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Preface

A variety of users from different industries, retailers, farmers, and medical care professionals are faced with growing pressure from society and legislation to minimize non-degradable packaging waste and to switch to biodegradable materials. The driving forces powering the development of these biodegradable materials are fourfold:

- the greenhouse problem, which urgently calls for reductions in CO_2 emissions in production processes;
- the increasing amount of Solid Municipal Waste (SMW) produced in Europe and the rest of the world;
- the environmental implementations of incineration and recycling of plastics; and
- the ever increasing price and expected future shortage of mineral oil.

Despite this pressure, there is at present no biodegradable alternative for disposable plastics combining all the features, functionalities, and – especially – economics necessary for it to be really competitive. Efforts to produce competitive biodegradable packaging have been frustrated by the problem of finding the optimal balance between mechanical properties, costs, and the level of biodegradability.

An increased emphasis on sustainability, eco-efficiency, and green chemistry has driven a search for renewable and environmentally friendly resources. Starch – a biodegradable polysaccharide produced in abundance at low cost – displays thermoplastic behavior under the right circumstances, making it one of the most promising candidates as an alternative for traditional plastics in certain market segments, such as the food packaging industry. Starch is a complex homopolymer composed of α-D-glucose units linked together in two different forms: the linear form amylose and the highly branched amylopectin. The compositions and structures of starch granules vary considerably between different plants, affecting the properties and function of starches from different crops.

The EU Agricultural-Industrial Research Commission studied the potential market for bioplastics on the basis of renewable resources and predicted 1.1 million tonnes of bioplastics with an increase in economic value and job potential of €2 billion and 20 000 new jobs (European Commission. DG XII: Study on Pro-

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duction of Thermo-Bioplastics and Fibers based mainly on Biological Materials, Science, Research and Development, EUR 16 102). This represents a tremendous market potential for competitive biodegradable packaging material, further stimulated through EU policies. Because landfill space is running short and because incineration may create toxic emission problems, national authorities and the European Commission have defined the reduction of the traditional packaging waste stream as an area to receive priority attention. If these authorities' efforts continue, sales volumes can meet the high figures quoted above.

Numerous studies have been conducted to optimize the performance of starch-based plastics. These studies show that important properties for evaluation of a packaging material include mechanical and thermoforming properties, gas and water vapor permeability, resistance, transparency, and availability. Designing and engineering a starch-based packaging product that possesses all of these required properties, however, is a significant challenge. Product cost and technical challenges – such as brittleness associated with high loads, and poor water and gas barrier properties – have to be overcome before renewable biomaterials can be commercialized. Currently, most research directed towards enhancing the functional properties and inherent bonding strength of starch has focused on incorporating additives, such as plasticizers, to improve the material's performance.

In the framework of the EU CRAFT program of the 5th FP BIOPACK a cooperative venture was established between the Department of Chemical Engineering of the University of Groningen (NL) and the Department of Food Process Engineering of Lublin University of Life Sciences (PL). They have joined forces to develop starch-based biodegradable packaging materials with physicochemical and physicomechanical properties, handling characteristics, shape, and end-product cost that must be competitive with those of the conventional stable and non-degradable plastics. The main results of these BIOPACK investigations, as well as other important information concerning thermoplastic starch and biodegradable plastics, are discussed in this book.

Bearing the figures on market potential in mind, packaging manufacturers and users nowadays see good opportunities to improve their competitiveness and to penetrate new markets. Many profit and non-profit organizations are looking for biodegradable packaging to improve overall waste management. Possible users are big companies, small enterprises, and public organizations in the food industry, retailing, agriculture, and medical care. Biodegradable materials meet current and future legislative demands and societal awareness on waste management.

Groningen and Lublin,
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1

Biodegradable Polymers and Their Practical Utility

Marcin Mitrus, Agnieszka Wojtowicz, Leszek Moscicki

The environmental impact of persistent plastic wastes is raising general global concern, and disposal methods are limited. Incineration may generate toxic air pollution, satisfactory landfill sites are limited, and recycling methods for commingled waste are expensive and often energy-intensive. In addition, petroleum resources are finite and are becoming limited. It will be important to find durable plastic substitutes, especially in short-term packaging and disposable applications. The continuously growing public concern in the problem has stimulated research interest in biodegradable polymers as alternatives to conventional nondegradable polymers such as polyethylene and polystyrene etc.

Several concerns must be addressed prior to commercial use of biobased primary packaging materials. These concerns include degradation rates under various conditions, changes in mechanical properties during storage, potential for microbial growth, and release of harmful compounds into packaged food products. Furthermore, the biopackaging must function as food packaging and meet the requirements of particular food products.

In Europe, the biopackaging field is regulated primarily by two EU directives: “Plastic Materials and Articles Intended to Come into Contact with Foodstuffs” (90/128/EEC), with later amendments, and “Packaging and Packaging Waste Directive” (94/62/EEC). Biopackaging often has difficulties in complying with the migration requirements of the directive on “Plastic Materials and Articles Intended to Come into Contact with Foodstuffs”. Furthermore, several of the raw materials and additives used to produce biopackaging materials are not included in the list of approved components. Polymers derived from renewable resources (“biopolymers”) are broadly classified according to the method of production. This gives the following three main categories:

- **Polymers directly extracted/removed from natural materials (mainly plants):** Examples are polysaccharides such as starch and cellulose and proteins such as casein and wheat gluten.

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- **Polymers produced by "classical" chemical synthesis from renewable bio-derived monomers:** A good example is polylactate, a biopolyester polymerized from lactic acid monomers. The monomer itself is produced by fermentation of carbohydrate feedstock.
- **Polymers produced by microorganisms or genetically transformed bacteria.**

The best known biopolymer types are the polyhydroxyalkanoates, mainly poly(hydroxybutyrates) and copolymers of hydroxybutyrate (HB) and hydroxyvalerate (HV). Such copolymers are produced by Monsanto and are better known by the generic trade name "Biopol2". Polyhydroxyalkanoates function in microorganisms as energy substrates and for carbon storage.

Most commonly available natural polymers (category 1 above) are extracted from agricultural or forest plants and trees. Examples are cellulose, starch, pectins, and proteins. These are cell-wall, plant-storage (starch), or structural polymers. All are by nature hydrophilic and somewhat crystalline; all factors may cause processing and performance problems.

Starch may offer a substitute for petroleum-based plastics. A renewable degradable carbohydrate biopolymer that can be purified from various sources by environmentally sound processes, starch, by itself, has severe limitations due to its water solubility. Articles made from starch will swell and deform upon exposure to moisture. To improve some of its properties, in the past decades a number of researchers have often blended starch with hydrophobic polymers in the form of petroleum polymers, both to increase biodegradability and to reduce the usage of petroleum polymer.

Fully biodegradable synthetic polymers, such as poly(lactic acid) (PLA), polycaprolactone (PCL), and poly(hydroxybutyrate-valerate) (PHBV), have been commercially available since 1990. However, these synthetic polymers are usually more expensive than petroleum-based polymers and also have slow degradability. Blending starch with these degradable synthetic polymers has recently become a focus of researchers. Advanced research results obtained by many scientists have established that blending of starch with poly(vinyl alcohol) and ethylene vinyl alcohol can be used for production of degradable films, and that biodegradable plastic substitutes can be produced by blending of starch with degradable poly(hydroxybutyrate-valerate) (PHBV). Preparation of new degradable polymers by blending of starch with degradable polycaprolactone (PCL) was the base for commercial trials. Unfortunately the mechanical strength properties of these blends were very limited. Of these biopolymers, because of its biodegradability and tissue compatibility, PLA has been extensively studied in medical implants, suture, and drug delivery systems since the 1980s. PLA is attractive for disposable and biodegradable plastic substitutes, due to its better mechanical properties, although it is still more expensive than conventional plastics. Also, its degradation rate is still low in relation to the waste accumulation rate.

1.1
Natural Polymers

Biopolymers are defined as polymers formed under natural conditions during the growth cycles of all organisms. Therefore they are also named natural polymers. They are formed within cells by complex metabolic processes. For materials applications, cellulose and starch are most interesting. However, there is an increasing attention in more complex hydrocarbon polymers produced by bacteria and fungi, particularly in polysaccharides such as xanthene, curdlan, pullulan, and hyduromic acid.

Starch is a polymer of hexacarbon monosaccharide – D-glucose. It is extremely abundant in corn seeds, potato tubers, and the roots and stems of other plants. The D-glucose structure can exist both in open-chain and in ring forms; the ring configuration is ascribed to D-glucopyranose. The pyranose ring is a more thermodynamically stable structure and it constitutes the sugar structure in the solutions.

Starch is mainly composed of D-glucopyranosis polymers bound by α-1,4- and α-1,6-glycoside links. These links are formed between the first carbon atom (C1) of one molecule and the fourth (C4) or sixth (C6) of the second one [1–5]. As the aldehyde group on one end of a starch polymer is always free, these starch polymers always possess at least one reducing tip. The other end of the polymer is an irreducible tip. Depending on the degree of polymer branching occurring in a starch molecule, there may be great numbers of irreducible tips. The formation of α links in a starch molecule enables some parts of starch polymers to generate helix structures; this is determined by the orientations of hydroxy (–OH) groups on the first carbon atom (C1) and the pyranose ring. Studies on starch's chemical properties and structure have established that it is composed of two components, both also polysaccharides: amylose (20–35%) and amylopectin. The ratio of these components varies, subject to the source of origin. Amylose is a linear polymer, whereas the amylopectin molecule is substantially bigger and branched. These structural differences cause marked differences in starch's characteristics and functions.

Starch appears in plants as granules (reserve material), the sizes, shapes, and structures of which depend on their sources of origin. Although the main components of all kinds of starch are the polymers amylose and amylopectin, there is considerable recorded diversity in the structures and characteristics of the natural starch granules [4]. The granule diameters vary from under 1 μm up to over 100 μm and their shapes may be regular (round, oval, angular) or totally irregular. Potato starch obtained from potato sprout tubers *Solanum tuberosum* L. has granules of varied size (from 10 up to 100 μm) and of different shapes (round, oval, oviform, oblong, shell-shaped, and other irregular forms).

Starch is employed in the cosmetics and pharmaceutical industries for producing dusting powders and powders and as a filler. In addition, it serves as a means to obtain glucose, ethyl alcohol, and dextrins, as well as for stiffening and binding in these industries. Wheat starch from wheat grains (*Triticum vulgare* Villars) exists as single granules of two types: large ovals of 15–45 μm in diameter and smaller, more rounded forms of 2–7 μm in diameter. This type of starch is applied as a neutral dusting powder or as an ingredient in pharmaceutical preparations. In some plants – in oats or rice, for example – complex starch granules develop through binding of single molecules in an organized way [6].

The distribution of amylose and amylopectin inside a starch granule is well ordered. However, during heating in the presence of water, the packing of the two polymers becomes chaotic. This loss of internal order occurs at different temperatures, depending on the starch type. With persistent warming in water, the natural granules swell and finally their structure gets destroyed. The polymers are then released into the water surroundings [4].

The starch degradation process proceeds very slowly: first dextrins are formed, and these in turn undergo hydrolysis to maltose disaccharide, to be eventually broken down into two glucose molecules [7].

Starch is a strongly hygroscopic, chemically neutral substance. It swells greatly in water, due to penetration of water molecules into its branched structure. As mentioned above, long boiling makes it dissolve in water or in weak acids, as well as in solutions with hydroxides of potassium, rubidium, cesium, or francium and concentrated solutions of chloral hydrate.

Soluble starch (*Amylum solubile*) is obtained as a result of long boiling of starch with water or weak acid; link cleavage at the amylopectin chain branching sites is then observed, and eventually a water-soluble product is formed. It is employed as an indicator in chemical analysis (iodometry) [6].

Studies on starch include examination of: water absorption, chemical modification of molecules, behavior under agitation, and high-temperature, thermomechanical abrasion resistance. Although starch is a polymer, its strength under stress appears to be low. At temperature above 150 °C, the glycoside bonds start cracking and over 250 °C starch granules subside endothermally. At low temperatures, however, some reorganization of hydrogen bonds is observed together with straightening of the molecule chains during the cooling process (retrogradation). In some extreme cases, under 10 °C, precipitation is reported. Starch may be hot-water-soluble and formed in thin films; its molecular orientation causes brittleness in both foils and solid packages produced in this way [3–5, 8–16].

Both amylose and amylopectin consist of glucopyranosis molecules, yet the structural differences between these two polymers determine their different properties. Amylose is mostly a linear polymeric molecule, consisting of α-1,4-linked D-glucopyranose (Figure 1.1). The molecular weight of amylose varies from 500 anhydroglucose units (AGU) in high-amylose maize starch to more than 6000 AGU in potato starch [6, 7]. Recent research, though, suggests that amylose also contains some branchings. For purposes of simplification, the polymer structure is presented as a normal chain, but amylose is often characterized with a helix structure. The helix structure contains C–H bonds, due to which it is hydrophobic, allowing a type of additive complexes with free fatty acids, fatty acid glycerides, some alcohols, and iodine to be generated [4].

Iodine addition proves to be an important diagnostic method for starch characterization. Amylose absorbs up to 20% iodine and stains blue. Bonding with lipids,

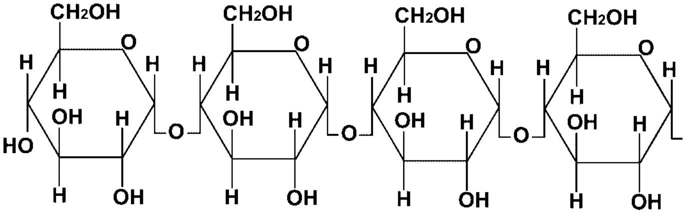


Figure 1.1 Amylose structure [9].

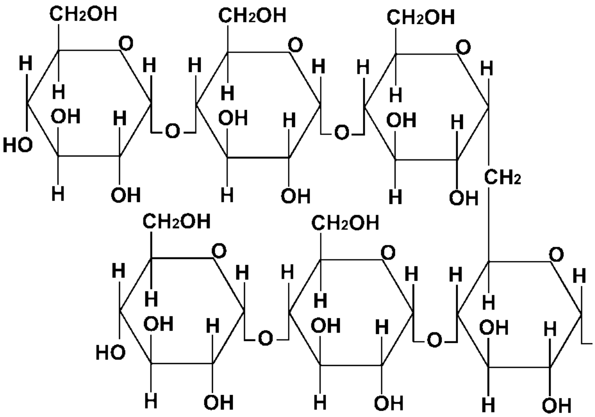


Figure 1.2 Structure of amylopectin [9].

especially mono- and diglycerides, is a well-known property of amylose helix. The configuration and structural indivisibility of amylose–lipid complexes are affected by numerous factors such as temperature, pH, fatty acid structure, or glyceride, as well as by the contact time and/or agitation time between an amylose "carrier" and a linked molecule. A developing complex can change the features of starch. Bonding of amylose to fats or to food emulsifiers such as mono- and diglycerides can change the starch gelatinization temperature or the textural and viscous profiles of the formed mass and can impede the retrogradation process.

After starch granules have been boiled, amylose possesses a gel formation capacity that allows rebinding of the dissolved amylose polymers. This property is noticeable in the behavior of some kinds of amylose-rich starch (wheat, rice, and high-amylose maize).

Amylopectin, dominant in most starch kinds, is a branched polymer of substantially larger size than amylose. Amylopectin consists of α-1,4-bonded glucose segments, linked by α-1,6 bonds at the branching sites (Figure 1.2). Estimates are that around 4–6% of bonds in a standard amylopectin molecule appear to be α-1,6 links, which results in over 20 000 branchings in a molecule, although the branchings are not large. Studies suggest a bimodal size distribution of polymer chains: namely small and large chains. Small chains have a average degree of polymerization (DP) of about 15, whereas the bigger chains have DPs of around 45. This unique configuration contributes to the crystalline nature of amylopectin and to ordered arrangements of amylopectin molecules within the starch granule. The branched chains of amylopectin behave just like those of amylose, but in the case of amylopectin whole chains – or more often their fragments – can be twisted spirally [4, 12].

Owing to this strongly branched structure of amylopectin, its properties differ from those of amylose: because of the large size of the amylopectin molecules and their structure, for example, retrogradation proceeds more slowly than in amylose and gel formation is inhibited. Starches consisting mainly of amylopectin (wax starches) are considered not to be gelating, but they usually show compact and rubbery textures. Amylopectin heated in water swells and forms a paste, it absorbs iodine poorly (around 0.6%), and stains violet or red-brown.

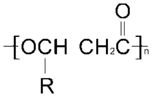
Amylose from different botanic sources shows varying degrees of polymerization (DPs), about 1500–6000, whereas the considerably bigger amylopectin molecules exhibit DPs from around 300 000–3 000 000. From these figures and from the molecular weight (MW) of anhydrous glucose (162), the MW of amylose can range from 243 000 up to 972 000. Reports say, however, that amylose from potato starch is of 1 000 000 MW, but its mean molecular weight is usually under 500 000. The MW of amylopectin varies between 10 000 000 and 500 000 000. The differences in the MWs of amylose and amylopectin are directly connected with their plant origins, methods of polymer isolation, and MW determination method [4].

Cellulose was isolated for the first time around 150 years ago. It is different from other polysaccharides produced by plants because the molecular chains forming it are very long and are made up of a single repeating unit. This structure is observed in the crystalline state. Isolated from the cell walls in microfibrils by chemical extraction, cellulose in all forms is a highly crystalline polymer of high molecular mass and is infusible and insoluble. As a result of this it is usually converted into derivative substances to make it easier for processing [17].

Chitin and chitosan: Chitin is a skeletal polysaccharide making up a basic shell constituent of crabs, lobsters, shrimps, and insects. Chitin can be degraded by chitinase. It is insoluble in its native form, although chitosan, a partly deacetylated form of chitin, is water-soluble. The materials are biocompatible and demonstrate antimicrobial activity as well as heavy metal absorptivity. They are widely used in the cosmetics industry, due to their water-retaining and moisturizing capacities. Used as carriers, chitin and chitosan allow the synthesis of water-soluble prodrugs. Chitinous fibers serve in the manufacture of artificial skin and absorbable sutures [18–20].

Proteins, used as materials, are mostly insoluble and infusible without prior modification, and so are used in natural form. This description is especially true for the fibrous proteins wool, silk, and collagen. All proteins are specific copolymers with regular arrangements of different kinds of α-amino acids; protein biosynthesis is thus an extremely complex process demanding many enzymes of different types.

Gelatin, animal protein, consists of 19 amino acids joined by peptide linkages. It can be broken up by a variety of proteolytic enzymes to obtain its constituent



$$-\!\left[\mathrm{OCH(R)\,CH_2C(=O)}\right]_n\!-$$

Figure 1.3 Structure of bacterial polyester (R = $-(\mathrm{CH_2})_x-\mathrm{CH_3}$, $x = 0$–8 or more).

amino acids or peptide components. Gelatin is a water-soluble, biodegradable polymer with wide industrial, pharmaceutical, and biomedical applications. In addition, it is also used for production of coatings and for microencapsulating various drugs and biodegradable hydrogels [21–25].

A method for gelatin application to produce thin flexible artificial skin adherent to an open wound to protect it from infection and fluid loss has been developed. This material was obtained as a blend of commercial gelatin and polyglycerol, either natural or after its epoxidation with epichlorohydrin, formed into thin films by casting on trays covered with Teflon. The films were tough and spontaneously adhered to open wounds. The films can contain bioactive molecules such as growth factors or antibiotics that will be released for a couple of days. The skin substitute prepared in this way could be sterilized with γ-rays or produced under sterile conditions [26].

In research into biodegradable materials, increasing interest has been reported in natural polyesters generated by various bacteria as reserve materials, due to fact that they are melt-processable polymers obtained from some renewable sources. The members of this thermoplastic biopolymer family, the general structure of which is shown in Figure 1.3, exhibit variation in their material properties from rigid brittle plastics through flexible to hard elastomers, subject to the alkyl group R and the polymer composition [27, 28].

1.2
Polymers with Hydrolyzable Backbones

Aliphatic polyesters are almost the only synthetic chemical compounds of high molecular weight that have been shown to be biodegradable. This is the result of the extremely strongly hydrolyzable backbones of these compounds. It has been stated that polyesters, being derivatives of diacids of medium-sized monomers ($\mathrm{C_6}$–$\mathrm{C_{12}}$), are more easily degraded by fungi (*Aspergillus niger* and *Aspergillus flavus*) than those derived from longer or shorter monomers. If synthetic polymers are to be biodegraded under enzyme catalysis, a chain of the polymer needs to fit into the active site of the enzyme; for this reason flexible aliphatic polymers can get degraded, whereas their rigid counterparts might not [29, 30].

Polyglycolic acid (PGA) is the simplest linear aliphatic polyester (Figure 1.4). Both PGA and the copolymer poly(glycolic acid-co-lactic acid) (PGA/PL) are used as degradable and absorbable sutures. Their vital advantage is degradability through simple hydrolysis of the ester backbone in aqueous surroundings, such as body fluids. Moreover, breakdown products are finally metabolized to carbon dioxide and water or are voided from an organism through the kidney [31].

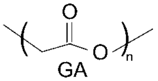


Figure 1.4 Structure of polyglycolic acid (PGA).

Polycaprolactone (PCL) has been thoroughly examined as a biodegradable medium and as a matrix in controlled drug-release systems. PCL is predominantly produced in the ε-caprolactone polymerization process [32–35]. Tokiwa and Suzuki [36] studied the hydrolysis process and PCL biodegradation by fungi and showed that polycaprolactone can be broken down enzymatically.

Polyamides contain the same amide linkage as polypeptides, but their biodegradation rates are so slow that they are regarded as undegradable. However, their degradation to low-molecular-weight oligomers under the influence of enzymes and microorganisms has been reported. Introduction of benzyl, hydroxy, and methyl substituents greatly improves polyamide biodegradation [37, 38].

Higher crystallinity of polyamides caused by strong interchain relations is responsible for the low observed biodegradation levels. Copolymers containing both amide and ester groups are easily degraded. As would be expected, the degradation rates increase with increasing ester content.

Natural protein structures are seldom composed of repeated units. Owing to this the substances do not tend to pack into highly organized morphologies, and for this reason enzymes can readily attack them. On the other hand, synthetic polyamides have short and regular repeating units. Their higher symmetries and strong hydrogen interchain bonds give rise to highly ordered crystalline morphologies that decrease their accessibility to enzyme attack. It was shown that polyamide esters and polyamide urethanes with long repeating chains undergo degradation at rates intermediate between those of proteins and of synthetic polyamides [39, 40].

Polyurethanes can be regarded as compounds combining the structural characteristics of polyesters and polyamides. Their susceptibilities to biodegradation are by some measure, as would be expected, similar to those of polyesters and polyamides and depend on their structures. Generally, it has been found that polyurethane biodegradation is conditioned by the matter of whether a basic polymer is a polyester or a polyether. Polyurethanes with structures based on polyethers are resistant to biodegradation, whereas polyester polyurethanes are susceptible to it. Many microorganisms (*Aspergillus niger, Fusarium solanii, Cryplococcus lacirentii,* etc.) and enzymes are highly effective in polyurethane degradation [41, 42].

1.3
Polymers with Carbon Backbones

Generally, vinyl polymers are, with some exceptions, not susceptible to hydrolysis. For their biodegradation, if any at all, an oxidation process is needed. Most of the biodegradable vinyl polymers contain readily oxidizable function groups.

Polyvinyl alcohol (PVA) undergoes biodegradation most easily. Microbiological and enzymatic degradation of PVA was studied under the influence of the soil bacterium *Pseudomonas*. It was shown that the first step of polyvinyl alcohol biodegradation is oxidation of the secondary alcohol groups to ketone groups. Subsequent ketone group hydrolysis results in polymer chain cleavage [43].

Polyvinyl alcohol can form complexes with many components, and so it can detoxify organisms. It is applied in low-molecular-weight form – below 15 000 – and is voided from the organism through the kidney. In addition, it is also used as a polymer carrier for plant protection (herbicides and pesticides) [44].

1.4
Practical Applications of Biodegradable Polymers

The biodegradable polymers are used in three main areas: medical, agricultural, and goods packaging. Intensive research in these fields has resulted in the development of commercial products. Because of their high specialization and greater unit values, medical applications have developed more rapidly than the others.

1.4.1
Medical Applications

The developed biodegradable synthetics serve as surgical implants in the blood vessels, in orthopedic surgery as implantable matrices for controlled long-term drug release in an organism, and as absorbable surgical sutures, as well as for eye treatment. Recently the term “biomaterial” has been defined as a non-living material used in medical device applications for interaction with a biological system. It is important that the term “biocompatibility” was also formulated; it determines how a tissue responds to foreign material. Biocompatibility is the ability of a material to coexist with some host’s reactions in a specific use [45, 46].

1.4.1.1 Surgical Sutures

Tissue damage causes loss of structural integrity: a deep cut in soft tissue or a bone fracture, for example, may or may not be capable of spontaneous healing. Insertion of material or an instrument to hold the wound edges together may facilitate the therapy. The classic example is application of sutures to hold both deep and surface wounds together. When the healing is complete, the sutures are redundant and may disturb healthy tissues. It is then helpful for the material to be removable from the site either physically or by degradation.

Synthetic, absorbable sutures were developed in the 1960s, and thanks to their good compatibility in tissues are widely used in general and tracheobronchial surgery. The sutures used most often are multifilament, with good handling characteristics. The most popular and commercially available are the sutures made from PGA, PLA and their copolymers. For laying continuous sutures, however, braided sutures with nonsmooth surfaces are not useful. In such cases only monofilament sutures with smooth surfaces are useful, because PGA or PLA proved to be too stiff and inflexible. The more flexible polydioxanones and polyglyconates can be used as sutures thanks to their low bending moduli. In addition, polymers of polycaprolactone are also bioabsorbable, elastic materials, so their clinical use is under study [47, 48].

Dexon is made of poly(glycolic acid), the first synthetic polymer developed especially for producing surgical thread. The fibers of the yarn obtained are precisely woven into a high-flexibility thread, very easily handled and with high knot security. This material undergoes hydrolytic decomposition in humans, causing minimal tissue reaction. The minimum absorbing period was observed 15 days after implantation, complete absorption took place within 60–90 days.

Polygalactin 910 is a copolymer of glycolide and lactide, obtained from glycolic and lactic aid in 9:1 ratio. The multi-fiber threads, called Victyl or Polisorb, are coated, transparent, or dyed purple. For Vicryl Rapid threads a material with smaller relative molecular mass is used, and as a result is absorbed more rapidly.

Mexon is a synthetic single-fiber thread with slow absorption characteristics, made of a copolymer of glycolic acid and trimethyl carbonate. Three weeks after implantation it retains about 55% of its initial resistance; compete absorption takes place after 26–30 weeks. The products of hydrolytic thread decomposition are: carbon dioxide, β-hydroxybutyric acid, and glycolic aid.

Monocryl (Poliglecaprone 25) is a glycolide and ε-caprolactone copolymer. The thread is nontoxic, but causes a delicate reaction during absorption, which take place in vivo by way of hydrolysis.

Polydioxanone (PDS) is a polyester of (*p*-dioxanone). Its key feature is essential mechanic resistance after implantation: after 14 days it retains 70% of the initial resistance, but after only six months it has undergone almost complete absorption by way of hydrolysis.

As well as natural threads (silk, flax, cotton), nylon (the general name of polyamides) is also biodegradable. Polyamide 6,6, polyamide 6, and their mixtures with other polyamides are used for thread production. Nylon sutures are water-absorbable and they cause moderate tissue reaction. After implantation they undergo slow biodegradation and fragmentation. After two years they have lost about 25% of their mechanic resistance.

1.4.1.2 **Bone-Fixation Devices**

Although metal fixation is an efficient method for undisturbed bone treatment, bone and metal have completely different mechanical properties. The elasticity constant of bone is only a tenth that of implanted steel, whereas its tensile strength is 10 times lower. Because of this, removal of metal implants can bring about bone weakness and refractures.

In contrast, biodegradable implants can adapt to the dynamic processes of bone healing through decreasing amounts of weight-bearing material. Over a few months the introduced material disappears and there is no need to operate on a patient to remove it. In this field, PGA, PLA, PHD, and polydioxanone can potentially be used. Polydioxanones have been recommended for clinical use to protect ligament augmentation, for securing ligament sutures, and as a sort of internal splinting suture to allow early motion after an operation.

Biodegradable polymers are also helpful in other applications. A marrow spacer can help to save autologous bone material. Plugs to close bone marrow are applied in the case of endoprosthetic joint replacement. To fill large bone defects, polymer fibers are used in order to avoid mechanical load [49].

1.4.1.3 Vascular Grafts

A great number of studies have been undertaken to develop acceptable vascular prostheses of small diameters. Nilu *et al.* [50] designed such small-diameter vascular prostheses with matrices that were absorbable into a growing anastomotic neointima. It was shown that a gelatin-heparin complex, when adequately crosslinked, can simultaneously function as a temporary antithrombogenic surface and as a perfect substructure for an anastomotic neointima.

1.4.1.4 Adhesion Prevention

Post-operation tissue adhesion can occasionally cause serious complications. Materials for tissue adhesion prevention should be flexible and tough enough to provide a tight cover over the traumatized soft tissue. In addition, they should be biodegradable and reabsorbable after the injured tissue has been completely regenerated. Matsuda *et al.* [51, 52] developed photocurable mucopolysaccharides for tissue adhesion prevention materials. These meet numerous requirements, such as nonadherent surface characteristics, biocompatibility, and biodegradability in accordance with the wound healing rate and nontoxicity.

Mucopolysaccharides partially functionalized with photoreactive groups, such as cinnamate or thymine, underwent UV irradiation to form water-insoluble gels through intermolecular photodimerization of the photoreactive groups. The photocured films with lower degrees of substitution and of high swellability and flexibility prevented tissue adhesion and showed enhanced biodegradability. It was assumed that newly developed gels might promote healing of injured tissues in a bioactive way.

1.4.1.5 Artificial Skin

Artificial skin substitutes and wound dressings made of biodegradable polymeric materials have been developed to treat burns. So far, most of the commercially available artificial skins have been composed of biodegradable polymers, such as collagen and chitin, which are enzymatically degradable polymers [53, 54].

Koide *et al.* [55] developed a new type of biomaterial in the form of a sponge that combines fibrillar collagen (F-collagen) with gelatin. The sponge was physically and metabolically stabilized by introduction of crosslinks. Although some types of collagen-based artificial skin have been developed, some unfavorable qualities of native collagen have still been reported; these mainly involve introduction of rodlike shapes and expression of collagenase genes to fibroblasts. New materials have been developed to cope with these problems.

Yasutomi *et al.* [56] developed a biosynthetic wound dressing with drug delivery capability. This medicated wound dressing consists of a spongy sheet based on a mixture of chitosan and derivatized collagen, laminated with a polyurethane membrane impregnated with antibiotics. From in vitro research it appeared that this wound dressing is capable of suppressing bacterial growth and of minimizing cellular damage. The studies on this new material were carried out in 80 clinical cases including superficial and deep second-degree burns, donor sites, and pressure sores and were very successful.

Another important goal in biomedical engineering is the development of hybrid artificial skins. Here, efforts are being made to combine synthetic polymers and cell cultures to form synthetic-biological composites. In such cases biodegradable polymers can be useful as media for growing cells and tissue cultures in vitro.

1.4.1.6 **Drug Delivery Systems**

Polymeric materials have been given a new dimension for use as drug delivery devices by the introduction of biodegradable polymers. Many degradable polymers, including various synthetic and natural substances, are potentially useful in this respect. The use of specially developed degradable polymers in medicine has been highlighted with the appearance of some innovations in drug delivery systems. The restrictions of classic methods for drug administration (by injection or tablet) are widely known. As a dose is applied, the plasma levels will go up but they will fall drastically when the drug has been metabolized and soon be below therapeutic levels. The next dose will make the plasma level high again and a cyclical pattern may be established. Therefore, in classical drug administration, most of the drug plasma levels can be outside the optimal range. The drug usually permeates throughout the body and is not targeted to the site where it is specifically required.

One of the possible solutions to this problem is to use a system of controlled drug delivery in which the drug is released at a constant, preset rate, preferably close to the specific location. One of the most notable approaches is when the drug is contained in a polymer membrane (or encapsulated in a polymer matrix), from which it diffuses out into the tissue in which the membrane/matrix is implanted. In some cases the mechanism of drug release is affected by erosion or polymer dissolution. Degradable polymers such as poly(lactic acid) or polyorthoesters can be used for drug delivery systems of this type [57, 58].

Some soluble polymers may be used as carriers for drugs. Duncan and Kapecek [59] reported the use of various polymers to which were attached, through lateral groups, certain drugs that could be released after cleavage of the bonds attaching them to the backbone. The drug targeting was achieved through the use of bonds that are cleaved only under certain conditions (e.g., by liver enzymes), thus allowing drug release only at the specific site of action.

Attempts have been made to obtain plastic biodegradable polymer materials. Lactic acid oligomers were plasticized with 1,2-propylene glycol and glycerol. Glycerol showed low compatibility, whereas glycol showed high polymer compatibility up to high concentrations. The prepared mixtures exhibited a substantial decrease in their processing temperatures and enhanced delivery of salicylic acid in the early stages of release. It therefore proved feasible to obtain easy and safe systems that can be injected into a body without the need for surgical retrieval after completion of the administration. Furthermore, the differential rates of drug release may be of great benefit in cases in which an increased drug dose is necessary at the beginning of therapy [60].

1.4.2
Agricultural Applications

Since the introduction in the 1930s and 1940s of plastic films for greenhouse covering, chemical plant protection, and mulching in fields, polymer use in agriculture has developed at a great rate. All the main classes of polymers – that is, plastics, coating, elastomers, fibers, and water-soluble polymers – are nowadays used for controlled release of pesticides and nutrients, soil fertilization, seed coatings, and plant protection. Degradable plastics are also of serious interest as materials for crop mulching in fields or as agricultural plant containers. Their biodegradation mode (i.e., composting) is of great significance because it allows various biodegradable materials to be combined and processed into useful materials to improve the state of the soil.

1.4.2.1 **Agricultural Mulches**

Agricultural mulches help farmers with crop growth. They are commonly used to reduce weeds, to maintain constant moisture level, and to increase soil temperature, improving the plant growth rate. It was reported that, thanks to the use of black polyethylene mulch, a two- to threefold increase in yield was achieved at a 6 ha melon farm, with ripening two weeks earlier. Thanks to application of mulches the weed growth was inhibited and soil compaction avoided, so the need for certain cultivation practices was eliminated. At the same time, root damage and plant stunting or dying were reduced, as were the fertilization and water requirements of the plants [61].

Transparent polyethylene is more efficient in heat trapping than black or smoke-gray film. Soil temperatures can increase by 5.5 °C under clear films, as against to 1.7–2.7 °C under black ones. The polymer films reduce radiative heat loss at night when the soil cools. In some cases inhibition of weed growth owing to solar heating of the polyethylene mulches has been reported. However, conventional films left in the field can cause some serious problems at harvest or during agricultural practices the next year. Film removal or disposal is troublesome and costly, and because of this, interest in the development of films that are biodegradable or have short service lifetimes has been noted. Despite a huge number of polymer types that can be designed for controlled degradation, only a few of them can be commercialized. The materials used usually contain light-sensitizing additives that make the material photodegradable [62–64].

The plastics used for mulch films are mainly low-density polyethylene, polyvinyl chloride, polybutylene or ethylene copolymer, and vinyl acetate. Especially interesting photogradable systems are composed of nickel and ferric dibutyldithiocarbamates in a ratio adjusted so that protection can be provided at specific growth periods. The material's stability is tuned, and when the growing period ends the material undergoes photodegradation. A further proposed system involves a combination of substituted benzophenones and titanium or zirconium chelates.

Biodegradable films based on starch with addition polyvinyl alcohol, copolymers of polyethylene, acrylic acid and polyvinyl chloride have been developed in laboratories in the USA. Films made from polylactone and polyvinyl alcohol readily degrade under the influence of soil microorganisms, whereas iron or calcium additives enhance polyethylene breakdown. The degradable mulches should break down into small, brittle pieces that will easily pass through harvesting machines without any negative interference with the following crops [46, 65–67].

Effective fumigant mulches need films of decreased porosity that reduce the potential escape of volatile chemicals (insecticides, herbicides) and therefore let lower doses be applied.

1.4.2.2 **Controlled Release of Agricultural Chemicals**

Controlled release (CR) is a method by which active chemicals are provided to specific plant species at preset rates and times. Polymers are mainly used to control the delivery rates, mobilities, and periods of effectiveness of the chemicals. The main benefit of the CR method is that if fewer chemicals are used for the protected plants over the predetermined period, then the effect on the other plant species is less, while leaching, volatilization, and degradation are reduced. The macromolecular character of polymers is the key to reduction of chemical loss throughout the production.

CR polymer systems can be divided into two categories. In the first, the active agent is dissolved, dispersed, or encapsulated within the polymeric matrix or coating. Its release takes place through diffusion or after biological or chemical breakdown of the polymer. In the second category, the active agent either itself constitutes a part of the macromolecular backbone or is attached to it. Here its release is the result of biological or chemical cleavage of the bond between the polymer and bioactive agent.

Physical systems into which agricultural chemicals have been introduced include microcapsules, physical blends, and dispersions in plastics, laminates, hollow fibers, and membranes. Kinetic models for chemical release have been developed for each of the above systems.

Of the natural polymers, starch, cellulose, chitin, alginic acid, and lignin are used in CR systems. Their advantages are availability, relatively low cost, and biodegradability. Although these materials have functionality for derivatization they have one significant drawback: that is, their insolubility in standard solvents for formulation, encapsulation, and dispersion. This drawback is overcome when a chemical is encapsulated in situ, with, for instance, gelatinized starch cross-linked with a chosen pesticide by calcium chloride or boric acid. As a consequence, the pesticide is trapped within the granular particles formed [68–71].

One of the most important applications of CR technology in agriculture is fertilization. Urea, a main nitrogen source, readily reacts with formaldehyde to form a polymer. The subsequent hydrolysis of polymer releases urea, so it is a simple and inexpensive CR system [72, 73].

A small niche for degradable plastics is the use of polycaprolactone for small agricultural planting containers. It is not a broad field for use of biodegradable synthetics, but it is one of the few applications in which the polymer used undergoes biodegradation within a reasonable period. Polycaprolactone planting containers have been used in automated machine planting for tree seedlings. It was found that the polycaprolactone had undergone substantial degradation after being in soil for six months, having lost 48% of its original weight, with 95% weight loss within a year [74].

1.4.3

Packaging

Physical characteristics of polymers for packaging are greatly affected by their chemical structures, molecular weights, crystallinities, and processing conditions. The physical characteristics required in packaging equally depend on the items to be packed and the environments in which the packages will be stored. Products to be stored frozen for some time require specific packaging. Foods demand stricter package requirements than solid products.

Intensive studies on the usability of starch-based materials for food packaging are being carried out. Holton *et al.* evaluated regular PE film and PE film with 5% maize starch content for packaging of broccoli, bread, and beef stored under standard conditions. Apparently the type of packaging film did not influence the assessed quality parameters, such as bread staling, broccoli color, and lipid oxidation in beef. In the case of PE film with starch content, however, a significant decrease in elongation was recorded. This may have been caused by interactions between film and free radicals produced during lipid oxidation in beef at frozen storage. Inconsistent results were obtained in the cases of broccoli and bread packaging in starch film. Owing to this fact it was suggested that PE films with starch content should be used for packaging of wet and dry low-lipid foods. Moreover, use of these materials for foods with high fat contents was not advised, due to possible interactions between the film and free radicals originating from lipid oxidation [75–77].

Over the past two years, packaging suppliers have introduced various forms of biodegradable plastics made from a variety of plants, mainly corn. This was driven by projections of growing demand for environmentally friendly packaging, a trend driven by environmentally conscious consumers and recycling regulations [78]. Some companies predict that the market will grow by about 20% annually, and bio-based packaging is increasingly being used as a replacement for petroleum-based plastics such as the widely used polyethylene terephthalate (PET), polyethylene (PE) resin, which is produced from natural gas, and polypropylene (PP), which is derived from crude oil. All these polymers are used to make a variety of containers and films for the food and beverage industries. Like PET, corn-based plastics permit a multitude of varied and complex bottle shapes and sizes that draw the attention of the consumer.

Many analysts believe that biodegradable packaging has a bright future. Growing environmental awareness and consumer power, coupled with the inexorable rise in pre-packaged disposable meals, means that food manufacturers and packagers are increasingly being targeted to improve their environmental performances. The demand is also being driven by anti-pollution legislation (e.g., traceability of compostable and degradable polymers).

The number of manufacturers of bioplastic products worldwide is strongly increasing, and more competition should give further momentum to the development of the sector. A growing number of food industry companies, including supermarkets and processors, have turned to biodegradable packaging as a means of meeting consumer demand for such ecofriendly products.

Two types of materials are included in the group of biodegradable polymers:

- polymers from renewable plant raw materials, which do not easily decompose, and
- polymers formed by chemical synthesis reactions, which are easily decomposed and mineralized by microorganisms.

In some important areas, technical developments have allowed bioplastic materials to achieve the quality of conventional products made of mineral oil. A new trend is the combination of commercialized biomaterials, thus creating new functional characteristics and special benefits. Other development efforts are focused on multi-layer films with altered characteristics that could, for example, improve the barrier characteristics of packaging materials. Another factor will be legislative support for the sector. There is less support for products made of renewable raw materials than there is for renewable energies and biofuels. Compostable or biodegradable plastic is usually made from plant-based starch or from fossil oil with additives that enable it to break down into CO_2 and water. Tests show that compostable packaging will break down more quickly than a banana skin, yet it takes many years for plastic packages or carrier bags to do the same.

1.4.3.1 Starch-Based Packaging Materials

Starch-based plastics are mostly made from maize, sugar-cane, or corn and potato starch. Corn is the operative word in packaging today, with more and more processors turning to biodegradable materials made from the crop and from other plants for packing their food products. Such packaging materials, which have appeared on the market for use by food companies, naturally break down in a garden compost heap, eradicating the need for packaging to be binned or bagged and sent to landfill. High-amylose corn starch (HACS) can produce films with higher barrier properties and physical strength than films made from a normal corn starch.

InnoWare Atlanta, USA, is producer of Expressions-ECO – effective, high-performing containers. They are more durable than typical compostable packagings and feature the ability to withstand higher temperatures, which is important during transport and storage. Solid bases and lids are safe up to 49 °C, whereas clear lids are safe up to 41 °C. These are ideal for cold applications such as salads, sandwiches, wraps, snacks, desserts, fruits, and more. Corn is harvested and broken down into dextrose. Dextrose is fermented and distilled into lactic acid, which is then modified with other biobased materials to reinforce its molecular structure. The result is an eco-friendly resin that is converted into Innoware's Expressions-ECO food containers. Expressions-ECO containers are recyclable and entirely compostable. The containers compost completely in 60–180 days, leaving no toxic residue.

Belu Mineral Water launched its compostable bottle (Figure 1.5), the UK's first bottle made from Ingeo^{TM} alternative bioplastic, in May 2006. Ingeo^{TM} bioplastics are ingenious materials made from plants, not oil. NatureWorks, Ingeo^{TM}, and the Ingeo logo are trademarks or registered trademarks of NatureWorks LLC in the USA and other countries. The revolutionary "Bio-bottle" is the latest initiative from London-based Belu, an environmental initiative that contributes 100% of its net profits to clean water projects. Through a collaboration with WaterAid, every bottle of water purchased in the UK provides someone in India or Africa with clean water for one month. KPMG (an audit, tax, and advisory firm) has been authorized to verify Belu's charitable donations. The bottle can be commercially composted back to soil in 12 weeks. Belu was formed in response to a challenge set by the UN's Global Compact, a movement to engage the business community in solving global social and environmental problems. Belu visited every natural mineral source in the UK to find the cleanest, freshest water. By sourcing its water in the UK, Belu minimizes long-distance transportation and the related environmental impact.

Amcor and Plantic Technologies (both from Australia) have teamed up to develop biodegradable, flexible plastic packaging for confectionary. Plantic will provide its patented material, a plastic created from plants that dissolves rapidly on contact with water. Plantic is based on corn flour, a renewable and biodegrad-

Figure 1.5 Ingeo^{TM} compostable bottles (with permission of Belu Water).

able raw material ideal for composting. Without contact with water the Plantic material starts to degrade after six months (according to EN1343).

Amcor intends to use the Plantic material to undertake trials of the resin in a commercial packaging film operation. Plantic materials have been used as rigid plastics in confectionery and biscuit trays. The goal of Plantic's collaboration with Amcor is to develop a thin and durable plastic for the flexible packaging of food and confectionery, such as chocolate bar wrappers and overwrap. Plantic is also developing its portfolio of resins to include injection-molding grades. Bottles made from biodegradable polymers for non-saturated drinks, milk, and plant oils have also been applied in the industry.

Australian scientists have developed revolutionary packaging materials that are fully biodegradable. Shopping bags based on wheat starch blended with other biodegradable materials will compost down fully in around 30 to 60 days. As well as for shopping bags, the materials could also be used to pack vegetables, in place of polystyrene trays for baked goods, and for other purposes such as mulch film for farming and gardening.

Modified starches such as cross-linked starch, substituted starch, acid-hydrolyzed starch, and pregelatinized starch have several functional uses as viscosity modifiers, thickeners, texture enhancers, and flavor encapsulation agents, in a host of products including soups, sauces, bakery products, dairy products, and confectionery. Dwindling non-renewable fossil fuel resources and the negative environmental impact of use of plastics has led researchers to focus efforts on utilizing starch as a biodegradable and virtually inexhaustible raw material for producing packaging materials including films, foams, and molded packages.

The utilization of TPS for the production of biodegradable plastics has increased and has been the object of several studies in the last decade. However, TPS has two main drawbacks: namely its water affinity and its poor mechanical properties. To overcome these problems, the addition of other materials to TPS is necessary. In order to increase its water resistance, TPS has been blended with synthetic polymers and modified by cross-linking agents such as Ca and Zr salts. Substances such as waxes and lignin have also been tested to decrease the water uptake of starch-based materials. TPS's mechanical properties have usually been improved by addition of synthetic polymers, such as ethylene-acrylic acid and ethylene-vinyl alcohol copolymers. Another approach requires the use of natural fibers and mineral fillers. The inclusion of reinforcing fillers such as fibers could, however, enhance the degradation of thermoplastic starch because of the increase in the melt viscosity [79–81].

One commercially processed TPS mixture is named Mater-Bi and it is shaped by pressing or extrusion techniques. This thermoplastic polymer is based on starch, natural plasticizers, and hydrophilic biologically degradable substances from synthetic polymers. This biopolymer is degradable, either in the presence of oxygen or in its absence. Another popular TPS biopolymer material is BIOPLAST, useful for Bioflex materials. Depending on processing methods it may be formed by film-blowing, thermoforming, or injection-molding [75, 76].

1.4.3.2 PLA-Based Packaging Materials

Applications of PLA include its use in compostable sugar-cane trays and in punnets or pallets. A starch derivative, PLA can be produced from maize and other plants and is a biodegradable, compostable plastic material. The material is available in a range of blends and can be used in sheet or film form for a diverse range of products including food containers. PLA can be used for rigid thermoforms, films, labels, and bottles, but because of its biodegradable features it cannot be used for hot-fill and gaseous drinks such as beer or sodas. PLA can also be used for non-carbonated beverages such as water, juices, and milk, as well as for edible oil products. It provides a flavor and aroma barrier comparable to that provided by PET and readily accepts coatings, inks, and adhesives. Its stiffness allows for a smaller thickness than is required with materials such as PET without any loss of strength. Heat seals can be made at temperatures as low as 80 °C, resulting in faster packaging times and increased output. Monolayer PLA bottles can be formed on the same injection-molding and stretch blow-molding equipment as used for PET, with no sacrifice in production rate.

Poly-L-lactic acid (PLLA) is formed by chemical condensation of lactic acid monomers; its breaking stress is about 47–70 MPa and its elongation 85–105%. PLLA could be used as packaging material, especially for garbage and shopping bags, wrappings, or fast-foods plates and cups. Nowadays, packaging manufactured from PLLA mainly consists of grocery and rubbish bags, coatings, six-pack rings, and fast-food containers.

Purac has invested in new lactides that should potentially provide the food, pharma, and cosmetics industries with cheaper and more effective bioplastic packaging. Netherlands-based Purac, a producer of lactic acid for the food sector, has stated that the new lactides will contain L-(+)- and D-(−)-lactic acids. The new lactides will be sold to companies that will use them to make bioplastics that can withstand greater heat than ever before. The new materials will be suitable for applications as diverse as hot-fill bottles, microwaveable trays, temperature-resistant fibers, and electronics, and will withstand temperatures of up to 175 °C.

In order to solve the problem of the inherent brittleness of poly(lactic acid) (PLA), which is due to poor elongation at break and impact strength, researchers at Michigan State University have recently developed biodegradable materials based on nanoscale hyperbranched organic particles (i.e., Boltrorn$^{\text{TM}}$ H2004 from the Swedish firm Perstorp) or on a poly(lactic acid) (PLA) matrix (i.e., Biomer® L9000 grade supplied by the German firm Biomer). This innovative modified PLA material exhibits an improvement in elongation at break of about 800 to 1000% in relation to traditional PLA grades with minimal impact on tensile strength and modulus.

NEC Corporation has developed a biodegradable plastic composite that is suitable for personal computer case applications. The composite material is made from poly(lactic acid) with fibers of the kenaf plant, a herbaceous annual related to cotton, incorporated to provide both increased strength and heat resistance. The material's heat resistance, processability, and strength are comparable to those of fiber-reinforced polycarbonate. It can withstand temperatures up to 120 °C before it begins to deform, which is 80% higher than normal poly(lactic acid). The material is also 70% stronger in terms of its ability to withstand bending forces. NEC plans to use the plastic in cases for its laptop computers and aims to have 10% of its line of laptops biodegradable by 2010. NEC uses commercial PLA sourced from several producers. The company has secured a source of kenaf fibers from Australia and is working to lower the manufacturing cost of the plastic.

Whereas scientists estimate that petroleum-based plastic products require thousands of years to decompose, PLA degrades under commercial composting conditions in 75 to 80 days. The compost can then be used to fertilize the next year's crop of corn, completing the cycle of a totally renewable resource. Since 2000, when NatureWorks PLA was introduced, the European market has been an early leader in adopting renewable resource-based products. Heightened environmental awareness in European countries, including Italy, France, Germany, Belgium, and the UK, has been the key for bringing nature-based plastics into the mainstream.

New BioPeel peelable lid film can be used for trays and pots. The film is made from corn-based PLA from the US-based NatureWorks, part of Cargill and one of the main movers behind the biodegradable packaging trend. The concept behind NatureWorks is relatively simple. Cargill essentially "harvests" the carbon from corn, which plants remove from the air during photosynthesis and store in grain starches. This is achieved by breaking down the starches into natural plant sugars. The carbon and other elements in these natural sugars are then used to make PLA through a simple process of fermentation, separation, and polymerization. Packaging made from NatureWorks is therefore 100 percent nature-based.

PLA is biodegradable and compostable and it can be free of genetically modified ingredients. PLA thus has wide appeal within the packaging industry, helping food packagers to meet EU waste targets. A few companies in the US (e.g., Naturally Iowa) have been using PLA for packaging of products such as organic milk.

BioPeel is a clear, peelable PLA lidding or flow-wrap film, suitable for use with chilled and frozen products such as fruit, vegetables, salads, and sandwiches. BioPeel has a broad sealing window and clarity, is available with antifog, and can be perforated. BioPeel can be tailored to seal and peel to any type of container.

The German-based BASF has also announced that it intends to launch a biodegradable plastic based on renewable raw materials in a bid to meet the growing demand for environmentally friendly packaging. BASF's Ecovio plastic is made up of 45% PLA from NatureWorks. Ecovio can be used to produce flexible films from which biodegradable carrier bags or other packaging can be made. Food packaging for products such as yogurt can be produced if other components are added to Ecovio. Biodegradable plastics are completely degraded within a few weeks under compositing conditions and may be produced from either petrochemical or renewable raw materials. The other component is the existing biodegradable plastic Ecoflex, which is derived from petrochemicals.

Huhtamäki Oyj, an international producer of consumption products packages, introduced BioWare products – disposals and one-use packages fabricated from

Figure 1.6 BioWare products (with permission of Huhtamäki Oyj).

renewable and compostable materials–as first on the market. BioWare is Huhtamäki Oyj's range of biodegradable products (Figure 1.6). BioWare fresh produce containers (drink cups and salad trays) are made from NatureWorks® corn starch biopolymers. The technology of NatureWorks® PLA is based on transformation of starch into natural sugars, with subsequent fermentation and separation; after composting the products are transformed into water, carbon dioxide, and organic materials. They can be processed on standard technological lines.

In the UK, Europackaging makes film bread bags from PLA. The bags allow steam to escape, so bakers can package items while still hot. A natural, biodegradable food packaging based on starch, called Starpol 2000, is also produced by the UK-based Stanelco.

Treofan uses PLA to make a packaging film branded as Biophan. The company intends to work on marketing Biophan to the food, cosmetics, and office materials markets and to promote Biophan as a film with "extraordinary" gloss and transparency, printability, and good sealing characteristics. Biophan laminated film is currently used for food packaging in the EU. The material is also being used for labels: for bottles in the US, for example. In an industrial composting plant, Biophan is completely transformed into carbon dioxide and water within 45 days.

1.4.3.3 **Cellulose-Based Packaging Materials**

Innovia Films produces the NatureFlex NVS line of films, which can be used for packaging of fresh foods. In addition to being biodegradable, the film is also compostable. It provides improved dimensional stability under chill conditions. This high-gloss film with enhanced transparency has inherent anti-static properties and is semipermeable to moisture, providing good anti-mist properties. NatureFlex films (Figure 1.7) are made from cellulose, which is derived from wood pulp from plantations operating under good forestry management standards. NatureFlex films also perform well on the packing line and have a wide heat sealing range–values from 70 °C to 200 °C are claimed. This means that the packaging film can be used on faster processing lines with no loss of seal performance. NatureFlex films are stiffer and more oriented than some other biopolymers,

Figure 1.7 NatureFlex film for vegetable wrapping (with permission of Innovia Films).

which makes them suitable for use on standard flow-wrap and form-fill-seal equipment, the company claims. They are also static-free for easier handling. Innovia is able to add specially formulated biodegradable coatings to the film, giving processors a choice of packaging with varying levels of thickness to meet the demands of different foodstuffs. The film is certified to meet both EU and US standards for compostable packaging. The film is first printed with the compostable logo and reference numbers before being micro-perforated, in order to tailor gas permeability to the products' requirements. The film can be used to flow-wrap a wide range of own-brand organic fruit and vegetables. NatureFlex NVS is currently available in 23 and 30 micron thicknesses.

A metalized biodegradable film targeting the confectionery business has been launched by Innovia Films. This is because biodegradable and recycled packaging may soon become viable alternatives for more food companies as the increasing price of plastics begins to be passed on by suppliers. NatureFlex NM is a unique cellulose-based film, manufactured from renewable wood pulp and metalized in-house. The film is printable with solvent and with water-based and UV inks and has an excellent luster and sheen for pack presentation. NatureFlex NM builds on the longstanding performance of cellulose film and has been designed to overcome the various issues commonly associated with polymeric films. The film is also static-free regardless of climatic conditions or contact with machinery or sugar dust. Not only does this mean that no static reduction equipment is required online, but it also prevents wrapped sweets from clinging to one another and to conveyor systems, which can often lead to unwrapped sweets. This anti-static performance, combined with the inherent stiffness of the film, also gives enhanced bag-fill, because products such as sweets do not slump to the bottom of a bag.

Biodegradable packaging material made from cellulose paper impregnated with wheat gluten boosts the shelf life of cultivated mushrooms, according to research conducted by scientists in Montpellier, France. The packaging is biodegradable, gas-selective, and permeable. Packaging of cultivated mushrooms with the material allows storage at 20 °C for four days, rather than for one day when using conventional synthetic film, according to France's Institute for Agronomy Research (INRA). Cultivated mushrooms packaged in trays give off high levels of moisture and are sensitive to carbon dioxide, both situations that rapidly give rise to opening of the cap and discoloration. The synthetic films currently used to package mushrooms in trays do not solve these problems. The poor permeability of synthetic films to water vapor causes condensation and the appearance of brown marks on the mushrooms. Preliminary studies by a sister unit in Avignon had demonstrated the usefulness of gluten films for the storage of plant products, enabling the maintenance of an atmosphere with low levels of both O_2 and carbon dioxide.

However, the weak mechanical properties of the materials did not allow their use for packaging. The use of paper as a substrate considerably improves the mechanical properties of the wheat gluten film, while still ensuring its biodegradability. Packaging of cultivated mushrooms with this composite material corresponds to "modified atmosphere packaging", providing an atmosphere containing low levels of both O_2 and carbon dioxide and preventing condensation.

The thermoplastic cellulose acetate Bioceta is a transparent granulate processed at 170 °C, and modified by addition of high amounts of liquid plant-based plasticizers to improve the complete biodegradability of acetylcellulose. Bioceta is slowly, but fully, biologically decomposed. Its forming can be accomplished by injection, pressing, or – in the case of film production – calendering or film blowing.

1.4.3.4 **Pullulan-Based Packaging Materials**

Pullulan is composed primarily of maltotriose units linked in α-1,6 fashion and is produced as an extracellular secondary metabolite of some fungi. Pullulan was commercialized in Japan as a food source, due to its natural origin, and has been accepted as a coating material for foods. It is a water-soluble polymer that provides transparent films of low oxygen permeability for foods. The film can be obtained by casting a 1–20% aqueous solution of pullulan on a metal plate roller, or, like starch, Pullulan can be molded with heat and pressure if a suitable amount of water is added as plasticizer [17, 82]. The challenge in biodegradable packaging materials is the development of completely biodegradable polymers for films or laminates with properties similar to those of synthetic polymers. For food applications pullulan can be use as a wrapping and as an edible film with limited oxygen permeability, with PHBV as an outside flexible cover with limited moisture permeability. The addition of pullulan to PHBV may reduce the oxygen permeability and improve product biodegradability because it increases the PHBV surface after the solution of pullulan in water.

Some other polysaccharides from cultivated plants are also being studied for film and coating production. One example of this is conjac flour from tubers of the perennial herb *Amorphophallus*, grown in Asia. The flour comprises around 1.6 mannose units to 1 glucose unit with β-1,4 linkages and randomly distributed acetyl groups. The polysaccharide is obtained as a flour termed Nuticol® conjac flour. Conjac flour (1%) is mixed with aqueous glycerol (1%) solution at 60 °C in the blender for 15 min and is then calendred into a film. Treatment of the conjac flour/glycerol mixture with 0.1% potassium carbonate or 0.2% sodium carbonate before casting can modify the film characteristics. Depending on the production process a film may be from transparent to opaque, from gelatinous to strong in hot water, and can demonstrate low to high tensile strength. The physical and chemical properties of the films have not been fully examined, but conjac flour has been recognized as safe according to the US Federal Food, Drug, and Cosmetic Act, so may in the future be used as food coating or packages [17].

ADM and Metabolix, a biotechnology company that has developed a form of PHA, intend to begin production of what they call a new generation of high-performance natural plastics. PHAs – polyhydroxyalkanoates – are polymers that are synthesized in the bodies of bacteria fed with glucose, such as corn sugar, in a fermentation plant. The process produces a range of plastics that are durable during use, but are compostable and biodegradable. ADM's plant will produce PHA natural plastics that have a wide variety of applications in products currently made from petrochemical plastics, including coated paper, film, and molded goods.

1.4.3.5 Other Bio-Packaging Solutions

Zip-Pak intends to feature a new line of biodegradable zippers, to allow film and bag converters to produce packaging that can help them meet the requirements with the convenience of a press-to-close format for easy storage. Brand owners can now specify zippered degradable packaging for food products such as produce, nuts, breads, and cheeses.

The packaging offered by RPC has been produced from PHAs – polyhydroxyalkanoates, polymers made from organic sugars and oils that break down in soil, composting installations, waste treatment processes, river water, and marine environments. The only products generated during decomposition are carbon dioxide and water. This means that, because these are the materials used to make the material, the life cycle is effectively a closed loop. The resulting moldings have, to date, proved to be far more heat-stable than the more familiar biodegradable polymer PLA, which according to RPC proves PHA's suitability for the cosmetics packaging market. The successful application of PHAs indicates that fully biodegradable cosmetics packaging can be a reality.

An example of a commercial biodegradable polyester is Biopol – a copolymer of hydroxybutyric and hydroxyvaleric acids, achieved during fermentation of sugars from sugar beet in the presence of bacteria that transform glucose into polymer. Biopol is one of the polymers with an ideal biodegradability profile, decomposing into carbon dioxide and water. Because of its stiff nature it is useful for bottles and canisters.

1.4.3.6 Partially Biodegradable Packaging Materials

In addition to completely biodegradable polymers, partly biodegradable polymers, such as mixtures of synthetic polymers with added starch, are also presented. The disadvantage of these materials is that only the starch is biodegradable and the rest is dissipated in the environment. The degradation of the synthetic film can be accelerated by means of starch used as filling. Low Density Polyethylene (LDPE) blends containing up to 10% maize starch have been produced by conventional techniques and the end products were used in bags for shopping or rubbish [83].

A challenge in the field of biodegradable packaging development is the combination of truly biodegradable polymers into blends of films or laminate films with qualities as good as in synthetic laminates. For instance, for food use, products may be coated with pullulan, an edible material of very low oxygen permeability and utilized as an outer packaging of high flexibility, thus acting as a moisture barrier. Pullulan film can be produced because it and the blending polymer can both undergo the same processing when melted under controlled moisture conditions. Pullulan as an additive reduces oxygen permeability. Some biopolymers based on polysaccharides are applied as coating materials or packaging films. They include starch, pullulan, and chitosan.

The Danish-based Danisco produces an additive from hardened castor oil and acetic acid. It is colorless, odorless, and completely biodegradable. The Toronto-based Diamant originally marketed its polystyrene-based stretch film as a non-plasticized food wrap that was eco-friendly and recyclable. The company developed the technology over the course of ten years as an alternative to PVC. Bioplastics were formed to develop and acquire new products and technologies for the manufacturing of totally biodegradable products. Diamant uses EPI Environmental Technologies' TDPA (Totally Degradable Plastic Additive) product for manufacturing the pallet wrap. When incorporated into commodity plastic resins, such as polypropylene (PP), polyethylene (PE) and polystyrene (PS), the TDPA additives render the plastics degradable and ultimately biodegradable. This product will degrade and ultimately biodegrade, and once biodegrading is complete all that remains is carbon dioxide, water, and biomass, all which are part of the normal biocycle.

The Californian-based company Cereplast claims that its biopropylene resin is an industry first and could replace traditional polypropylene in the vast majority of applications. These bio-resins replace a significant portion of petroleum-based additives with materials such as starches from tapioca, corn, wheat, and potatoes, meeting the demand from consumers and manufacturers for sustainable plastics. Also notable is Cereplast's already existing line in compostable resins in which bio-based starch products, such as corn, wheat, and potato starches, replace nearly 100 percent of petroleum-based additives. This results in products that will compost in commercial facilities within 180 days, leaving no chemical residue.

Cereplast Compostables® resins are renewable, ecologically sound substitutes for petroleum-based plastic products, replacing nearly 100% of the petroleum-based additives used in traditional plastics (Figure 1.8). Cereplast Compostables® resins are starch-based, made from corn, wheat, tapioca, and potato starches that come primarily from the Midwest. Resin manufacturing begins once the Cereplast production team has selected the right biopolymer matrix made from renewable, cost-stable resources. These biopolymers include poly(lactic acid) (PLA), soy proteins, PHA, PHBs, or starch from corn, wheat, or potatoes. The selected biopolymer is blended with other biodegradable components to reinforce its molecular

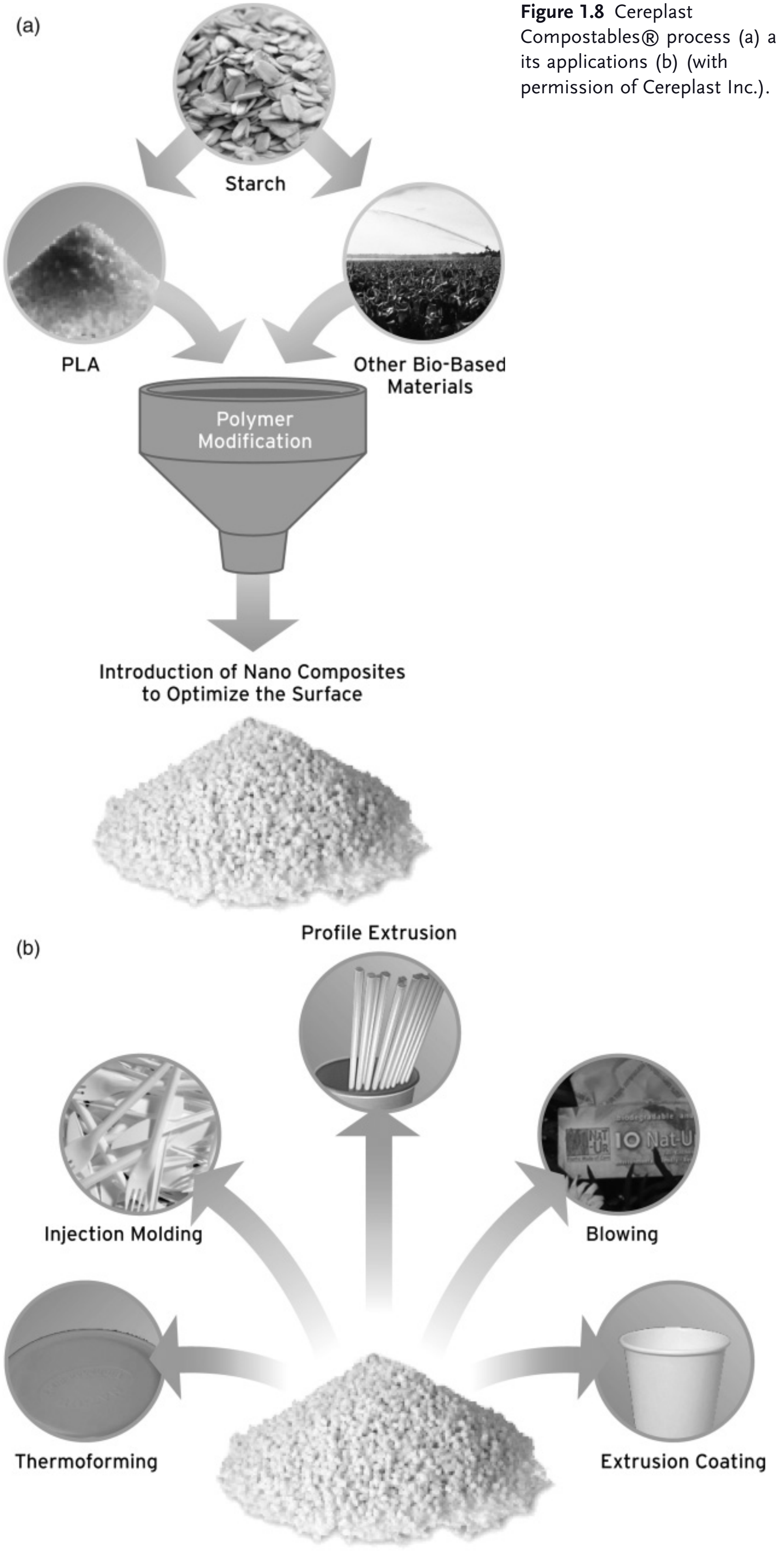


Figure 1.8 Cereplast Compostables® process (a) and its applications (b) (with permission of Cereplast Inc.).

structure through a proprietary process developed by Cereplast. The blend is then polymerized and treated with nano-composites for surface optimization and further reinforcement. The entire green composite process is high-speed and low-cost. The final product is then packaged and shipped to converters, which are able to process the resin using traditional equipment. Cereplast manufactures ten grades of resins for various applications: injection-molding, extrusion, and more. Cereplast proprietary resins are a cost-competitive alternative to traditional fossil-fuel-based resins. Cereplast can be substituted in a wide range of applications for manufacturing. There are currently 12 resin formulations available to manufacturers. All Cereplast resins are made from renewable resources and are certified as 100% compostable.

Cereplast Hybrid Resins^{TM} products are bio-based, with 50% or more of the petroleum content in traditional plastic products being replaced with bio-based materials such as starches from corn, tapioca, wheat, and potatoes. Cereplast Hybrid Resins^{TM} products can be processed with the same cycle times as traditional plastics, but require less energy in the production process thanks to the use of significantly lower machine temperatures. The first product from the Cereplast Hybrid Resins^{TM} family (Biopolyolefins^{TM}) is Biopropylene 50^{TM} (CP-BIO-PP-50), a 50% petroleum and 50% starch-based resin exhibiting physical characteristics similar to those of traditional polypropylene. Biopropylene^{TM} resin can be used in a variety of manufacturing processing including injection-molding, thermoforming, profile extrusion, and extrusion blow-molding.

The Harvest Collection^{TM} from Genpak (USA) is a new and exciting line of compostable plates, compostable food containers, and compostable cups produced from naturally occurring, annually renewable resources such as corn, rice, and wheat. They will completely compost and biodegrade in a commercially run composting facility. The compostable products in the Harvest Collection^{TM} line look and feel just like traditional top-of-the-line plastic items, but have the added benefit of being produced from annually renewable resources. The Harvest Collection offers a wide variety of biodegradable products including compostable food containers, compostable cups, and compostable dinnerware items for food service applications.

Starch mixed with polyethene is also known as biobased (hydrodegradable) material and reaches the American Standards for Testing Materials as well as the European norms for compostability degrading in 60% under 180 days.

Polymers that usually use starch are polycaprolactone (PCL), polyvinyl alcohol (PVA), and poly(lactic acid) (PLA), all used to control the microbial breakdown, only allowing breakdown in the presence of microbes, heat, moisture, and proper aeration, such as those conditions found in traditional compost piles. Additive-based plastic bags, on the other hand, are our traditional plastic bag films with a special chemical adjustment so as to make them breakdown more readily under certain conditions. In the first stages of decomposition, oxygen, light, heat, and/or stress react on a molecular level, fragmenting the film in such a way that water can wet and surround its molecules, thus making it readily biodegradable, leaving only CO_2, water, and biomass once microorganisms get a hold of it. These oxodegradable/photodegradable plastic bags may make things easier without causing much change in the consumer's lifestyle today and right now cost a little less.

Nowadays, industrial processing of partly biodegradable polymers containing starch includes: Mater-Bi by Novamont, Bioplast by Biotec, Greenpol and Eslon Green by Yukong LTD and Cheil Synthetics Int., Starpol 2000 by the UK-based Stanelco, Cargill's NatureWorks, and many others.

1.4.3.7 **Protective Loose-Fill Foams**

As an alternative to very popular polymer foams such as expanded polystyrene (EPS), loose-fill (foamed chips for filling space around goods within a packing box) extruded from thermoplastic starch is probably the most successful application of starch-based material in cushion packaging. Starch-based loose-fill foams are biodegradable and have competed well with EPS-based loose-fill even though starch-based loose-fill costs approximately $21 per cubic meter delivered, which is about 30% higher than the price of EPS-based loose-fill [84]. Several patents relating to extruded foams based on starch and blends of starch with various additives have been filed [85–88] and the material is commercially available. Considerable effort has been made to study the influence of extrusion conditions, moisture content, and composition on the physical properties of starch-based foams [84, 89, 90].

Extruded starch foams are generally water-soluble, and their properties are sensitive to moisture content. Greatest expansion and lowest densities are generally achieved through the use of modified high-amylase starches. Various synthetic polymers, such as poly(vinyl alcohol) or polycaprolactone, have been blended with unmodified starches to produce foams with lower densities and increased water resistance.

Although the use of starch in loose-fill products gives advantages in the form of biodegradability and environmental protection, these products have been criticized for their imperfection in relation to EPS loose-fill products. EPS- and starch-based foams have differences, but the differences do not compromise performance.

These products differ with respect to composition and method of manufacture. Foam and bulk densities, which are higher than those of EPS-based foams by factors of two to three, are attributable to the density of starch, which is 50% higher than that of polystyrene homopolymer, and to the direct water-to-steam expansion process, which creates a predominately open cellular structure that stops foam expansion. Starch-based foam loose-fill is very hygroscopic. The foam densities of starch-based products significantly increase, between 10 and 30%, after conditioning at high humidity.

The compressive stresses of most starch-based foams do not differ significantly from those of EPS products. Chemically modified starches gives foams with good retention of compressive stress over a broad humidity range.

The resiliencies of starch-based foams, with values between 69.5 and 71.2%, are, as a group, about 10% lower on a relative basis than those of EPS foams. Although starch-based foams absorb 13 to 16 wt% moisture after conditioning at 80% r.h. (relative humidity) and 23 °C, these products retain between 62 and 67% resiliency.

Fragmentation of both starch- and EPS-based foam amounts to 2 to 6 wt%, but starch-based foams break down into fine dust, whereas EPS-based foams break into large fragments.

All starch-based foams have significantly higher foam and bulk densities and open-cell and moisture contents than EPS-based foams. Both product types have similar compressive stresses, resiliencies, and friabilities. Starch-based foams are more sensitive to changes in relative humidity and temperature than EPS-based foams, but the larger amounts of absorbed moisture do not compromise mechanical integrity.

Generally, extrusion techniques can be successfully employed for production of starch-based foams. The physical properties of loose-fills, such as density, porosity, cell structure, water absorption characteristics, and mechanical properties, are highly dependent on the raw materials and additives. The mechanical behavior of foamed pellets can be adjusted effectively by controlling the cell structure through use of different additives. At room temperature and 50% relative humidity, some mechanical properties, such as compressive strength or compressive modulus of elasticity, are comparable to those of commercial EPS foams.

Starch-based foams can be prepared from different starch sources, with 70% of the polystyrene being replaceable with biopolymer starch. Functional starch-based plastic foams can be prepared from different starch sources, depending on their availability.

Starch-based foams with polymer addition (e.g., PS, PM, PHEE) show improved properties in comparison with 100% starch foams. The addition of polymers significantly increases radial expansion and gives low-density foams. Compressive strength depends primarily on foam density, and not on starch type or polymer structure. Friability is reduced when polymer is present in the foam.

PLA/starch foams can be successfully prepared by using water as a blowing agent in the presence of talc, which acts as an effective nucleation agent. Water is a good blowing agent for the PLA/starch system. Talc at 2% gives the PLA/starch foam a fine foam cell size and uniform cell size distribution.

The addition of Mater-Bi® affects the foam expansion characteristics. High levels of MBI result in low radial expansions and high densities. The resiliency improves as the levels of MBI and moisture contents are increased. The MBI-starch foams have the potential to be used as an environmentally friendly loose-fill packaging material.

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2
Blends of Natural and Synthetic Polymers

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2.1
Introduction

In recent times, biodegradable materials have been growing in importance, particularly for the protection of the environment from ever-increasing plastic waste. The use of partially biodegradable polymers obtained through the blending of biodegradable and non-biodegradable commercial polymers can effectively reduce the volume of plastic waste thanks to partial degradation. The reasoning behind the approach for blends of starchy biodegradable polymers with inert polymers, such as PE, is that if the biodegradable component is present in sufficient amounts, and if it is removed by microorganisms in the waste disposal environment, the plastic or film containing the remaining inert components should then disintegrate and disappear.

The biodegradable products market and its perspectives are closely monitored by the different groups involved. According to a new technical market research report from BCC Research [1], the global market for biodegradable polymers reached 245 million kg in 2007. This market is expected to increase to over 545 million kg by 2012, with a compound average annual growth rate (CAGR) of 17.3%. The report breaks the market down into the separate applications of compost bags, loose-fill packaging, and other packaging, including medical/hygiene products, agricultural, and paper coatings and miscellaneous (Table 2.1). Currently the compost bags have the largest share of the market. At nearly 110 million kg in 2007, this segment is expected to reach 266 million kg by 2012, with a CAGR of 19.4%. Loose-filled packaging has the second largest share of the market, with production estimated at 73 million kg in 2007 and set to reach 97 million kg by 2012. The third largest segment, other packaging, is currently a 37 million kg segment predicted to reach 105 million kg by 2012, for a CAGR of 23.4%. BCC Research explains that growth rates are very high because the base volumes of biodegradable polymers are still relatively low in comparison with petrochemical-based polymers.

The loose-fill packaging growth rate is mainly attributable to two factors: lack of an effective infrastructure for disposal, and the popularity of air-filled plastics and

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Table 2.1 Global biodegradable polymer market by application – million kg (million lbs.)[1].

Application	2006	2007	2012	CAGR% (2007–2012)
Compost Bags	78 (173)	110 (242)	266 (586)	19.4
Loose-Fill Packaging	69 (152)	73 (162)	97 (214)	5.7
Other Packaging[a]	23 (51)	37 (81)	105 (232)	23.4
Miscellaneous[b]	15 (33)	25 (56)	78 (171)	25.0
Total	186 (409)	245 (541)	545 (1203)	17.3

a Includes medical/hygiene products, agricultural, paper coatings, etc.
b Unidentified biodegradable polymers.

other materials for packaging. The biodegradable polymer market, although commercial for over 20 years, is still at a very early stage in its product life cycle. This market still has several major problems, the most important of which are relatively high prices and lack of an infrastructure for effective composting – an extremely critical aspect for biodegradable polymer market success. The North American biodegradable polymer market has not progressed as rapidly as in Europe and Asia, but is now beginning to show its potential. Major drivers for the U.S. market would be mandated legislation and prospective increases in landfill pricing – none of which are foreseen within the next five years, although recent increases in petroleum-based plastics have rekindled interest in biodegradable polymers.

2.2
Starch in Blends with Polymers

There exist an important number of biodegradable polymers (biopolymers) that are derived from both synthetic and natural sources. The utilization of agricultural products in plastic applications is considered an interesting way to reduce surplus farm products and to develop non-food applications.

Thermoplastic starch (TPS) or plasticized starch (PLS) is processed, like synthetic plastics, through extrusion and injection units [2]. Unfortunately, TPS is a very hydrophilic product, and additional processing of starch to reduce the hydrophilic character of the starch chains is sometimes necessary. There are some strict limitations to the development of starch-based products, due to its poor mechanical properties and high sensitivity to moisture. Starch is a very common, environmentally friendly, biopolymer. Raw, granular starch comes from a variety of sources, including corn, wheat, rice, and potatoes; wheat and rice granular starch tends to be the least expensive. However, pure starch is brittle and rapidly degrades when exposed to water. In efforts to overcome this disadvantage, there have been many attempts to combine starch with synthetic polymers. If starch were used as an additive in blends with polymers, it should not only increase their biodegradability, but should also make them less expensive to synthesize. Mixtures of starch and polymers have resulted, however, in materials with poor physical qualities. The starch generally does not mix well with the polymers. In attempts to improve the mixtures, some researchers have used high-amylose starch [3]. Although high-amylose starch slightly improves the physical properties of the mixtures, it is relatively expensive and so reduces or eliminates the cost benefits of these mixtures. Gelatinized starch obtained from processing of raw starch has also been used in attempts to improve these mixtures. However, both gelatinized starch and high-amylose starch require the addition of a plasticizer (e.g., glycerol), and this poses another disadvantage: as well as requiring processing of the starch, it increases the cost. In addition, plasticizers such as glycerol increase the water absorption of polymer/starch mixtures. The addition of glycerol (plasticizer) not only damages the mechanical properties of starch-filled PE but also has a negative effect on the mechanical properties of starch-filled PE after storage, because glycerol is not compatible with PE.

Starch and more hydrophobic compounds such as biodegradable polyester are rather immiscible, and mixing produces blends with separated phases with poor interfacial properties. One strategy to overcome these weaknesses is to associate the starch with a moisture-resistant polymer with good mechanical properties, while maintaining the overall biodegradability of the product. Moisture sensitivity and critical aging have led to the necessity to associate TPS with other biopolymers, to preserve the biodegradabilities of the final blends. Association between polymers can be in the form either of blends or of multilayer products. Multilayers can be obtained by coating or by coextrusion processes; multilayer coextrusion has been widely used in the past decades to combine the properties of two or more polymers into one single multilayered structure. The preparation of starch-based multilayers may also be carried out through compression molding of plasticized starch and polyesters. These considerable research efforts have led to starch-based blends being commercialized, by Mater-Bi from Novamont (Italy) or by Bioplast from Biotec (Germany) [2]. To produce these commercial starch blends, starch can be blended either with non-biodegradable polymers (polyolefins) or with biodegradable polyesters (e.g., PCL). Applications involve packaging, disposable cutlery, gardening, leisure, hygiene, and the like.

Most research is focused on the blending of PLS with biodegradable polyesters: PCL (polycaprolactone), PEA (polyesteramide), PHBV (polyhydroxybutyrate co-hydroxyvalerates), PHBO (polyhydroxybutyrate co-hydroxyoctonoate), PBSA (poly(butylene succinate/adipate)), PBAT (poly(butylene adipateco-terephthalate)), PLA (poly(lactic acid)), or PHEE (poly(hydroxy ester ether)) [3–5]. These commercially available polyesters show some interesting and reproducible properties, such as more hydrophobic characters, lower water permeabilities, and some improved mechanical properties, relative to PLS. The preparation of the blends is the main factor affecting their properties and their behavior during processing. The solid-state properties of the blends depend on the nature of the polyester phase. At ambient temperature, polyesters can be rigid (e.g., PLA) or soft (e.g., PCL, PBSA, PBAT), so the corresponding mechanical properties are tunable. Research results have shown that PEA presents the highest surface tension, because of the highly polar component, and PLA the lowest. These different determinations allow the establishment of a classification from the least compatible (PLA) to the most compatible polyesters (PEA). However, low compatibility induces special behavior and properties: during the injection molding process, a preferential migration of the polyester, the low-viscosity polymer, toward the mold surface was observed. After cooling, a polyester-rich skin and a starchy core can be obtained.

PLS has been widely used in blends with other polymers, and a lot of patents have been published on this topic. This stratified pseudo-multilayer structure gives the blend rather good water resistance, in comparison with PLS itself, due to the polyester surface protection. Water sensitivity, determined by contact angle measurements with water drops, decreases drastically for polyester contents lower than 10% in the blend. The biodegradabilities of such blends are modified, with degradation occurring from the starchy core toward the skin.

A provisional patent application proposed by Wang *et al.* [6] presents biodegradable materials from starch-grafted polymers cross-reference to related applications. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polybutylene (PB), poly (styrene-ethylene-butylene styrene) (SEBS), polyvinyl fluoride (PVF), polyvinyl chloride (PVC), and poly(ethylene terephthalate) (PET) are some of the more common plastics. They are non-biodegradable and are generally synthesized from petroleum products. Several alternative materials to replace these plastic polymers have been investigated. Different starch varieties include high-amylose starch, processed starch such as gelatinized starch and starch ethers and esters may also be used. The innovation requires only granular starch and provides a blend that has physical characteristics very similar to those of the pure polymer. Furthermore, it is claimed that any type of starch is usable, including wheat and rice starch. The capacity to use these inexpensive types of starch greatly enhances the cost efficiency of the invention. With use of granular starch, no additional processing step is needed to prepare plasticized or gelatinized starch. The starch can be from different sources, such as corn, rice, and potato, and can be in either modified or unmodified form. PE can also be of different types, such as linear low-density PE (LDPE) or high-density PE (HDPE). It is also very important to note that the use of starch to replace PE significantly (–15%) reduces production costs.

The patent [6] relates to mixing of starch with a primary polymer and a compatibilizer that has grafted compounds attached to it. These grafting compounds covalently bond to the hydroxyl groups located on granular starch. Starch hydroxyl groups are susceptible to binding by these grafting compounds. Because the starch is chemically grafted to the compatibilizer, which in turn physically interacts with the polymer, the resulting mixture has substantially the same physical properties as the polymer in its pure form. Up to 30% of the mixture may be granular starch. In addition, the starch greatly enhances the biodegradability of the mixture. Polymers with grafting compounds already attached to them are presently commercially available and are only slightly more expensive than the unaltered polymers.

Granule size may vary greatly without significantly affecting the physical properties of the invention. Although granules of approximately 25 micrometers in diameter are preferred, large variations in granule diameter have only a minimal effect on the physical properties of the end product. Different starches are more plentiful in different parts of the world, so the ability of the invention to utilize a variety of starches is highly advantageous. Starches such as those derived from wheat, corn, rice, and potatoes are only some of the many starches that are suitable.

U.S. Patent No. 6218532 [7] discusses a method of synthesizing materials from amylose starch derivatives. The starch is chemically modified to form starch ethers or esters. No cross-linking of starch to polyethylene occurs. Amylose derivatives with various degrees of substitution and amylose/amylopectin ratios can be used. These chains are chemically cross-linked and are then mechanically stretched to produce a biodegradable and mechanically superior material. Specifically, the process involves starch derivatives such as starch ethers and starch esters. It is claimed that the polymers have degrees of substitution from about 35% to about 95% (degree of substitution is from about 1.05 to about 2.85) and preferably have degrees of substitution from about 1.95 to about 2.70. The starch derivatives are cross-linked to produce permanent entanglements and are processed into sheets, films, fibers, threads, or other articles. After processing, the articles are swollen to the desired volumes in thermodynamically acceptable solvents or solvent mixtures and are deformed in uniaxial or biaxial extensions. The polymer materials are preferably stretched from about 1% to about 500%. Finally, the solvents are removed, yielding homogeneous, highly-ordered materials. The associated increase in van der Waals bonding between the molecules improves the quality of sheets, films, fibers, threads, or other articles with respect to their mechanical properties.

Mixing of starch with a hydrophilic biodegradable polymer–such as polyethylene oxide, for instance–does not need the use of a compatibilizer for covalent attachment of polyethylene to granular starch [8]. For conversion of native starch or starch derivatives into thermoplastic starch, at least one hydrophilic biodegradable polymer has to be added. This hydrophilic biodegradable polymer, which serves as a plasticizer or swelling agent, may be a polymer selected from the following list: an aliphatic polyester, a copolyester with aliphatic and aromatic blocks, a polyester amide, a polyester urethane, a polyethylene oxide polymer and/or a polyglycol, and/or mixtures of these. When the starch, such as in particulate native starch or derivatives thereof, is mixed in the melt with the hydrophilic biodegradable polymer as a plasticizer or swelling agent, to homogenize the mixture, the water content is reduced to <1% by weight based on the weight of the mixture.

Starch polymer can also have polyester grafted onto it [9]. Such a polyester-grafted starch/polymer alloy is capable of imparting practical flexibility and toughness to moldings with no or only a little plasticizer. The polyester-grafted starch/polymer alloy comprises a blend of a polyester-grafted starch (a starch which has polyester graft chains on the starch molecule, with the terminal hydroxyl groups of the polyester graft chains and the hydroxyl groups connected directly to the starch entirely or partly blocked with the ester group) and an independent polyester (a polyester constructed of the same unit as said polyester graft chain, with its terminal hydroxyl groups entirely or partly blocked with the ester group) which are uniformly mixed together. A method of preparing the alloy and thermoplastic resin compositions containing the alloy are also disclosed.

U.S. Patent No. 5569692 [10] describes a starch-based composition for the production of articles of biodegradable plastic materials. The starch is heated with a destructuring agent in order to destructure the starch. It is then mixed with a polymer, preferably polyvinyl alcohol or ethylene vinyl alcohol. This patent does not mention covalent grafting of granular starch onto polyethylene. In order to prepare a starch-based composition usable for the production of articles of biodegradable plastics material, starch is mixed in a heated extruder with a plasticizer with high boiling temperature. A destructuring agent is added for a time sufficient to cause the starch to be destructured. The process temperature should be below the boiling point of the plasticizer and between 120–170 °C. The composition thus obtained is particularly suitable for the formulation of mixtures with polymers of relatively high melting points, because it can be processed at temperatures higher than 120 °C and is suitable for extrusion at low pressure. In particular, compositions thus obtained and mixed with polyvinyl alcohol and/or ethylene vinyl alcohol are suitable for the formation of films by blowing, since they have the desired characteristics of mechanical strength and resistance to tearing and perforation, or for the formation of articles finished by injection molding, thermoforming, or mold blowing.

The most popular method for processing of starch/polymer blends is injection molding for rigid biodegradable products, because of high production rates and accurate product size. During flow, a polymeric material is simultaneously subjected to mechanical and thermal influences, and depending on the morphology, introduces orientation under residual stress. Shrinkage in injection-molded products affects the physical properties and dimensional stabilities of the finished products.

Biodegradable PLS-based multilayer films are useful for packaging or coatings. Multilayer structures present some advantages over blends. Moisture sensitivity is not fully addressed in a blend because of the presence of starchy material close to the surface. Better resistance to moisture in starch-based products can thus be achieved by use of multilayers, allowing the preparation of sandwich-type structures with PLS as the central layer and a hydrophobic component as the surface outer layers. These blends can, for instance, be obtained by different processes – that is, coextrusion, casting, and hot-melt techniques – to protect starch-based materials with waxy layers. Stratified materials can also be obtained by a multistep process based on compression molding. Instances of coating have also been mentioned in the literature. Coating has been achieved by spraying or painting solutions made from biodegradable polyester onto the starch-based material.

Coextrusion seems the best option, because it offers the advantages of being a one-step, continuous, and versatile process [11]. Multilayer coextrusion has been widely used in the past decades to combine the properties of two or more polymers in one single multilayered structure. However, some problems inherent to the multiphasic nature of the flow are likely to occur during coextrusion operations;

these include non-uniform layer distribution, encapsulation, and interfacial instabilities, which are critical because they directly affect the quality and functionality of the multilayer products. Layer encapsulation is essentially the surrounding of the more viscous polymer by the less viscous one. Different stratified structures have been processed by coextrusion and studied: with PCL, PBSA, PEA, PLA, PBAT, or with PHBV. Some research into PLS/PEA/PLS systems has shown that the key parameters are the skin-layer viscosity and thickness, the global extrusion rate, and the die geometry after determination of the stable and unstable flow conditions [6]. The occurrence of instabilities is strongly related to the shear stress at the interface.

2.3
Mechanical Properties of Starch/Polymer Blends

In recent years there has been significant interest in the development of materials from blends of natural and synthetic polymers such as PE or EVOH (ethylene-vinyl-alcohol). To maintain the compostability feature, different biodegradable blends have been developed. These blends can be processed into useful disposable end products with potential to alleviate disposal problems by degrading in selective environments. The mechanical properties of polymer blends depend greatly on the adhesion of the different phases. Poor interfacial adhesion leads to lower ultimate properties, whereas strong interfacial adhesion leads to good mechanical properties and reduced molecular mobility.

There are two fundamental types of transient experiments that can be used to assess viscoelastic properties over time: these are stress relaxation and creep. In the stress relaxation mode, the time decay of stress at a constant strain can be determined; in creep the decrease in strain with constant stress can be investigated. The stress relaxation experiments are useful in predicting the long-term mechanical behavior of materials from short-time experiments.

The primarily studied partially biodegradable starch-based polymer blends are based on polyolefins. Griffin [12] found a biodegradable composition containing a high proportion (over 50%) of biodegradable starch. He proposed a process for making LDPE blown films containing native or modified starch such as thermoplastic starch or plasticized starch and antioxidants such as unsaturated fatty acids and their derivatives. The composition is particularly useful for making trays for meat packaging. These trays are liquid-repellant but gas-permeable.

The mechanical properties and biodegradation of starch/PE blends have been studied extensively. Generally the starch/polyolefin blends are incompatible, and as a result they have larger phase domains than those in a compatible blend. Larger nondegradable residues are therefore produced and can further give rise to secondary pollution in the natural environment. In addition, this incompatibility also leads to poorer mechanical properties. For these reasons, the modification of starch can be advantageous, because smaller domain sizes in the blends can be obtained.

Thakore *et al.* [13] presented results relating to the use of up to 30% of potato starch and stath (starch phthalate) blends with LDPE for injection molding with a comparison of morphologies of specimens by SME microscopy. The rough surface that a starch granule exhibits after esterification provides a site for better adhesion and anchoring, so starch phthalate acts as a better filler than starch. The morphology of a tensile-fractured surface of LDPE shows a uniform continuous matrix. However, the SME pictures of a 70:30 LDPE/starch blend showed voids due to the partial removal of loosely embedded starch granules. This causes phase separation in spite of good dispersion, leading to poor tensile properties for these blends. On the other hand, the morphologies of corresponding LDPE and esterified starch (starch phthalate) blends showed stath particles uniformly distributed and firmly embedded into the LDPE matrix. In addition, the two phases were not easily distinguishable as in the case of LDPE/starch blends. Most of the blends showed lower tensile strength and percentage elongation than LDPE (9.92 MPa and 92.5%, respectively). An increasing percentage of biodegradable component in the blend resulted in decreases both in tensile strength and in elongation at break, although when a proportion of the starch was replaced by stath these properties were both improved. Esterification of starch leads to improvements in its thermoplastic character, thermal stability, hydrophobicity, and crystallinity, so LDPE/stath blends showed better mechanical, thermal, and morphological properties, as well as better biodegradation.

Martin *et al.* [11] reported on the effects of the adhesion strength between the layers on properties of multilayer films. Parameters that affected this adhesion were, among others, polyester type (PCL, PBSA, PEA, PLA, and PHBV) and plasticizer (glycerol) content. The polymers were chosen as the outer layers of the stratified “polyester/plasticized wheat starch/polyester” film structure. The main purpose of the polyester layers was to improve the properties of plasticized wheat starch (PWS) significantly in terms of mechanical performance and moisture resistance. Starchy films (65:35 starch/glycerol ratio) showed elongations at break of 109%, whereas the addition of polyesters increased the elongations at break from 122 to 179% and the tensile strengths from 2.1 for starchy film to 12.3 MPa when polyesters were added. Polyesteramide showed the best adhesion to the PWS layer, which can be attributed to its polar amide groups. PCL and PBSA showed medium adhesion values, and PLA or PHBV were the least compatible polyesters. The same trend in the magnitude of adhesion strength was observed between coextruded and hot-pressed multilayers. It was possible to increase the adhesion properties of the film by up to 50%. This could be achieved by use of polyester blends in the cap layer or PWS/polyester blends in the central layer. Finally, the presence of a polyester cap layer slightly improved the mechanical properties of plasticized starch. These multilayers also have satisfactory water resistance properties [11]. Blending PWS with these polyesters resulted in significant improvements in the properties of plasticized starch, but coating should be preferred.

Walker *et al.* [14] reported on the application of a mechanical process called solid-state shear pulverization (SSSP), creating blends and composites of polyethylene (PE) and damaged starch granules. Starch granules are generally unchanged when polymer/starch blends are made by melt mixing, and this is the first time that damage (surface roughening, cracking, and clustering) of the starch granule has been reported. The damaging of the starch granule reduces the oxygen permeability. In a 70:30% PE:starch mixture processed by SSSP the permeability was reduced by 29%, in comparison with 21% permeability reduction when melt processing was used and the starch particles were not damaged.

Liu *et al.* [15] tested starch-filled polypropylene (PP) and reported the effect of starch granule size on the crystallization behavior of PP. Differential scanning calorimetry and scanning electron microscopy were used to monitor the changes in energy of crystallization and to characterize the morphologies of PP/starch composites. Little interaction between starch and PP was observed despite the variation in starch granule size. The crystallization temperature of PP decreased with the addition of starch and this decrease became more apparent with increasing starch granule size. The addition of starch also decreased the overall crystallization rate of PP, which can be attributed to an increase in the activation energy of crystallization under nonisothermal conditions. An increase in the size of the starch granules increases the crystallization activation energy of PP and consequently decreases its crystallization rate.

Averous [16] tested biodegradable PLS-based blends that can be useful as fillers in different petroleum polymers. Blending is an easy process by which to obtain materials with improved property/cost performances. This approach is cheaper than the development of new polymers. In addition, blends can be used as models for testing the compatibility between polymeric phases, because a blend presents a large interfacial surface in comparison with, for example, multilayer structures.

Averous *et al.* [17] presented results obtained with different compositions of wheat thermoplastic starch (TPS) and polycaprolactone (PCL) on melt blending by extrusion and injection molding. A large range of blends with different glycerol contents and different starches (wheat starch and PCL) was analyzed. They noted fairly low compatibility between the two polymeric systems, but the addition even of small amounts of PCL to TPS (10%) overcomes the weaknesses of pure TPS: low resilience, high moisture sensitivity, and high shrinkage.

Battachaya [18] processed starch and synthetic polymer blends compounded in a co-rotating extruder. Each blend contained 70% starch, 5% functionalized polymer (HDPEMA, EMA, or EVAMA), and 25% non-functionalized synthetic polymer (high-density polyethylene (HPDE), low-density polyethylene (LDPE), or ethylene vinyl acetate (EVA)). Starch was also blended in amounts of 15%, 30%, 50%, and 60% with synthetic polymer and a compatibilizer was kept constant at a 5% level for all blends. To obtain test samples, all materials were processed by injection molding in the 80–150 °C temperature range. A small amount of maleic anhydride-functionalized synthetic polymers (5% by weight) was added to compatibilize the starch and the synthetic polymer. Starch/HDPE and starch/LDPE blends exhibited stress–strain curves similar to those of ductile polymers, whereas with starch/EVA blends the material was more rubbery. The elastic moduli of starch/HDPE and starch/LDPE blends range between 450 and 550 MPa for the various types of starch (70% starch content), whereas for starch/EVA blends the elastic moduli ranged from 80 to 110 MPa. As the starch content is increased, the moduli of the blends increase while the elongations at break decrease. Starch/HDPE and starch/LPDE blends showed ductile behavior, whereas starch/EVA blends displayed rubbery characteristics. Blends containing EVA relaxed most rapidly, whereas those containing LPDE took the longest times. The longer relaxation times of LDPE or HDPE blends are probably due to the crystallinities of these synthetic polymers. The slightly longer time required for LDPE melts to relax to a particular reduced stress level could be due to the lower mold temperature (40 °C for LDPE blends as opposed to 45 °C for HDPE blends). In general, as the amylose content in the blend increased, the time taken for the material to relax increased. This is due to the fact that amylose, which is the linear fraction in starch, experiences greater interaction with the anhydride group in the synthetic polymer. Starch/EVA blends showed the fastest relaxation, whereas blends containing LDPE had the slowest.

Blends of recycled LDPE with corn starch have two environmental advantages:

- virgin synthetic thermoplastic material can be substituted by post-consumer materials, and
- the end product can be biodegradable and cheap.

Recycled LDPE/corn starch blends containing 30, 40 and 50 wt% starch were prepared by extrusion [19]. The addition of starch to LDPE reduced the melt flow index values, the tensile strengths, and the elongations at break, whereas the moduli increased. The decreases in the melt flow index and tensile properties were most evident when 40 and 50 wt% starch was added. SEM showed that the interfacial interaction was weak for blends containing virgin and recycled LDPE.

Remkumar *et al.* [20] evaluated the mechanical properties of various compositions of starch/PE blends with addition of EVA (ethylene vinyl acetate), EVAMA (ethylene vinyl acetate maleic anhydride), and EMA (ethylene maleic anhydride), and also with addition of cellulose fibers. The blends were melted in an extruder and were then injection-molded under different conditions. Tensile testing and flexural testing were performed. The corn starch/EMA blends had higher tensile strengths (8.6–11.2 MPa) and were brittle in relation to corn starch/PE blends. Both EMA and PE had comparable elongation and tensile strengths. Blends containing corn starch had higher tensile strengths (9% higher) than wheat starch blends, but elongation of blends containing corn starch was approximately 33% lower. The addition of fibers increased the tensile strength but not the flexural strengths. The mechanical properties of starch/EMA blends were better than those of starch/EVAMA blends.

Park *et al.* [5] presented the first report on blends of potato starch with commonly used plastics such as LDPE and the aliphatic polyester APES (starch/aliphatic polyester, chemical name: poly-(butylene succinate-co-adipate)) with addition of an ionomer. The ionomer used in this study was essentially polyethylene (PE) with a small amount of methacrylic acid copolymerized randomly into the ethylene chain. This was neutralized with Na cation. For each blend, a different level of starch (from 10 to 90% by weight) was used. Measurements of tensile properties such as tensile strength, elongation at break, and tensile modulus were performed. The biodegradation of the prepared polymer films by microorganisms was investigated in activated compost soil mixtures. Tensile strength values continue to decrease with increasing starch content in starch/LDPE and starch/APES blends. This happens because the hydrophobic LDPE or APES is not compatible with hydrophilic starch. It is a general trend that the better the dispersion of the starch in the thermoplastics matrix, the better are the mechanical properties. In fact, addition of starch generally results in an increase in stiffness. This corresponds to smaller tensile strengths and decreasing elongation at break. For the starch/LDPE and starch/APES blends, the elongation at break and modulus showed the same trend with variation of starch loading. This can be explained by the lack of good phase adhesion, as well as poor dispersion. Park *et al.* [5] also tested the microstructural morphologies of starch/polymer mixtures. It was seen in SEM diagrams that increasing starch loading in starch/LDPE blends decreases the interfacial adhesion and homogeneity. The biodegradation of PE/starch blends suggests that microbes consume starch and create pores in the materials, leading to increases in the surface areas of the PE matrixes and providing susceptible groups for their biodegradation.

Petersen *et al.* [21] reported properties of commercial and semicommercial biobased materials blended with wheat and corn starch and processed by film extrusion, thermoforming, and injection-molding as a basis for primary food packaging and for other uses. The tensile strength and elongation at break showed poorer mechanical properties for the biobased packaging materials than for LDPE and HDPE. The tensile strengths of starchy materials were in the 8 to 20 MPa range, relative to 25 to 50 MPa reached for tested polymers. Wheat and corn starch materials showed water vapor permeabilities three to four times higher than those of the LDPE or HDPE used in the experiments. Use of these materials in combination with edible coatings could improve the water vapor permeability as well as the utilization of films with multiple layers of complementary properties. Furthermore, gas permeability is a limiting factor during food packaging. An increase in the starch content in LDPE-starch blends resulted in higher gas permeabilities, so the biobased materials might be good alternatives for packaging of highly respiring foods.

Processing of wheat starch/polyesteramide blends with addition of glycerol and water were reported by Averous *et al.* [2]. The starch content was kept as the major phase, more than 50%. Mixtures of starch with plasticizers were extruded and granulated, and samples were injection-molded after mixing with polyester. The behavior of pure TPS showed that its tensile strength decreases with increasing glycerol content, whereas the elongation at break increases with higher glycerol content. However, at the highest contents the elongation at break decreases again because of phase separation. The maximum elongation at break was observed when the glycerol/starch ratio was close to 0.2. For brittle materials (10% glycerol content) the addition of polyesteramide resulted in an improvement in impact properties. For more flexible TPS formulations (from 18 to 35% glycerol) the addition of polyesteramide improves all the mechanical characteristics. Addition of polyesteramide also influences the shrinkage significantly, to provide acceptable values, so this polymer can be considered a dimensional stability enhancer. The polyesteramide did not prevent aging, however, increasing rigidity of the material during the first six weeks was observed. Blending of the starch with polyesteramide was also an efficient way to increase the hydrophobicity. Different combinations of TPS and polyesteramide give a wide range over which mechanical properties could be varied to fit different applications and might represent an interesting approach by which to produce cheaper biodegradable materials.

2.4
Compatibilizers

Environmental threats restrict the use of nondegradable polymers and provide incentive for the development and use of degradable plastics. To obtain a cost-effective biodegradable plastic, starch-filled polyethylene (PE) is still the best alternative, but starch/PE blends are incompatible at the molecular level and often give poor performance. In order to overcome this drawback, either the PE or the starch should be modified. This comparatively new method of producing compatible thermoplastics blends by reactive blending extends to the formation of copolymers or interacting polymers. This differs from other compatibilization methods, which require the addition of separate compatibilizers. In reactive blends, the blend components themselves may be chosen or modified in such a way that reactions occur during melt blending and interfacial adhesion/compatibility of immiscible polymers becomes possible. The small amount of graft polymer formed during the blending and reactions between the components is enough to stabilize the morphology and to improve the blend's properties.

To improve compatibility between two phases, compatibilization strategies are generally developed. This strategy entails the addition of a compound: the compatibilizer, which can be obtained by modification of at least one polymer initially present in the blend. For compatibilization, the following different approaches may be applied [6]:

- the functionalization of the polyester, with maleic anhydride, with pyromellitic anhydride, with polyacrylic acid, or by production of telechelic polyester phosphate;
- the functionalization of starch with polyglycidyl methacrylate, or with urethane functions by treatment with *n*-butylisocyanate;
- starch/polyester reticulation with coupling agents such as peroxides or polyisocyanates;
- the development of copolymers: starch-graft polyester.

The grafting may be achieved by different methods based on the polymers transformed: by the ROP (ring-opening polymerization) technique, for example, or by atom transfer radical polymerization (ATRP). Wide application of these polymerization methods for synthesis of glycopolymer-polypeptide triblock copolymers have been reported by Dong *et al.* [22]. Reactions can be catalyzed with stannous octanoate and initiated with aluminium alkoxides. The length of the grafts can be controlled to obtain a comb structure. The same approaches can be used with PLA-grafted polysaccharides.

The compatibilizer, a commercially available polymer with a grafting compound attached, is mixed with granular starch and the polymer under heat and pressure. The heat and pressure cause the grafting compound in the compatibilizer to bind covalently to hydroxyl groups on the granular starch. The resulting blend has mechanical properties very similar to that of the pure polymer. Furthermore, the reported blend is significantly less expensive than a pure polymer as well as significantly more biodegradable [6]. In the embodiments described below, maleic anhydride is preferred as the grafting compound for the compatibilizer, facilitating covalent bonding of granular starch to the compatibilizer. This is generally because of its ready availability [3].

The compatibilizer improves the mechanical properties of PE/starch, and addition of a plasticizer is actually detrimental to the finished products. Although PE is used here to demonstrate the results of this invention, results are practically the same with other combinations of polymer and compatibilizer as disclosed therein. Incorporation of compatibilizer is easily accomplished by mechanical blending of the polymer, starch, and compatibilizer prior to extrusion. Typically, the compatibilizer is composed of the same polymer as the primary polymer itself. The polymer component of the compatibilizer may be selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-stryrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinyl chloride, or derivatives thereof [6].

Under the heat and pressure conditions used for extruding and curing most hydrophobic polymers an anhydride group will react with a hydroxyl group in order to form a covalent, ester linkage [6]. When a compatibilizer is added to a mixture of starch granules and a hydrophobic polymer, its anhydride groups will react with the hydroxyl groups of the starch granules, causing them to become covalently bound. Typically, the concentration of the compatibilizer is about 10% of that of the starch. However, the amount of compatibilizer may be as much as 80% by weight of the starch.

The starch binding compound is preferably a relatively small percentage of the overall weight of the compatibilizer, typically around 5% [18]. Because of this, large portions of the compatibilizer have no starch binding compound and therefore, no hydrophilicity. These regions of the compatibilizer are very hydrophobic and strongly interact with the polymer in the mixture. A synthetic polymer and starch blend comprises 1–30% starch, 1–24% compatibilizer, and the remainder polymer. The compatibilizer is made up of 75–98% polymer and 2–25% grafting compound, in which grafting compound is covalently attached to the polymer. The compatibilizer should be selected from the group consisting of maleic anhydride or chemicals with similar reactive properties [6]. The resulting mixture is less expensive and more biodegradable than pure polyethylene and has similar mechanical properties, and the mixture absorbs relatively little water.

Maleic anhydride (MA) is an effective starch-binding compound for use in any of a variety of compatibilizers at an amount of 0.01–10 weight % [23]. This is especially so because of the availability of polymers to which maleic anhydride has been grafted. Generally, the polymer component of the compatibilizer should preferably be the same as the polymer being mixed with the starch granules [20]. For example, maleic anhydride-grafted polyethylene (PE-g-MA) is especially suitable for use with PE, both high-density and low-density. Similarly, maleic anhydride grafted polypropylene (PP-g-MA) is especially suitable as a compatibilizer for polypropylene. Both PE-g-MA and PP-g-MA are suitable for use with PET. In addition, it is been found that styrene/ethylene-co-butylene/styrene grafted with maleic anhydride (SEBS-g-MA) is a good compatibilizer for PE, PP, PS, PB, PET, PVC and PVF. For PB, SEBS-g-MA, maleic anhydride grafted polybutylene (PB-g-MA) and glycidyl methyl acrylate grafted polybutylene (PB-g-GMA) are all suitable compatibilizers. In addition, glycidyl methyl acrylate grafted poly(methyl methacrylate) (PMMA-g-GMA) is a good compatibilizer both for PVC and for PVF. Those skilled in the art will appreciate that any polymer that blends well with the polymer being mixed with starch granules should serve well as the polymer compatibilizer.

The European patent registered by Menceloglu and Inceoglu [24], relates to biodegradable thermoplastic nanocomposite materials comprising a melt blend of natural polymer/clay hybrid with polyolefin in the presence of compatibilizer and plasticizer. It presents a method for the preparation of a natural clay nanocomposite and a process for preparing a biodegradable thermoplastic nanocomposite. The combination of polyethylene with the natural polymer and clay in the presented invention increases the processability and melt strength of the natural polymer and the biodegradability of the synthetic polymer and decreases the moisture sensitivity of the biopolymer. The material is superior in mechanical strength, gas barrier properties, biodegradability, processability, and transparency in the presence of plasticizer. The natural polymer component described in this invention may be any natural polymer such as a carbohydrate, keratin, chitosan, cellulose, a protein, or derivatives thereof. It is used in an amount of from 10 to 50 wt%, based on total amount. Derivatives may be modified biopolymers such as acetylated, hydroxypropylated, polyester-grafted, or thermo-plastified starch, carboxymethylated cellulose, or ester-grafted chitosan. Corn starch is preferred because it has the smallest particle size and provides better dispersions in blends with thermoplastic polymer, but starch obtained from wheat, rice, and potato may also be used.

Compatibilizer may be used to provide adhesion between natural polymer/clay hybrid and synthetic polymer. It can be maleic anhydride-grafted polyethylene, glycidyl epoxidized polyethylene, acrylic acid-grafted polyethylene, 3-isopropenyl-α,α-dimethylbenzene isocyanate-grafted (TMI-grafted) polyethylene, or a silane-grafted polyolefin, depending on the biopolymer, and it can be used in an amount of 5 to 30% based on the total weight [24]. Typically, the compatibilizes are incorporated in an amount of 5 to 20 wt%. Suitable plasticizers may be glycerin (glycerol), formamide, ethylene glycol, propylene glycol, polyethylene glycol, sorbitol, or urea and/or may also be a polymer in the form of an aliphatic polyester, a copolyester with aliphatic and aromatic blocks, a polyester amide, a polyester urethane, a polyethylene oxide polymer, a polyether polyol, polyglycol, and/or mixtures thereof. The plasticizer content can be 25 to 80 wt%, based on the natural polymer. Preferably, the amount of the plasticizer is 25 to 60 wt% [24]. The synthetic resin used may be any thermoplastic material with a melting temperature lower than the degradation temperature of the natural polymer. Polyethylene oxide, low-density polyethylene, high-density polyethylene, polypropylene, and combinations thereof may be chosen as suitable thermoplastic resins. The novel biodegradable nanocomposite materials have relatively rapid biodegradabilities together with excellent mechanical and optical properties, and so are suitable for various applications including the production of agricultural covering mulch films, packaging materials, yoghurt containers, marketing bags, or waste containers for composting, The addition of starch significantly decreases the tensile strength and elongation properties of polyethylene. However when PEgMA was used as a compatibilizer it provided better tensile strengths and elongation values in films, but these were still insufficient for many applications such as as packaging bottles etc.

Processes for preparing biodegradable thermoplastic nanocomposite granules comprise the following steps:

a) dissolution of a natural polymer selected from the group comprising starch, chitosan, carbohydrates, keratin, cellulose, proteins and derivatives thereof such as carboxy-methylated cellulose (CMC), or ester-grafted chitosan, polylactic acid, etc. in a solvent;

b) adjustment of the pH of the solution to acidic;

c) addition of 2% to 50 wt% natural clay based on the weight of the natural polymer;

d) stirring of the solution to obtain a natural polymer/clay nanocomposite precipitate;

e) melt blending of the natural polymer/clay nanocomposite in an extruder at a suitable temperature of between 110–250 °C with a synthetic polymer selected from the group comprising: polyethylene oxide, low-density polyethylene, high-density polyethylene, polypropylene, and combinations thereof, as well as any polyolefin with a melting temperature lower than the degradation temperature of the natural polymer;

f) granulation of the material obtained in a pelleticizer [24].

Biodegradable thermoplastic nanocomposite polymers obtained by this method are characterized by being transparent and by having improved tensile strengths and good elongation properties.

Yoo *et al.* [25] characterized the interfacial reaction of the polyethylene (PE)/starch blend system containing the reactive compatibilizer maleated polyethylene (m-PE) by FTIR spectroscopy. A significant amount of the anhydride groups on the m-PE existed as their hydrolyzed forms, resulting in a large amount of carboxyl groups. With the aid of a vacuum heating cell designed in the laboratory, the carboxyl groups were successfully transformed back into the dehydrolyzed state (i.e., anhydride groups). This result enabled the direct spectroscopic observation of chemical reaction occurring at the interface. For the PE/starch blend system containing m-PE, the chemical reaction at the interface was verified by the evolution of ester and carboxyl groups in the FTIR spectra. The effect of the reactive compatibilizer on the interfacial morphology was also examined by scanning electron micrography (SEM). Enhanced interfacial adhesion was clearly observed for the blend system containing reactive compatibilizer. The tensile strengths of blend systems containing m-PE were also significantly increased in comparison with the corresponding system without compatibilizer. Similar observations were made for the breaking and elongation data.

Corn starch and LDPE (25/100) were pre-mixed with different amounts of compatibilizer (PE-g-MA 0, 5, 10, 15, 20, 25, and 35% w/w based on starch) in order to determine the critical saturated interfacial concentration of PE-g-MA for the corn starch and LDPE system. These mixtures were then melt-blended in a lab-scale twin-screw counter-rotating extruder at 170 °C and 50 rpm. When PE-g-MA was added to the blends, the tensile strengths and elongations at break of the blends were improved, and the improvement was more pronounced at higher starch contents. PE-g-MA increased adhesion between the LDPE matrix and the starch filler. The improved interfacial adhesion between LDPE and corn starch had a positive impact on the stress transfer, thus reducing the chance of interfacial de-bonding and leading to improved tensile properties. In addition, these results also supported the conjecture that the interaction between the starch and the PE-g-MA was based on chemistry between the hydroxyl groups in corn starch and the anhydride groups in PE-g-MA, because the polar interaction between them would not improve their properties to any significant extent.

Chandra and Rustgi [26] reported the processing of modified linear low-density polyethylene (LLDPE) blends with starch. Maleic anhydride (MA) was grafted onto LLDPE in xylene in the presence of dicumyl peroxide (DCP) as an initiator. This was needed to bring about some compatibility between starch and synthetic polymers containing polar functional groups that can interact with starch. Corn starch in varying concentrations (between 10 and 60%) was blended with MA-g-LLDPE in a torque rheometer. The same blend compositions of nonfunctional LLDPE with starch were prepared for blends, except in the case of 60% starch content. The tensile strengths and moduli increased and the percentage elongations decreased with increasing starch content in the blends, suggesting interfacial adhesion of the two components of the blend due to reaction. The water absorptions and opacities of the blends also increased with increasing starch content. MA-g-LLDPE/starch blends showed better water resistance than LLDPE/starch blends. Even blends with high starch content (50–60%) could be made significantly water-resistant.

Studies of the biodegradabilities of MA-g-LLDPE/starch blends in soil environment over a period of six months and in mixtures with fungi inoculum for 28 days showed that the samples containing starch contents of more than 30% supported heavy fungus growth and that blends exposed to soil environment degraded more

Table 2.2 Mechanical properties of MA-g-LLDPE/potato starch blends [26].

Blend composition MA-g-LLDPE/starch	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
100/0	13.65	533.49	300.12
90/10	14.36	277.56	342.19
80/20	14.72	237.36	352.22
70/30	14.84	162.36	371.27
60/40	15.01	139.80	417.36
50/50	15.64	124.84	489.21
40/60	16.34	104.27	520.16

than those exposed to fungi alone. This may be because other environmental factors in soil, such as oxygen, humidity, heat, or microorganisms, play synergetic roles and further degrade the samples. The percentages of crystallinity decreased as the starch contents increased, and biodegradation resulted in increases the cristallinity in the tested blends.

Mani and Battachaya [3] also presented results relating to maleic anhydride application to starch/polymer mixtures processed by injection molding. The objective of this work was to study the influence of amylose content on the properties of injection-molded starch/ethylene-vinyl acetate (EVA), starch/ethylene-vinyl acetate maleic anhydride (EVAMA), starch/low-density polyethylene maleic anhydride (EMA) and starch/high-density polyethylene maleic anhydride (HDPEMA) blends. The corn starches used had amylose contents of approximately 0, 25, 50, and 70%. The starch content in the blends was 70% by weight. The properties of injection-molded starch blends with synthetic polymers (ethylene-vinyl acetate, low-density polyethylene, and high-density polyethylene) containing different amounts of amylose and amylopectin in starch were improved by the addition of a small amount (5% by weight) of anhydride-functionalized polymer. The tensile and flexural strengths were increased at an amylose content of 70% and were higher in waxy maize starch (highly branched) blends, presumably due to more crosslinking. In starch/EVA blends, the strength increased with increasing amylose content in the starch, but the values of the mechanical properties for corn starch were much lower than those for potato starch, presented in Table 2.2. Starch blends containing EVA showed greater elongations than blends containing LDPE and HDPE, but lower strengths.

2.5
Conclusions

Many ideas have been proposed for controlling plastics' lifetimes and to accelerate their decomposition to enhance waste reduction. The blending of stable synthetic polymers with biopolymers and the chemical or physical modification of polymeric composites are examples of solutions used for inducing degradability. Starch is considered a useful material in certain thermoplastic applications because of its biodegradability, availability, non-toxicity, high purity, and low cost. Starch promotes the biodegradability of a non-biodegradable plastic and it can also be used together with a fully biodegradable synthetic polymers, producing biodegradable blends of low costs.

The starch remains in granular form in the plastic matrix and so may act as a filler. On mixing, starch enhances the biodegradability of the synthetic polymer, mainly because of the increase in polymer surface created after consumption of the starch by microorganisms. The mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and the degree of adhesion of the filler to the polymer matrix.

The amount of starch in a blend plays an important role in its biodegradability, as indicated by the soil burial biodegradability test. At present, biopackaging materials are most suitable for foods with high respiration (fruit and vegetables) or for food with short shelf lives (bread, convenience food, etc.), because of poor water barrier properties of these packagings. A main concept for biobased materials applications could be as organic food wrappings in biobased food packaging materials that are environmentally friendly. Additional processing may be needed to improve moisture barrier, by coatings or multilayer coextrusion, for example. It is to be expected that extensive further developments will occur in this field in the near future.

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3
Biodegradability and Compostability of Biopolymers

Agnieszka Wojtowicz

3.1
Definitions and Norms

The “biodegradability” of plastics is dependent on the chemical structure of the material and on the constitution of the final product, not just on the raw materials used for its production. Therefore, biodegradable plastics can be based on natural or synthetic resins.

Bioplastics differ from conventional plastics in two important features:

- the use of renewable resources for their production, and
- their biodegradability/compostability.

For the first feature, no standardized measures for evaluation exist. It is subject to individual interpretation how big the proportion of renewable resources in a plastic product has to be in order for it to be called a bioplastic. No standard to approve this is available, although scientific methods to measure the “renewable carbon” in a given product exist.

For biodegradability and compostability, scientific methods to determine these qualities accurately in terms of plastics have been developed. The European Norm EN 13432 [1] was introduced in Europe in 2000. As a harmonized standard it is valid in all EU member states. The EU Directive on Packaging and Packaging Waste (94/62/EC) defines requirements for packaging to be considered recoverable. The harmonized standard EN 13432 amplifies these requirements with respect to organic recovery and biodegradable packaging. EN 13432 lays down laboratory test procedures for biodegradability and compostability and for the determination of potential harmful material constituents in packaging and in packaging materials. Whenever a packaging product is launched onto the market as “degradable”, conformance with the requirements of 94/62/EC is to be assessed through the use of EN 13432.

European Bioplastics calls for plastic products to be approved according to EN 13432 [1] if the marketer advertises the product as “compostable” or “biodegradable”. Because these terms are not always used correctly, the association has published information on “degradable” or “ox-degradable” plastic products. Pro-

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ducers have signed a voluntary self-commitment on product certification, which has been acknowledged by the European DG Enterprise.

The bioplastics industry's measures to secure highest product quality have established that products and materials that have been validated according to EN 13432 are usually also certified. Certification is a guarantee that it is not only the plastic element of the product that is completely biodegradable and eligible for composting: other components of the product, such as inks, glues, labels, and even the content – if the product is itself a packaging – also have to meet the requirements for composting. For this certification the complete set of components of the plastic product have to be disclosed to the certification institute. This also offers the opportunity to determine the proportion of renewable resources.

The certification process involves the assignment of a protected label, which is a valuable and necessary tool in communication. The terms "compostable" and "biodegradable", however, cannot be protected. The compostability logo, also called the "seedling", enables the user/consumer to identify the product. It is also usually required for the correct sorting and disposal of compostable plastic waste. The European Bioplastics association is currently implementing a unified certification and labeling scheme for bioplastic products in Europe.

Many polymers that are claimed to be "biodegradable" are in fact "bioerodable", "hydrobiodegradable", or "photo-biodegradable". These different polymer classes all come under the broader category of "environmentally degradable polymers". The classes of biodegradable plastics considered, in terms of their degradation mechanisms, are:

- Biodegradable
- Compostable
- Hydro-biodegradable
- Photo-biodegradable
- Bioerodable

European standards of biodegradability and compostability are collected in EN 13432:2000 (Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the acceptance of packaging) [1]. Australian Standard AS 4736 – 2006 (Biodegradable plastics – Biodegradable plastics suitable for composting and other microbial treatment) [2] specifies requirements and procedures to determine the compostability, or anaerobic biodegradation, of plastics by addressing biodegradability, disintegration during biological treatment, effect on the biological treatment process, and effect on the quality of the resulting compost. These standards provide a basis to allow labeling of materials or products made from plastics as "compostable" for use in facilities such as municipal or industrial composters. Definitions according to these standards are as follows:

- **Biopolymer** refers to a material that is partially made up of natural starch additives with the characteristics of a plastic product.

- **Degradable plastic** refers to a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of plastic properties. Changes and degradations are measured by standard test methods appropriate to the particular material.
- **Biodegradable plastic** refers to a degradable plastic in which the degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi, and algae. This plastic type is classed as a biopolymer.
- **Photodegradable plastic** refers to a degradable plastic in which the degradation results from the action of natural daylight.
- **Oxidatively degradable plastic** refers to a degradable plastic in which the degradation results from oxidation.
- **Hydrolytically degradable plastic** refers to a degradable plastic in which the degradation results from hydrolysis.
- **Compostable plastic** refers to a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with those of other known, compostable materials and leaves no other distinguishable or toxic residue.

The failure of early "biodegradable" plastics to degrade properly led to the American Society for Testing and Materials (ASTM) creating definitions on what constitutes "biodegradability". The ASTM created new standards of testing methods and labeling terminology for biodegradable and compostable packaging materials.

The ASTM defines "biodegradable" as: "capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal conditions." It is important to note that the definition of biodegradation should specify a time limit. If the biodegradation process is sufficient to mineralize organic matter into carbon dioxide or methane, water, and biomass, the material can be termed "biodegradable".

Biodegradation is degradation caused by biological activity, particularly by enzyme action leading to significant changes in the material's chemical structure. In essence, biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment, such as carbon dioxide and water. Biodegradation rates are highly dependent on the thicknesses and geometries of the fabricated articles. Although rapid breakdown rates are often quoted, these generally apply to thin films. Thick-walled articles such as plates, food trays, and cutlery can take up to a year to degrade biologically.

According to the EN 13432 [1] standard, a material or product can be called biodegradable if it is able to undergo, under specific environmental conditions within a given time, a certain degradation process that is caused by biological activity and can be measured by a standardized test method. EN 13432 requires that for a material/product to be defined as biodegradable and compostable it has to fulfill the following criteria:

- biodegradation level: >90% in comparison with cellulose (positive standard) in 180 days under conditions of controlled composting measured through respirometric methods (EN 14046 [3]),
- disintegration level: >90% in 3 months (EN 14045 [4]),
- ecotoxicity: toxicity tests (germination and plant tests), and
- chemical testing according to product safety.

Biodegradable and compostable polymers can be produced from agricultural renewable raw materials, including in combination with materials of fossil origin. Evaluation of the ultimate aerobic biodegradability of packaging materials under controlled composting conditions can be achieved on the basis of ISO 14855-1999 [5] or EN 14046-2003 [3].

Compostable biodegradable plastics must be demonstrated to biodegrade and to disintegrate in a compost system during the composting process (typically around 12 weeks at temperatures over 50 °C). The compost must meet quality criteria such as heavy metal content, ecotoxicity, and the absence of obvious distinguishable residues caused by the breakdown of the polymers. Compostable plastics are a subset of biodegradable plastics.

“Compostable” is defined by the ASTM as: “capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials (e.g., cellulose).”

A polymer is “compostable” when it is biodegradable under composting conditions. The polymer must meet the following criteria:

- it breaks down under the action of micro-organisms (bacteria, fungi, algae),
- total mineralization is achieved (conversion into CO_2, H_2O, inorganic compounds and biomass under aerobic conditions), and
- the mineralization rate is high and is compatible with the composting process.

The degree of degradability of the material shall be measured under controlled composting conditions as per ASTM D 5338-92 [6]. Those materials with degrees of biodegradation equivalent to that of cellulose (maximum permissible tolerance of 5%) will be considered to meet the compostability criteria. The following requirements must therefore be fulfilled for compostable plastic products:

- compliance with all criteria of the EN 13432 standard [1],
- product certification based on EN 13432, and
- labeling with a protected compostability mark.

Users/vendors of compostable bioplastic products are strongly recommended to ask their supplier about product certification and to demand the certificate with the certification number. Even if composting of the product is not intended, certification guarantees high product safety. Certification, moreover, distinguishes between bioplastic and conventional plastic and offers marketing and communication possibilities.

The norm EN 13432 [1] incorporates the definitions of biodegradability and compostability by reference and is recommended for the applications of compostable packaging according to the Directive on Packaging and Packaging Waste 94/62/EC. EN 13432 can be also the basis for other compostable plastic products or semi-finished goods. For a material to be called compostable it has to be biodegradable and to disintegrate in a composting system in such a way that this disintegration occurs during a period of end-use of the compost.

Product certification guarantees that it is not only the plastic that is compostable, but also all other components of the product, such as colors, labels, glues, and – in the case of packaging products – residuals of the content. The protected "compostability label" (or "seedling") may only be used for certified products. Both the logo and the number of the certificate printed on the product allow identification of the producer and confirmation of conformity: the product that has been tested and the marketed one must coincide.

Certification of compostable polymer products based on EN 13432 [1] is performed by DIN CERTECO and other EU certification bodies according to quality management systems such as EN 45011/EN 45012 [7, 8]. DIN CERTECO, the certification organization of DIN, established the scheme in 1997 and has gained internationally renowned expertise ever since, as witnessed by, for example, their participation in the International Network for Compostability Certification together with institutions from the USA, Japan, and Taiwan, or with other certification bodies in Europe in order to implement harmonized supranational certification schemes. As from June 2004, participants are: The Composting Association from the UK, Keurmerk from the Netherlands, and COBRO from Poland.

Hydro-biodegradable and photo-biodegradable polymers are broken down in a two-step process: an initial hydrolysis or photo-degradation stage, followed by further biodegradation. Single-degradation-phase "water-soluble" and "photodegradable" polymers also exist.

Many polymers that are claimed to be "biodegradable" are in fact "*bioerodable*" and degrade – at least initially – without the action of micro-organisms. This is also known as abiotic disintegration, and may include processes such as dissolution in water, "oxidative embrittlement" (heat aging), or "photolytic embrittlement" (UV aging).

3.2
Biodegradability of Starch-Based Products

Biodegradation of starch-based polymers is a result of enzymatic attack at the glucosidic linkages between the sugar groups, leading to reductions in chain length and splitting-off of sugar units (monosaccharides, disaccharides, and oligosaccharides) that are readily utilized in biochemical pathways.

3.2.1
Starch Composites (10% Starch)

Starch can be used as a biodegradable additive or replacement material in traditional oil-based commodity plastics. If starch is added to petroleum-derived polymers (e.g., PE), it facilitates disintegration of the blend, but not necessarily biodegradation of the polyethylene component. Starch accelerates the disintegration or fragmentation of the synthetic polymer structure. Microbial action consumes the starch, thereby creating pores in the material that weaken it and enable it to break apart.

3.2.2
Starch Composites (50% Starch)

Also called plastified starch materials, such materials exhibit mechanical properties similar to those of conventional plastics such as PP and are generally resistant to oils and alcohols, but degrade when exposed to hot water. Their basic content (40–80%) is corn starch, a renewable natural material. The balance is performance-enhancing additives and other biodegradable materials.

3.2.3
Starch Composites (90% Starch)

Usually referred to as thermoplastic starch, these are stable in oils and fats, but depending on the type they can be either stable or unstable in hot/cold water. They can be processed by traditional techniques for plastics. At lower starch contents (less than 60%) the starch particles act as weak links in the plastic matrix and as sites for biological attack. This allows the polymer matrix to disintegrate into small fragments, but not for the entire polymer structure actually to biodegrade. Along with the biodegradation of the polymers by sugar molecules, certain TPS grades are also fully water-soluble. The wheat starch-aliphatic polyester blend studied by Lim *et al.* [9] demonstrated excellent biodegradability. Soil burial tests revealed complete biodegradation within eight weeks. The excellent properties exhibited by these blends make them ideal as commodity biodegradable plastics. Polyvinyl alcohol (PVOH) is blended with starch to produce readily biodegradable plastics. PVOH is readily water-soluble, and the starch/PVOH blends are therefore degraded through hydrolysis and biodegradation of the sugar molecules.

3.3
Biodegradability of Polyesters

Aliphatic polyesters such as PHAs, and more specifically homopolymers and copolymers of hydroxybutyric acid and hydroxyvaleric acid, have been confirmed to be readily biodegradable. Such polymers are actually synthesized by microbes, with the polymer accumulating in the microbes' cells during growth. PHAs are biodegradable through composting. Optimum conditions for the commercially available Biopol™ (PHA) degradation during a 10-week composting period were 60 °C, 55% moisture, and a C/N ratio of 18:1. Biopol™ reached close to a 100% degradation rate under these composting conditions. The aliphatic polyesters function like starch or cellulose to produce non-humic substances such as CO_2 and methane. These aliphatic polymers are suited to applications with short usage and high degradation rate requirements. Shin *et al.* [10] found that bacterial PHB/PHV (92:8 w/w) degraded nearly to completion within 20 days of cultivation by anaerobic digested sludge, whereas synthetic aliphatic polyesters such as PLA, PBS, and PBSA did not degrade at all in 100 days. Cellophane, which was used as a control material, exhibited degradation behavior similar to that of PHB/PHV. Under simulated landfill conditions, PHB/PHV degraded within six months. Synthetic aliphatic polyesters also showed significant weight losses through one year of cultivation. The acidic environment generated by the degradation of biodegradable food wastes, which comprise approximately 34% of municipal solid waste, seems to cause weight loss in synthetic aliphatic polyesters. Poly-hydroxybutyrate-co-polyhydroxyhexanoates (PHBHs) resins are one of the newest type of naturally produced biodegradable polyesters. The PHBH resin is derived from carbon sources such as sucrose, fatty acids, or molasses by fermentation processes. PHBH resins biodegrade both under aerobic and under anaerobic conditions, and are digestible in hot water under alkaline conditions.

PLA: Lactic acid is produced (by starch fermentation) as a co-product of corn wet milling. The ester linkages in PLA are sensitive both to chemical hydrolysis and to enzymatic chain cleavage. PLA is often blended with starch to increase biodegradability and to reduce costs. PLA is fully biodegradable when composted in a large-scale operation with temperatures of 60 °C and above. The first stage of degradation of PLA (two weeks) is through hydrolysis to water-soluble compounds and lactic acid. Rapid metabolization of these products into CO_2, water, and biomass by a variety of micro-organisms occurs after hydrolysis. PLA does not biodegrade readily at temperatures less than 60 °C, due to its "glass transition" temperature being close to 60 °C.

Polycaprolactone (PCL) is a biodegradable synthetic aliphatic polyester made by the ring-opening polymerization of caprolactone. PCL has a low melting point (between 58–60 °C) and low viscosity and is easy to process. Although not produced from renewable raw materials, PCL is fully biodegradable when composted. The low melting point of PCL makes the material suited for composting as a means of disposal, because the temperatures obtained during composting routinely exceed 60 °C. Rutkowska *et al.* [11] studied the influence of different processing additives on the biodegradation of PCL film in the compost with plant treatment active sludge. It was found that, without additives, PCL had completely degraded after six weeks in compost with activated sludge. The introduction of additives to processing gave better tensile strengths of the materials but made them less vulnerable to micro-organism attack. The rate of marine biodegradation of PCL has been studied by Janik *et al.* [12] by measurement of the tensile strength and percent weight loss over time both in seawater and in a buffered salt solution. It was found that the weight loss, as a percent of total weight, decreased more rapidly in seawater than in the buffered salt solution. After eight weeks, the PCL in seawater was completely decomposed, whereas that in salt solution had lost only 20% of its weight. The same trend was seen for the tensile strength: after eight weeks, the PCL in seawater had been destroyed and that in buffered salt solution had decreased to roughly one-sixth of its original value. It is therefore apparent that enzymes in the seawater solution assist to accelerate the biodegradation of PCL and other biodegradable plastics.

Aliphatic-aromatic copolyesters (AAC)s combine the biodegradable properties of aliphatic polyesters with the strength and performance properties of aromatic polyesters. This class of biodegradable plastics is seen by many as the answer to making fully biodegradable plastics with property profiles similar to those of commodity polymers such as polyethylene. To reduce costs, AACs are often blended with TPS. Although fossil fuel-based, AACs are biodegradable and compostable. ACCs fully biodegrade to carbon dioxide, water, and biomass. Typically, in an active microbial environment the polymer becomes invisible to the naked eye within 12 weeks. The extent and rate of biodegradation depends, apart from on the inherent biodegradability of the polymer itself, on several environmental factors, such as moisture, temperature, surface area, and the manufacturing method of the finished product.

Modified PET (polyethylene tetraphthalate) is PET that contains co-monomers, such as ether, amide, or aliphatic monomers, that provide "weak" linkages that are susceptible to biodegradation through hydrolysis. Depending on the application, up to three aliphatic monomers are incorporated into the PET structure. Typical modified PET materials include PBAT (polybutylene adipate/terephthalate) and PTMAT (polytetramethylene adipate/terephthalate). Modified PET is hydro-biodegradable, with biodegradation steps following an initial hydrolysis stage. It contains weak linkages that create sites for microbial attack. The mechanism involves a combination of hydrolysis of the ester linkages and enzymatic attack on ether and amide bonds. With modified PET it is possible to adjust and control degradation rates by varying the co-monomers used.

Degradability of other polyesters: There are two main water-soluble polymer types commercially available: polyvinyl alcohol (PVOH) and ethylene vinyl alcohol (EVOH). PVOH is a readily biodegradable, water-soluble polymer. The degradation of PVOH is influenced by its crystallinity and molecular weight. PVOH does not biodegrade, but simply dissolves in water or can be biodegraded by activated sludge treatment. EVOH is another water-soluble synthetic plastic.

3.4
Photo-Biodegradable Plastics

Photodegradable plastics are thermoplastic synthetic polymers into which light-sensitive chemical additives or copolymers have been incorporated for the purpose of weakening the bonds of the polymer in the presence of ultraviolet radiation. Photodegradable plastics are designed to become weak and brittle when exposed to sunlight for prolonged periods. In photodegradable systems, biodegradation occurs only after an initial photodegradation stage. Degradation of the polymer is triggered by UV light and is assisted by the presence of UV sensitizers in the polymer. The polymer is initially converted into low-molecular-weight materials (i.e., waxes) and is then converted into carbon dioxide and water by bacterial action.

3.5
Controlled Degradation Additive Masterbatches

The use of additives that impact controlled degradation behavior to conventional thermoplastics, as well as to inherently biodegradable plastics, is becoming a popular strategy because of price competition. Such additives are known as prodegradant concentrates, and are generally based on catalytic transition metal compounds such as cobalt stearate or manganese stearate. The additive is typically used at levels of 1–3% and leads to additional costs of between 10–35% over those of polyethylene. Plastic products manufactured with prodegradant additives such as TDPA™ (abbreviation for Totally Degradable Plastic Additive) or degradable and compostable polymer (DCP) additives progressively degrade to lower and lower molecular weights. They become brittle, disintegrate, and are ultimately digested by microorganisms back to the basic elements of carbon dioxide (CO_2), water (H_2O), and biomass with no harmful residues. TDPAs have been shown not to affect bacteria, fungi, or earthworms and they leave no hazardous residues. TDPAs can control the degradation rates of plastics to various degrees, from as short as a few weeks to months or years, at a competitive cost. Prodegradant-containing films represent a significant development over earlier biodegradable films based on starch-filled polyethylene. The additive, such as AMCOR Flexibles (a metal chelate), initiates chain scission processes that cause the polymer chain to be reduced to molecular weights 20% of that of the original, at which point bacterial degradation takes over. The addition of a "masterbatch" (i.e., concentrate) to a plastic base resin allows for degradation behavior to be controlled. Polyethylene containing 3% of the additive is claimed to degrade to a 95% weight loss after four weeks at 60 °C. Such environmentally degradable plastic compositions are not strictly biodegradable but rather "bioerodable".

DCP-containing polymers do not initially biodegrade, but rather chemically oxidize to lower and lower molecular weights, becoming brittle and fragmenting. The fragments are then ingested slowly by microorganisms, ultimately leaving carbon dioxide, water, and biomass. The additives promote an oxidation process of the polymer, neither light nor heat is essential, and the additives can function at ambient temperature. When the molecular weight of the plastic has dropped sufficiently, the plastic is effectively converted into wax and at this point it will naturally biodegrade.

3.6
Methods of Biodegradability Measurements

There are a range of international standards, and test methods, developed specifically for biodegradability, product safety, and also for compost-derived products. The main point of differentiation between the various international standards is the percentage of biodegradation required for compliance.

The main international organizations that have established standards or testing methods are:

- American Society for Testing and Materials (ASTM),
- European Committee for Standardization (CEN),
- International Standards Organization (ISO),
- Institute for Standards Research (ISR),
- German Institute for Standardization (DIN),
- Organic Reclamation and Composting Association (ORCA) (Belgium).

A family of ASTM standards addresses physical property deterioration under a variety of specific environmental conditions including simulated composting (D5509, D5512 [13, 14]), simulated landfill (D5525 [15]), aerobic microbial activity (D5247 [16]), and marine floating conditions (D5437 [17]).

A second group of ASTM standards addresses CO_2 generation in aerobic environments including sewage sludge (D5209 [18]), activated sewage sludge (D5271 [19]), and controlled composting (D5338 [6]).

A third group of ASTM standards addresses CH_4/CO_2 evolution in anaerobic environments such as anaerobic sewage sludge (D5210 [20]), anaerobic biodegradation (D5511 [21]), and accelerated landfill (D5526 [22]). D6400 [23] differentiates between biodegradable and degradable plastics.

3.6.1
ASTM D5338-98 [6] **(Composting)**

For biodegradable plastic materials to be accepted in composting plants, both biodegradability and disintegration are important. Disintegration is the physical falling apart of the biodegradable plastic material, or more precisely of the product that has been made from it, into fine visually indistinguishable fragments at the end of a typical composting cycle.

A compostable material is understood to be a material in which:

- the polymer chains break down under the action of micro-organisms (bacteria, fungi, algae);
- total mineralization is obtained (conversion into CO_2, H_2O, inorganic compounds, and biomass under aerobic conditions); and
- the mineralization rate is high and is compatible with the composting process.

Those materials showing a degree of biodegradation equivalent to that of cellulose (maximum permissible tolerance of 5%) are considered to meet the compostability criteria under these standards. To measure compostability, the ASTM in the United States has developed the key standard ASTM D5338-98. This is a standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions. In this method the plastic is mixed with stabilized and mature compost derived from the organic fraction of municipal solid waste. The net production of CO_2 is recorded relative to a control containing only mature compost. After determination of the carbon content of the test substance, the percentage biodegradation can be calculated as the percentage of solid carbon of the test substance that has been converted into gaseous carbon in the form of CO_2. In addition to carbon conversion, disintegration and weight loss can be evaluated.

To meet the ASTM D5338-98 standard, 60% of the original mass of a single-polymer material must mineralize in six months, whereas 90% must do so in a blend. Materials should give way to intense microbial activity and be converted from carbon into carbon dioxide, biomass, and water. Materials should also begin to fragment, at which point disintegration begins. In this phase, the material must completely physically and visually disintegrate. Ninety percent of the disintegrated material must not adversely affect the quality of the compost. Finally, even after land application, remaining materials should be safely converted into carbon dioxide by microorganisms. The resultant compost should not be toxic and should not deter plant growth.

ISO CD 14855 [5] and the CEN test procedures are similar to ASTM D 5338-98. The only difference is the temperature profile, which in both the ISO and the CEN procedures is continuously at 58 °C, whereas in the ASTM test it follows a temperature profile of 35–58–50–35 °C.

3.6.2
ASTM D5209-92 [18] **(Aerobic, Sewer Sludge)**

The Sturm test (ASTM D5209-92) was developed to measure the biodegradability of both water-soluble and insoluble compounds in an aquatic environment. As with ASTM D5338-98 these tests are based on the measurement of CO_2 produced during biodegradation of the plastic test material. The percentage biodegradation is calculated from the CO_2 produced by the plastic sample in relation to the total theoretical amount. Continuous aeration ensures that there is sufficient oxygen in the bioreactor at all times. The measurement of carbon dioxide evolved during degradation gives direct information on the bioconversion of the carbon backbone of the polymer to metabolic end products. A 10 mg plastic sample is used in the test. For this reason it gives an artificially high breakdown rate. Although the measurement of evolved CO_2 is very accurate the rate of biodegradation can have an error of up to 80%.

The Technical Research Center of Finland (VTT) has developed a “headspace test” that, like the Sturm test, is also based on the measurement of carbon dioxide under aerobic conditions. The VTT test is performed in “headspace” bottles (volume 125 mL) containing 50 mL of a mineral nutrient medium and sewage sludge. The benefits of the VTT test are its simplicity and the capacity for an extensive number of samples to be processed simultaneously, thereby allowing statistical evaluation. The carbon dioxide evolved during biodegradation is determined from the gas and liquid phases at weekly intervals.

3.6.3
ASTM D5210-92 [10] (Anaerobic, Sewage Sludge)

Anaerobic degradation is biodegradation in the absence of oxygen. A mixed population of microorganisms is needed for complete degradation of the polymer. In the first stage, acidogenic bacteria convert organic substances into components of lower molecular weight, such as alcohols and short-chain fatty acids. Subsequently, acetogenic bacteria further degrade these substances into acetone, carbon dioxide, and hydrogen. In the final phase, methane and carbon dioxide are the end products of anaerobic degradation.

The standard test method for determining the anaerobic degradation of plastic materials is ASTM D5210-92. This test measures the amount of biogas released during polymer biodigestion by microorganisms. The biodegradation percentage is the ratio of biogas produced by the test sample in relation to the theoretical amount produced in the case of complete mineralization.

3.6.4
ASTM D5511-94 [21] (High-solids Anaerobic Digestion)

ASTM D5511-94 is the standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic digestion conditions. This method determines the inherent biodegradability of plastic in an anaerobic solid waste digester or a sanitary landfill under optimal conditions. In this case the total volume of biogas produced per unit weight of sample is measured. With knowledge of the carbon content of the test material, the percentage of biodegradation can be calculated as the percentage of solid carbon in the sample that has been converted into gaseous carbon in the form of CH_4 and CO_2.

3.6.5
Tests for Specific Disposal Environments

Tests to evaluate the generation and quality of humic substances in landfills or in composting or aquatic environments are beginning to appear. Aerobic composting with activated vermiculite provides the opportunity to recover and to quantify the polymeric residues, allowing the determination of more complete carbon balances as well as assessments of toxic compound generation and humus quality. The properties of disintegration of biodegradable plastics can be measured on a pilot scale or in full-scale composting tests. The test substance is subjected to a spontaneous composting process for a duration of 12 weeks. At the end, sieving over 2 mm followed by a precise sorting analysis is executed. It may be that a bioplastic passes the test at a specific thickness but fails the test at a higher thickness. It must also be demonstrated that the bioplastic materials have no negative effect on compost quality. This involves chemical analyses (e.g., heavy metals) as required in the evaluation of conventional compost quality. In addition, ecotoxicity tests, including both plant germination tests and animal toxicity tests, are advised. The purpose of these tests is to make sure that small quantities of additives (e.g., from the plastics) do not have an adverse effect on compost quality.

3.6.6
International Standards Research

The performance of biodegradable plastics in composting facilities and under laboratory conditions has been studied by Institute for Standard Research (ISR). ISR has determined that plastics need to meet the following three criteria in order to be compostable:

- They must biodegrade at the same rate and to the same extent as known compostable materials such as garden waste and paper, and leave no persistent or toxic residues.
- They must disintegrate during active composting so there are no visible or distinguishable fragments found on the screens.
- They must display no ecotoxicity or phytotoxicity that might impact on the ability of the compost to support plant growth.

Three International Standards Organization (ISO) standards have set the criteria by which European biodegradable plastics are currently assessed. These are:

- ISO 14855 [5] (aerobic biodegradation under controlled conditions);
- ISO 14852 [24] (aerobic biodegradation in aqueous environments); and
- ISO 15985 [25] (anaerobic biodegradation in a high solids sewerage environment).

ISO 14855 is a controlled aerobic composting test, and ISO 14851 [26] and ISO 14852 are biodegradability tests specifically designed for polymeric materials. An important part of assessing biodegradable plastics is testing for disintegration in the form in which they will ultimately be used. Either a controlled pilot-scale test or a test in a full-scale aerobic composting treatment facility can be used. Because of the natures and conditions of such disintegration tests, the tests cannot differentiate between biodegradation and abiotic disintegration, but instead demonstrate that sufficient disintegration of the test materials has been achieved within the specified testing time.

The European Committee for Standardization (CEN) established the norm standard (CEN EN 13432 [1]) in 1999. The norm provides the European Commission's *European Directive on Packaging and Packaging Waste* with appropriate technical regulations and standards. This norm is a reference point for all European producers, authorities, facility managers, and consumers.

The standard specifies requirements and procedures to determine the compostability of plastic packaging materials based on four main areas:

- biodegradability,
- disintegration during biological treatment,
- effect on the biological treatment process, and
- effect on the quality of the resulting compost.

Importantly, the packaging material that is intended for entering the bio-waste stream must be "recognizable" as biodegradable or compostable by the end-user.

3.6.7
Standard EN 13432 – Proof of Compostability of Plastic Products

Plastic products can provide proof of their compostability by successfully meeting the harmonized European standard EN 13432 [1]. The European Packaging Directive 94/62 EC makes reference hereto with regard to compliance with recovery directives.

Scope of testing under EN 13432:

- **Chemical test:** Disclosure of all constituents, threshold values for heavy metals are to be adhered to.
- **Biodegradability in watery medium (oxygen consumption and production of CO_2):** Proof must be given that at least 90% of the organic material is converted into CO_2 within six months.
- **Disintegration in compost:** After three months' composting and subsequent sifting through a 2 mm sieve, no more than 10% residue, relative to the original mass, may remain.
- **Practical test of compostability in a semi-industrial (or industrial) composting facility:** No negative influence on the composting process is permitted.
- **Compost application:** Examination of the effect of resultant compost on plant growth (agronomic test), ecotoxicity test.

The maximum material gauge of a plastic is determined by its compostability in standard practice composting operations. All tests must be passed. Success in individual tests will not be sufficient. The EN standard test methods are based on the scientific definitions of the ISO standards 14851 [26], 14852 [24] (aerobic degradability in water), 14853 [27] (anaerobic degradability in water), and 14855 [5] (aerobic composting). The tests must be conducted by recognized test laboratories.

European Bioplastics calls for plastic products to be approved according to EN 13432 if the marketer advertises the product as "compostable" or "biodegradable". Because these terms are not always used correctly, the association has published information on so-called "degradable" or "oxo-degradable" plastic products. Producers have signed a voluntary self-commitment on product certification, which has been acknowledged by the European DG Enterprise.

The strictest European standard for biodegradability is CEN 13432. This standard can apply to other packaging materials in addition to polymers, and incorporates the following tests and standards:

- ISO 14855,
- ISO 14855 (respirometric),
- ISO 14852,
- ASTM D5338-98,
- ASTM D5511-94,
- ASTM E1440-91 [28],
- modified OECD 207 [29, 30], and
- CEN TC 261/SC4/WG2 [31].

For a material to pass the standard, it must not persist for longer than six months under any of the conditions stipulated in the above tests and have a pass level of 90%. In addition, the material must not exceed contaminants content above 50% of that for "normal" compost, as follows: Zn 150 ppm, Cr 50 ppm, Cu 50 ppm, Mo 1 ppm, Ni 25 ppm, Se 0.75 ppm, Cd 0.5 ppm, As 5 ppm, Pb 50 ppm, F 100 ppm, Hg 0.5 ppm, according to EN 13432 [1].

3.6.8
Other Standards

The Canadian certification program BNQ for compostable plastic bags has been open to companies since September 07, 2007. The objective of the BNQ certification program is both to permit consumers and other users easily to identify bags that are compostable in municipal composting operations through the use of a logo and also to permit operators of composting facilities to receive organic material in plastic bags of known compostability, thus ensuring improved quality of the compost [32]. The certification mark of the certified products is a mark shared between the BNQ ("Bureau de Normalization du Québec") and the Composting Council of Canada.

Australian standards, based on EN, determine procedures for biodegradability and disintegration of plastics according to several methods: for example, AS 4736-2006 [2] (Biodegradable Plastics – Biodegradable plastics suitable for composting and other microbial treatment), or AS 4351.1-1996 [33] (Organic compounds in an aqueous medium – Method for determining and reporting biodegradability), and AS 4351.6-1996 [34] (Organic compounds in an aqueous medium – Guidance for the determination of biodegradability of poorly soluble organic compounds). The labeling of compostable products is also limited and certified.

3.6.9
"OK Compost" Certification and Logo

The "OK Compost" logo can be used on the labeling of biodegradable plastics and other materials to signify that the material is 100% compostable and biodegradable. The logo is owned and managed by AVI, and is based on the CEN 13432 standard.

All the laboratory tests have to be performed only for materials, intermediates, and additives. In these tests the chemical properties are checked, the ultimate biodegradability is verified, and the disintegration properties are determined. Chemical testing serves to ensure that neither harmful organic substances, such as polychlorinated biphenyls (PCB)s and dioxins, nor heavy metals, such as lead, mercury, and cadmium, pass into the soil through the compost.

The methods specified for the testing of biodegradability and of disintegration serve to verify the complete degradation of the materials within the processing period of normal composting plants. An ecological nontoxicity test that is also prescribed ensures that the plastics used have no adverse effect on the quality of the compost. Additionally the maximum compostable layer thickness is determined.

If the results of the tests are in conformity with the standard(s) and/or the certification scheme, the material, intermediate, or additive is registered and included in a positive list. Products that have been manufactured from registered materials, intermediates, and additives may be certified if they meet the maximum compostable layer thickness of the used materials or intermediates. Verification tests are performed in order to confirm that the same base materials as those declared on application for certification are being used. For this purpose, infrared spectra are recorded and compared.

3.7
Environmental Aspects of Biopolymers

Plastics can in general be considered to perform well with respect to their environmental impact. These lightweight materials make efficient use of resources and energy during their manufacture, transport, and application. After use they offer high energy potential that can be exploited in thermal recovery. Other recovery options can also be applied.

Bioplastics have the additional advantage of using renewable resources. This does not necessarily go together with an advantage over conventional plastics, but it has often proven advantageous when the criteria “consumption of fossil resources” and “reduction of CO_2 emissions” are being assessed. Using agricultural resources also allows a regional closed-loop management. The environmental performance, however, should be validated by standardized assessment criteria. Especially in countries with a lack of humus (arid zones) the compostability of many of the products offers an additional advantage. They allow the production of compost, which can be used as fertilizer and substrate to improve the soil quality.

Even if many bioplastics are biodegradable, they are not intended to be disposed of in nature. They must be recovered in a controlled and eco-efficient way. European Bioplastics has a clear anti-littering position.

3.7.1
Climate Protection

Manmade influences are today considered to be the main reasons for climate change. Burning of fossil resources increases the levels of CO_2 in the atmosphere, which causes an increase in the average temperature (greenhouse effect). Scientists see a distinct connection between CO_2 increase in the atmosphere and increasing numbers of thunderstorms, floods, and aridity. Climate protection is nowadays a central part of environmental policy, due to the fact that climate change can create far-reaching negative consequences. Governments and organizations work against this threat with targeted measures.

The increased use of renewable resources is an important step toward a solution. Life cycle analysis shows that bioplastics enable CO_2 savings of 30 to 80% in relation to conventional plastics. This does not apply generally and inevitably it depends on the product and its application. The saving (in the case of the same application) results from the use of renewable resources.

Plastics in general are considered to be “climate-friendly” materials: in comparison with materials such as metal or concrete they can be easily produced, transported, or used without much energy expenditure. In the automotive engineering sector (lightweight construction) or as thermal insulating materials, plastics enable significant “secondary” effects by protecting resources and thus saving CO_2 production. Examples of the successful use of bioplastics exist already: Goodyear’s car tires contain a proportion of starch material, which decreases the tires’ rolling resistance and is therefore also able to reduce fuel consumption.

3.7.2
Life-Cycle Economy

The principle of sustainable development and the lack of landfill capacity in Europe are reasons for the introduction of the closed-loop economy in the European Union. Products have to be produced and used in a manner that conserves resources and have to be recovered after use, if their use cannot be avoided entirely. Landfill of waste is not allowed anymore, so the question of disposal is already an issue during the development of a product. If easily disposed materials are used for the production, the disposal cost will decrease, and so in consequence will the overall product costs.

According to these guidelines, bioplastics have been developed, with composting considered to be the most cost-effective method of disposal. Only by use of renewable resources can a genuine closed loop be achieved. Assessments of the impacts of products on the environment require objective and standardized criteria. Life-cycle analyses complying with ISO 14040 [35] are a suitable means of quantifying the impact of products on the environment. Their primary use in industry is to optimize process-engineering aspects of production with regard to the environment (Figure 3.1).

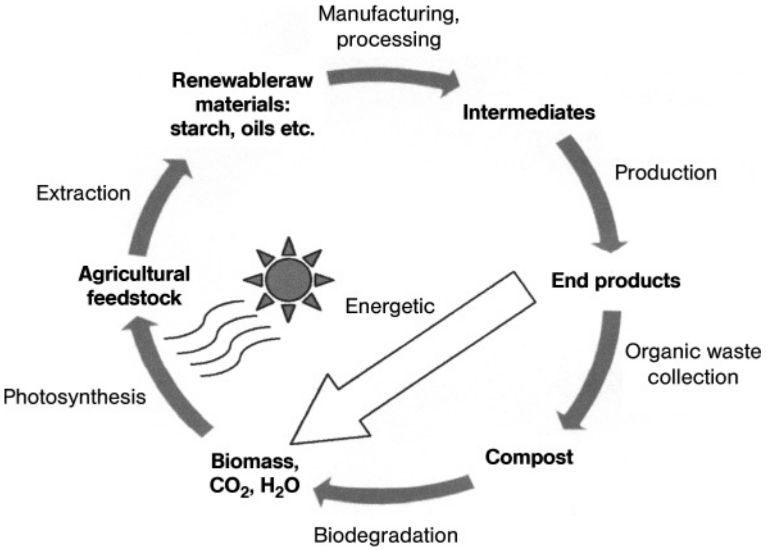

Figure 3.1 Life cycle of biodegradable materials.

3.7.3
Recovery Options

The objective of the EU to close material cycles has led to a different understanding and handling of the term “waste”: “waste” can be regarded as “raw material for new after-life options”. Bioplastics have been designed on the concept of closed-loop material management – as is found in nature. Bioplastics can be recovered and recycled like conventional plastics by all available methods: by thermal recovery, back to plastics, or by chemical recovery.

Unlike conventional plastics, most bioplastics types can be organically recycled by composting, provided that they comply with EN 13432 criteria. Diverse investigations and studies show that there is no “best” option in recovery and recycling for plastics. Ecological and economical evaluation results differ with regard to different application of plastics, even if the same resin type is considered.

Composting is a useful and often preferred method for mulch film and bio-waste bags, as well as for gardening articles, which additionally offer shoppers the “second life option” of also serving as organic waste bags. In all these applications biodegradability represents added value. Used food packaging can be processed with high eco-efficiency by composting, especially for packing of easily spoiled food with a short shelf-life. Then the packaging can be recovered together with the spoiled content without further treatment. Nevertheless, the eco-efficiency is also dependent on the given infrastructure at a place or in a region.

Short characterization of recovery options for bioplastics:

- **Thermal recovery:** Use of the high calorimetric value of the substance to produce heat and electricity (legislative criteria have to be met).

- **Organic recycling (composting):** The resulting compost is used to improve soil quality and as a replacement for fertilizers.
- **Chemical recycling:** This can be an option, especially for polyester types such as PLA or PHA. By chemical treatment the polymer chain can be de-polymerized, and the resulting monomers can be purified and polymerized again. Sufficient amounts of source-separated collected plastic waste are a precondition for application of this method. The same arguments apply for recycling back to plastics.

3.7.4
Waste Management and Bioplastics Treatment

Waste management will be a key success factor of bioplastics in two different ways. On the one hand, for compostable plastic products it is crucial to have composting infrastructures in place. That is the reason why European Bioplastics advocates separate collection of organic and residual waste and installation of composting sites across Europe. The association welcomes all political initiatives that support this goal, as the latest announcement of the German Environmental Ministry did. The ministry intends to draw up a national organic waste recycling strategy. This includes the question of whether organic waste should be dried, burnt, fermented, or composted, or whether it should be processed to create biofuels. The German Federal Government has also started to introduce its organic waste strategy at the European level. In the EU, organic waste accounts for around 38% of municipal waste. This amounts to around 120 million tonnes of organic waste per year, with the potential to provide over 50 million tonnes of compost annually (in EU 25). One problem, however, is the European Landfill Directive. Although the directive includes several requirements to reduce the organic component of waste, it explicitly permits burning, treatment in a mechanical biological facility, and mixed composting of organic waste components, with the result that the waste can no longer be used for soil improvement. Like the EU parliament and the "biowaste coalition" (Austria, Belgium, Cyprus, the Czech Republic, Estonia, Hungary, Italy, Portugal, Slovakia, Spain, Romania, and Germany), European Bioplastics supports the idea of a dedicated Organic Waste Directive, which is unfortunately not yet on the agenda of the EU Commission.

On the other hand, European Bioplastics strongly supports appropriate treatment of bioplastics in view of the quantities of material available. Organization of the best-suited waste-management system is dependent on local infrastructures for collection and recycling, local and regional regulations, the total available volume on the market, and the compositions of waste streams. This is also a primary reason why conventional packaging is not always treated in the same way across the EU. Most countries have set up systems to recover and to recycle post-consumer plastic bottles. For most other packaging, the results are more fragmented and not always very well developed. In many cases, mixed fractions are being incinerated, and in doing so, (fossil) energy is being recovered.

With both bioplastics and biopackaging in their infancy, the development of the market should not be delayed, even though optimal recovery systems have often not been ascertained by local authorities. The risks associated with existing recovery schemes should be monitored. These will be limited at present, given the relatively small volumes that are currently entering the market. Once volumes reach a critical mass, waste-management systems that make most sense from an environmental and economic point of view can be set up. Over time, recycling may be the best option for certain bioplastics, especially if a homogenous stream can be organized, like that in place for plastic bottles. The German government acknowledged these considerations in an amendment to its Packaging Ordinance by releasing bioplastic bottles from deposit obligation. The ordinance states that bottles with more than 75 percent RRM content will not be subject to a deposit charge. This exemption postpones the obligation to install recovery systems to a point of time after market introduction.

European Bioplastics is the representative body of the European bioplastics industry. The association comprises companies along the whole value chain of bioplastics: from the agricultural feedstock, chemical, and plastics industries, as well as industrial users and recycling companies.

Founded in 1993 as IBAW (interest group biodegradable plastic materials), in 2007 the association represented the interests of 75 member companies. Between 2004 and 2007 the number of members more than doubled. The goals of the association are to shape the political, business, and public landscape for the bioplastics industry.

It is recommended that commercial users or retailers of compostable bioplastic products ask distributors about their product certifications and demand the certification numbers. Even if composting of the product is not intended, certification guarantees high product safety. Certification, moreover, distinguishes between bioplastic and conventional plastic and offers marketing and communication opportunities.

The certification program for compostable plastic products has been set up by experts responsible for waste-management recycling and compost quality assurance.

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4
TPS and Its Nature

Marcin Mitrus

The interest in using starch as a basis for packaging material originated in the 1970s, when environmental awareness was increasing drastically. Since then a steady development of new products can be seen. The ability to compete in price with traditional materials, such as plastics, has always been indispensable for the general acceptance of these new materials.

Griffin [1, 2] was the first to use starch as filler in synthetic plastics. Polyethylene films containing starch and other items based on this technology are available on the market. In this technology starch addition is restricted to a maximum of 10% by weight. The starch has to be dried to under 1% moisture to avoid steam formation during extrusion processes, and the starch granules are surface-treated (with silanes, for example) to increase the compatibility of the hydrophilic starch with the hydrophobic plastic matrix.

At almost the same time as Griffin's investigations, Otey [2–5] and his co-workers at the National Center for Agricultural Utilization Research (NCAUR) were studying the composites of starch and plastics in which the starch granular structure was totally disrupted. Blends of starch and polyethylene-co-acrylic acid (EAA) with addition of urea were used for film blowing, for example. In these materials, starch can develop into a continuous phase rather than being present as a particulate filler, so starch loading in these composites can reach 50% by weight while the mechanical parameters remain acceptable. The Feruzzi Group (Novamont) in Italy is marketing composites of this general type.

Starch-thermoplastic polymer composites have also been prepared by graft polymerization. Chemical treatment of starch leads to the development of free radicals in the starch backbone, and these can act in the presence of various polymers (polystyrene, polyethylene, and poly(vinyl halides)) as macroinitiators to yield polymer grafts of high molecular weight [6–8].

Starch biodegrades to carbon dioxide and water in a relatively short time relative to most synthetic polymers. In view of certain drawbacks in existing technologies for manufacture of biodegradable materials, there have in recent years been large-scale investigations into increasing the amounts of starch that can be used in starch-plastic composites to the highest possible level. The final objective of these

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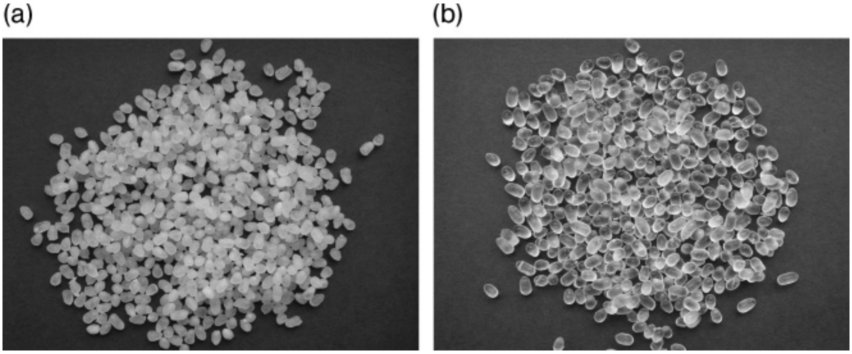

Figure 4.1 Thermoplastic starch with different glycerol contents: a) 15% glycerol, and b) 25% glycerol.

investigations is to obtain commercial items produced from pure starch for one-time use, and to exclude synthetic polymers from the formulation. Thermoplastic starch (TPS) seems to be a perfect solution because it can be processed with conventional technologies used in synthetic plastics manufacture (extrusion, injection-molding) [9–11].

To obtain thermoplastic starch (Figure 4.1), thermal and mechanical processing should disrupt semi-crystalline starch granules. As the melting temperature of pure starch is substantially higher than its decomposition temperature there is a necessity to use plasticizers, such as water. Under the influence of temperature and shear forces, disruption of the natural crystalline structure of starch granules and polysaccharides to form a continuous polymer phase has been reported [10, 12–22].

TPS produced from starch plastified only with water becomes very brittle at room temperature. To increase the material flexibility and to improve processing, other plasticizers, such as glycerol, propylene glycol, glucose, sorbitol, and others, are also used [12, 16, 17, 19, 20, 22].

To improve the mechanical properties of TPS-based materials, other additives can also be applied. These include emulsifiers, cellulose, plant fibers, bark, kaolin, pectin, and others [13, 14, 23–26].

4.1
Structure and Properties

Starch granules include both amorphous and ordered regions, the latter made up of short chains of amylopectin arranged in a cluster form. With regard to crystallographic net arrangement in the ordered zones there are two types of crystalline structure or polymorphic A and B types. A-type polymorphs are formed from the orthogonal packing of double helices with a small amount of tightly bound structural water. B-type polymorphs are formed by a more open hexagonal packing of the double helices, with 36 water molecules per unit cell, some of them located in channels formed by the hexagonal packing [27].

Starch is termed A, B, or C type, depending on the kind of crystallographic structure contained in the starch granules. A-type starches contain the polymorphic A pattern, B-type starches the polymorphic B pattern, and C-type starches both the polymorphic A and the polymorphic B patterns. This crystallographic structure depends on the botanical source of origin. There are also a few types of so-called crystalline V: the structure formed by amylose. Such crystalline amylose configurations develop when an amylose suspension is supplemented with an agent that enhances the whole structure formation.

The crystallites distributed inside granules in a specific way are recognizable by X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC). As starch exhibits birefringence, it is possible to detect the presence of a crystalline structure under polarized light by a characteristic interference pattern called the Maltese cross. Scanning electron microscopy (SEM) has been used to examine the surfaces and inner structures of the materials. It is thus possible to observe a plasticizer effect on the formation and homogeneity of the amorphous TPS structure. All the residues of starch granules, crystalline structures, and structural defects are clearly visible in the obtained material [10, 15, 27–32].

Thermoplastic starch can be obtained by suitable treatment with temperature and pressure in the presence of a plasticizer, such as water, glycerol, or sorbitol. The plasticizer penetrates into the starch granules and disrupts the initial crystallographic structure. Because of temperature and shear forces, the material undergoes a melting process and forms a continuous amorphous mass that no longer exhibits diffraction. If the total thermal and mechanical energy provided to the starch is insufficient the product will show nonmolten starch granules of clear A- or B-type crystallographic structure and with characteristic patterns in X-ray diffractograms. Similarly, use of an insufficient amount of plasticizer may result in incomplete destruction of the crystallographic structure of starch [20–22, 29, 30, 32–34].

Immediately after the processing (e.g., extrusion cooking) the starch does not show any residual crystallinity (or values lower than one percent). However, some hours after the manufacture a new type of crystallinity will develop. The structures are formed by single helices of amylose and they can be divided into three types, called the V_A type (non-hydrated), the V_H type (hydrated), and the E_H type. The E_H structure is not stable and under the influence of moisture it changes during storage into the V_H type, although the total amount of amylose crystallinity remains the same [20–22, 30, 34].

The amount of V-type crystalline structure depends on the processing parameters. The longer the material stays in the extruder, the more E_H-type crystalline structures are formed. This is likely to be the result of more severe destruction of the starch granules and the release of amylose. Similarly, an increase in screw rotation and processing temperature causes a rise in V-type crystallites. Below 180 °C V_H-type structures develop preferentially, whereas above this temperature structures of the E_H type are formed.

The number of amylose crystallites generated is also influenced by the composition of the blend. This number is proportional to the quantity of amylose in the starch. If the TPS materials contain only amylopectin, no amylose crystalline structure formation occurs. The V_H-type structures are formed in extruded TPS with a water content over 10%, whereas E_H- and V_A-type structures mainly occur in materials containing relatively small amounts of water (under 10%). If the water content in the mixture increases, the number of E_H-type crystallites formed decreases [21, 22, 30, 34].

A second type of recrystallization has been reported if the starch is plasticized with glycerol. During storage the amylose and amylopectin can recrystallize into structures of type A or B. The recrystallization rate depends on the starch source, amylose content, and storage conditions. When the ambient moisture content increases, the amount of crystalline structures rises. Similarly, with an increase in storage time (particularly at ambient moisture levels over 60%) the number of B-type crystallites increase [20, 28].

The rate of TPS crystallization during storage is affected substantially by plasticizer content. A large amount of plasticizer induces increased mobility of starch chains and lowers the glass transition temperature. Crystallization rates increase with water content growth. The presence of glycerol on the contrary, was found to decrease crystallization rates at constant water content through some interaction between starch and glycerol, reducing both the starch chains' mobilities and water stabilization. Because of glycerol's hygroscopicity, however, the water content usually increases, which lowers the glass transition temperature and intensifies the crystallization [21, 22, 28].

The structure of a TPS granulate surface depends to a great extent on the starch type used. In the case of potato starch application there is a reported gradual smoothing of the granulate surface with increasing glycerol content (Figure 4.2a–c). Owing to the great viscosity caused by glycerol migration, a granulate surface containing 30% of this plasticizer acquired defects due to granule stickiness. The material obtained from potato starch exhibited a relatively smooth structure with visible creases of irregular size and broadened contours of gelatinized, swollen starch clusters [35].

In the case of corn starch with 20% glycerol content, a smoother surface with smaller creases was observed, without clear marked starch fractions (Figure 4.2d). The surface with the most uniform structure was noted for granulate manufactured from wheat starch (Figure 4.2e). In the case of this material there is a visible parallel configuration of long polymer chains that give rise to the grooved character of the surface [35]. A similar fibrous structure was reported by Soral-Smietana *et al.* [36] on analyzing the structure of wheat starch heated at 121 °C in the presence of water.

On analysis of photos of cross-sections of the potato TPS granulate (Figure 4.3), similar conclusions can be made as in the case of the surface: that is, the homogeneity of the internal structure of the material increases with increasing percentage of glycerol in the material blend. In granulate containing 20% glycerol there are visible clusters of starch grains with free volume, implying non-uniformity of

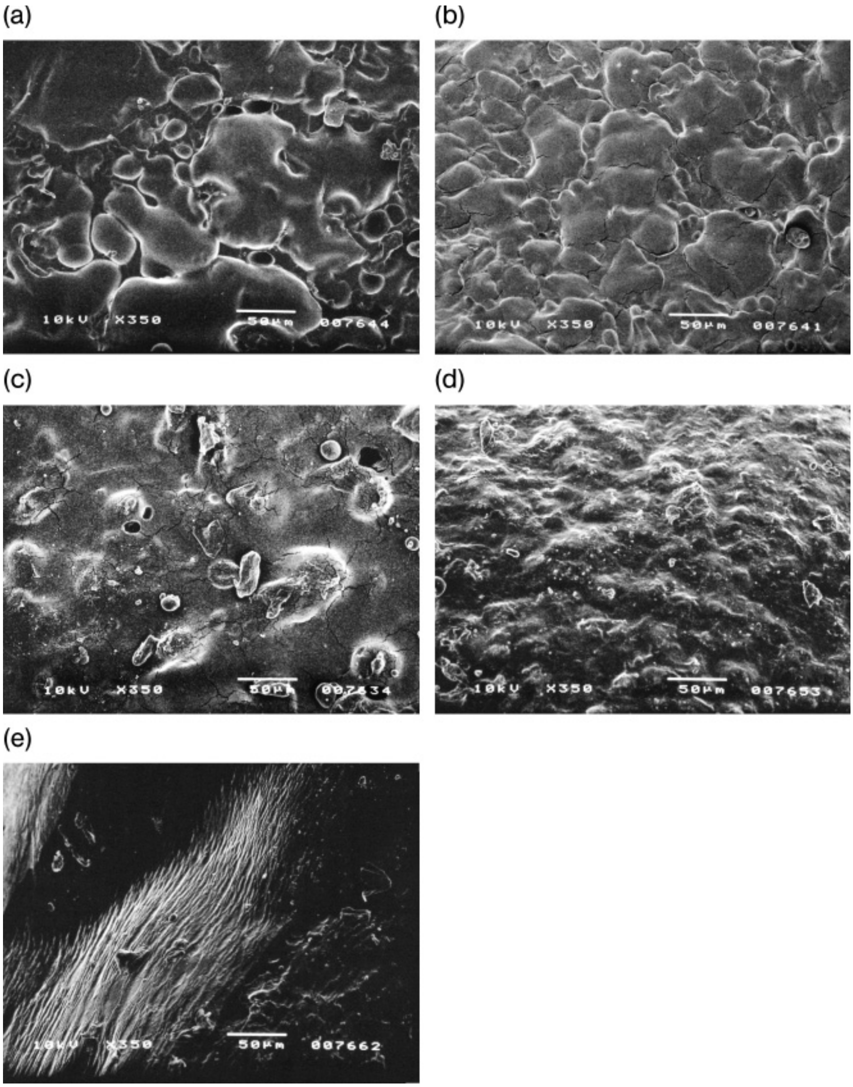

Figure 4.2 Surfaces of TPS granulates produced with differing glycerol contents, enlargement ×350: a) potato starch with 20% glycerol, b) potato starch with 25% glycerol, c) potato starch with 30% glycerol, d) corn starch with 20% glycerol, and e) wheat starch with 20% glycerol.

material. With an increased glycerol content of 25%, further flowing of starchy structures is recorded, inducing smoothing and uniformity of the whole mass. Irregular shapes of gelatinized starch granules are also noticed. A further increase in the amount of plasticizer up to 30% resulted in the development of a compact, gelatinized inner structure of the granulates, where few single starch granules

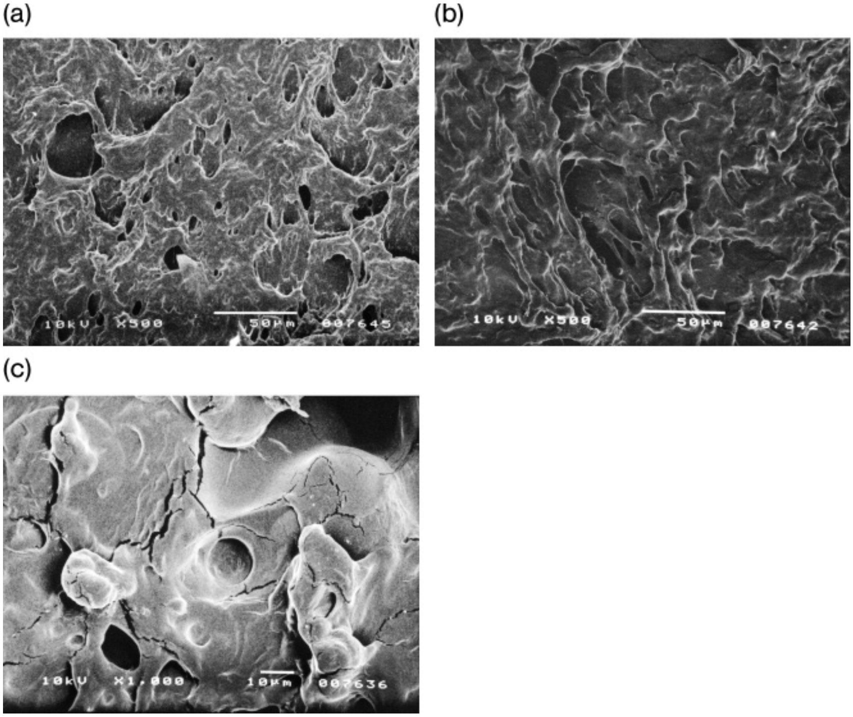

Figure 4.3 Cross-sections of potato TPS granulates developed from varied glycerol contents, enlargement ×500: a) 20% glycerol, b) 25% glycerol, and c) 30% glycerol.

appeared. In Figure 4.3c some free volumes are the residues of steam bubbles formed in the extrusion cooking process [35].

TPS materials obtained from corn and wheat starch exhibit spongy structures with numerous pores, along with size equalization and uniform spatial distribution of granulate masses. The pores are the result of excessive granulate expansion under barothermal treatment, making up a characteristic honeycomb structure reported for many plant extrudates [37–39]. Increased plasticizer content in the blend composition of the mixture processed induces enlargement of the forming pores (Figure 4.4).

At high enlargement (×1000) the changes in the granulate inner structure resulting from the use of different starch types are even more visible. Gelatinized starch surrounded with polymer matrix present in the materials obtained from potato starch with 20% glycerol undergoes gradual flowing into more homogeneous structures with an increase in glycerol content, constituting a relatively uniform, compact mass at 30% plasticizer presence [35].

In the cases of the materials obtained from corn and wheat starch there is clearly marked formation of larger pores with growth in glycerol content from 20% to

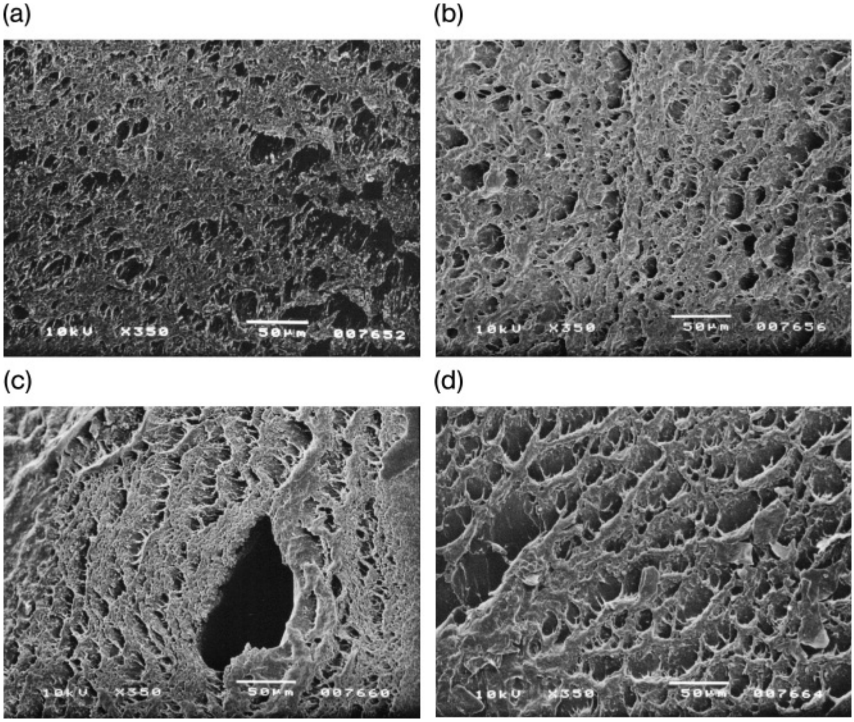

Figure 4.4 Inner structures of granulates from corn and wheat starch with varied glycerol contents, enlargement ×350: a) corn starch, 20% glycerol, b) corn starch, 25% glycerol, c) wheat starch, 20% glycerol, and d) wheat starch, 25% glycerol.

25%. A relatively dense material structure is reminiscent to a greater extent of a honeycomb structure [35].

4.2
Glass Transition Temperature

One of the major drawbacks associated with starchy materials is their brittleness. This is related to a relatively high glass transition temperature (T_g). This temperature marks the transition from a highly flexible state to a glassy one. T_g is considered the most important parameter for determining the mechanical properties of amorphous polymers and for control of their crystallization processes [40, 41].

The effect of starch plastification with water has been repeatedly studied, and various techniques for glass transition temperature have been compared. Differential scanning calorimetry (DSC) is used most commonly, but the glass transition temperatures found by DSC can be 10–30 °C higher than the T_g values obtained by NMR (nuclear magnetic resonance) or DMTA (dynamic mechanical thermal analysis). Analysis of the influence of water on the T_g values of amylose and amylopectin showed that the highly branched amylopectin had a slightly lower glass transition temperature than the amylose. On the grounds of published research and practical observation it can be stated that starchy material containing water is generally in the glassy state and therefore brittle under natural conditions [41–44].

However, the results of measurements published by various authors are inconsistent to a high degree, due to complex changes that occur in starch as a result of high temperatures and different measurement conditions.

Estimates found the T_g values of dry amylose and amylopectin to be 227 °C, whereas Bizot *et al.* [42] determined that the glass transition temperature of dry starch is 332 °C. An increase in water content in extruded TPS caused a drop in T_g irrespective of the starch type used. To decrease the T_g of potato TPS close to room temperature, about 0.21 g water is needed for 1 g starch [44–46].

Zeleznak and Hoseney [47] found that the glass transition temperature of wheat starch with 13–18.7% moisture varies between 30 and 90 °C and that T_g is likely to be lower than room temperature if the starch humidity increases above 20%. Van Soest *et al.* [48] determined a T_g value of 5 °C for extruded potato starch with 14% moisture content, whereas at higher moisture content the T_g could not be determined. Shogren showed that the glass transition temperature for starch with 7–18% moisture content ranged from 140 to 150 °C [49, 50].

Myllarinen *et al.* [44] indicated that the T_g values of amylose and amylopectin may equal the room temperature when the water content in a blend is 21%; however, at the same glycerol content it goes up to 93 °C. This leads to the conclusion that glycerol is a less effective plasticizer than water. Moreover, on the basis of calculations they found that a glycerol content as high as 35% is required to let the T_g value drop to room temperature [28].

For other plasticizers, such as sorbitol, the T_g value of TPS also decreases at increasing concentrations. Yu *et al.* [31] found that TP maize starch with 10% moisture and 25–35% glycerol shows T_g values running from 83–71 °C. Van Soest *et al.* [22, 34] showed that potato TPS with 11% moisture and 26% glycerol content had a T_g of 40 °C, whereas for the materials of higher moisture and glycerol content it fell below 20 °C. Lourdin *et al.* [51] reported that potato starch of 13% moisture with 15% glycerol content had a T_g around 25 °C, whereas at 25% glycerol content the T_g dropped to around 0 °C [8, 51, 52].

Three-phase systems obtained through starch plastification with water and glycerol behave in a very complex way. In studies on the influence of glycerol and other plasticizers on the T_g of potato starch it was found that glycerol plastifies starch in marked consistency with Coachman's model in the case of single-phase polymer/solvent systems. In research into barley starch plastified with water and glycerol a phase separation was detected, and calorimetric measurements showed two glass transition temperatures. Moreover, in a dielectric-mechanical analysis, investigations in which amylose and amylopectin were plastified with glycerol showed increasing phase separation with growth in glycerol content over 25%. Only recently has it been determined, on examination of the behavior of the two-component amylase/glycerol system, that the systems comprise amylose-rich phases and glycerol-rich ones [43, 53, 54].

Determination of glass transition temperatures of TPS by DSC is a hard task, as a result of the fact that starch is made up of two polysaccharides: amylose and amylopectin. Depending on the starch composition, DSC thermograms can show either the so-called "higher" or "lower" T_g values, or both at the same time. The higher and lower phases are detected in most cases in blends containing less than 30% glycerol. As implied earlier, this behavior is likely to be caused by the formation of starch-rich or glycerol-rich regions, which induces partial phase separation. The higher and lower transitions seem to be attributes of the glycerol-plastified starch, irrespective of processing method [53].

Mitrus [35] showed that the T_g of the obtained material decreases almost linearly with growth in glycerol content in the material blend. The highest observed T_g was 132.7 °C for 15% glycerol; the lowest was 18.1 °C at a glycerol level of 30%. Figure 4.5 shows the change in glass transition temperature with changing glycerol content. The moisture content of all the mixtures was 15%.

Research shows that, over the measured range, the moisture content of the processed blends has only a minimal influence on the T_g of thermoplastic starch. At 20% glycerol content there is a slight decrease in T_g with an increase in moisture content, consistently with scientific reports published in the literature [15, 17, 51]. In the case of a 25% glycerol level a reversed tendency was noticeable. With mixture moisture growth the T_g value went up as well. In these two cases, however, the T_g value changes are very small, and blend moisture content, over the measured range, has no significant influence on T_g changes. Figure 4.6 shows the influence of mixture moisture content on the T_g values of potato starch plasticized with 20 and 25% glycerol.

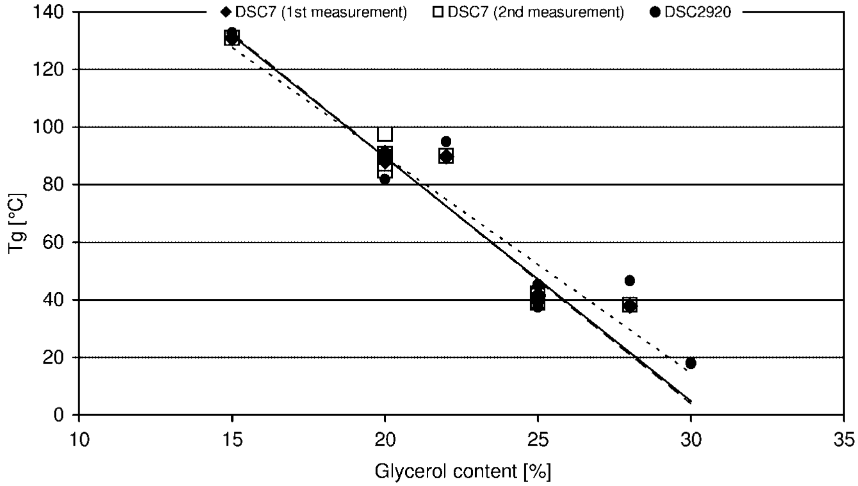

Figure 4.5 Influence of the glycerol content on the T_g of thermoplastic starch.

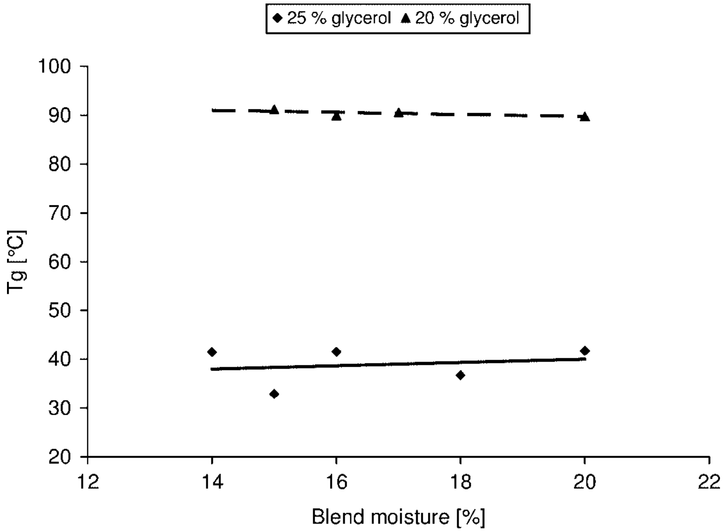

Figure 4.6 Influence of blend moisture on the T_g of thermoplastic starch.

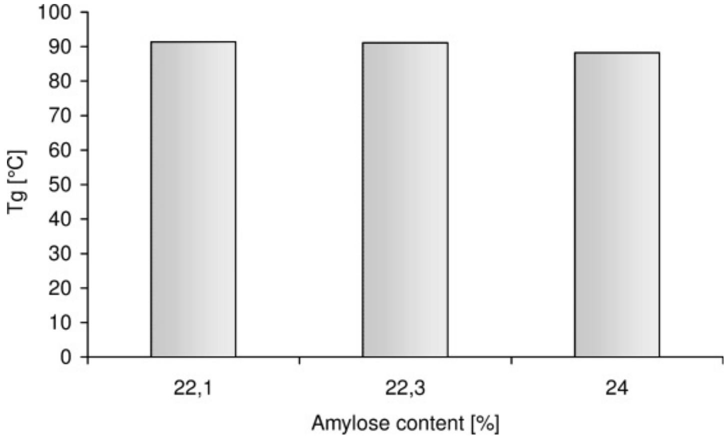

Figure 4.7 Influence of amylose content on T_g for samples with 20% glycerol.

Figure 4.7 illustrates the influence of amylose content on the T_g of thermoplastic starch for blends with 20% glycerol. A slight drop in T_g with amylose content increase was noted. It is possible that the differences in amylose content in our starches were too low for significant differences in the T_g values of the thermoplastic starch to be observable.

Figure 4.8 illustrates the influence of repeated extrusion on the T_g of thermoplastic starch for blends with 25% glycerol. A slight drop in the T_g can be noted on reprocessing thermoplastic starch. The maximum decrease in the glass transition temperature did not surpass 0.15 °C. However, it should be mentioned that

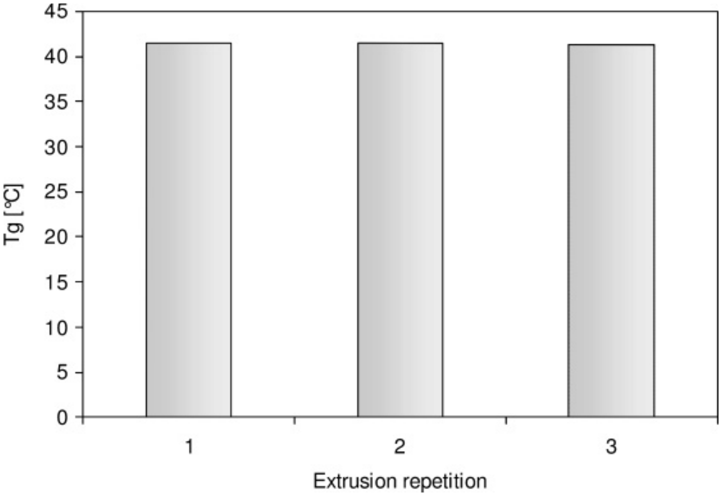

Figure 4.8 Influence of multiple extrusions on the T_g of thermoplastic starch.

to avoid thermal destructuring the repeated extrusion experiments were performed at slightly lower temperatures (by around 10 °C).

4.3
Mechanical Properties of Granulates

The mechanical properties of TPS depend on the starch production temperature and water content, as well as the quantity and type of added plasticizers and auxiliary materials. The most notable influence on changes in mechanical properties proved to be the amounts of plasticizer and auxiliary materials.

The most common plasticizers, such as glycerol, glycol, or sorbitol, possess hydroxy groups similar to those that appear in starch, and so are compatible with starch macrogranules.

Mitrus [35] showed that the radial expansion index value determined for TPS granulates strongly depended on extruder working conditions. This parameter was greatly affected by extruder screw rotation and, regardless of the mixture's material composition, the expansion index of the manufactured granulates increased with higher screw rotation speed.

No information concerning the expansion index of TPS is available in the professional world literature. Therefore, the results of research into this parameter can only be considered by reference to expansion indexes of other starchy products, for which it varies over a broad range from 1 to 10 or, in the case of expanded grains, even up to a factor of 17.

For TPS granulate produced in a modified TS-45 extruder a relatively low radial expansion index was determined: for the samples examined it did not exceed a value of 3.5 (Figure 4.9), thus being a favorable property. A clear upward tendency

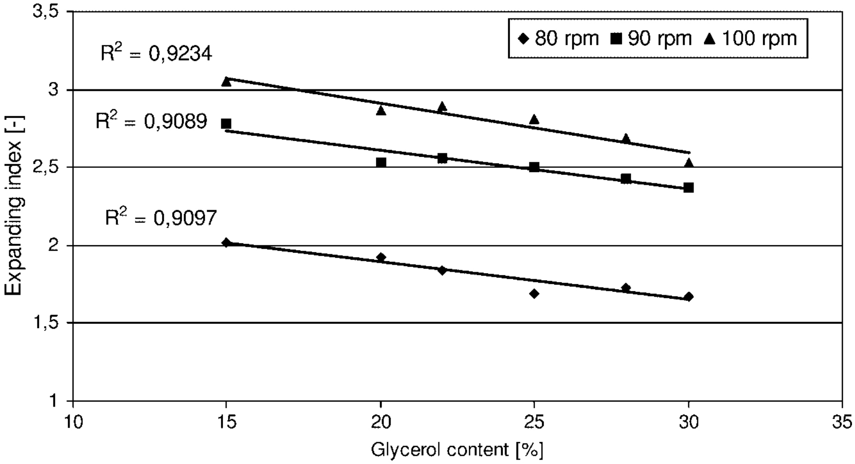

Figure 4.9 Changes in granulate expansion index produced from potato starch as a function of glycerol content for varied screw rotations.

was recorded with increasing screw rotation speed, irrespective of material mixture composition.

For extrudates manufactured from blends with varied glycerol contents a clear dependence of expansion index on screw rotational speed has been reported. The lowest expansion index was recorded for granulate production from mixtures of the highest glycerol content (30%), and the highest for mixtures with 15% glycerol. This index showed a downward tendency with increasing glycerol percentage in the material mixture.

Analysis of the expansion indexes of potato starch granulate with different amylose contents established a relation between this parameter and glycerol percentage (Figure 4.10).

For blends with 20% glycerol content a fall in the expansion index was recorded in the extrudates with higher amylose contents. In the case of mixtures containing 25% glycerol, however, a reverse tendency was reported. A rise in amylose content in starch brought about an increase in the radial expansion index. Studies on the expansion indexes of TPS granulate produced from various starch types revealed that, irrespective of starch type, the expansion index declines with increasing glycerol content in the mixture (Figure 4.11). The lowest values of this parameter were detected for potato starch, the highest for wheat starch.

Multiextrusion cooking of granulate affected the changes in the granulate expansion index, with the radial expansion index declining at a higher extrusion ratio (Figure 4.12). This effect is associated with processed material homogenization with repeated extrusion cooking.

Investigations showed that TPS density depends to a high degree on blend composition and moisture content (Figure 4.13). Assessment of this parameter established that granulate density increases with increasing glycerol content in the

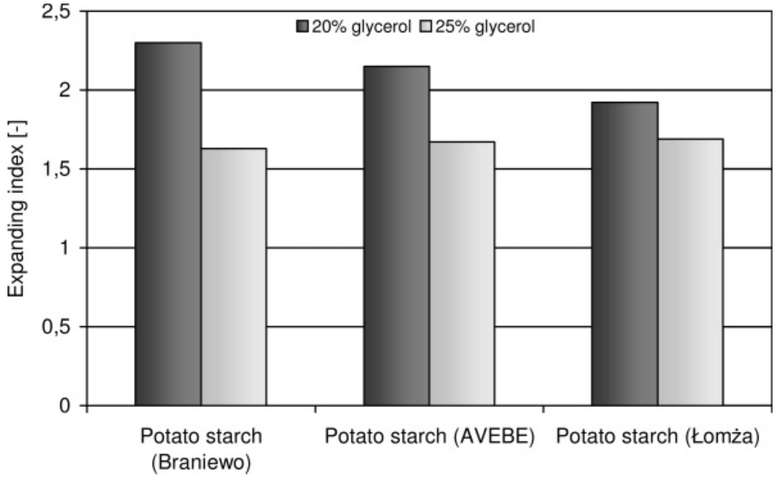

Figure 4.10 Changes in expansion index of granulate manufactured from potato starch with varied amylose content.

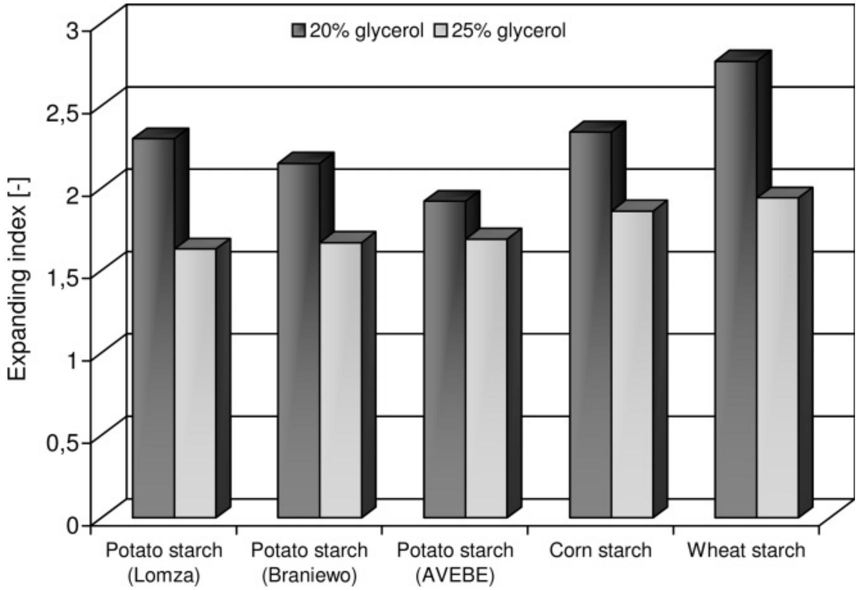

Figure 4.11 Changes in expansion index of granulate produced from different starch types.

mixture. The lowest density values were found for mixtures with 15% glycerol content, the highest for mixtures with 30% glycerol. It was also established that increasing mixture moisture content induces a rise in granulate density. If mixture moisture was increased by 5%, the density increase was 5–15% depending on the glycerol percentage.

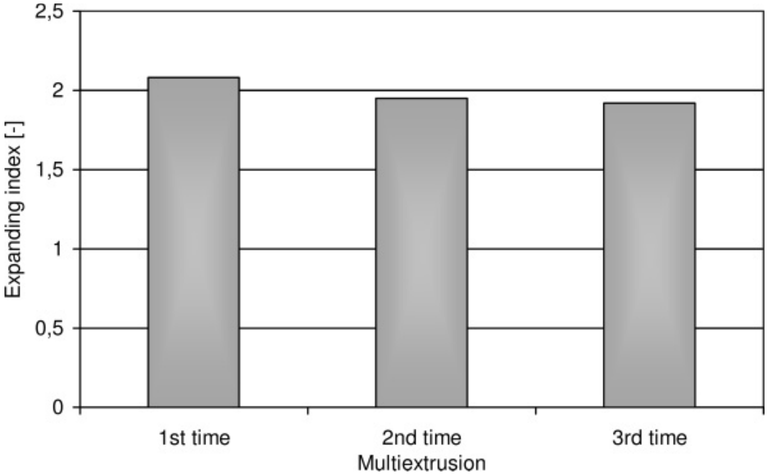

Figure 4.12 Impact of extrusion repetition on expansion index of granulates from potato starch.

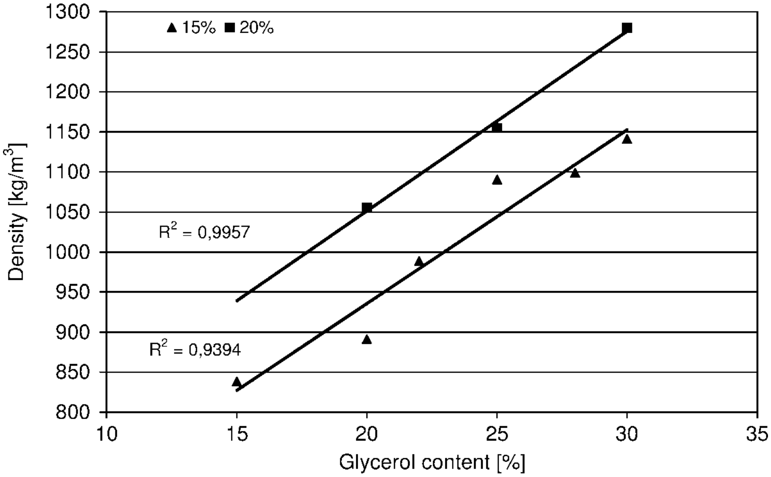

Figure 4.13 Influence of glycerol percentage on densities of granulates produced from potato starch for varied mixture moisture.

Density evaluation of granulate manufactured from different starch types established that, regardless of starch type, density increased with increasing glycerol percentage in the mixture (Figure 4.14).

In cases of mixtures with 20% glycerol content, the lowest density was recorded for granulate obtained from potato starch, and the highest for “maize” granulate. Turning to the mixtures with 25% glycerol content, the lowest density values were

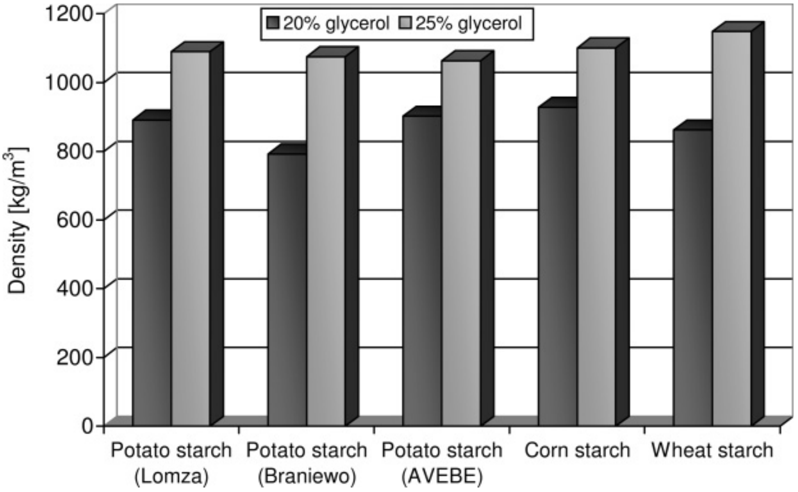

Figure 4.14 Densities of granulates obtained from different starch types.

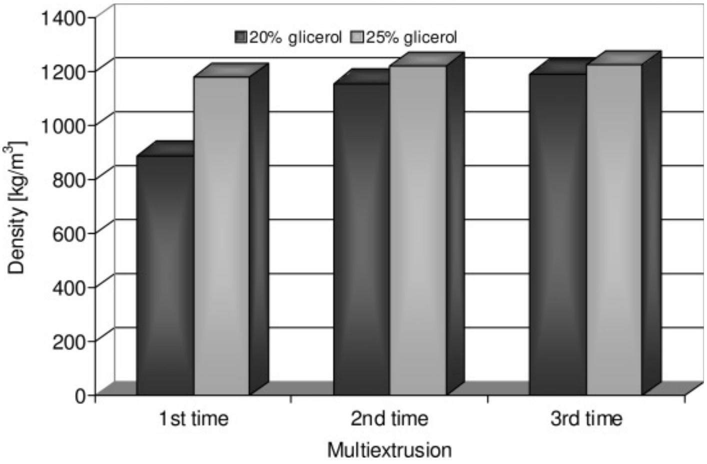

Figure 4.15 Impact of extrusion repetition on densities of potato starch granulates.

again observed for potato granulates and the highest now for those produced from wheat starch.

Research revealed an explicit influence of extrusion repetition on TPS density (Figure 4.15). Greater extrusion repetition induced an increase in granulate density irrespective of the material composition. This relationship was at its most pronounced in cases of extrusion of mixtures with 20% glycerol content. A considerable density rise was observed on double repetition of the mixture extrusion.

The densities of all the granulates produced ranged from 790 to 1280 kg m^{-3}, varying with material composition and mixture moisture. The lowest values of this parameter were attributed to excessive expansion of material. For investigation of material containing pores – that is, granulate of high expansion index – the measured density is actually a so-called apparent one. Apparent densities have been determined for potato starch mixtures with 15% glycerol content and for wheat and maize starches with 20% glycerol content.

The obtained density measurements for TPS were comparable with the data for typical polymer densities: polyethylene 920–940 kg m^{-3}, polystyrene 1030–1050 kg m^{-3}, poly(vinyl chloride) 1300–1410 kg m^{-3} [40].

Increasing plasticizer content brings about a decrease in the tensile strength of thermoplastic starch, whereas the elongation at break increases. Starch is a natural polymer containing numerous hydrogen bonds between the hydroxy groups in its molecules, and so it manifests substantial tensile strength values. Glycerol, sorbitol, or glycol behave as diluents and decrease the interaction between molecules, and consequently they diminish tensile strength. At the same time they act as plasticizers, which improves macromolecular mobility and leads to a rise in elongation at break [31, 32].

The increase in elongation at break with increasing plasticizer content occurs only for some ranges of glycerol content. If it surpasses 35%, a reduction in the elongation at break is noted. This effect is caused by a too-high percentage of glycerol, the molecular interactions therefore becoming so weak that some interactions between starch molecules are replaced by interactions between glycerol and the starch molecules [31, 36, 49, 51, 52, 55].

An increase in water content in the blend induces a decrease in the tensile strength of the TPS and an increase in the elongation at break. If water content exceeds 35%, however, a drop in the elongation at break of the TPS is detected [15, 49].

Addition of filler materials such as cellulose fibers, flax, kaolin, or pectin increases the tensile strength but reduces the elongation at break. In turn, addition of urea or boric acid improves the elongation at break but reduces the tensile strength [8, 14, 31, 56].

During storage of TPS some recrystallization of amylose and amylopectin occurs. With a longer storage period – and consequently greater TPS crystallinity – the tensile strength increases and elongation at break decreases. An increase in moisture content in the starchy materials under storage conditions brings about an intensification in the changes in their mechanical properties [20, 34].

In investigations carried out by Mitrus [35] it was found that with increasing glycerol content in a material mixture, a decrease in the maximum stress produced in granulate compression could be detected (Figure 4.16). In addition, blend moisture was also observed to have an effect on the maximum stress generated in a compressed granulate. The stresses produced with increasing mixture moisture are greater, but a faster drop in stress values with increasing glycerol content was recorded (see trend lines). In the case of granulate produced from mixtures with glycerol contents over 27% the stresses generated in granulate from moister blends are lower than those for drier ones. The results highlight the fact that an increase in glycerol percentage is accompanied by a lower tensile strength of the thermoplastic starch. Although water content increase may improve the strength

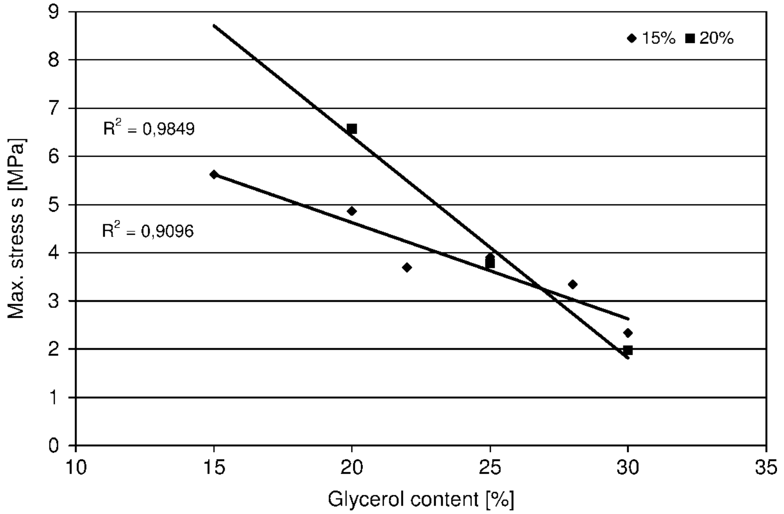

Figure 4.16 Influence of glycerol content on maximum stress of granulates from potato starch at compression depending on blend moisture.

of the obtained material, it is still most probable that some boundary value of total plasticizer content exists and that when it has been surpassed the material will become softer.

Excessive expansion and the presence of pores adversely affects TPS tensile strength (Figure 4.17). In an investigation of granulate from corn and wheat starch with 20% glycerol content very low stress values were detected. The presence of pores had a significant impact on tensile strength, weakening the obtained extrudate. In trials with 25% glycerol content the highest tensile strength values were recorded for the materials made from corn starch, and the lowest for those containing wheat starch.

On the basis of the studies carried out by Mitrus [35] it can be stated that repetition of extrusion affects the maximum stress value generated in compressed granulate (Figure 4.18). It was reported that the maximum stress value increases with repetition of extrusion, regardless of glycerol content in a blend mixture. Moreover, there is an increase in the difference in stress maximum value with progressing repetition of pressure-thermal treatment. Only at single extrusion was the stress maximum of material obtained with 20% glycerol smaller than that observed with a 25% glycerol content. This was a consequence of a small number of steam bubbles in the material of lower glycerol content, which induced its attenuation.

Studies on the mechanical properties of TPS granulate showed that a decrease in the Young modulus (*E*) was recorded with increasing glycerol content in the material blend (Figure 4.19). An increase of 15% in the glycerol percentage brings about a drop of over 50% in the Young modulus. This amounts to material

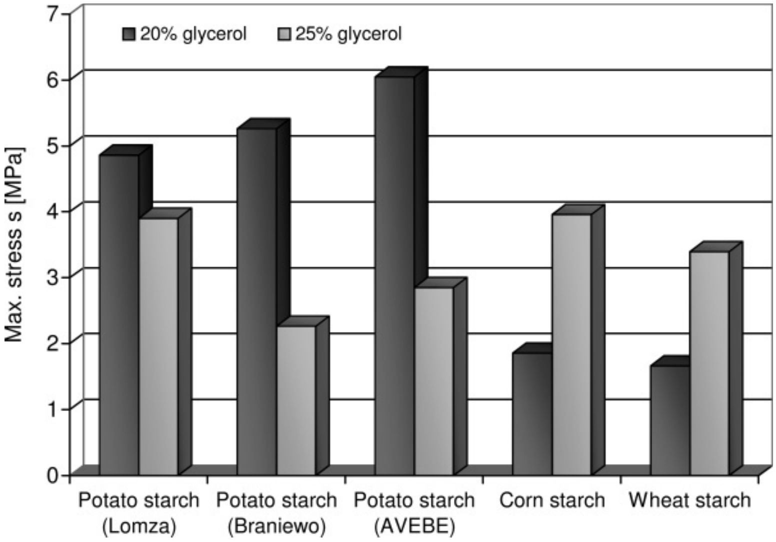

Figure 4.17 Impact of glycerol percentage on maximum stress of granulates at compression for varied starch types.

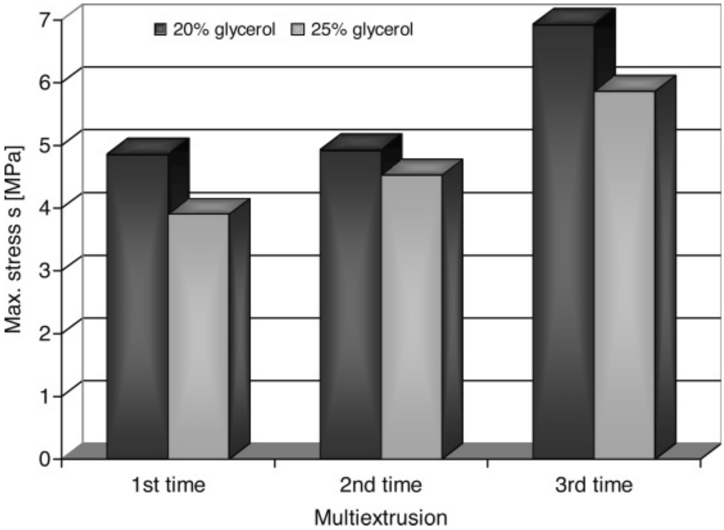

Figure 4.18 Influence of extrusion repetition on stress maximum at compression of granulates from potato starch.

elasticity weakening and confirms the results obtained during testing of the viscoelastic properties of granulate. Moreover, it was found that a mixture moisture content rise caused an increase in the Young modulus, just as an increase in glycerol content in the blend induced a decrease.

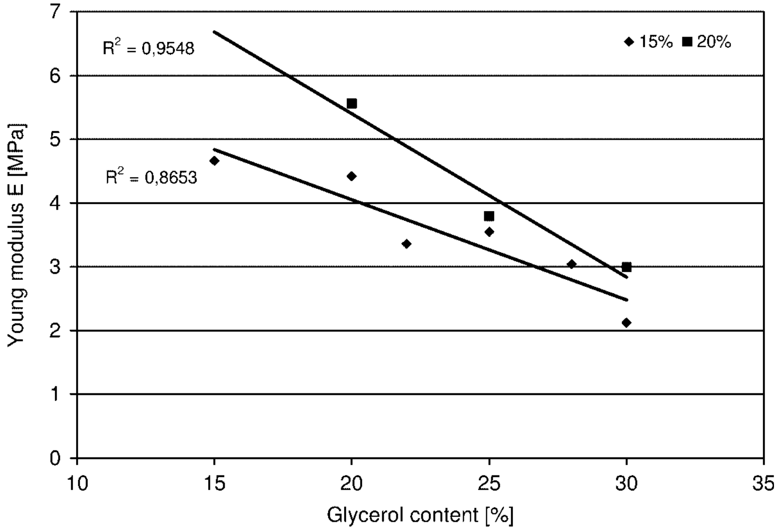

Figure 4.19 Influence of glycerol content on Young modulus of granulates produced from potato starch at compression depending on material blend moisture.

In the case of granulate from corn or wheat starch containing 20% glycerol, low values of Young modulus were obtained because of the presence of pores in the extrudates (Figure 4.20). This means that the pores stiffened the material to a great extent and at the same time decreased its elasticity. For samples with 25% glycerol, the highest Young modulus values were recorded for potato TPS and the lowest for wheat and corn thermoplastic starch.

Research has shown that repetition of extrusion influences the value of the Young modulus (Figure 4.21). Regardless of the glycerol content in a mixture, the Young modulus value rises – that is, the TPS elasticity increases – with repetition of extrusion . These results are in accordance with the findings made in investigations of the viscoelastic properties of thermoplastic starches.

Irrespective of the plasticizer type and amount, melted TPSs exhibit non-Newtonian flow behavior typical of pseudo-plastic liquids. Increasing plasticizer content causes decreasing viscosity, as a result of which TPS materials' flowing capacities increase. Thermoplastic starch shows a clear relationship between viscosity and temperature, also a well-known effect in the case of conventional polymers [8, 12, 26, 31, 32, 55].

The most common method for testing viscoelastic properties of materials is dynamic mechanical thermal analysis (DMTA). With this technique the changes in storage modulus (E') and loss modulus (E'') are evaluated as well as an internal friction parameter ($\tan \delta = E''/E'$) as a function of the temperature for several frequencies. E' is a measure of material flexibility and elasticity: the higher the modulus, the more flexible the material. E'' is related to deformation energy

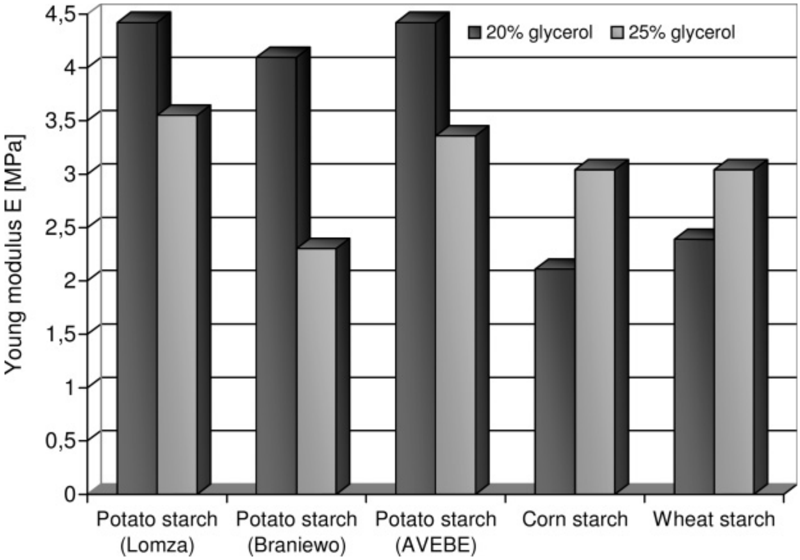

Figure 4.20 Impact of varied glycerol content on Young modulus at compression of granulates from different types of starch.

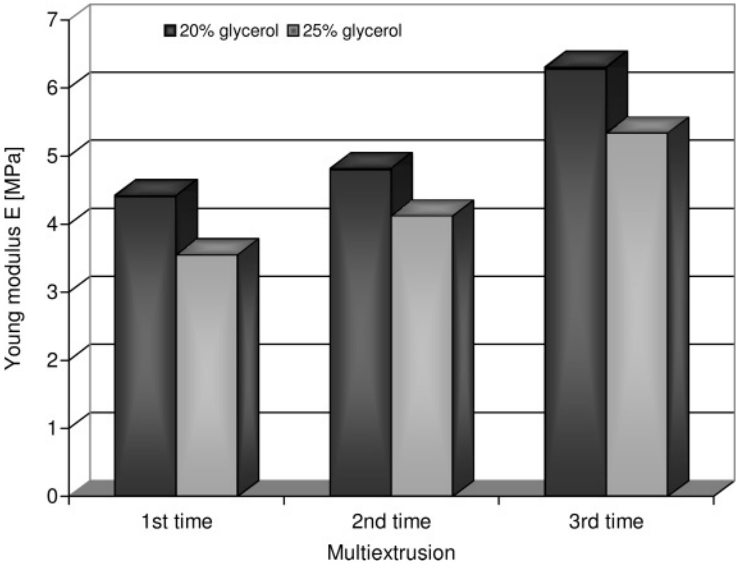

Figure 4.21 Influence of extrusion repetition on Young modulus at compression of granulates from potato starch.

dissipated as heat of friction and is related to viscosity. This technique is one of the major methods for T_g determination in plastics and TPS. Because of the considerable accuracy of the measurements it allows the so-called “lower” and “higher” T_g values to be fixed. The higher and lower glass transition temperatures are recorded for most blends with glycerol contents below 30% and are most likely to rise as a result of phase separation. They seem to be an attribute of starch plastified with glycerol, regardless of the processing method. Similar behavior has been reported for starch/sorbitol systems [29, 40, 41, 43, 46, 52–54].

Investigations into the viscoelastic properties of TPS were performed by Mitrus [35] for granulate from blends of potato, wheat, and maize starch with 20% and 25% glycerol contents. In the case of granulates from potato starch the impact of extrusion ratio on the changes in viscoelastic properties was studied.

During the research it was found that storage modulus (E') increases with extrusion repetition followed by a decrease in the potato granulate tan δ value with 25% glycerol content (Figures 4.22 and 4.23). In the case of triple extrusion the increase in elasticity in the obtained material relative to the primary value was 30%.

The results of research into TPS produced from different types of starch with 25% glycerol content indicated that the highest storage modulus values were obtained for potato starch and the lowest for maize starch material (Figure 4.24). Consequently, the highest internal friction tan δ values were recorded for maize starch and the lowest for potato starch (Figure 4.25). The highest elasticity difference in the produced materials occurred at temperatures approaching room temperature, and in the case of potato starch, E' was five times as high as in corn

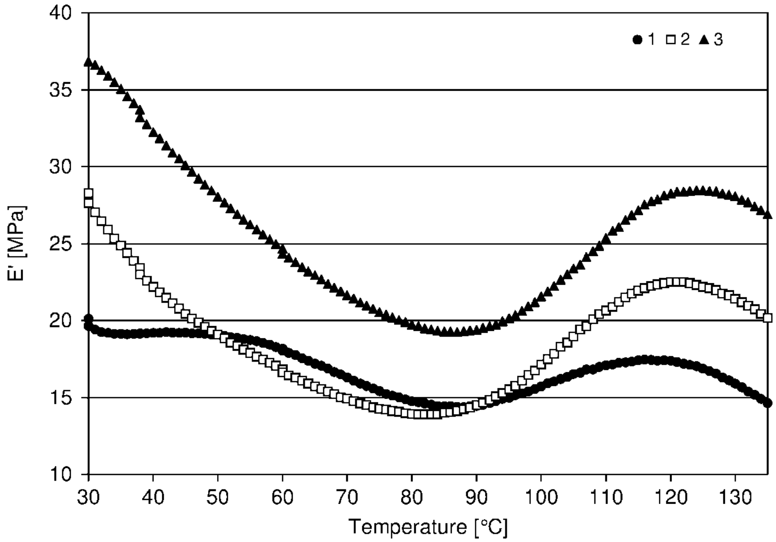

Figure 4.22 Changes in storage modulus as a function of the temperature of granulate from potato starch mixture with 25% glycerol (notation: 1- single extrusion, 2- double extrusion, 3- triple extrusion).

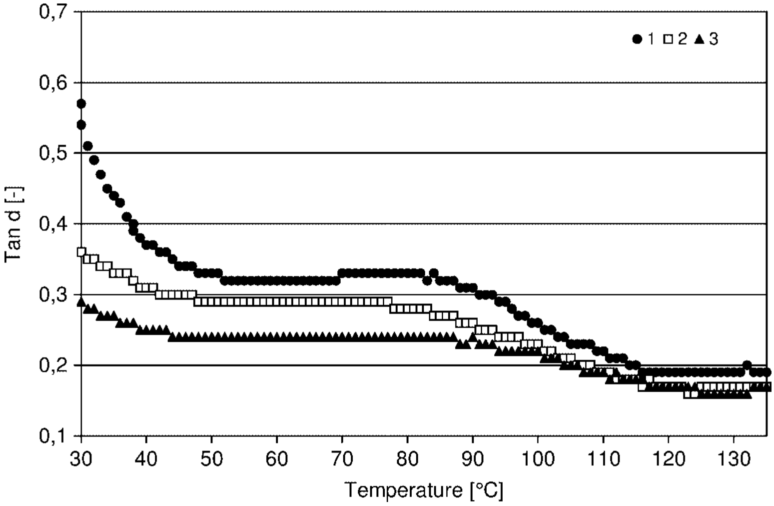

Figure 4.23 tan δ as a function of the temperature for granulate produced from potato starch/25% glycerol mixtures (notation: as in Figure 4.22).

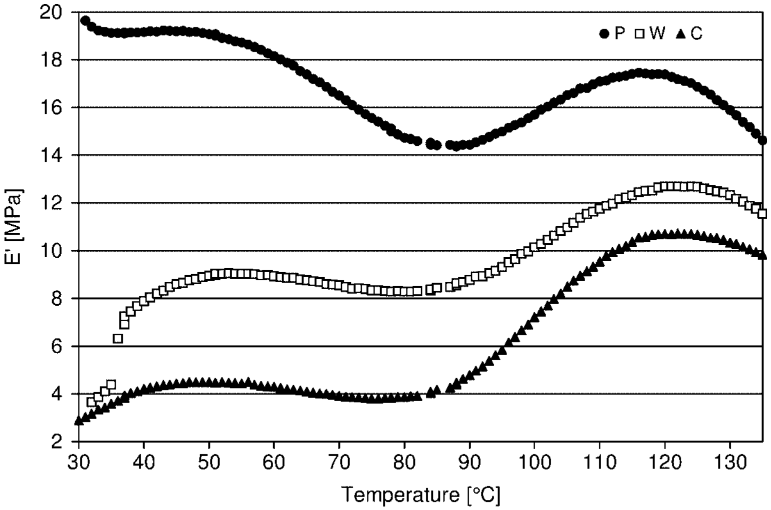

Figure 4.24 Changes in storage modulus in a function of the temperature for granulate obtained from different starch types with 25% glycerol contents (notation: P–potato starch, W–wheat starch, C–corn starch).

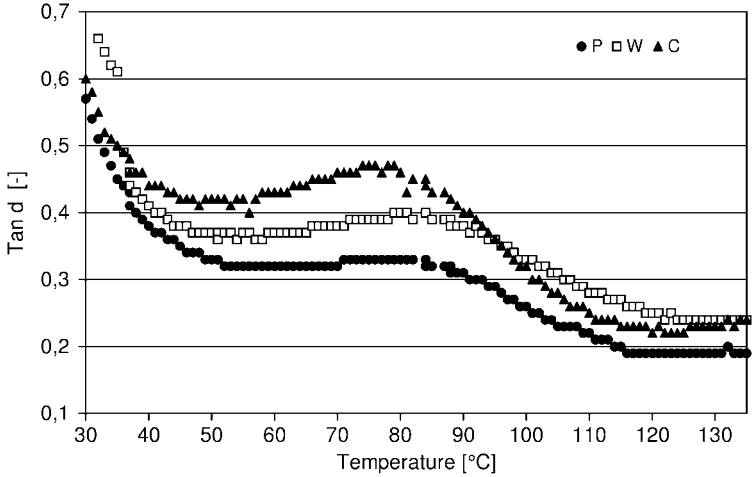

Figure 4.25 tan δ as a function of the temperature for granulates produced from varied starch types with 25% glycerol contents (notation: as in Figure 4.24).

starch. With increasing temperature the differences between the storage modulus values of the materials decreased, although potato starch granulates still kept elasticity higher by at least 30% than those obtained from corn starch.

The shapes of curves illustrating the changes in storage modulus reported for all the TPS types with 25% glycerol content indicate the formation of cross-linking in the extrudate structure. Because there do not appear to be any factors to induce such behavior in the composition of the raw material, it is most likely starch recrystallization that takes place. A relatively high glycerol content and the elevated temperature cause increased mobility of the polymer chains, thus facilitating new crystalline structure development. This effect needs to be investigated more thoroughly.

Investigations into the viscoelastic properties of granulates produced from different types of starch containing 20% glycerol showed that potato TPS demonstrated the highest values of *E′* and corn TPS the lowest, over nearly the whole temperature range studied (Figure 4.26). Over the 40–50 °C temperature interval, however, the highest values of storage modulus were exhibited by the materials obtained from corn starch and the lowest from potato starch. In the 50–70 °C temperature range it was also observed that the materials from wheat starch had the highest elasticity, whereas those from corn starch had the lowest.

Changes in *E′* values were manifested in the form of internal friction changes (Figure 4.26). The chart shows peaks for corn and potato starch associated with drops in *E′* values (Figure 4.27), suggesting glass transition appearance. The glass transition temperatures estimated from the charts (39 °C for potato starch and 42 °C for corn starch) are substantially lower than T_g values obtained by DSC. This corroborates the presence of materials with so-called higher and lower transition

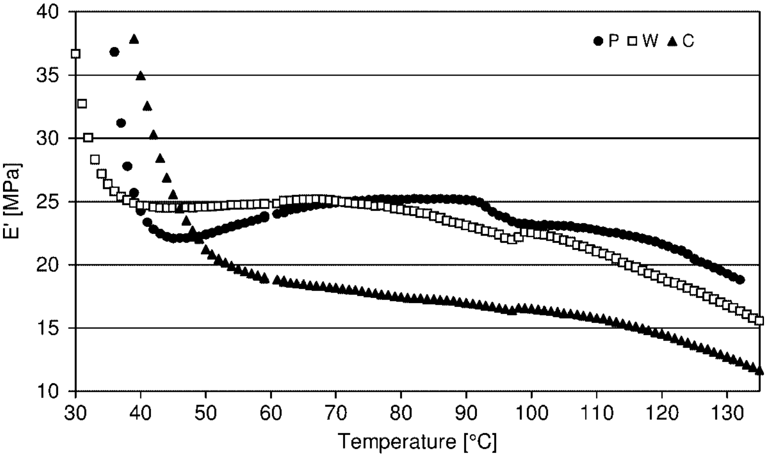

Figure 4.26 Changes in storage modulus as a function of temperature for granulates produced from different starch types with 20% glycerol contents (notation as in Figure 4.24).

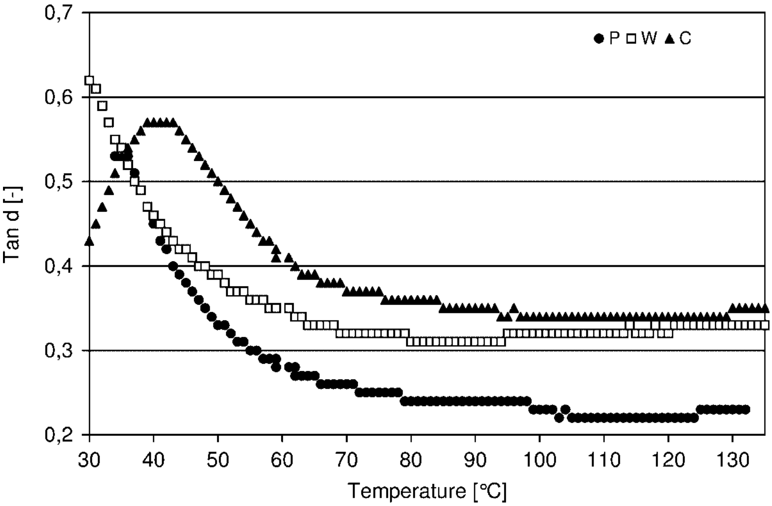

Figure 4.27 tan δ as a function of the temperature for granulates obtained from mixtures of different starch types with 20% glycerol content (notation as in Figure 4.24).

temperatures, as has been confirmed in papers by many scientists [29, 41, 43, 46, 51–53].

Comparison of storage modulus values obtained for materials of differing glycerol contents indicates that a decrease in the elasticity of the obtained material is recorded with increasing glycerol percentage in a mixture regardless of starch type used.

Investigations into water absorption by starch without a plasticizer found that amylopectin absorbs less water than amylose. The influence of glycerol addition on water absorption is similar for both starch components [42, 44].

At low relative ambient moisture, that is, below 50%, water content for both, amylopectin and amylose is lower in the presence of glycerol than without glycerol. This effect is probably associated with the replacement of strongly structurally immobilized water by glycerol. Similar behavior has been observed for starch plastified with sorbitol.

At relative ambient moisture levels higher than 50% the mixtures with highest glycerol concentrations showed the highest water contents. When ambient moisture exceeded 70%, water content in the starch plastified with glycerol proved to be higher than in starch without glycerol.

Although both starch components behave similarly with regard to water absorption, in the case of high ambient moisture levels amylose absorbs greater amount of water than amylopectin because the crystallization reduces water absorption by the hydrophilic polymers [17, 44, 53, 54].

4.4
Conclusions

The properties of TPS depend on the amount of water contained and the properties of the additives, as well as their amounts added to the starch.

Thermoplastic starch can be obtained by the extrusion cooking technique in the presence of a plasticizer, such as water, glycerol, or sorbitol. The plasticizer penetrates into the starch granules and disrupts the initial crystallographic structure. Scanning electron microscopy studies on the extrudate microstructures confirmed the differentiated structure of TPS as a result of the material compositions of the processed mixtures. The materials produced from potato starch had uniform and compact structures and their structure quality improved with increasing glycerol percentage. The materials from corn and wheat starch showed structures similar to honeycomb, rather unfavorable in this case. The structures of these materials indicate the necessity to observe technological procedures very strictly during the biopolymer extrusion cooking, with maintenance of appropriate barothermal treatment parameters for particular materials. Testing of structural changes occurring during extrusion can be helpful for evaluation of the functional behavior of the processed TPS.

Investigations have revealed that granulate specific density was predominantly affected by mixture composition and glycerol content. Increasing plasticizer content in a blend caused an increase in the density. The density of TPS can be comparable with the data for the densities of typical polymers: polyethylene 920–940 $\mathrm{kg\,m^{-3}}$, polystyrene 1030–1050 $\mathrm{kg\,m^{-3}}$, poly(vinyl chloride) 1300–1410 $\mathrm{kg\,m^{-3}}$.

Measurements of TPS glass transition temperatures demonstrate a direct influence of the plasticizer on the values. Generally, studies have revealed that the glass transition temperatures of the obtained materials decrease with increasing plasticizer content in the material mixtures.

Table 4.1 Influence of selected components on properties of TPS.

Component	T_g	Tensile strength	Elongation
water	–	–	+
plasticizer	–	–	+
fiber	n.d.	+	–
kaolin	n.d.	+	–
urea	n.d.	–	+
boric acid	n.d.	–	+

+, increase; –, decrease; n.d., no data.

An increase in the plasticizer content brings about a decrease in the tensile strength of thermoplastic starch, whereas the elongation at break increases. Starch is a natural polymer containing numerous hydrogen bonds between the hydroxy groups in its molecules, so it manifests substantial tensile strength values. Glycerol, sorbitol, or glycol act as diluents and decrease the interactions between molecules, and consequently they diminish tensile strength. At the same time they act as plasticizers, which improves macromolecular mobility and leads to an increase in elongation at break. Addition of filler materials such as cellulose fibers, flax, kaolin, or pectin increases the tensile strength but decreases the elongation at break. In turn, addition of urea or boric acid improves the elongation at break but reduces the tensile strength (Table 4.1).

At lower moisture contents, thermoplastic starch become very brittle, whereas at higher moisture levels it become more flexible and soft. It also rapidly loses strength when wet. This sensitivity to moisture obviously severely limits the usefulness of TPS in environments where humidity is very low or high.

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5
The Melting Process in Thermoplastic Starches

Agnieszka Wojtowicz

5.1
Introduction

Water is most often used as a plasticizer during starch transformation, and the minimum moisture content required for starch gelatinization is around 33%. There are many studies relating to different transformations of starchy material into thermoplastic forms with intermediate and high water levels. Specific mechanical energy (SME) values necessary for transformations decrease with increasing levels of water in raw material. A high water content in the mixture also influences the onset temperature, glass transition temperature, and rheological properties of the molten material [1–4]. In many scientific publications other plasticizers – that is, monoglycerides or glycerol – have also been examined as flexibility improvers [5]. Addition of glycerol influences the onset of gelatinization and results in an increase in the activation energy for the melting of the starch crystallites and in higher glass transition temperatures and stronger interaction forces between glycerol and starch polymers [4–8]. During the extrusion process high shear stresses and high values of energy input are present, and under these conditions the melting process may be enhanced [9]. The DSC technique or X-ray wide-angle diffractometry have been used for investigations with different types of starchy materials and with different combinations of starch/glycerol/water contents. Corn or waxy corn and wheat or barley starch have most often been investigated as basic thermoplastic raw materials [3, 10–18].

Time and temperature are the most important factors for melting of the crystalline components in starch, but the intensity of the shearing actions should also be taken into account [19]. Higher breakdown and degradation of corn starch molecules have been observed with increasing process time [20]. Starch breakdown was also more intensive when higher shear forces were used, which in turn increased the cold-water solubility of the starch [2]. There are some differences between the results of starch modifications during heating-shearing treatment, depending on the investigation method, the starch origin, and the treatment conditions.

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DSC is the most popular method for evaluation of melting enthalpy [21]. Test results achieved with different types of rheometers used to simulate the thermomechanical conditions differ and depend on the equipment used. The influence of the intensity of the treatment can be tested with a batch mixer, a cone and plate rheometer, a shear cell device with well-defined shear rate, a Couette-type device with variable eccentricity, or a compression molding device. All these devices can, to a certain extent, simulate different temperature and treating time processes: that is, mixing-kneading, extrusion-cooking, or injection-molding [9, 22–26]. The shear rate, temperature profile, and residence time during treatment simultaneously influence the starch behavior and properties. Changes in properties in excess water have also been observed in these research results. Most studies on the influence of water on properties have been carried out at high water content, but it is well-known that extrusion-cooking or injection-molding processes are done with limited (10–30%) water content. Properties of products can be measured by wide angle X-ray scattering (WAXS) or intrinsic viscosity [10]. Product behavior and properties after extrusion with a high level of water content are not always acceptable because of crystallinity, retrogradation, and stress-strain profiles of the materials expressed by the tensile strength or elongation [6].

Depending on the amount of glycerol in the TPS the product may be in a glassy or rubbery state at ambient temperature [24]. In the presence of sufficient amount of water or glycerol under gelatinization conditions native starch becomes gel-like in appearance or properties, but during the thermoplastic processing behaves like a polymer melt. Tests with different starch origins can be found in the literature [9, 20, 24].

5.2
Melting Process

The heating-shearing behavior of potato starch/glycerol mixtures with limited water addition (below 30%) was investigated by Wojtowicz and van der Goot [26] and by Wojtowicz (paper in print). The goal of the treatment was to use Brabender Mixograph simulating mixing-kneading and a specially designed shearing device-shear cell to obtain a starchy molten phase under well-defined thermomechanical processing conditions. This new equipment is based on the cone and plate rheometers approach, with the capability to isolate singular parameters, such as temperature, rotation speed, or shear stress in the equipment, during processing [20]. The base material was potato starch with addition of glycerol (20%, 22.5%, and 25%), together with added water (5, 10, 15, and 20% w/w). To compare the behavior of the starch, different starches were also tested under the same conditions (unpublished data). In the Brabender Mixorgaph and shear cell device the mechanical shearing and heating are simultaneously delivered to treated raw materials and transformation of starch/glycerol/water mixtures occurred.

Wojtowicz (in print) reports on mixing tests performed in a two-bladed counter-rotating batch mixer (Do-Coder E330, Brabender OHG, Germany) interfaced with a computer and control unit. Samples of starch/glycerol/water mixtures were placed inside the chamber and mixed for 2 minutes with 5 rpm screw rotation speed. The mixer temperature was set to 85 °C, heating was started directly after closing of the chamber, and the screw rotation was increased from 5 to 100 rpm over 3 minutes. Comparison of starch origins was performed with the same temperatures and times, but the screw rotation was increased from 5 to 80 rpm. Samples were treated for 10 minutes in total. During mixing the torque was recorded continuously.

The second shearing device was a shear cell, based on the cone and plate rheometer on a pilot scale (Figure 5.1). The details of this shearing device can be found elsewhere (Einde *et al.* [20] and Veen *et al.* [26]). Views of the equipment with starch before and after the treatment are shown in Figure 5.2. The mixture sample should be carefully loaded onto the plate at a uniform rate and the apparatus should be closed precisely, because of the pressure increase during the heating-shearing process. The treatment temperature was selected as 85 °C for samples with 15 and 20% added water, 88 °C for samples with 5 and 10% added water, and 115 °C for starch/glycerol mixtures. The rotation speed was 10 rpm during the first two minutes and was then increased gradually to 100 rpm over three minutes.

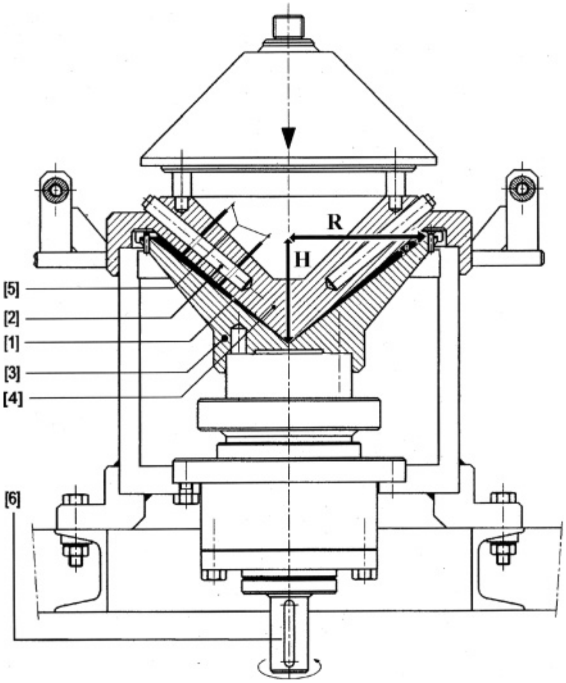

Figure 5.1 Shear cell equipment: 1) shearing zone, 2) heating elements, 3) rotating plate, 4) non-rotating cone, 5) thermocouple, 6) torque measurement point. Cone angle = 100°, shear zone angle = 2.5 °, R = 0.1 m, H = 0.082 m [25].

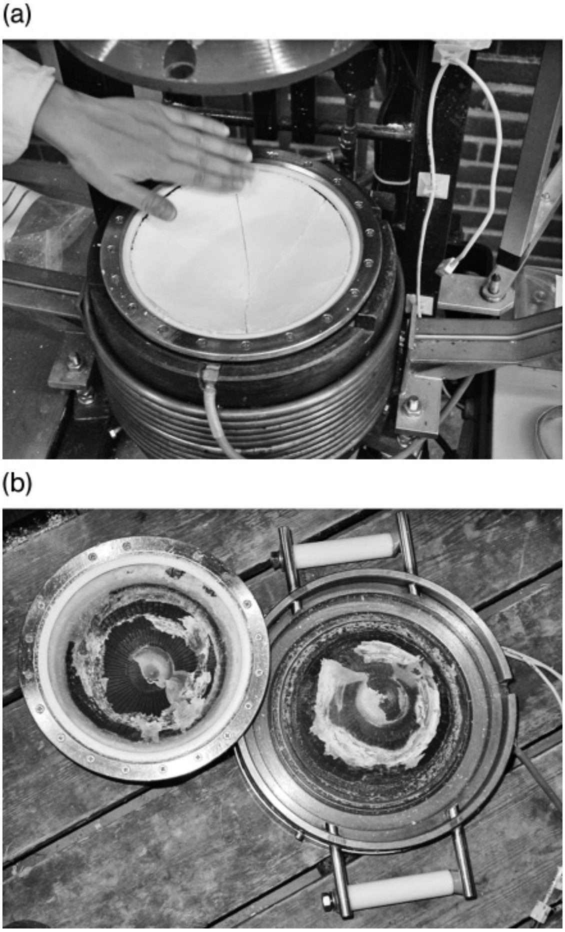

Figure 5.2 Starch/glycerol mixtures a) before and b) after shearing–heating process in shear cell device.

The torque changes during the treatment were recorded by use of a calibrated measurement device and used for further calculations. The shear stress (τ), shear stress multiplied by time ($\tau \cdot t$), and SME values were calculated and analyzed as a function of glycerol and water levels in the tested mixtures. The intrinsic viscosity (η) is very sensitive for thermomechanical treatment and the degradation of molecular weight compounds in starch, and so can be used as a method for molecular weight measurement. The authors [25] report intrinsic viscosities of native starch and of sheared-heated samples measured by the Ubbelohde viscometer method [20] at 25 °C. They also tested the microstructures of samples by optical microscope (Axioskop, Zeiss, Germany) with polarized light.

5.3
Influence of Plasticizers on Melting Behavior of Starch

Wojtowicz reported that the addition of water in amounts from 5 to 20% influenced almost every recorded parameter during treatment in the Brabender Mixograph. In treatment of starch/glycerol/water mixtures, decreasing start melting temperatures were observed from 80 °C for mixtures with limited water addition (5%) to 65–70 °C for samples with 20% added water. In addition, the time needed for melting of samples to begin also decreased with increasing water addition. It seems to be that water becomes a plasticizer for starch, and this is in accordance with previous reports [4]. The effects of addition of water on torque values and the decrease in torque with increasing water content in mixtures were also observed (Table 5.1), but torque values during mixing were quite low in comparison with those seen in the extrusion process and shear cell treatment.

It was also found that potato starch displayed lower melting temperatures than wheat and corn starch with glycerol and water addition, but at the same time higher maximum torque values were reported during the melting tests. The lowest torque values were reached for corn starch samples, independent of water addition. The temperature ranges from the start of melting were 80–95 °C for corn starch/glycerol mixtures, 78–91 °C for wheat starch/glycerol mixtures, and

Table 5.1 Results of main parameters calculated for potato starch/glycerol/water mixtures processed in the shear cell [25].

Starch/glycerol ratio (%)	Water (%)	Max torque (Nm)	Max shear stress (Pa)	Max SME (kJ/kg)	Shear stress multiplied by time (Pa*s)
80 : 20[a]	–	170.80	$5.21*10^4$	$1.02*10^4$	$7.82*10^6$
	5	200.79	$6.13*10^4$	$6.38*10^4$	$31.98*10^6$
	10	155.20	$4.74*10^4$	$3.76*10^4$	$17.95*10^6$
	15	132.12	$4.03*10^4$	$1.66*10^4$	$8.06*10^6$
	20	132.82	$4.05*10^4$	$1.78*10^4$	$8.28*10^6$
77.5 : 22.5	–	175.00	$5.34*10^4$	$2.12*10^4$	$11.22*10^6$
	5	174.71	$5.33*10^4$	$5.10*10^4$	$29.19*10^6$
	10	146.16	$4.46*10^4$	$1.27*10^4$	$8.79*10^6$
	15	135.78	$4.14*10^4$	$1.79*10^4$	$8.62*10^6$
	20	121.92	$3.72*10^4$	$1.66*10^4$	$7.78*10^6$
75 : 25	–	155.44	$4.74*10^4$	$3.91*10^4$	$23.19*10^6$
	5	138.85	$4.24*10^4$	$4.39*10^4$	$19.67*10^6$
	10	126.47	$3.86*10^4$	$1.38*10^4$	$6.48*10^6$
	15	121.65	$3.71*10^4$	$1.42*10^4$	$6.61*10^6$
	20	93.90	$2.86*10^4$	$2.11*10^4$	$10.18*10^6$

[a] Glycerol was replaced by water (80% starch – 20% water).

78–88 °C for potato starch/glycerol mixtures mixed at 80 rpm, depending on water content in the treated sample (unpublished data). Higher levels of water resulted in lower melting temperatures and lower maximum torque values in the tests (Figure 5.3).

During intensive thermomechanical treatment in the shear cell, shorter times necessary for the start of changes inside the structure were observed (Figures 5.4 and 5.5). This may be explained by the much higher shear stress during shearing-heating in the shear cell. It was not possible to start the melting process in potato starch/glycerol mixtures without addition of water, however, because the maximum temperature that could be achieved during heating in the water-heated Brabender device was 98 °C. After tests in shear cells it is now known that the starting melting temperatures for these preparations are about 115 °C at the 100 rpm used [25].

Mixtures with small amounts (5%) of added water show the highest values of torque, and increases in the water content lead to lower torques in both types of treatment.

Wojtowicz and van der Goot [25] noted that there were also visible differences in transparency and flexibility of samples produced after different types of treatment. After treatment in the Brabender equipment, samples became elastic with foamy consistencies and non-transparent, milky white colors. Only for samples of potato starch without and with small amounts of water did added material become brittle, as well as partially transparent with 5% added water or completely transparent and glassy in appearance for potato starch without additives. This last sample, though, was much stickier after treatment then the others. When they were warm, the samples were flexible and easy underwent elongation and formation into different shapes. After cooling at room temperature the materials had become hard and were no longer flexible.

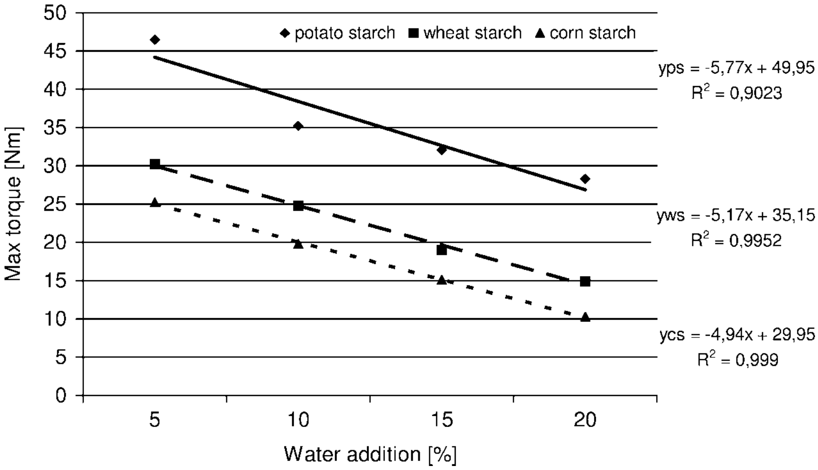

Figure 5.3 Influence of water addition on torque values for starch of various origins with 20% glycerol addition and different levels of added water.

All the samples with added glycerol that were heat-sheared in the shear cell were of visibly transparent glassy-like appearance and smooth surface; directly after processing they were easily prone to elongation and showed rubbery properties even after cooling to room temperature.

Glycerol addition also had a strong effect on test results. Nashed *et al.* [3] reported DSC observations of glycerol behaving as an anti-plasticizer by hindering the gelatinization process, and linear increases in onset temperature with increasing glycerol content were observed during treatment of wheat starch/water/glycerol mixtures. During thermomechanical treatment of starch/glycerol mixtures it was clear that addition of larger quantities of glycerol resulted in decreasing melting or gelatinization times and temperatures, and torque also decreased during treatment (Figures 5.6 and 5.7).

The influence of shearing-heating treatment on mechanical parameters calculated on the basis of the torque was also studied [25]. Comparison of data acquired from results during treatment of cornstarch and waxy cornstarch [20] showed higher values of maximal shear stress than for measurements with potato starch without or with small amounts of water, and almost identical values for initial moisture content in the 30–34% range. With increasing water addition the maximal shear stress values decrease; increasing glycerol content also results in decreases in the values of this parameter. Van der Veen [23] observed for potato starch/enzyme/glycerol mixtures (30% of moisture content (m.c.)) in a shear cell device at 50 rpm that the shear stress had increased after 30 s of shearing because of starch gelatinization, but that after 2 min of treatment it had decreased, due among other factors to degradation of starch.

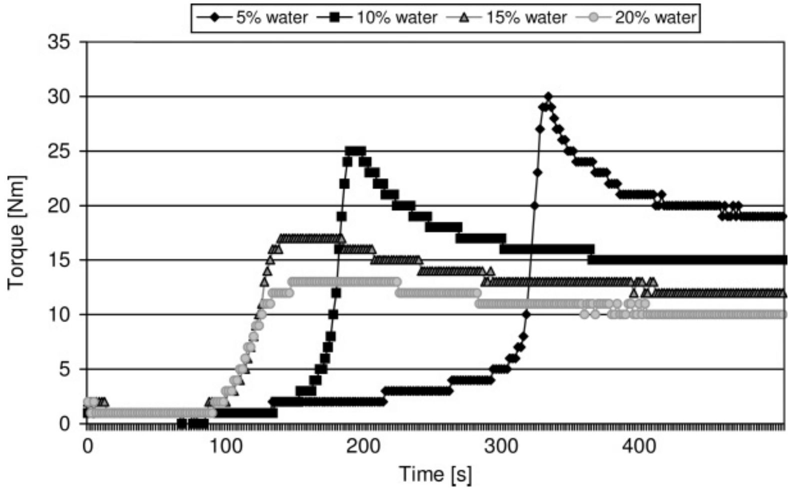

Figure 5.4 Influence of water addition on torque value during thermomechanical treatment of potato starch/glycerol (80 : 20) mixtures in the Brabender Mixograph (Wojtowicz, in print).

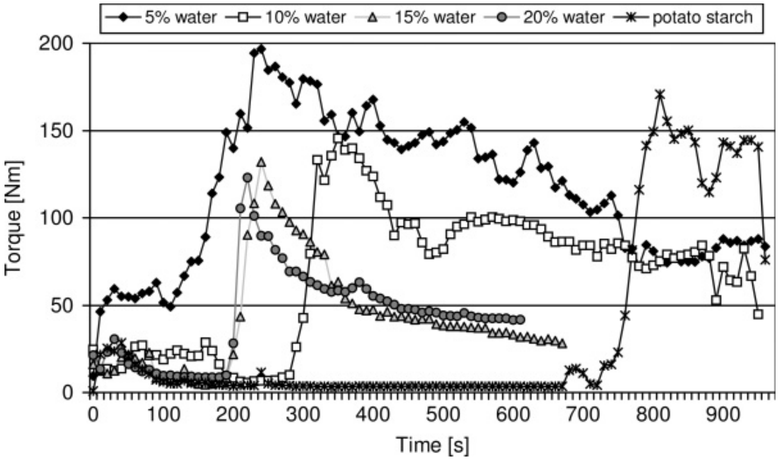

Figure 5.5 Influence of water addition on torque value during thermomechanical treatment of potato starch/glycerol (80 : 20) mixtures in the shear cell [25].

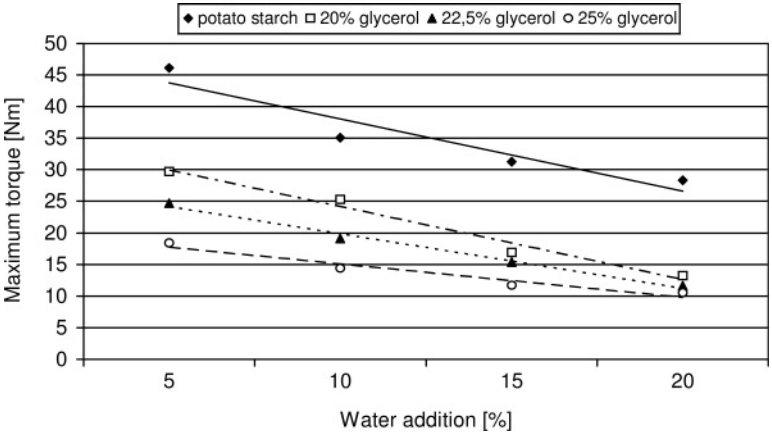

Figure 5.6 Effect of glycerol and water addition on maximum torque during treatment in the Brabender Mixograph (Wojtowicz, in press).

Almost all parameters calculated for samples of starch/glycerol mixtures without water addition showed lower values than with 5% added water [26]. Much lower values in SME and in shear stress multiplied by time were noted. According to previous data [20] it may be concluded that increasing moisture content should lower values of maximal shear stress and should thus reduce the macromolecular degradation. This can be confirmed by intrinsic viscosity measurement.

There are some differences in the extrusion behavior of potato and of cornstarch, as reported by Della Valle *et al.* [27]. Molten potato starch under the same conditions

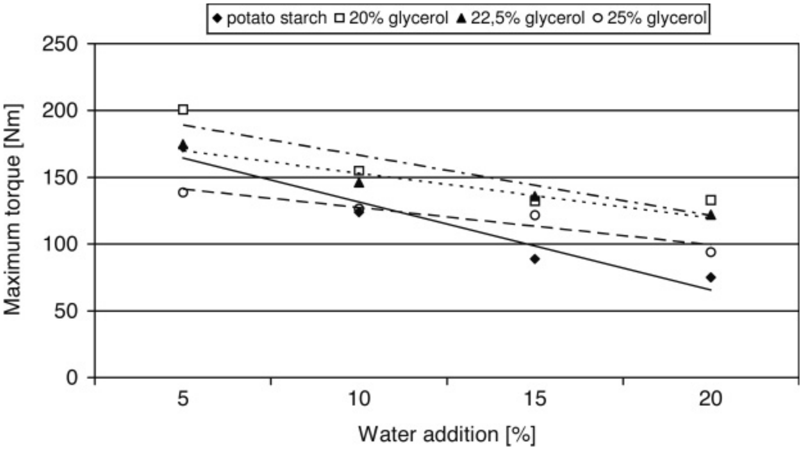

Figure 5.7 Effect of glycerol and water addition on maximum torque during treatment in shear cell device [25].

exhibits higher melt viscosity, earlier melting inside the extruder, and higher energy requirements. The first may be the result of the higher molecular weight of potato starch, whereas early melting requires lower transition temperatures than needed for the cereal starches. It has been found that increasing molecular degradation is observed with increasing extrusion temperature, but the influence of SME should also be taken into account [27]. Increasing the moisture content influenced the lower maximal shear stress, reducing the macromolecular degradation, but here the influence of the temperature on starch/water mixtures is strong [20]. Della Valle *et al.* [27] reported that an increase in moisture content increases the SME values and therefore decreases the molecular weight as measured by intrinsic viscosity.

The intrinsic viscosity of native potato starch was determined to be 369.8 mL g^{-1} [25]. Without addition of any plasticizer (water or glycerol), the starch seems quite thermostable. By comparing those data with data reported by van den Einde [20], it can be concluded that potato starch is less thermostable than cornstarch. With addition of plasticizer, a significantly reduced thermostability of starch can be observed. All achieved results are much lower than for native starch, and variation of the values is between 111 and 219 mL g^{-1} [25]. This means that high macromolecular degradation takes place during shearing-heating treatment in the shear cell. This is in accordance with the findings of Fujio *et al.* [28] for potato, corn, and wheat starches, of van den Einde [20] for cornstarch, of Rushing and Hester [29] for polymers, and also of van der Veen [23] for corn starch with added glycerol and enzymes. Intrinsic viscosity is very sensitive, especially to thermomechanical degradation (Figure 5.8). Low values of shear stress resulted in lower intrinsic viscosities of treated starch/glycerol mixtures. Larger amounts of glycerol, and also water, in the mixtures resulted in decreasing molecular degradation of starch granules whereas intrinsic viscosity values were a little higher, but these differences are not easy to explain.

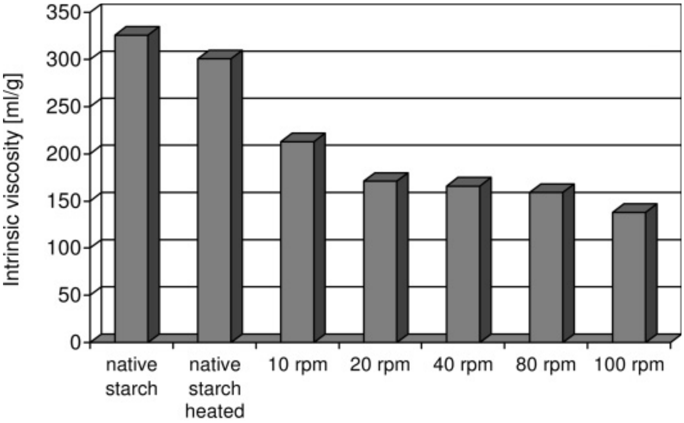

Figure 5.8 Effect of rotation speed on intrinsic viscosity during heat-shear treatment (87 °C, 10 min) of a mixture of potato starch with 20% of glycerol and 20% of water added (unpublished data).

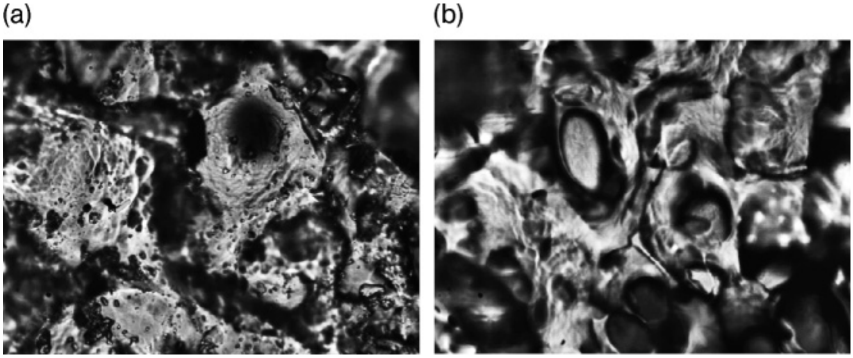

Figure 5.9 Microstructure of potato starch/glycerol/water treated in the shear cell without water addition: a) 20% glycerol, b) 25% glycerol [25].

Through comparison with native starch intrinsic viscosity values, this means that over 50% of residue starch molecules were broken by thermomechanical treatment. It has been suggested that increasing moisture content decreases the degree of starch degradation due to reduction of the stresses because the melt viscosity is reduced. On the other hand, water might be involved in the chemical reactions leading to thermal degradation and the effect of moisture content might be more complex [20].

The microstructures of shear-heated samples differ with glycerol and water levels (Figure 5.9). Figure 5.10 shows the structures of starch/glycerol mixtures with 10% added water. The smaller starch granules, in comparison with Figure 5.9,

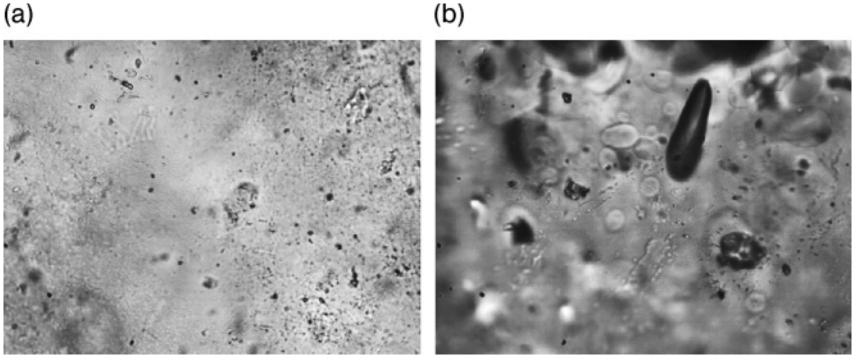

Figure 5.10 Microstructure of potato starch/glycerol/water treated in the shear cell with 10% of water added: a) 20% glycerol, b) 25% glycerol [26].

are clearly visible. That means the starch gelatinization process has taken place. There are only a few visible starch granules in the smooth homogenous network inside the samples. They start to become transparent and the milky color disappears.

Lower levels of glycerol caused better homogeneity of the mixtures than was achieved with 25% glycerol. In this sample individual starch granules are visible, but most of the product has been transformed into a compact mass with small amounts of gas bubbles.

Levels of water higher than 10% influenced starch gelatinization. Swollen starch granules in the gelatinized starch network were observed in samples with 15% of water added, but 20% added water resulted in smooth and homogenous structures in all the samples after the shearing process.

5.4
Conclusions

Gelatinization of thermoplastic potato starch is dependent on water and glycerol contents. Higher water and glycerol contents result in earlier melting and even gelatinization of the samples. Treatment only in the Brabender Mixograph is not in itself enough to gelatinize the raw materials even when using the same temperature and rotation speed range as during treatment in the shear cell. Water and glycerol contents also influence the shear stress: higher levels of water and glycerol cause lower shear stress values. Addition of larger quantities of plasticizers to starch during heat-shear treatment leads to lower breakdown of starch, expressed in higher intrinsic viscosity levels after treatment. Microstructure pictures show that the complete gelatinization process can easily be achieved by addition of 25% glycerol and 10–20% water to potato starch with use of the suggested thermal shearing parameters.

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6
Extruders

Leon P.B.M. Janssen

6.1
Introduction

Although there are a variety of different types of extruders, a main division that can be made is between single-screw extruders and twin-screw extruders. The most important difference between these two types of machines is the transport mechanism. A single-screw extruder consists of one screw rotating in a closely fitting barrel; the transport mechanism is based on friction between the material and the walls of the channel. If the material slips at the barrel wall, it is easy to envisage that it will rotate with the screw without being pushed forward. This makes these types of machines strongly dependent on the frictional forces at the wall and the properties of the material processed. Therefore, in the processing of natural polymers, single-screw extruders are less suitable for extrusion of mixtures with high water or high fat contents. However, many starch processes are possible in this (inexpensive) type of machine.

An exceptional type of single-screw extruder is the pin extruder. In this extruder the screw has interrupted flights and it rotates in a barrel with stationary pins. The effect is twofold: because of the rotation of the screw a good mixing action can be achieved, and because of the increased resistance against slip the throughput is more stable than in ordinary single-screw extruders. However, the pressure built up in this type of machine is rather poor. In some special types the screw not only rotates but also oscillates in an axial direction.

A twin-screw extruder consists of two screws, placed in an "8"-shaped barrel. In the case of intermeshing extruders the flights of one screw protrude into the channel of the other screw. Because of this, the polymer cannot rotate with the screw, irrespective of the rheological characteristics of the material. This indicates the most important advantage of intermeshing twin-screw extruders: the transport action depends on the characteristics of the material to a much lesser degree than in the case of a single-screw extruder.

Figure 6.1 represents the main types of extruders.

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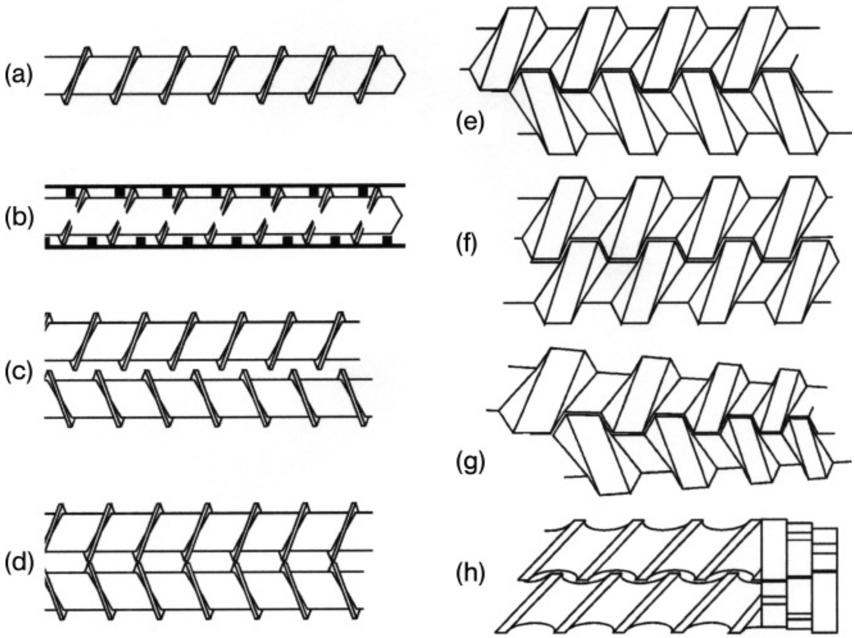

Figure 6.1 Different types of extruders: a) single-screw; b) co-kneader; c) non-intermeshing, mixing mode; d) non-intermeshing, transport mode; e) counter-rotating, closely intermeshing; f) co-rotating, closely intermeshing; g) conical counter-rotating; h) self-wiping, co-rotating.

- **The single-screw extruder (a)** is the most common machine, if no problems in transport are envisioned. The working characteristics of this relatively inexpensive machine are strongly dependent on the material properties. Very short single-screw extruders with high rotation rates are often used in the starch industry for gelatinization purposes. The barrel can be equipped with grooves to increase the friction and to prevent the material from rotating with the screw.

- **Pin extruder and co-kneaders (b)** have one single screw while the barrel is equipped with kneading pins and the screw flight is interrupted at the pin locations In co-kneaders the screw rotates and oscillates, giving a very good mixing action. In both types of extruders different pin geometries can provide different mixing actions. The pins can also be used for monitoring the temperature or as injection points. An important feature is that the pins prevent the material from rotating with the screw and therefore ensure a more stable operation than can be provided in an ordinary single-screw extruder.

- **Tangential twin-screw extruders (c and d)** are not closely intermeshing; they can be envisaged as a parallel connection of two single-screw extruders with mutual interaction. A model based on three parallel plates is often used to describe this type of twin-screw extruder. This model shows a strong resemblance to the two-parallel-plate model that is used for single-screw extruders. This type of machine has clear advantages if very elastic materials have to be extruded. The screws can be arranged in two different ways: a mixing mode (c) or a transport mode (d). All commercial tangential twin-screw extruders are counter-rotating.

- **The closely intermeshing twin-screw extruders, both counter-rotating (e) and co-rotating (f)** can best be modeled as series of C-shaped chambers. Because of the rotation of the screws these chambers transport the material from hopper to die, while interactions between the chambers occur through leakage flows. In general these leakage gaps are larger in co-rotating machines than in counter-rotating ones. Because of the large resistance to back-flow through the narrow gaps, these extruders have strong positive conveying characters and their stabilities are high.

- **The screws and the barrel of a closely intermeshing twin-screw extruder can also be conical (g)** This has advantages for the feeding process if the material has a low bulk density. While it is passing through the extruder the chambers gradually decrease in size and compress the material. Moreover, conical screws provide a larger space for the bearings of the screws and the screws can easily be removed from the barrel.

- **Depending on the exact geometry, self-cleaning co-rotating twin-screw extruders (h)** can be described in two ways. They can be modeled as series of C-shaped chambers with very wide leakage gaps or, more commonly, they can be considered to be constructed as continuous channels with some flow restrictions at regular intervals. This type of machinery imposes high shear forces on the material, and special shearing elements to increase shear even further are common. Both screw configurations with two or three lobes or thread starts per screw exist. Two-lobe screws possess a better conveying capacity and provide a higher throughput, whereas three-lobe screws have greater mechanical strength and higher shear rates in the channel. Most modern machines have two-lobe screws.

Closely intermeshing extruders, both co-rotating and counter-rotating, have in general deeply cut channels and narrow leakage gaps. Their rotational speeds are usually low, due to the large shear forces on the material in the gaps, so the average shear level imposed on the material in the chambers is low. Self-wiping extruders, on the other hand, have shallow channels (especially if equipped with triple-flighted screws). They operate with high rotational speeds and the transport efficiency (the amount of material transported per revolution) is lower than in closely intermeshing machines. In these machines the material is subjected to high average shear forces and the viscous dissipation is much larger than in closely intermeshing machines.

Conical twin-screw extruders have the advantage that the space provided for the bearing is large. Moreover, by moving the screws axially it is possible to compensate for wear of the screws. A disadvantage of machines of this type is that screw elements with different geometries are not easily interchangeable.

Tangential extruders are often used in situations in which the elasticity of the material would pose problems in the leakage gaps. Extruders of this type are mainly found in the rubber industry.

In general it can be concluded that, because of the large shear forces in the channel and the simple application of mixing elements, self-wiping extruders are often used in processes in which high shear is desirable. Their high shearing action is particularly convenient if intensive mixing or devolatilization is required. When working with thermoplastic starches the low average shear in closely intermeshing extruders is an advantage because degradation of the starch results in deterioration of mechanical properties. Moreover, because of the low shear levels the heat generated by viscous dissipation is low, allowing for good temperature control. On the other side, self-wiping extruders generally display better mixing action and higher throughput at comparable screw diameters.

6.2
Single-Screw Extruders

Single-screw extruders can be used in processes in which no slip occurs at the wall and in which high shear during the process is not a problem. Their working mechanism and modeling is well covered in the literature and an extensive description can be found in various books such as those by Rauwendaal [1] and by Tadmor and Klein [2]. The basis of the fluid flow in single-screw extruders can also be generalized to other types of extruders, so here we introduce a simple analysis based on Newtonian behavior of the liquid. For this analysis the channel of the screw is simplified into a flat plane geometry. The single-screw extruder consists of a barrel containing a rotating screw. As a first step in the simplification we will keep the screw stationary and let the barrel rotate. The next step is to unwind the screw channel into a straight trough. Figure 6.2 shows the results. The rotation of the screw can now be transformed into the movement of a plate over the channel. The velocity of this plate is of course the circumferential velocity of the screw and equals πND, whereas its direction relative to the channel equals the screw angle (ϕ). N is the rotation rate of the screw and D is the screw diameter.

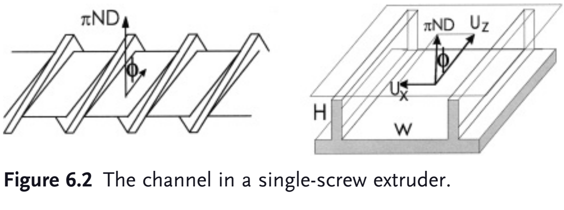

Figure 6.2 The channel in a single-screw extruder.

The velocity profile in the down-channel direction can, under the approximation of a Newtonian rheology, easily be calculated and, after integration, the throughput follows:

$$Q = AN - B\frac{\Delta p}{\eta} \tag{6.1}$$

where N is the screw rotation rate, Δp is the pressure difference over the zone and η is the viscosity. A and B are parameters that depend only on the screw geometry as shown in Section 6.8.1. The interesting aspect of this equation is that the influence of the rotation rate (the drag flow) and the influence of the pressure (the pressure flow) are uncoupled (Figure 6.3).

If the flow across the flights of the screw can be neglected (which is generally the case for the hydrodynamics in single-screw extruders) the velocity profile in the direction transverse to the channel is given by:

$$v_x = 3\mathrm{U_x}\frac{\mathrm{y}}{\mathrm{H}} * \left(\frac{2}{3} - \frac{\mathrm{y}}{\mathrm{H}}\right) \tag{6.2}$$

The profile of which, in combination with the down-channel direction, shows a helical path of the fluid elements through the channel.

The cross-channel flow forms a circulatory flow as sketched in Figure 6.4. The center of circulation, where v_x equals zero, lies at 2/3 of the channel height. This cross-channel profile must of course be combined with the down-channel profile; the cross-channel flow should be superimposed on the flow in the channel direction. As a result the polymer elements follow a helical path through the channel. The center of rotation of this helical flow lies at 2/3 of the channel height. Particles in this location follow a "straight" line through the channel without being interchanged with particles at other locations. Therefore these fluid elements will never

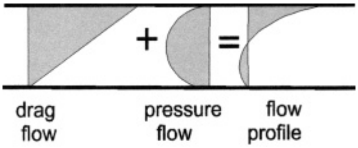

Figure 6.3 Superposition of drag flow and pressure flow in a single-screw extruder.

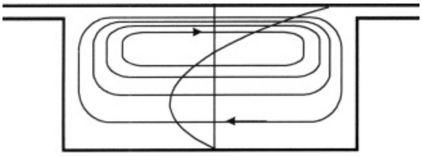

Figure 6.4 Rotating flow in the cross–channel direction.

approach the wall closer than 1/3 of the channel depth if no mixing elements are used in the screw design. This will appear to be particularly important when considering heat transfer and thermal homogenization in processes with viscous dissipation.

6.3
Pin Extruders

A particular type of single-screw extruder that can be used for starch processing is the pin extruder. An extruder of this type may have two different designs: one with stationary pins and a simple rotating screw and interruptions of the flights, called the expander, and one with a rotating and axially oscillating screw, generally known as a co-kneader. The latter type of machine is also often used in the rubber industry and in processes in which intensive mixing is required. Though discovered in 1945 and commonly used in industry, its application is far ahead of theoretical understanding.

The co-kneader also consists of a single screw with interrupted flights [3]. A schematic representation is given in Figure 6.5. Its working principle is based on the rotation and axial oscillation of the screw, causing transportation and mixing. The mixing is enhanced by stationary pins in the barrel. During one passage of the pin, the material is subjected both to high shear stress and to reorientation. The dispersive mixing process is promoted by the local weaving action of the pins and screw flights, in which the distributive mixing is enhanced by the reorientation that is introduced by the pins. Figure 6.6 displays an unrolled screw and barrel. The trajectories of the kneading pins are visualized in relation to the rotating screw. It is clear that all surfaces are subjected to wiping actions.

The expander extruder is a relatively simple machine. The function of the pins is twofold: to provide a more stable throughput and to improve mixing. Because of the stationary pins, slip at the wall is prevented and the material cannot rotate with the screw. This provides a more stable throughput. The mixing is increased

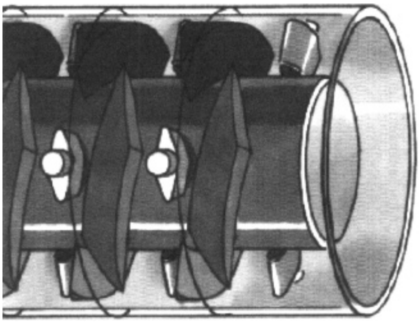

Figure 6.5 The co-kneader (from [3]).

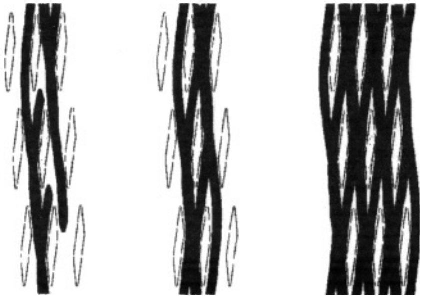

Figure 6.6 Paths of the kneading pins with respect to the screw flights (from [4]).

relative to an ordinary single-screw extruder. Pin extruders provide both distributive and dispersive mixing. The distributive mixing is caused by the geometry of the screw flights. The interruptions in the flights divide material in the screw channel into two streams. After the following interruption of the screw flight the streams recombine partially and the material is divided again. The kneading pins also provide a rearrangement of the stream lines. Because of these two effects the distributive mixing of a pin extruder is very good and the distributive mixing process requires relatively low energy.

Through the rotating and oscillating movement of the screw in a co-kneader, the screw flights slide along the pins and barrel. This results in high shear stresses and disperse mixing. It also leads to good self-cleaning properties, which is much less the case in expander extruders.

The temperature can be controlled by the thermostatted barrel and screw. The large area/volume ratio, together with the radial mixing, contribute to good heat transfer capacities. These characteristics make pin extruders well-suited for processes in which good dispersive mixing is required, although a disadvantage is that the relatively high shear can easy give rise to degradation of the starch. Because of the large interruptions of the flights it is not possible to use this machine for pressure build-up. If, at the end of the line, pressure is needed, a normal single-screw extruder is generally placed behind the pin extruder. The mixing mechanism in the co-kneader is rather complex.

6.4
Closely Intermeshing Twin-Screw Extruders

If the chambers of a closely intermeshing twin-screw extruder are fully filled with material, the maximum throughput of a zone (Q_{th}) can be written as the number of C-shaped chambers (Figure 6.7) that is transported per unit of time, multiplied by the volume of one such chamber:

$$Q_{th} = 2mNV \tag{6.3}$$

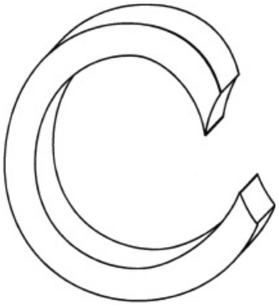

Figure 6.7 The C-shaped chamber (from [4]).

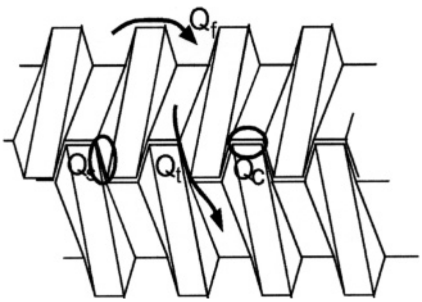

Figure 6.8 Leakage gaps in a counter-rotating, closely intermeshing twin-screw extruder (from [4]).

Here N is the rotation rate of the screws, m is the number of thread starts per screw, and V is the volume of a single chamber. In reality the output of a twin-screw extruder is, of course, smaller than the theoretical throughput, because the chambers are not completely closed. Four different kinds of leakage flows can be distinguished [4] (see Figure 6.8):

- Leakage (Q_f) through the gap between the flights and the barrel wall. This leakage shows clear parallels with the leakage that occurs in a single-screw extruder. The gap through which this leakage flows is called the flight leak.
- Leakage (Q_c) between the flight of one screw and the bottom of the channel of the other screw. Because the flow through this gap resembles the flow in a calender this leak is called the calender leak.
- Leakage (Q_t) through the gap between the sides of the flights, which is called the tetrahedron leak. In principle, this leak is the only leak that leads from one screw to the other. In closely intermeshing counter-rotating twin-screw extruders, this gap is generally very narrow. In self-cleaning counter-rotating twin-screw extruders this gap is very wide and the major part of the material passes through this gap regularly.

- Leakage (Q_s) through the gap between the sides of the flights, normal to the plane through the two screw axes. This leak is called the side leak. In its behavior this leak most resembles the calender leak.

The throughput through the different leakage gaps consists partly of drag flow and partly of pressure flow. The pressure flow, in its turn, is a consequence of the internal pressure build-up in the chambers and of the pressure that is built up at the die, resulting for the leakages in:

$$\begin{aligned} Q_\mathrm{f} &= A_\mathrm{f} N + B_\mathrm{f} \frac{\Delta P}{\mu} \quad Q_\mathrm{s} = A_\mathrm{s} N + B_\mathrm{s} \frac{\Delta P}{\mu} \\ Q_c &= A_\mathrm{c} N + B_\mathrm{c} \frac{\Delta P}{\mu} \quad Q_\mathrm{t} = A_\mathrm{t} N + B_\mathrm{t} \frac{\Delta P}{\mu} \end{aligned} \tag{6.4}$$

here the subscripts f, s, c, and t stand for flight, side, calendar, and side gap. The total amount of leakage through a section of the extruder is the sum of the individual leakage flows. For a screw with *m* thread starts this can be written as [4]:

$$\Sigma Q_\mathrm{l} = 2Q_\mathrm{f} + Q_\mathrm{t} + 2m(Q_\mathrm{c} + Q_\mathrm{s}) = AN + B\frac{\Delta P}{\mu} \tag{6.5}$$

in which ΔP is the pressure drop between two consecutive chambers, μ the viscosity, and N the rotation rate of the screw. Numerical values for A and B and for the chamber volume (V) follow from the geometrical parameters of the screws only and are given in Section 6.8.2 of this chapter. The real throughput of a pumping zone in a twin-screw extruder, completely filled with polymer, can now be determined easily.

$$Q = Q_\mathrm{th} - \Sigma Q_\mathrm{l} = (2mV - A)N - B\frac{\Delta P}{\mu} \tag{6.6}$$

For Newtonian liquids the use of dimensionless numbers for throughput and pressure drop leads to simple relations:

$$\begin{aligned} Q^+ &= \frac{Q}{2mNV} \\ P^+ &= \frac{\Delta P}{N\mu} \end{aligned} \tag{6.7}$$

Here ΔP is the pressure drop per chamber, caused by the pressure in front of the die, and μ is the Newtonian viscosity. These two dimensionless groups for throughput and pressure are very powerful. When these groups are used, the characteristics for the completely filled pumping zone of twin-screw extruders are straight lines that are independent of viscosity and speed of rotation of the screws. Figure 6.9 presents an example of these lines and their dependence on the size of the

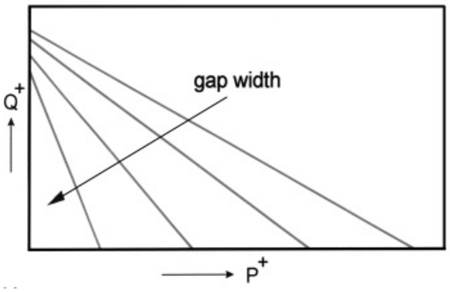

Figure 6.9 Dimensionless pressure-throughput characteristics of a counter-rotating twin-screw extruder.

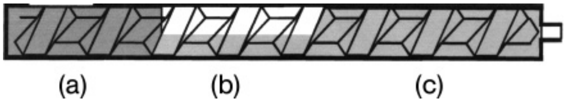

Figure 6.10 The different zones in a twin-screw extruder when fed with solid material: a) solids transport, b) partly empty, c) fully filled.

calender gap. As these lines are only dependent on geometrical parameters, they keep their validity when the pumping zone of a twin-screw extruder is scaled up geometrically. If, for instance, the screw diameter, the pitch, the chamber height, and the different leakage gaps are all enlarged by the same factor, the lines do not change.

6.4.1
The Different Zones

If a twin-screw extruder is stopped and opened, several zones can be distinguished clearly (Figure 6.10). Depending on whether the extruder is fed with a solid or a liquid material, two different situations occur. In the case of a solid feed (which is generally the case in starch processing) the chambers near the feed hopper are more or less filled with solids. This material plasticizes, and a zone with only partly filled chambers can be seen. At the end of the screw, close to the die, the chambers are completely filled with material.

If the extruder is fed with a liquid, as in some candy processes, the first part does not necessarily need to be partly empty. However, as will be explained later, for reasons of stability it is advisable to create a zone in which the chambers are not fully filled.

In particular, the fully filled zone is very important for proper functioning of the extruder. In this zone the pressure is built up, mixing and kneading mainly take place, and the major influence of viscous dissipation also occurs. In order to explain the existence of the fully filled zone, we need to realize that the different zones in a twin-screw extruder cannot be viewed separately, but are interconnected. This can be shown by the throughput.

The actual throughput of a twin-screw extruder is determined by the feeding zone. What comes into the extruder here will also have to leave the extruder at the other end. Because the chambers are only partially filled no pressure can be built up in this zone and the leakage flows will be limited to the drag component only. Under normal circumstances, the throughput of this zone is therefore independent of pressure at the die end of the extruder.

In the last part of the extruder, where the pressure that is needed for squeezing the polymer through the die is built up, the chambers are fully filled with material, a pressure gradient is present, and considerable leakage flows are dependent on this gradient.

The effect of the throughput is as follows:

As derived, the actual throughput through the completely filled zone is given by:

$$Q = 2mNV - \Sigma Q_l \tag{6.8}$$

but the real throughput is determined by the feeding zone:

$$Q = 2m_v N V_v \varepsilon \tag{6.9}$$

in which ε is the degree of filling of the chambers in this zone and the index v indicates that volume and number of thread starts of the screws relate to the geometry in this zone. For reasons of continuity, the difference between theoretical throughput and real throughput should equal the sum of the leakage flows:

$$\Sigma Q_l = 2N(mV - m_v V_v \varepsilon) \tag{6.10}$$

Because the degree of filling (ε) does not depend on the final pressure and because all other parameters in the right-hand term of this equation are also independent of pressure it becomes clear that the sum of the leakage flows in a twin-screw extruder must be independent of pressure. However, if the equation for the leakage flows is taken into consideration:

$$\Sigma Q_l = AN + B\frac{\Delta P}{\mu} \tag{6.11}$$

the pressure drop per chamber is fixed and dependent on viscosity and geometry only. If geometry and viscosity were not to change, the pressure gradient would be constant over the whole completely filled zone. In addition, a fixed pressure is built up in the die of the extruder, depending on throughput, viscosity, and die geometry. Therefore, within reason, there will be a point in the extruder at which the actual pressure becomes zero. Between this transition point of partly and fully filled chambers and the die there exist pressure gradients, there are leakage flows, and the chambers are completely filled with polymer. Between this transition point

Table 6.1 Influence of extrusion parameters on the filled length.

Influence of	Q	P	ΣQ_l	dp/dx	Filled length
die resistance	0	+	0	0	+
rotation speed	+	+	+	+	0
degree of filling	+	+	–	–	++
wall temperature	0	0	0	–	+
die temperature	0	–	0	0	–
gap size	0	0	0	–	+

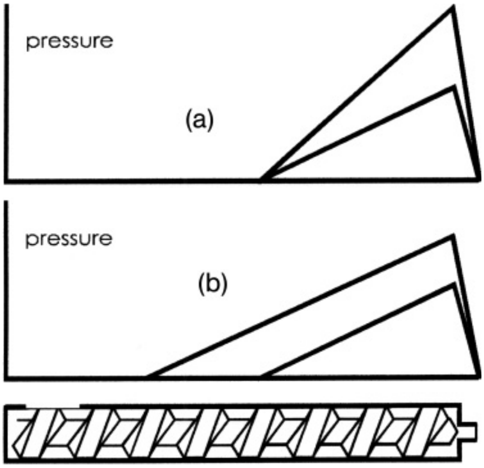

Figure 6.11 Pressure build-up: a) changing rotational speed, b) changing die resistance.

and the feed hopper, there is no difference in pressure between consecutive chambers, the leakage flows are zero or consist only of drag components, and the chambers are only partly filled with material.

The length of the completely filled zone is an important factor, and for good process control, knowledge of the different parameters that influence the length of the completely filled zone is indispensable. Table 6.1 gives this influence schematically.

- If, for instance, for the simplified case that the extruder is filled with an iso-viscous liquid, the resistance of the die is doubled, the pressure in front of the die will also double, because the output remains constant. However, the leakage flow is not influenced by the die pressure, so the pressure gradient in the extruder remains constant. Ergo, the completely filled length increases as indicated in Figure 6.11.
- If the rotation speed is doubled, while the specific throughput (throughput per revolution) is kept constant, the throughput will also double and consequently

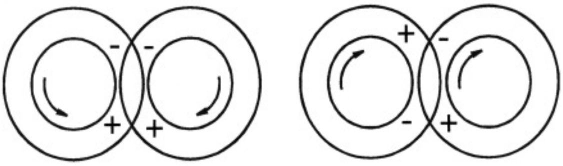

Figure 6.12 Internal pressure generation in a) a counter-rotating, and b) a co-rotating twin-screw extruder.

the die pressure will do so too. Because the leakage flows also double, the pressure gradient will double and the length of the completely filled zone will remain the same (Figure 6.11).

If the viscosity is not constant, the ability to build up pressure is proportional to the viscosity. Changes in consistency – by gelatinization of the starch or by mixing with polyols, for instance – influence the local pressure gradient and therefore the filled length. In addition, the influence of the temperature in this scheme is based on a change in the local viscosity and, because of that, on pressure drop.

6.4.2
Co-Rotating Versus Counter-Rotating Closely Intermeshing Extruders

Both co-rotating and counter-rotating twin-screw extruders can be modeled by a C-shaped chamber model. However, there are some differences. For reasons of construction (the screws must fit into each other) the tetrahedron gap in a co-rotating machine is generally bigger than in a counter-rotating machine. Moreover, the drag flow in the tetrahedron gap in a co-rotating extruder is parallel to the direction of this gap. Whereas in a counter-rotating extruder the direction of internal pressure generation favors the flow through the calender gap, in co-rotating machines this pressure generation favors the tetrahedron flow (Figure 6.12). Because the tetrahedron leakage is the only leakage connecting the chambers on one screw with the chambers on the other screw, the mixing between material on the different screws is better in co-rotating machines. In counter-rotating extruders both drag flow and internal pressure generation favor the calender leak. Because the material is elongated and kneaded in the calender gap it can be concluded that counter-rotating extruders favor a good kneading action.

6.5
Self-Wiping Twin-Screw Extruders

An important difference between closely intermeshing and self-wiping twin-screw extruders is the way the screws fit into each other. In self-wiping extruders the screw geometry is such that in the plane through both screw axes there is a very close fit between the two screws (Figure 6.13). This requires a special geometry

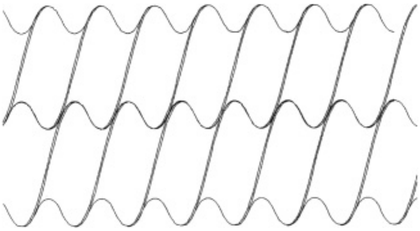

Figure 6.13 Transport elements in a self-wiping extruder.

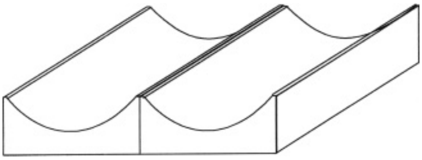

Figure 6.14 Unwound channel in a self-wiping extruder.

with, as a consequence, a very large tetrahedron gap between the "chambers". Because of this special character of most self-wiping extruders, the C-shaped chamber concept has to be abandoned; a model based on continuous channels can better be used. Therefore, the self-wiping extruder acts more as a drag pump than as a displacement pump. Figure 6.14 shows, analogously to single-screw extruders, the unwound channel. Each time when the material changes screw during its transport through a channel there exists a certain flow restriction. This can give an extra pressure build-up, which is, however, in general very minute, and for practical purposes this effect is often neglected.

Screws of self-wiping extruders consist of one, two, or three thread starts. With increasing numbers of thread starts the distance between the screw axes has to increase and as a consequence the maximum channel depth decreases, which in turn influences the maximum throughput per screw rotation. For this reason extruders with four or more thread starts are not common. Because there exist hardly any parallel planes close to each other in the geometry of a self-wiping machine, their rotational speed can be chosen to be much higher than for closely intermeshing twin-screw extruders. Combined with the shallow channels this leads to a high average shear level, which is in practice five to ten times higher than in closely intermeshing machines. The shear levels can be increased further by the use of so-called mixing or kneading elements. Changes in the angle between these elements determine the kneading action, as will be seen later.

6.5.1
Screw Geometry

Because the screws have to fit closely in the plane through the axes, the degrees of freedom in screw geometry are very limited. Because of the requirement of close

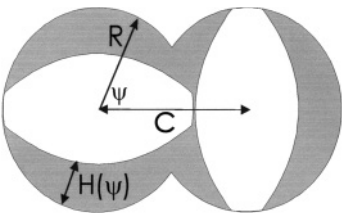

Figure 6.15 Cross section through the screws.

fitting in a cross section perpendicular to the axes, the surfaces of the screws must always (nearly) touch. This is shown in Figure 6.15. The channel depth as a function of the angle ψ can be written in its most elementary form as:

$$H(\psi) = R(1+\cos\psi) - \sqrt{c^2 - R^2\sin^2\psi} \tag{6.12}$$

where c is the center line distance [5]. More complicated geometries exist, with use of different radii of curvature to obtain geometries with a larger flight width or deeper channels. The cross section of the screw elements is the same as the cross section of the kneading elements. If extra pressure build-up is required, elements with a narrower pitch (pumping elements) are used. Nearly all self-wiping extruders are based on screws with separate screw elements and, depending on process requirements, different screw lay outs can be constructed.

6.5.2
Transporting Elements

The transporting elements in a self-wiping extruder, similarly to single-screw extruders, can be modeled by a channel with a plate moving over it and their working is again basically by drag flow. The throughput can therefore be expressed as:

$$Q = \left(m - \frac{1}{2}\right) ANf_{ds} - (2m-1)B\frac{\Delta p}{\mu} f_{ps} \tag{6.13}$$

where A and B are geometrical parameters and m is the number of tread starts per screw. The most common value for m is two or three, extruders with double tread starts (m = 2) having a larger throughput and triple start screws (m = 3) exerting a higher shear on the material. The correction factors f_{ds} and f_{ps} account for the curvature in the channel.

It can be seen that the throughput can also be divided into a drag component and a pressure component–not interrelated under the assumption of Newtonian rheology–in the case of a self-wiping transport element.

6.5.3
Elements for Pressure Build-Up

Through the construction of screws with a large overlap in the intermeshing region, the pressure build-up abilities can be increased considerably. In the limiting case the self-wiping profile will be lost and C-shaped chambers will emerge. Figure 6.16 shows these so-called pressure build-up elements. The chosen pitch is generally smaller than in transport elements. A model based on C-shaped chambers leads to good results for this type of elements.

6.5.4
Kneading Elements

The third type of elements present in self-wiping twin-screw extruders is the kneading element (Figure 6.17). These elements consist of kneading discs that have the same cross sectional shape as the transport elements. The angle between the individual kneading discs, the so-called stagger angle, determines the kneading action. Stagger angles of 30, 60, 90, 120, and 150 ° are frequently used; the last two angles (120 and 150 °) are also sometimes referred to as –60 and –30 °. As a general rule it can be stated that the larger the angle between the discs (30, 60, 90, 120,

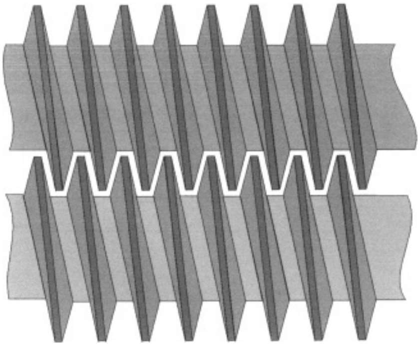

Figure 6.16 Pressure-generating elements.

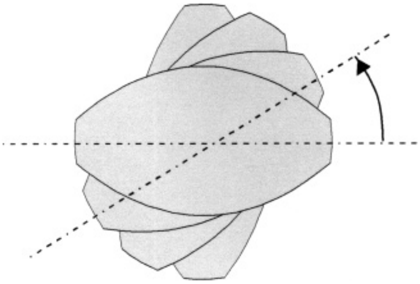

Figure 6.17 Kneading elements.

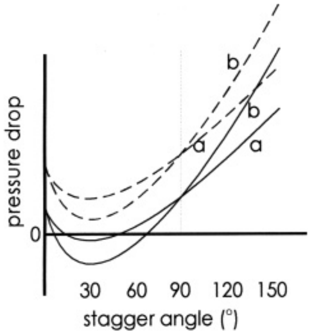

Figure 6.18 Pressure losses over kneading elements: a) low rotational speed; b) high rotational speed.

150), the larger the kneading action, but this also results, of course, in a larger energy dissipation in the element. In addition, the pressure drop over the kneading element is dependent on the stagger angle. At moderate throughputs a kneading element with a stagger angle up to 60° can still build up some pressure; in all other situations pressure is needed to transport the polymer through the element. This dependence on the stagger angle can be understood if we regard the kneading element as an interrupted screw flight.

At angles of 30 and 60° there exists a certain pumping action that depends on the rotational rate. At larger throughputs, the pressure drop over the element will decrease or, as stated, even become negative. In kneading elements with a stagger angle of 90° the pumping action is absent. This implies that the pressure needed to pump the polymer through the kneading element is independent of the rotation rate but proportional to the throughput. At stagger angles larger than 90° the kneading element acts as a screw element with reversed pitch. The transport elements in front of the kneading element have to pump against the reversed pumping action of the kneading element, and high shear levels and large energy dissipation will be attained. Figure 6.18 shows an example of the pressure drop over the kneading elements as a function of the stagger angle at two different rotation rates at large and at small throughput. At increasing throughput the curves will be shifted upward, resulting in higher pressure drops at large stagger angles and disappearance of the pressure generation at low stagger angles. For reactive extrusion the kneading elements have two functions: they improve the mixing and, as will be seen in the next paragraph, they increase the filled length in front of the element and therefore the hold-up in the extruder-reactor.

6.5.5
The Fully Filled Length

Similarly to the situation in closely intermeshing twin-screw extruders, in self-wiping extruders it is possible to distinguish different regions where the screws are either fully filled with material or only partially filled. Again, in the fully filled region pressure is built up, whereas in the partially filled zone the pressure gradient equals zero. This implies that a fully filled zone must be present before the die and before pressure-consuming kneading elements. The lengths of these zones before the die (L_d) and before a kneading section (L_m) can be simplified to:

$$
\begin{aligned}
L_d &= \frac{p}{\mu(AN - BQ)} \\
L_m &= \frac{A'Q + B'N}{C'N - 2Q}
\end{aligned}
\qquad (6.14)
$$

The above equations can be used to quantify the influence of different extrusion parameters on the filled length. It is striking that the filled length in front of a kneading section is independent of viscosity. This is due to the simplification we have made in assuming an iso-viscous process: if the viscosity changes, a relative viscosity factor has to be introduced. The fact that the filled length is independent of the absolute value of the viscosity can be understood if we realize that both the pressure-generating capabilities of the transport elements and the pressure drop over the kneading elements are proportional to the viscosity: the absolute viscosity therefore has no influence on the length of the fully filled zone. Moreover, the equations show that if we change the rotational speed and the throughput in the same way – or, in other words, if we keep the relative throughput constant – the fully filled length does not change. If the throughput increases at constant rotation speed the filled length will increase, and if the rotation rate increases at constant throughput the filled length decreases. Finally, an increase in the stagger angle in kneading elements (increasing B') will also increase the filled length. Application of kneading elements with a more severe kneading action (larger stagger angles) will not only increase the kneading action in the elements themselves, but will also result in a larger filled length, resulting in extra mixing. Figure 6.19 shows an example of the pressure profile in a screw, consisting of transport elements, followed by pressure build-up elements, a kneading zone, transport elements, and finally pressure build-up elements before the die. At loca-

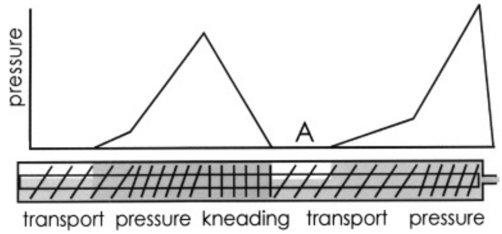

Figure 6.19 A possible screw lay-out and the pressure profile. At location A material can be added or removed.

tion A the material is pressureless and the channel is not necessarily fully filled. This location can be used for, for instance, devolatilization or for an easy feeding of an extra component. However, it should be realized that at increasing throughput the filling of the extruder increases and the pressureless zone will disappear.

6.6
Non-Intermeshing Twin-Screw Extruders

Non-intermeshing twin-screw extruders can be seen as a first approximation as two parallel single-screw extruders (Figure 6.20). This would be accurate if the open area that connects the two barrel halves (the apex area) were zero. Because of the existence of the apex area, the screws interact with each other and the throughput of a non-intermeshing twin-screw extruder will be less that that of two single-screw extruders. The screws can be arranged in two different ways (Figure 6.21): in the staggered configuration mixing is enhanced, but pressure build-up abilities are low, whereas in the matched configuration a better pressure build-up is achieved at the cost of some mixing abilities.

The conveying action of this type of machine can be derived from a three-parallel-plate model, in which the outside plates represent the screw surfaces and the middle plate (with zero thickness) represents the barrel. The apex is accounted for by parallel slots in the middle plate, perpendicular to the circumferential

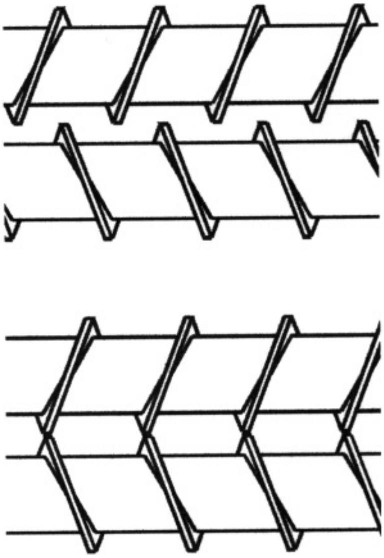

Figure 6.20 Cross section through a non-intermeshing twin-screw extruder with staggered configuration.

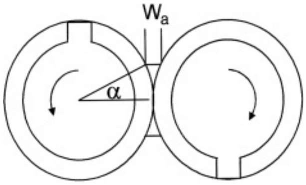

Figure 6.21 Two different configurations for non-intermeshing twin-screw extruders: staggered configuration (top) and matched configuration (bottom).

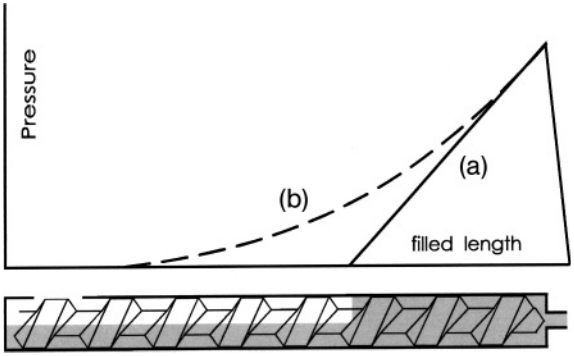

Figure 6.22 Pressure generation with a) an iso-viscous fluid, and b) a reacting fluid.

velocity. This model leads (again) to a throughput that can be divided into a term dependent on the rotation speed (the drag flow) and a term dependent on the pressure difference (the pressure flow), leading to:

$$Q = AN - B\frac{\Delta p}{\mu} \tag{6.15}$$

6.7
Influence of Low-Viscosity Monomeric Feed

In the simplified case of an iso-viscous process the pressure built up along the filled length appeared to be constant. In reactive extrusion, however, the material is generally far from iso-viscous, which influences the filled length considerably. Figure 6.22 shows the influence of increasing viscosity on the pressure built up in the extruder. For a simple screw with uniform geometry this pressure build-up is uniform in the simplified case of an iso-viscous material (a). For reactive extrusion the viscosity increases in the direction of the die and the low viscosity in the filling region results in poor local pressure build-up abilities (b). This makes the extruder more sensitive to disturbances, and small fluctuations in pressure may

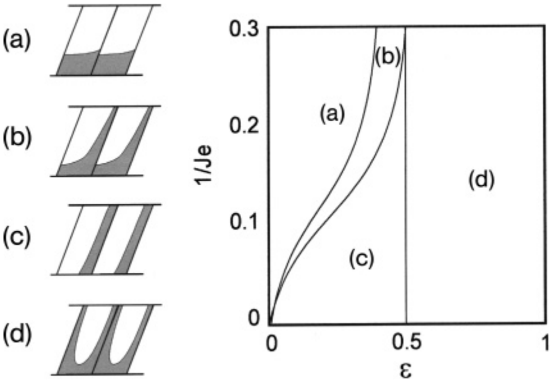

Figure 6.23 Influence of viscosity and filling degree on the material distribution in partially filled chambers.

result in large changes in the fully-filled length and therefore in residence time. Moreover, overfilling of the extruder can easily occur [9].

A low-viscosity feed stream also influences the working of the feed zone. In this partially filled zone, material with low viscosity is not likely to be dragged properly along the channels of the screw but tends to flow on the bottom of the extruder because gravitational forces predominate rather than viscous forces. A dimensionless parameter that relates gravitational and viscous forces is the Jeffreys number:

$$Je = \frac{\rho g D}{\mu N} \tag{6.16}$$

where g is the gravitational acceleration. This Jeffreys number equals the ratio between the Reynolds number and the Froude number. De Graaf *et al.* [10] described experiments in which the pattern of the fluid in the chambers was correlated to the Jeffreys number and to the degree of fill. Three different patterns could be distinguished (Figure 6.23):

- at low degrees of filling and high Jeffreys numbers the material remained basically at the bottom of the channel and was not carried over the screws,
- at low degrees of filling and low Jeffreys number the material collected at the pushing flight, and
- at high degrees of filling the material sticks to both flights.

6.8
The Mathematics of Extrusion

Very sophisticated numerical models for different types of extruders exist, and computational fluid dynamics nowadays plays an important role in extruder modeling. Nevertheless, the different extruders can also be described with relatively simple models. Extensive description of these models can be found, mainly in the literature for extrusion of synthetic polymers [1, 2, 4]. Nevertheless, many features of these theories can also be used for starch processing, and therefore some simple mathematical models with general validity are presented here.

6.8.1
Single-Screw Extruders

As stated before, the rotation of the screw can be transformed into the movement of a plate over a flat channel. The velocity of this plate is of course the circumferential velocity of the screw and equals πND, whereas its direction relative to the channel equals the screw angle ϕ. N is the rotation rate of the screw and D is the screw diameter.

The movement of the plate has a component in the down-channel direction and a component in the cross-channel direction; both drag the liquid along and introduce flow profiles with components parallel and perpendicular to the direction of the channel.

$$\begin{aligned} U_\mathrm{z} &= \pi ND\cos\phi \\ U_\mathrm{x} &= \pi ND\sin\phi \end{aligned} \tag{6.17}$$

The flow in the down-channel direction can be calculated from a force balance:

$$v_\mathrm{z} = \pi ND\cos\phi\frac{y}{H} - \frac{H^2}{2\mu}\frac{\mathrm{d}P}{\mathrm{d}z}\left\{\left(\frac{y}{H}\right)-\left(\frac{y}{H}\right)^2\right\} \tag{6.18}$$

where dP/dz denotes the pressure gradient in the down-channel direction. A closer look at this equation reveals that the right-hand side consists of two terms. The first part (apart from geometric parameters) only depends on the rotational speed and the second part is a unique function of the pressure, so the effects of screw rotation and pressure can be separated. This is shown in Figure 6.3. The actual flow profile is a superposition of the (linear) drag flow and the (parabolic) pressure flow. However, strictly speaking, this separation is only valid for Newtonian liquids.

From the velocity profile in the down-channel direction the throughput of the pump zone of a single-screw extruder can be obtained by integration:

$$Q_\mathrm{v} = W\int_0^H v(z)\,\mathrm{d}y = \frac{WH}{2}\pi ND\cos\phi - \frac{H^3W}{12\mu}\frac{\mathrm{d}P}{\mathrm{d}z} \tag{6.19}$$

The effects of drag flow and pressure flow can also be separated in this equation; the drag flow is proportional to the rotational speed of the screws and the pressure flow is proportional to the ratio of pressure gradient and viscosity.

This equation is often written as:

$$Q = \frac{1}{2}\pi^2 N D^2 H (1-a) \sin\theta \cos\theta \tag{6.20}$$

θ is the flight angle and a is the throttle coefficient, which signifies the ratio between the pressure flow and the drag flow:

$$a = \frac{H^2 \Delta P \tan\theta}{6\mu(\pi N D) L} \tag{6.21}$$

In the analyses above the width of the flight is neglected; it can be shown that this simplification has no significant influence on the final outcome.

An analogous calculation can also be set up for the transverse direction of the channel, and if the flow across the flights of the screw can be neglected (which is generally the case for the hydrodynamics in single-screw extruders), the velocity profile in the direction transverse to the channel can easily be calculated.

$$v_{\mathrm{x}} = 3U_{\mathrm{x}} \frac{y}{H} * \left(\frac{2}{3} - \frac{y}{H}\right) \tag{6.22}$$

This profile, in combination with the down-channel direction, shows a helical path of the fluid elements through the channel.

The cross-channel flow produces a circulatory flow as sketched in Figure 6.4. The center of circulation, where v_{x} equals zero, lies at 2/3 of the channel height. This cross-channel profile must of course be combined with the down-channel profile; the cross-channel flow should be superimposed on the flow in the channel direction. As a result the polymer elements follow a helical path through the channel. The center of rotation of this helical flow lies at 2/3 of the channel height. Particles in this location follow a “straight” line through the channel without being interchanged with particles at other locations. Therefore these fluid elements will never approach the wall closer than 1/3 of the channel depth if no mixing elements are used in the screw design. This will appear to be particularly important when considering heat transfer and thermal homogenization for reactions in which large amounts of reaction heat are released.

6.8.2
Correction Factors

Strictly speaking, Equations 6.18 and 6.19 are only valid for straight extruder channels of infinite width. To account for the curvature of the channel and the finite width, correction factors can be used and Equation 6.19 can be written as:

$$Q_{\mathrm{v}} = \frac{WH}{2}\pi N D \cos\phi . f_{\mathrm{d}} - \frac{H^3 W}{12\mu}\frac{\mathrm{d}P}{\mathrm{d}z} . f_{\mathrm{p}} \tag{6.23}$$

The correction factors follow from an analytical solution of a two-dimensional stress balance:

$$f_\mathrm{d} = \frac{16W}{\pi^3 H} \sum_{i=1,3,5}^{\infty} \frac{1}{i^3} \tanh\left(\frac{i\pi H}{2W}\right)$$
$$f_\mathrm{p} = 1 - \frac{192H}{\pi^5 W} \sum_{i=1,3,5}^{\infty} \frac{1}{i^5} \tanh\left(\frac{i\pi W}{2H}\right) \tag{6.24}$$

For practical purposes (H/W < 0.6) these factors can conveniently be approximated by:

$$f_\mathrm{d} = 1 - 0.57\frac{H}{W}$$
$$f_\mathrm{p} = 1 - 0.62\frac{H}{W} \tag{6.25}$$

Basically these correction factors can be used not only for single-screw extruders but for all types of extrusion processes.

6.8.3
Counter-Rotating Closely Intermeshing Twin-Screw Extruder

The equations for the different leakage gaps are mathematically simple [4]. The variables are defined in Figure 6.15. For the tetrahedron gap in a counter-rotating twin-screw extruder an empirical equation exists:

$$Q_\mathrm{t} = 0.0054\left(\frac{H}{R}\right)^{1.8}\left[\psi + 2\left(\frac{\varepsilon + \sigma\tan\psi}{H}\right)\right]^2 * \frac{\Delta P R^3}{\mu} \tag{6.26}$$

The derivation of the flight leakage is similar to that for the flight leakage in a single-screw extruder:

$$Q_\mathrm{f} = (2\pi - \alpha)R\left\{\frac{NB\delta}{2} + \frac{\delta^3}{6\mu B}\left[3\mu\frac{NB}{H^2}\left(\frac{B}{m} - B\right) + \Delta P\right]\right\} \tag{6.27}$$

The equation for the calender leakage follows the classical derivation for the throughput of a two-roll calender, with the only difference being that the velocities of the two calender surfaces are different because of the different radii:

$$Q_\mathrm{c} = \frac{4B}{3m}\left\{\frac{2m\Delta P\sigma^3}{6\pi\mu\sqrt{(2R-H)\sigma/2}} + N\pi(2R-H)\sigma\right\} \tag{6.28}$$

For the side leak a semiempirical equation is used:

$$Q_s = \pi N(2R-H)(H-\sigma)(\varepsilon+\sigma\tan\psi) + \frac{m\Delta P(H-\sigma)(\varepsilon+\sigma\tan\psi)^2\cos\psi^2}{12\mu R\sin\frac{\alpha}{2}} * \left[1-0.630\frac{\varepsilon+\sigma\tan\psi}{H-\sigma}\cos^2\psi+0.052\left(\frac{\varepsilon+\sigma\tan\psi}{H-\sigma}\cos^2\psi\right)^5\right] \tag{6.29}$$

From the equations above it can simply be deduced that every leakage flow has two components: one drag component, proportional to the rotational speed, and one pressure component, proportional to the pressure difference between two consecutive chambers and inversely proportional to the viscosity. The proportionality factors are only dependent on geometrical parameters. The only exception is the tetrahedron gap, which only depends on pressure differences. The total amount of leakage can now be written as:

$$\sum Q_{\mathrm{l}} = AN + B\frac{\Delta P}{\mu} \tag{6.30}$$

in which, as can be seen from the equations, A and B are constants that only depend on the geometry of the screws.

The volume of a C-shaped chamber can also easily be determined by straightforward calculations. For this we subtract the volume of the screw over the length of one pitch from the free volume of the barrel over the same length. The volume of the barrel follows from Figure 6.15:

$$V_1 = \left\{\left(\pi-\frac{\alpha}{2}\right)R^2+\left(R-\frac{H}{2}\right)\sqrt{RH-\frac{H^2}{4}}\right\}S \tag{6.31}$$

The volume of the screw root is:

$$V_2 = \pi(R-H)^2 S \tag{6.32}$$

and the volume of the flight is:

$$V_3 = \int_{R-H}^{R} b(r) * 2\pi r\, dr \tag{6.33}$$

For a screw with straight-sided flights this yields:

$$b(r) = B + 2(R-r)\tan\psi \tag{6.34}$$

and the integral can be written as:

$$V_3 = 2\pi\left\{\left(RH-\frac{H^2}{2}\right)B+\left(RH^2-\frac{2}{3}H^3\right)\tan\psi\right\} \tag{6.35}$$

The total volume of one chamber can now be calculated from:

$$V = \frac{V_1 - V_2 - mV_3}{m} \tag{6.36}$$

6.8.4
Self-Wiping Twin-Screw Extruders

Because the working of self-wiping twin-screw extruders is mainly based on drag in an open channel, the equations derived for single-screw extrusion can be used. Combination of drag flow and pressure flow in one single channel leads to an equation for the throughput per channel:

$$Q = \frac{1}{2} W H_0 U_z f_{\mathrm{ds}} - \frac{W H_0^3}{12\mu} \frac{\mathrm{d}P}{\mathrm{d}z} f_{\mathrm{ps}} \tag{6.37}$$

Here f_{ps} and f_{ds} are correction factors for the channel geometry and H_0 is the maximum channel depth. In cases involving rectangular screw channels the correction factors can be calculated analytically; for the complex geometries of self-wiping extruders they can be approximated or can be calculated numerically [6]. The number of parallel channels in a screw with m thread starts equals $2m$–1. This leads to a throughput for a self-wiping twin-screw extruder of [5, 6]:

$$Q = \left(m - \frac{1}{2}\right) W H_0 U_z f_{\mathrm{ds}} - (2m-1) \frac{W H_0^3}{12\mu} \frac{\mathrm{d}P}{\mathrm{d}z} f_{\mathrm{ps}} \tag{6.38}$$

Apart from this, an extra pressure build-up will occur in the intermeshing region. This can be expressed by means of a correction factor κ, a function of the relative flow area in the intermeshing region, leading to the final equation:

$$Q = \left(m - \frac{1}{2}\right) W H_0 U_z f_{\mathrm{ds}} - (2m-1) \kappa \frac{W H_0^3}{12\mu} \frac{\mathrm{d}P}{\mathrm{d}z} f_{\mathrm{ps}} \tag{6.39}$$

In practical situations this factor κ is close to one and its influence is often neglected. For shallow channels the shape factors f_{ds} and f_{ps} can be approximated by [7]:

$$f_{\mathrm{ds}} = \int_{-W/2}^{W/2} \frac{H(x)}{W H_0} \mathrm{d}x$$

and (6.40)

$$f_{\mathrm{ps}} = \int_{-W/2}^{W/2} \frac{H(x)^3}{W H_0^3} \mathrm{d}x$$

The pressure gradient in the fully filled zones can be calculated from the equation for the throughput and equals for an iso-viscous process:

$$\frac{\Delta P}{Z}=\frac{\mathrm{d}P}{\mathrm{d}z}=\left\{\frac{WH_0}{2}(\pi ND\cos\phi)\,f_{\mathrm{ps}}-\frac{Q}{2m-1}\right\}*\frac{12\mu}{\kappa WH_0^3 f_{\mathrm{ds}}} \tag{6.41}$$

As a consequence the fully filled length before the die in axial direction is :

$$L_{\mathrm{f}}=Z\sin\phi=\frac{\kappa WH_0^3 f_{\mathrm{ds}}P}{12\mu\left\{\frac{WH_0}{2}(\pi ND\cos\phi)\,f_{\mathrm{ps}}-\frac{Q}{2m-1}\right\}}\sin\phi \tag{6.42}$$

For kneading elements the pressure drop can be written as:

$$\Delta P=\mu\{AQ+\xi BN\} \tag{6.43}$$

in which A and B are geometrical constants and ξ denotes the dependence of pressure on the stagger angle. ξ is negative for angles smaller that 90°, zero for 90° and it increases with increasing stagger angle. If the pressure is zero after the kneading element, indicating a partially filled zone in that region, an expression for the filled length in front of the kneading element can be obtained:

$$Z=\frac{(2m-1)*(AQ+\xi BN)}{(2m-1)WH_0(\pi ND\cos\phi)\,f_{\mathrm{ps}}-2Q}\frac{\kappa WH_0^3 f_{\mathrm{ds}}}{6} \tag{6.44}$$

obtained from:

$$L_{\mathrm{f}}=Z\sin\phi \tag{6.45}$$

6.8.5
Non-Intermeshing Twin-Screw Extruders

The mathematical description of the conveying action of non-intermeshing twin-screw extruders consists of a three-parallel-plate model, similar to the two-parallel-plate model used in single-screw extrusion. The outside plates represent the screw surfaces and the middle plate (with zero thickness) represents the barrel. The apex is accounted for by parallel slots in the middle plate, perpendicular to the circumferential velocity. Using this model Kaplan and Tadmor [8] derived an expression for the throughput for Newtonian flows:

$$Q=WHU_{\mathrm{z}}f_{\mathrm{dn}}-\frac{WH^3}{6\mu}\frac{\mathrm{d}P}{\mathrm{d}z}f_{\mathrm{pn}} \tag{6.46}$$

This throughput is of course twice the throughput for a single-screw extruder, except for the correction factors, which can be written in their simplest forms as:

$$f_{\mathrm{dn}} = \frac{4f}{1+3f}$$
$$f_{\mathrm{pn}} = \frac{4}{1+3f} \tag{6.47}$$

where f is the ratio between the uninterrupted barrel circumference and the total barrel circumference, or:

$$f = \alpha/\pi \tag{6.48}$$

More accurate descriptions of the correction factors are based on a model in which the middle plate has a final thickness [10]:

$$f_{\mathrm{dn}} = \frac{f.f_{\mathrm{d}}.f_{\mathrm{p}}(2+W_{\mathrm{a}}/H)^3}{f(2+W_{\mathrm{a}}/H)^3+2f_{\mathrm{p}}(1-f)}$$
$$f_{\mathrm{pn}} = \frac{.f_{\mathrm{p}}(2+W_{\mathrm{a}}/H)^3}{f(2+W_{\mathrm{a}}/H)^3+2f_{\mathrm{p}}(1-f)} \tag{6.49}$$

W_a is the apex width and f_p and f_d are the shape correction factors, as defined for single-screw extruders (Eq. 6.24 and Eq. 6.25).

6.9
Concluding Remarks

Various types of extruders exist, all with their specific characteristics. For starch processing the consistency of the material changes from a solid to a highly viscous dough with addition of some polyols. This requires good pumping abilities, preferably independent of viscosity and slip. If the slip is limited, single-screw extruders can do a good job, especially if the barrel wall has grooves to increase friction and to prevent slip. Generally a more stable process can be obtained in (more expensive) twin-screw extruders.

A special type of single-screw extruder is the pin extruder. This type of extruder is provided with mixing pins through the barrel wall and the flights of the screw are interrupted. This extruder provides a very good mixing action and good transporting characteristics, but poor abilities to build up pressure. Especially when extensive micro-mixing is required this extruder is a good alternative, although care has to be taken that no significant degradation occurs.

Twin-screw extruders can be divided into different classes: non-intermeshing (counter-rotating), closely intermeshing (counter- or co-rotating), and self-wiping extruders (co-rotating). The last two types in particular have good pumping capabilities. Specific for twin-screw extruders is the occurrence of a fully filled zone and a zone where the screws are only partially filled with material. The operating conditions and screw geometries determine the length of the fully filled zone and as a consequence the hold-up in the reactor as indicated in Table 6.1.

Symbol List

α	apex angle	–
ψ	angle	–
	degree of chamber or channel filling	–
δ	flight gap width	m
κ	pressure correction factor for the intermeshing zone	–
σ	calender gap width	m
ξ	pressure factor for kneading elements	–
ϕ	screw angle	–
ε	tetrahedron width at the channel bottom	m
μ	viscosity	Pa.s
ΔP	pressure difference	Pa
ΣQ_l	total of leakage flows	$m^3 s^{-1}$
A	geometry parameter	m^3
B	chamber width	m
B	geometrical parameter	m^3
c	distance between screw axes	m
D	screw diameter	m
f_d	drag flow correction factor single-screw extruder	–
f_p	pressure flow correction factor single-screw extruder	–
f_{ds}	drag flow correction factor self-wiping extruder	–
f_{ps}	pressure flow correction factor self-wiping extruder	–
f_{dn}	drag flow correction factor non-intermeshing extruder	–
f_{pn}	pressure flow correction factor non-intermeshing extruder	–
g	gravitational acceleration	$m s^{-2}$
H	channel depth	m
H_o	maximum channel depth	m
Je	Jeffreys number	–
L_f	filled length in axial direction	m
m	number of thread starts of one screw	–
N	rotation rate of the screws	s^{-1}
P	pressure	Pa
P^+	dimensionless pressure	–
Q^+	dimensionless throughput	–
Q_f, Q_c, Q_t, Q_s	leakage flow through the flight gap, calender gap, tetrahedron gap and side gap	$m^3 s^{-1}$
Q_l	leakage flow	$m^3 s^{-1}$
R	screw radius	m
S	pitch of the screw	m

U_x	wall velocity in the cross-channel direction	$\mathrm{m\ s^{-1}}$
U_z	wall velocity in the down-channel direction	$\mathrm{m\ s^{-1}}$
v	local velocity	$\mathrm{m\ s^{-1}}$
V	volume of a C-shaped chamber	$\mathrm{m^3}$
W	width of the channel	m
y	height coordinate in the screw channel	m
z	down-channel coordinate	m
Z	length of the extruder channel	m

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7
Extrusion-Cooking of TPS

Marcin Mitrus, Leszek Moscicki

Application of extrusion-cooking techniques to processing of starch/glycerol mixtures is one of the most economical and efficient ways to produce TPS byproduct (granulates) used for film-blowing or mold-injection of packaging material. The process conditions are very stable and strictly determined according to the expected quality of the extrudates. In addition, the raw materials used (starchy components mixed with plasticizers) have to be gauged properly. Altogether, many trials and detailed measurements are needed in order to find optimal process conditions that can guarantee the best quality of the product.

One of the most interesting questions connected with extrusion-cooking is energy consumption. Specific Mechanical Energy (SME) consumption is defined as the amount of energy that is consumed per kilogram of product. Knowledge of SME is not only important for design purposes, but is also an indication of the mechanical forces on the material and consequently of degradation and viscous heating during the process. Specific mechanical energies for extrusion-cooking of thermoplastic starch are of the order of $2.52 \cdot 10^5\,\mathrm{J\,kg^{-1}}$, equivalent to $0.07\,\mathrm{kWh\,kg^{-1}}$. These rather low SME values depend on the material compositions of the mixtures, the temperature, and the rotation speed.

7.1
Process Stability

The stability over the course of the process was evaluated by Mitrus [1] on the basis of temperature changes recorded in each extruder section in the processing of all the applied materials with different process parameters. The stability of temperature behavior of a final product immediately after it had left the extruder die was also studied. Temperatures in the cylinder were measured by means of thermocouples fixed in each section and connected to meters installed in the extruder control board. The product temperature was recorded with a digital thermometer (CIE 370 type) equipped with an appropriate measuring lance. All the data were registered by PC.

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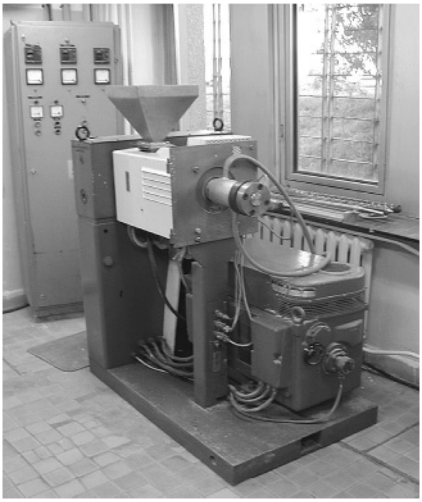

Figure 7.1 Modified TS-45 single-screw extruder (without cutting device).

Feeding stability and mass flow through the barrel and extruder crosshead were assessed by recording and from evidence of extruder shutdowns, problems with material feeding, and blocking of die openings. These data are of great importance for determining the optimal parameters for TPS production, taking account both of production stability maintenance and of invariant process parameters, in particular in long production cycles.

The use of a modified TS-45 extruder (Polish design) fitted with an additional cooling system allowed the process temperature to be maintained at the appropriate level within the 80–100 °C range for almost all the trials (Figure 7.1). Slight mean fluctuations of temperature (±5 °C) during TPS extrusion were detected at each extruder section for all the starch types. Evident influences of screw rotation speed, mixture composition, and moisture content on temperature changes were recorded in all the extruder sections (Figures 7.2 and 7.3). Temperature increases were observed with increasing screw rotation speed and were highest for the mixtures with both the lowest moisture (15%) and glycerol (15%) contents. This effect was caused by friction heat inside the cylinder and conversion of mechanical energy into heat energy.

Temperature decreases in all the extruder sections were noted with an increase in glycerol content in the mixtures up to 25% (Figure 7.2). Processing of mixtures with higher glycerol contents than this induced temperature increases throughout the length of the plastifying system (section II).

A reverse impact on the extrusion temperature changes was noted in cases of changes in material moisture levels (Figure 7.3). Temperature increases in all the extruder sections were recorded with mixture moisture level rises of up to 25%. Above this value, however, only an insignificant temperature increase was recorded.

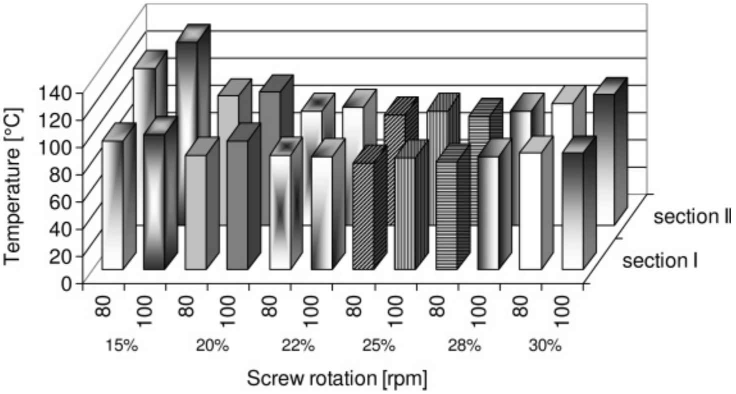

Figure 7.2 Temperature changes over the course of extrusion of potato TPS of varied glycerol content for different screw rotation speeds.

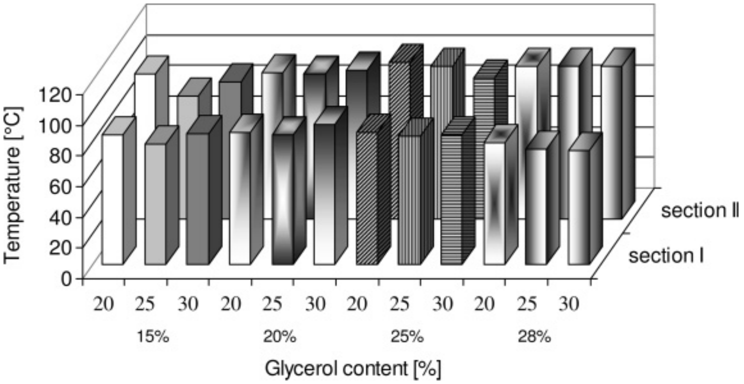

Figure 7.3 The course of temperature changes during the extrusion-cooking of potato thermoplastic starch of varied glycerol content and different mixture moisture levels at 80 rpm screw rotation speed.

The influence of the nature of the starch applied on the TPS granulate temperature is illustrated in Figures 7.4 and 7.5. It was found that the highest extrusion temperatures, regardless of glycerol content, were observed for wheat starch, whereas the lowest were for potato starch. In granulate manufacture with use of potato starch of different amylose contents the extrusion process proceeded more stably with potato starch mixtures of the highest amylose contents.

During investigations in cases of material mixtures, material clogging in the extruder charging hopper and some difficulties with material delivery by the screw were noted. For these reasons it was necessary to feed in material manually. The disturbances with uniform material feeding induced uncontrolled changes in the extrusion-cooking temperature, even by as much as ±20 °C. In cases of failure of

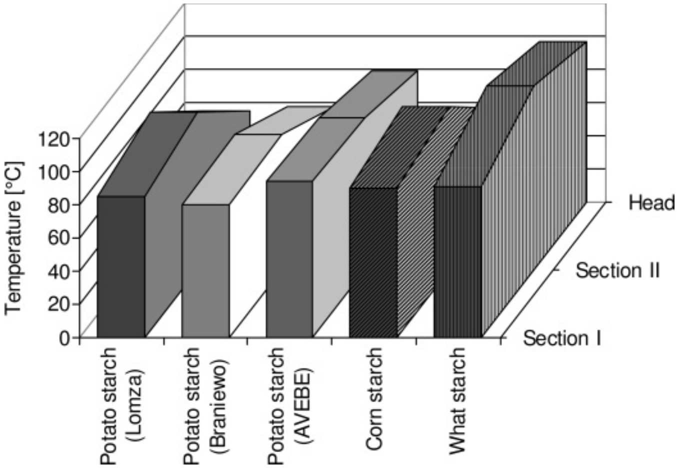

Figure 7.4 Temperature distribution for extrusion-cooking of different starch types with 20% glycerol content.

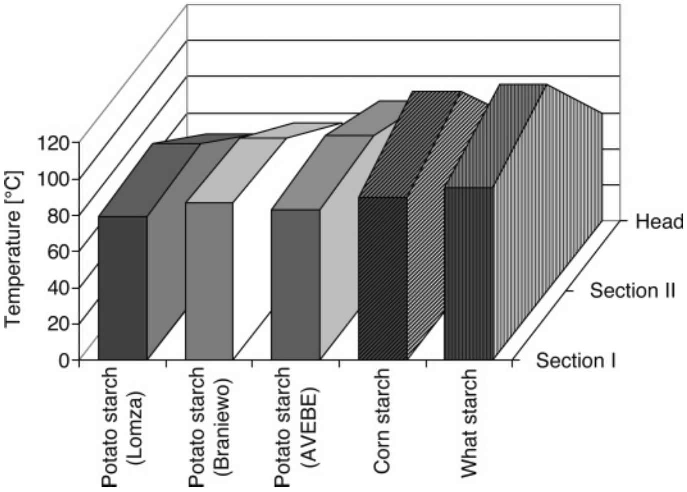

Figure 7.5 Temperature distribution for extrusion-cooking of different starch types with 25% glycerol content.

or reduction in material feed-in, the temperature at the extruder sections dropped, to be followed by a drastic rise after feed-in restart. The temperature changes caused excessive TPS expansion, formation of steam bubbles, and granulate surface destruction. For blends with glycerol contents over 20%, granulate stickiness that disabled its separation was also recorded. To avoid this effect the materials need to be fed in meticulously and precisely, thus with careful control of their flow and delivery to the screw.

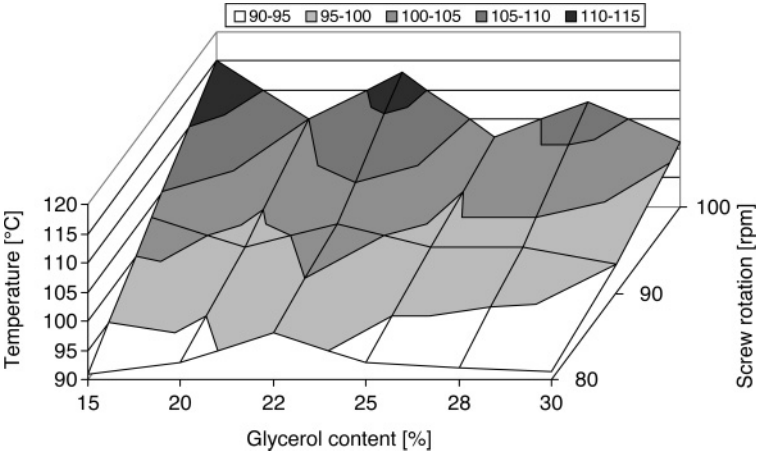

Figure 7.6 Potato TPS temperature at die opening in relation to glycerol content and screw rotation speed.

Water contents of over 15% in blends brought about excessive expansion of the obtained granulates. The extrudates showed damaged surfaces with numerous steam bubbles. Application of the extended extruder variant TS-45 with the final part of the cylinder cooling system with the aid of a variable flow of cold water definitely improved stabilization of the final product. The maximum water flow through the refrigeration component of the cylinder final part was 400 $\mathrm{L\,h^{-1}}$ and was used for processing maize and wheat starches, as well as potato starch mixtures with 15% glycerol content. In other cases the water flow was 140–370 $\mathrm{L\,h^{-1}}$.

It was found out that changes in the TPS temperature at the slit die depended predominantly on the screw rotation speed used. Irrespective of moisture and mixture composition, if screw rotations are increased, the temperature of the final products also increases (Figure 7.6). The temperature of TPS produced at 100 rpm was 9–24 °C higher than that of TPS produced at 80 rpm. With increasing glycerol content in the material mixture, drops in the temperatures of products leaving the die were noted. For screw speeds of 80 and 90 rpm, the product temperature varied over a small range of ±5 °C. At 100 rpm application, however, the fluctuations in the product temperature reached as high as 12 °C.

7.2
Specific Mechanical Energy

The power consumption of an extruder was measured with a standard wattmeter connected to the extruder drive unit. These results were converted into an index of specific mechanical energy (SME) consumption according to an equation formulated by Levin [2, 3]:

$$SME = \frac{n \cdot P \cdot O}{n_m \cdot Q} (\text{kWhkg}^{-1}) \quad (7.1)$$

where,

N = screw rotations (min^{-1}),
n_m = maximal screw rotations (min^{-1}),
P = power (kW),
O = engine loading (%), and
Q = extruder capacity (kg h^{-1}).

Application of the extrusion-cooking technique for processing of plant starch into TPS needs a very significant factor: determination of the specific mechanical energy (SME) necessary to obtain a product mass unit. As Bindzus *et al.* [4] found, when wheat, maize, and rice starch was processed in a twin-screw extruder the SME values were spread over the 0.081–0.365 kWh kg^{-1} range. Brummer and others [5] reported that in maize starch extrusion on a twin-screw extruder the SME reached values from 0.1 to 0.25 kWh kg^{-1} and this parameter value is related to the material moisture to a very small degree. Research into potato starch extrusion carried out by Della Valle *et al.* [6] on a twin-screw extruder indicated that specific mechanical energy varied over the range from 0.1 to 0.32 kWh kg^{-1}. Wiedmann and Strobel [7], in their investigations into the extrusion of wheat TPS, recorded SMEs ranging from 0.1 to 0.55 kWh kg^{-1} depending on material moisture content.

Mitrus [1] showed that material composition and extruder screw rotation speed have a substantial impact on SME during TPS processing. An increase in glycerol content clearly leads to a decrease in SME, as can be seen in Figure 7.7. Moreover,

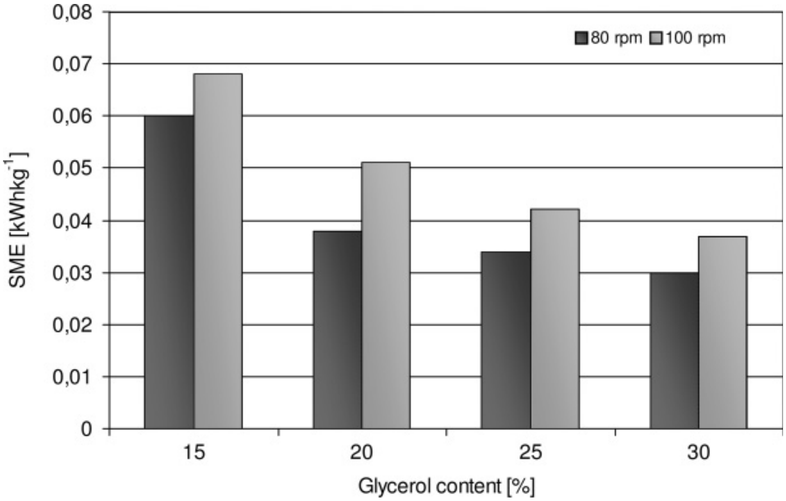

Figure 7.7 SME changes for potato TPS extrusion in relation to glycerol percentage in mixture.

an increase in extruder screw rotation speed causes the specific mechanical energy to rise. The SME values reached 0.068 kWh kg^{-1} for mixtures with a 15% glycerol content processed at a rate of 100 rpm, whereas at 80 rpm for the same mixtures a value of 0.06 kWh kg^{-1} was obtained. As would be expected, the lowest SME values were recorded for mixtures with a glycerol content of 30%.

In the case of barley starch extrusion, Mollymäki *et al.* [8] demonstrated a significant influence of glycerol content and material moisture on specific mechanical energy. They observed SME values ranging from 0.087 to 0.24 kWh kg^{-1}. With increasing material moisture and glycerol percentage the SME values decreased, although if glycerol was used the SME values were higher than those observed for starch plastified exclusively with water. For extrusion in single-screw extruders when potato, wheat, and maize starch were plastified only with water, the SME values were 0.072, 0.079, and 0.094 kWh kg^{-1} respectively.

The investigations firmly established that changes in SME during TPS production are affected by material blend moisture content: the higher the material moisture, the higher the SME values. The highest SME values recorded (0.076 kWh kg^{-1}) related to potato starch of 20% moisture and 20% glycerol content.

All of the starch types investigated were found to show lower SME values with increasing glycerol contents in the mixtures (Figure 7.8). The lowest SME values were obtained for potato starch extrusion, the highest for wheat starch processing. Differences in SME values were also detected for potato starch with varied amylose contents. The highest SME values were found for potato starch with 24% amylose, the lowest for starch with 22.1% amylose content.

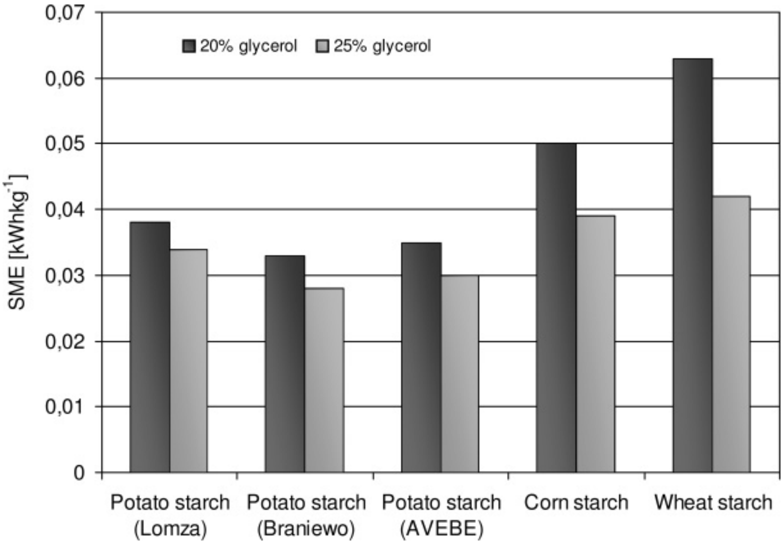

Figure 7.8 Specific mechanical energy of extruder for mixtures with differing starch type contents.

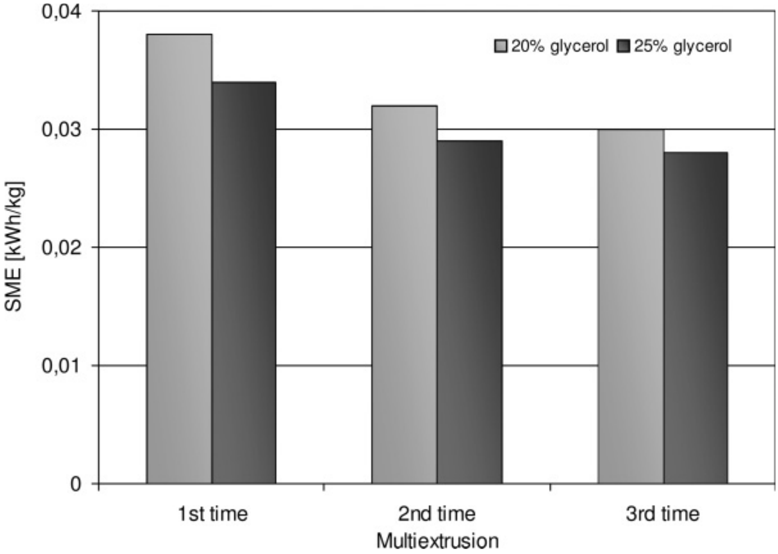

Figure 7.9 SME changes associated with repetition of potato TPS extrusion.

For repeatedly extruded potato TPS it was found that the SME decreases with extrusion repetition (Figure 7.9). The higher the number of extrusions, the lower the SME becomes. This result might indicate that a certain amount of crystallographic structure is destroyed during processing. Unprocessed, half-crystalline starch needs a higher energetic input to be melted and processed than thermoplastic starch of amorphous structure, which has no crystallographic structures at all.

7.3
Conclusions

Application of the modified TS-45 single-screw extruder produced by Z.M.Ch. Metalchem (PL), fitted both with an extended plastifying system and with an additional cooling system, proved to be useful for extrusion-cooking of TPS. TPS granulates can be used for manufacture of biodegradable packaging materials (e.g., films). The use of the additional cooling system allowed process temperatures to be maintained at appropriate levels, within the 80–100 °C range, for almost all the trials.

Evident influences of the screw rotation speed, the mixture composition, and the moisture content of the raw materials on the temperature profile along the barrel of the extruder were recorded. Changes in the TPS temperature at the slit die depended predominantly on the screw rotation speed used.

It has been reported that application of a temperature range running from 80–100 °C and an extruder screw rotation range of 80–100 rpm for thermal treatment of potato starch allowed a product of good quality, without any visible damage or steam bubbles, to be obtained. Granulate produced from wheat and corn starch blends with glycerol addition under the same conditions has not met the required quality parameters to the full.

Thermoplastic starch extrusion-cooking is associated with a rather low energy input: 0.07 kWh kg^{-1} on average. The extruder power required for extrusion-cooking of TPS depends on material composition: an increase in the glycerol content in a mixture causes the process energy consumption to decrease.

The SME value also depends on the type of starch. The lowest SME values were obtained during potato starch extrusion, whereas the highest were found for wheat starch processing. It was also found that there are differences in SME values for potato starch of varying amylose contents.

The specific mechanical energy also changes with repetition of extrusion. The higher the number of extrusion repetition cycles for the same material, the lower the SME recorded.

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8

Influence of Process Conditions on the Physical Properties of TPS

Leon P.B.M. Janssen

A major challenge in the development of operational methods for the manufacture of products from thermoplastic starches is the use of classical polymer technology. The use of processes designed for synthetic polymers should make it possible to produce starch plastics that act as supplements to existing synthetic products [1, 2]. Moreover, similarity of production methods should facilitate the acceptance of thermoplastic starches in the plastics industry. Still, however, starch plastics have not yet become widely introduced as consumer goods, due to some major drawbacks. One of the main problems of starchy material is its brittleness. This brittleness is caused by the relatively high glass transition temperature (T_g) and a lack of the so-called sub-T_g mainchain relaxation areas [3]. On storage this brittleness even increases, due to retrogradation and volume relaxation processes. During the retrogradation process the starch recrystallizes; this process can be divided into two parts. The recrystallization of the amylose component is an irreversible and very fast process. However, the reversible crystallization of amylopectin is much slower, and retrogradation can be regarded as the long-term recrystallization of the amylopectin component [4]. This spontaneous recrystallization process is caused by the tendency of macromolecules to form hydrogen bonds with expulsion of trapped water molecules or other solvents [5]. Retrogradation and volume relaxation also cause another problem: namely shrinkage. Dependent on the processing technology, these phenomena can last for a few weeks, with total shrinkage of more then 10%.

The T_g or glass transition temperature is an important and measurable parameter giving information about the retrogradation behavior. Besides that, the T_g is also of great importance for the mechanical properties of the material. Beneath the glass transition temperature the material exists in an amorphous, “frozen” liquid structure with stiff and brittle behavior. Below its T_g the intermolecular bonds are not broken, due to the small amounts of room left for Brownian movement, as is stated in Eyring’s “free volume theory” [6]. The specific volume increases relatively slowly with increasing temperature. When the material is heated up, at temperatures close to T_g the cohesive forces decrease drastically, the polymer expands, and the free volume increases to such an extent that there is

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room for migration of segments containing about 20 to 40 monomer units. The polymer now starts to flow, its characteristics being determined by the temperature increase above T_g and the crystalline structure, if any. The free volume is equally distributed throughout the material and in an unperturbed state the movements of the segments are random. However, when an external stress is applied, the segment migration will no longer be random but will occur in the direction that tends to relieve the applied stress, so the polymer will show a rubbery behavior. A sub-T_g (a glass transition temperature occurring at a lower temperature than expected) is in general of great importance for the product quality.

Starches from different sources, such as waxy maize, wheat, potato, and pea starch, behave differently when extruded with the plasticizer glycerol, this in concentrations of 15, 20 and 25% (w/w). De Graaf *et al.* [2] measured the glass transition temperatures of the resulting thermoplastic products by Dynamic Mechanical Thermal Analysis (DMTA). As well as their mechanical and structural properties, the transition temperatures of the materials during tensile and impact tests were also evaluated. Above certain glycerol contents, depending on the starch source, a lower glass transition temperature (T_g) resulted in decreased moduli and tensile strengths and increased elongations. Lowered T_g vales at different glycerol contents did not influence the impact strength. When the amylose/amylopectin ratio was increased a decrease in T_g was found. For pea, wheat, potato, and waxy maize starch the T_g values are 75 °C, 143 °C, 152 °C and 158 °C, respectively. This leads to the viewpoint that products with higher percentages of amylose are more flexible. The shrinkage of the specimens effected by injection-molding can be considerably higher than that produced in specimens made by pressing. The strength of the glassy polymer is that it offers the capability to dissipate energy in situations of shocks on short timescales, so the polymer is less brittle. A sub-T_g can be caused by the release of limited motion potential in parts of the main chain or lateral groups or it can be caused by the presence of a second, smaller polymer. Sub-T_gs always occurs at lower temperatures than main T_gs. Addition of plasticizers such as water, glycols, sugars, and amides will lower the T_g and therefore make the thermoplastic starch more rubber-like.

8.1
Plasticizers

Plasticizers act by spacing out the molecules and reducing interactions. Efficient plasticizers generally have low viscosities and low temperature coefficients of viscosity. This is to be expected from theories of T_g based on free volume concepts because free volume and viscosity are related. A plasticizer is often a polymer with a low molar mass, and consequently a greater free volume. Because of this, polymer chains will have increased mobility and so the T_g will shift to a lower value, resulting in a less brittle polymer. An important requirement is that the plasticizer be perfectly mixed on a molecular scale, such that the plasticizer is homogeneously blended in the polymer, or the polymer in the plasticizer. The resulting T_g of such a homogeneous mixture is given by the following equation [7]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{8.1}$$

where T_g is the glass-transition temperature of the blend, T_{g1} that of polymer 1, and T_{g2} that of polymer 2, whereas W is the weight fraction. Plasticizers may also serve another purpose: they decrease the melt viscosity. The lower the melt viscosity, the more easily can the material be processed or fabricated at lower temperatures. Furthermore, the plasticizer should have a high boiling point to avoid its evaporation during further processing and storage of the final product [8].

Besides plasticizer features, properties of the starch itself, such as the amylose/amylopectin ratio, also have an influence on the final material. As mentioned above, amylose and amylopectin recrystallize in different ways. Amylose will form the more crystalline part of a thermoplastic and amylopectin the amorphous component; the opposite behavior is found in the native starch granule, in which amylopectin is predominantly the crystalline part. The source of the starch determines the ratio and the molar mass distribution of amylose and amylopectin, and consequently the properties of the thermoplastics made out of it [7]. In this chapter the effects of and relations between the plasticizer, the amylose/amylopectin ratio, and the mechanical properties of four starches from different sources – potato, pea, wheat, and waxy maize – are described and discussed. Besides an overview of the properties, this should finally lead to better insight into the behavior of starch materials during processing.

8.2
Extrusion of Thermoplastic Starch

Thermoplastics are extruded from four starches together with different amounts of glycerol. The potato starch used (Avebe, Veendam, the Netherlands) is food grade and has a moisture content of 13% (w/w). The pea starch, from Parrheim foods (Manitoba, Canada), is also food grade and contains 9% (w/w) moisture. Cerestar Benelux BV (Sas van Gent, the Netherlands) supplied the waxy maize starch, with 9% (w/w) moisture. The wheat starch was supplied by Cerestar Germany (Krefeld) and contained 8% (w/w) moisture. The amylose/amylopectin ratios (information obtained from the starch suppliers) of the starches are shown in Table 8.1. Starch was introduced into an intermeshing co-rotating twin-screw extruder (APV Baker MPF-50, Peterborough, UK) with a double, round die opening of 3 mm. The APV has a length/width ratio of 25 : 1 and consists of 10 heating sections. The screws were constructed with transport, kneading (30 °), and pressure elements in the following order: 9D transport – 1D kneading – 5D transport – 2D kneading – 3D transport – 5D pressure. Glycerol (0.3% w/w water and technical grade, Chemproha, Dordrecht, the Netherlands) was added 10 cm

Table 8.1 Extrapolated glass transition temperature and related amylose/amylopectin ratios of the starches used, according to de Graaf [9] and Whistler *et al.* [10].

Source of origin	T_g extrapolated from Figure 8.2 (°C)	Amylose/amylopectin[a]
pea	75	2:1
potato	152	1:4
wheat	143	1:4
waxy maize	158	1:99

a Information from starch suppliers.

downstream from the starch feed. The starch was gelatinized by use of a screw speed of 110 rpm and a linearly increasing wall temperature varying from 45–150 °C from the feed zone to the die. The processed material was subsequently chopped to provide granulate, after which test specimens were produced by injection-molding and pressing. In the case of the pea starch an extra amount of water (~10% with respect to the starch throughput) had to be added, to avoid degradation during extrusion. The obtained products were immediately packed in airtight bags and stored in dark, cool surroundings. The products were analyzed within two days.

8.3
Test Methods

Specimens, shaped according to ASTM-D 638, were prepared with an injection-molding machine from Arburg BV (Nieuw-Vennep, the Netherlands) (Allrounder type 221-55-250). The injection-molding temperatures were 150 °C. The obtained products were immediately packed in airtight bags and stored in dark, cool surroundings. The water contents of most of the test specimens used varied only a little, around 9–10% w/w moisture, although in the cases of pea and potato starch higher moisture contents were found (around 12–13% w/w). An Instron Corporation model 4301 machine (Canton, Massachusetts) with clamps of 5.0 kN, operating at a grip distance of 23.0 mm and a crosshead speed of 10.0 mm min^{-1}, was used for tensile tests. At least five specimens of each type of material were tested. Impact tests were done with specimens, unnotched according to ASTM-D 256-56, which were made on a press at ±150 °C under 30–103 N m^{-2}. The unnotched type was used because of the brittleness of some materials, which made notching impossible. A Cantilever Beam (Izod type) impact machine from Zwick Materialprüfung with hammers exerting an impact from 0.5–4.0 J was used for the impact tests. Unnotched specimens of some synthetic polymers (PS, PP, LDPE, and HDPE) were also tested for comparison. At least ten specimens of each material type were tested

8.3.1
Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis tests were used to measure the glass transition temperatures of the batches. With this technique the modulus of a polymer can be monitored against the frequency of an oscillating deformation of a sample bar at different constant temperatures. For a viscoelastic polymer two moduli can be distinguished: a storage modulus (E'), which is related to recoverable elastic energy stored in the sample, and a loss modulus (E''), related to deformation energy dissipated as heat of friction. Both moduli show decreases around the glass transition temperature and the dissipation factor (damping), $\tan\delta = E''/E'$, will give a peak around phase transitions. The temperature at which this occurs is referred to as the glass transition temperature [11] Actually, the conventional T_g is 5 to 15 °C higher then the temperature of maximum damping [12]. The analyzer used was from Rheometric (Piscataway, NJ, type: Solids analyzer RSA II). The specimens were made by pressing and each had a width of 6 mm and a thickness of 1.5 mm. During testing, the temperature of each sample was raised by 2 °C min^{-1} and the angular frequency was 6.28 rad s^{-1}.

8.4
Glass Transition Temperature

The influence of the amylose/amylopectin ratio and the amount of glycerol on the glass transition temperature (T_g) was determined by comparing the results for thermoplastic starches produced from various sources and with three different glycerol percentages (15, 20 and 25%, w/w). Figure 8.1 shows broad tanδ peaks for starches with 15% glycerol. The products with 20 and 25% glycerol, not illustrated, show comparable characteristics. The existence of a broadened transition region diminishes the temperature sensitivity of the mechanical material properties. This broadening is caused by heterogeneity [12] in the tested material and decreases with increasing glycerol content and increases with increasing amylose/amylopectin ratio (Figure 8.1). This means that a certain level of heterogeneity exists between amylose and amylopectin, so the glycerol acts not only as a plasticizer but also as a solvent in which both amylose and amylopectin dissolve, forming a more homogeneous mixture. After the T_g has been passed the measurement is no longer smooth. High-amylose starch (pea) will break down less quickly than high-amylopectin starch (waxy maize), indicating increased temperature processibility of the former. The temperature region between the T_g and the flow point will thus increase for materials containing higher percentages of amylose. This difference in heat resistance can be attributed to the irreversible retrogradation of amylose, in contrast with the reversible retrogradation of amylopectin. The initial rate of development of stiffness of starch gels after gelatinization is dependent on the botanical source and the degree of solubilization of amylose during gelatinization. This initial crystallization is not reversed on heating to 100 °C.

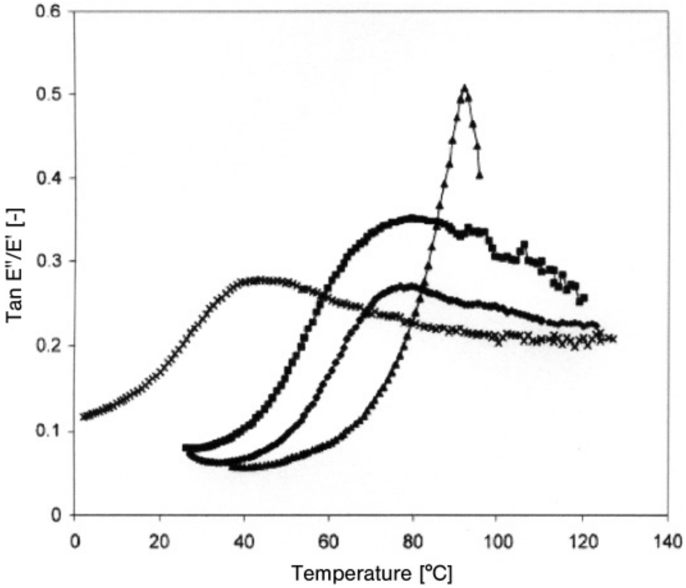

Figure 8.1 Plots of DMTA tests for potato (♦), wheat (■), waxy maize (▲), and pea starch (×) with 15% glycerol content.

However, there is also a long-term increase in gel stiffness, which is thermally reversible below 100 °C and can be attributed to amylopectin crystallization [13]. This is why waxy maize can be processed at lower temperatures than pea starch, because it is already in a flowing state at lower temperatures.

Figure 8.2 shows glass transition temperatures as a function of glycerol content. It is clear that the T_g values decrease in the order waxy maize > wheat > potato > pea starch and, with regard to the glycerol content, in the order 15% > 20% > 25%. Products containing higher levels of amylopectin (waxy maize) have higher T_g values than materials with less amylopectin (pea). The lower molar mass of amylose and its lack of branches results in a greater free volume of pea starch, so that (parts of) the chains can move more easily. This explains the lower T_g of amylose in relation to the branched amylopectin, so materials with higher amylose weight fractions will give lower T_g values. It can be expected from Equation 8.1 that glycerol should lower the transition temperature. Characteristically, the T_g of an undiluted polymer is much higher than that of a typical low-molar-mass, glass-forming diluent. As the diluent concentration of a solution is increased, the T_g decreases monotonically, because the average molar mass of the homogeneous polymer/plasticizer mixture decreases, and its free volume increases [13]. The small plasticizer molecules make chain movements easier. The greatest effect of glycerol is seen for waxy maize, so glycerol has a greater impact on materials containing more amylopectin. This effect can be explained by the fact that the T_g values of amylopectin and glycerol are more different from each other than those

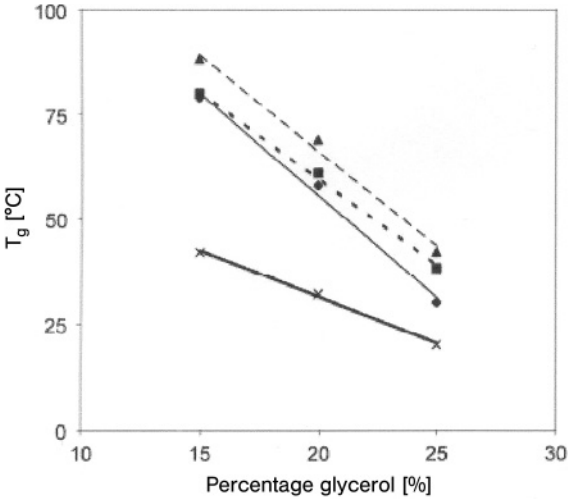

Figure 8.2 Glass-transition temperatures of potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of the glycerol content. The drawn lines are trend lines.

of amylose and glycerol. Extrapolation of the glycerol contents in the starch mixtures to zero results in approximations to the T_g values of the pure starches. These T_g values are listed in Table 8.1.

8.5
Tensile Strength

Figure 8.3 shows different stress/strain behavior as a function of the glycerol percentage and the starch source. For a low glycerol content (15%) the samples break in brittle fashion for potato, wheat, and waxy maize; for this last material the sample even fractures while the stress is still increasing. This occurred despite the fact that the glycerol reduced the T_g values of these materials relative to those of the pure starches; obviously these decreases were not sufficient to make them flexible. With higher percentages of glycerol (and in all cases for pea starch), a stress maximum is observed together with a clearly higher elongation. High glycerol levels decrease the stress, with the stress maximum becoming less dominant or not being observed at all. At a temperature of 20 °C and a low glycerol content the materials with higher amylopectin percentages are far below their T_g values. Therefore, their chain mobilities are very low and the samples show brittle stress/strain behavior. Pea starch, which has a much lower percentage of amylopectin, and therefore a lower T_g, is more flexible. At higher glycerol/starch ratios the starch chain mobility increases as the glycerol molecules weaken the interchain hydrogen bonding. The T_g is lowered, approaching the usage temperature. The starch chains

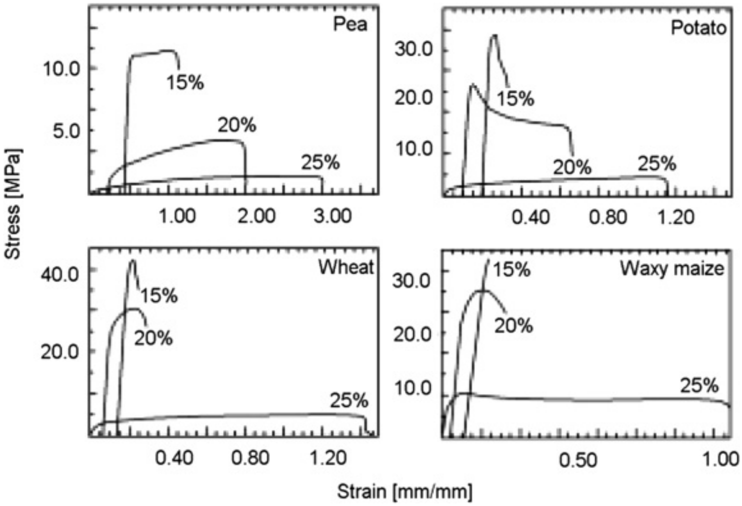

Figure 8.3 Stress/strain diagrams for potato, waxy maize, pea, and wheat starch.

can adapt to the applied stress and the possible elongation increases because the chain mobility is increased. If the T_g is lowered below 20 °C, no stress maximum is observed at all, because chain movements are again facilitated, leading to lower stress and greater elongation [6].

Figure 8.4 shows mean tensile strengths and elongations as functions of glycerol content for the four different sources of starch at 20 °C and 50% humidity. The courses of the moduli against glycerol content are not illustrated, as these are comparable to those of the tensile strengths. The moduli vary from 900 MPa for waxy maize with 15% glycerol to 7.3 MPa for pea starch with 25% glycerol. It is obvious that pea starch has a low tensile strength and modulus, which steadily decreases with increasing glycerol percentage. Besides that, the pea starch product shows a large elongation at break, as already observed in the plots. The relatively large content of linear amylose molecules means that the entanglement between the chains is not very strong, so they will slide easily along each other with low stress and large elongation. The maximum tensile strength and modulus, obtained with 15% glycerol, can be compared with that of LDPE (10 MPa), the elongation at break with that of polypropylene (250%). The starches of potato, wheat, and waxy maize became very brittle at low levels of glycerol (15%). This results in moduli between 700 and 900 MPa, comparable to that of HDPE, and tensile strengths around 35 MPa, which is equal to the value for polystyrene. The higher amylopectin contents mean that the chains, because of the branched structure, are less ordered and therefore have a greater degree of entanglement, causing brittle fracturing with higher stress. Glycerol gives the chains more mobility and because of this the interactions between the chains are lowered. This is the reason why the

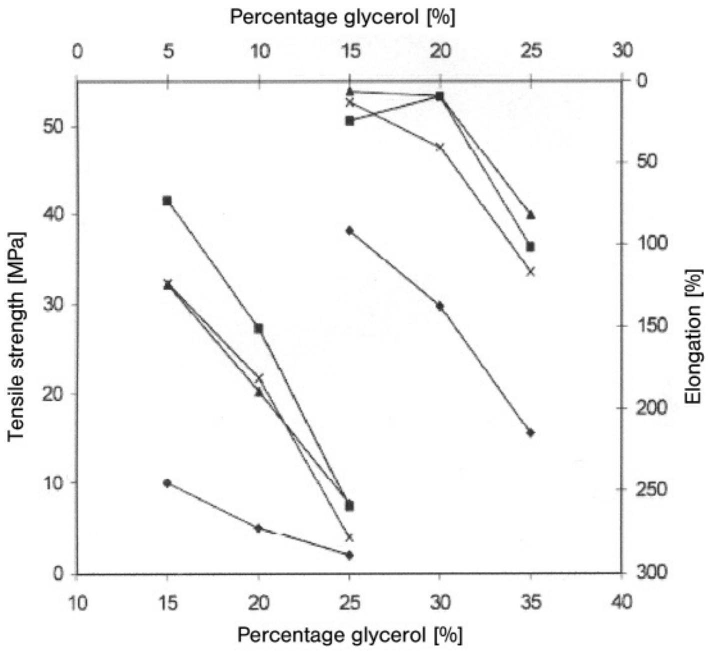

Figure 8.4 Tensile strength and elongation of potato (×), wheat (■), waxy maize (▲), and pea (♦) starch after 1 day as a function of glycerol content.

tensile strengths and moduli decrease and the elongations increase with increasing glycerol content. With regard to the tensile strengths, a smaller effect of glycerol is observed for pea starch, the high-amylose starch, than for the other starches with lower amylose contents. The difference in tensile strength between potato and wheat starch, in which the amylose/amylopectin ratios are nearly the same, can be explained by the difference in moisture content. The higher moisture level in potato (13%) relative to wheat (9%) will lower the T_g and consequently the tensile strength [14].

However, it is not directly explainable why the tensile strength of wheat starch is higher than that of waxy maize starch in spite of the considerably lower amylopectin content. More research needs to be performed to confirm this conclusion. The aging of starch is illustrated in Figure 8.5 for waxy maize and pea starch. As can be seen, moduli and tensile strengths increase, whereas the elongations decrease with time. The assumption is that the starch retrogrades further during storage. Recrystallized amylopectin acts as physical cross-links and increases the strength and decreases the elongation [15].

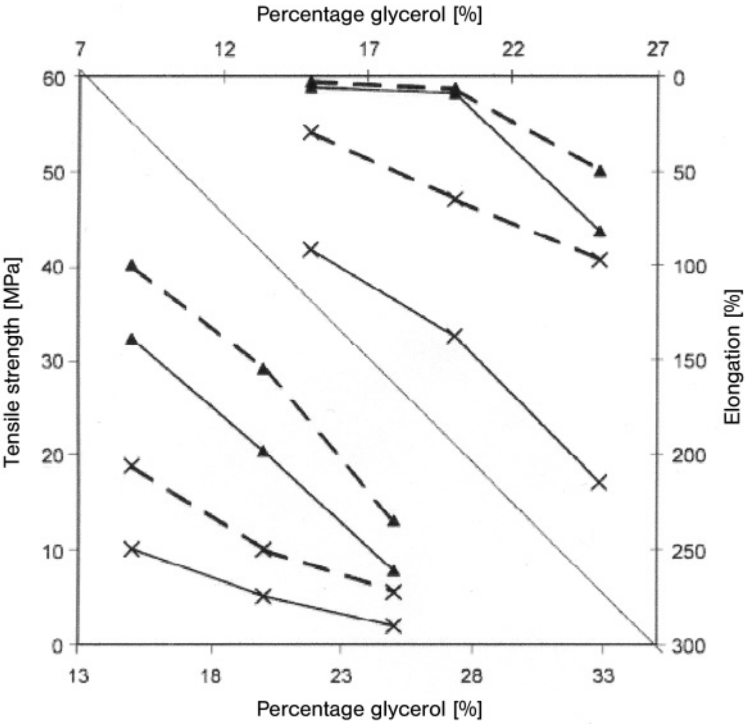

Figure 8.5 Aging of waxy maize (▲) and pea (×) starch reflected in the tensile strength and elongation after 1 day (—) and after 21 days (– – –) as a function of the glycerol content.

8.6
Impact Strength

As depicted in Figure 8.6, the impact strengths of all samples are very low and around the impact strength of PS. The T_g is lowered by glycerol, as would be expected from Equation 8.1, and this is of great importance for the impact strength. The T_g indicates the temperature above which the polymer can react through deformation; below the T_g it is a stiff and often brittle material. In our case the T_g values decrease, which means that the polymer toughness and impact strength should increase. There is a large difference in behavior on slow deformations as in the tensile tests with a movement of 10 mm per minute, and deformations on a short timescale, like the impact tests. Potato starch with 20% glycerol and a T_g of 57 °C, for instance, is very flexible, as is also illustrated by the elongation of 40% during the tensile tests, but nevertheless has a very low impact strength. The same phenomenon occurs for potato, wheat, and waxy maize starch with 25% glycerol and pea starch with 15, 20, and 25% glycerol. The assumption is that the broad

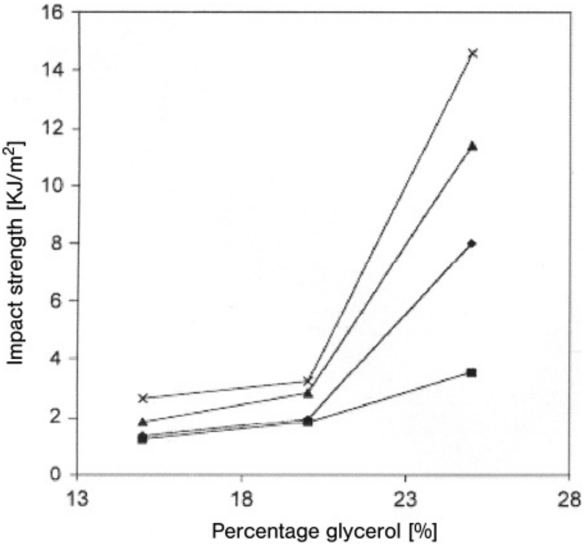

Figure 8.6 Impact strength of potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of glycerol content.

peaks of tanδ, generated by the DMTA tests, are the basis of this phenomenon. With a peak around 57 °C, the T_g of potato starch with 20% glycerol is far above the temperature of testing, which is 20 to 25 °C. However, tanδ is already increasing before the test temperature. With regard to the acclivity of tanδ there is a matter of limited mobility of the chains. This is apparently enough to distort the material during slow deformations, such as bending and the tensile tests, but deformations on a short timescale, such as impact tests, will cause a brittle fracture at this point.

8.7
Shrinkage

Sample bars made by injection-molding change in size during storage. In the injection direction there is obvious shrinkage, whereas in the direction perpendicular to it an increase in size is detectable. Figure 8.7 shows the results relating to the shrinkage of the sample bars after 1 week; no further shrinkage was measured after this period. At lower glycerol contents (15%) there is hardly any shrinkage of starch with a higher percentage of amylopectin, so it can be concluded that the chains need a certain amount of plasticizer, which enables the relaxation process. When the starch contains more amylose a lower amount of glycerol is necessary, due to the more mobile linear amylose chain. The injection of the polymer in the mold induces an elongation flow [16], and the chains of the polymers are consequently orientated in the injection direction. The chains are there-

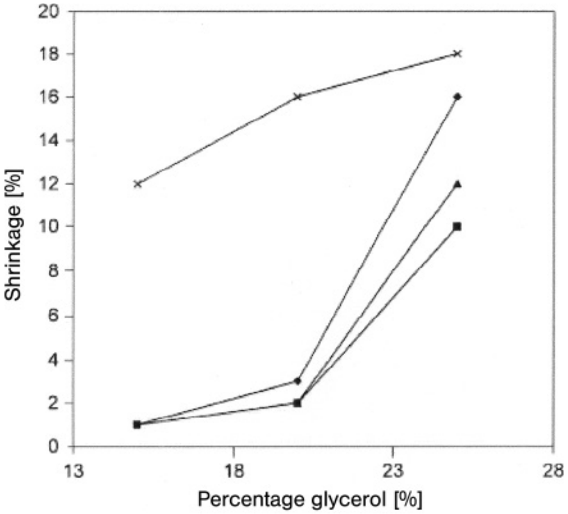

Figure 8.7 Shrinkage (in the injection direction) of injection-molded specimens after 1 week for potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of the glycerol content.

fore in a stretched conformation and lie parallel to each other. When the injection is stopped, reorientation starts and the chains realign in a helix configuration. This explains the shrinkage in the injection direction and the swelling in the width. Besides that, retrogradation will also cause shrinkage through the formation of hydrogen bonds between the chains with repulsion of water molecules. As would be expected, the shrinkage becomes faster with increasing glycerol fraction. This is due to the decreased local viscosity and the concomitant increased mobility of the chains, which make a faster relaxation possible. The shrinkage of waxy maize starch takes much more time than that of the other starches. The large proportion of amylopectin means that the chains are more entangled, which causes a lot of interactions and consequently a limited freedom to move relative to starch with higher amylose content. Finally it can be stated that the specimens made by pressing do not shrink to the same degree as the injection-molded specimens. During pressing there is no elongation flow present, resulting in less relaxation of the chains.

8.8
Conclusion

Addition of glycerol tends to reduce the glass transition temperatures of extruded starches and to narrow the transition regions. However, with glycerol contents of up to 25%, the T_g values are not lowered below 20 °C for the starches used. Lower

T_g values cause increases in impact strength, but with glycerol contents of 15 to 25% these increases remain quite low (up to $15\,\mathrm{kJ\,m^{-2}}$). The moduli and tensile strengths decrease with glycerol content whereas elongations increase. The same effect is noticeable in the case of the amylose/amylopectin ratios of the starches: an increase in this ratio lowers the modulus and tensile strength and increases the elongation. Shrinkage of thermoplastic starch products made by injection-molding is considerable for those with glycerol contents above 20%. This shrinkage is caused by the elongation flows during injection.

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9
TPS Film-Blowing

Andrzej Rejak, Leszek Moscicki

Film-blowing is the most popular method of polymer processing, commonly used in manufacturing of packaging materials [1, 3]. TPS is expected to be a promising raw material for biodegradable folia, which can have enormous potential application in that field too [2, 4, 5].

During the investigations TPS granulates produced earlier underwent thermal treatment according to appropriate working parameters. Because the basic properties of the granulates had already been determined, it was possible to establish a temperature profile and screw rotations for film processing. Over the blow-molding, film sleeves of 150–700 mm diameter and 0.15–0.6 mm thickness were manufactured, over a range of granulate compositions, applied temperatures, screw rotations, and configurations. Some of the film samples were subjected to further treatment, among others spray-coating of the top surface with drying prevention agents.

The TPS granulate was produced from different starchy raw materials (mixed with glycerol, partly enriched with emulsifiers), by use of a modified TS-45 extrusion-cooker and process conditions as described in Chapter 7.

The process of film extrusion by the film-blowing method was conducted on a line specially designed for film manufacture in the Department of Food Process Engineering, Lublin University of Life Science (PL), based on a single-screw plastic extruder of L/D = 35 (Figure 9.1). The line was produced by SAVO Ltd Co., Poland.

TPS film was produced by use of two screws of different geometries (compression ratios: 2.0 and 3.5), and the screw rotational speeds were varied from 50 to 90 rpm. The film was extruded with barrel and crosshead temperatures ranging from 70 to 155 °C.

Tensile testing of the films was carried out with a Zwick type Z2.5/TN1S tester by the standard ISO 527 tensile test. At the crosshead, 1 kN was applied to a sample of length 100 mm and sample width 17 mm, each sample thickness being measured with a micrometer. The crosshead speed for initial stress was 10 mm min^{-1}, with speed up to flexibility limit of 50 mm min^{-1} and test speed of 200 mm min^{-1}. Measurements were made for maximum strength, tensile strength, elongation at the maximum strength, and tensile strength (Figure 9.2).

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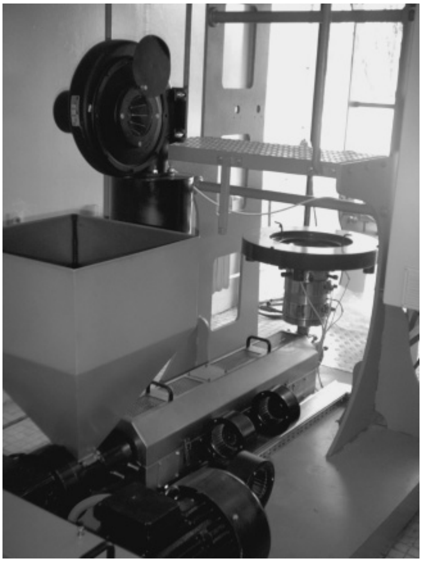

Figure 9.1 Stand for film extrusion processing.

Figure 9.2 TPS film-blowing.

9.1
Mechanical Properties of Films

The test results for film extrusion from granulates manufactured from maize and wheat starch blends showed that the product obtained in the range of the process parameters considered demonstrated a very brittle structure, thus being unfit for packaging. The resulting opaque and thick films, not suitable for making by blow-molding, cracked after cooling.

Far better results were obtained with the granulate derived from potato starch, with the best results being recorded for the starch mixtures with 20–25% glycerol. At processing temperatures below 120 °C the material was not fully processed and some granulate residuals appeared on the film surface. The obtained films were thick and either opaque or semi-transparent, after some time losing flexibility and becoming brittle due to their drying up. When higher pressing temperatures were applied, together with a screw with a mixer arm, films of good quality were obtained. These were flexible, semi-transparent films readily amenable to blow-molding. Unfortunately, because of the use of a crosshead with 1 mm slit application and a low-powered compressor the resulting films had a minimum thickness of 120 mm, but the production of much thinner ones is possible.

Addition of two emulsifiers – polyoxyethylenesorbitan monolaurate (Tween 20) and glycerol monostearate – at amounts of up to 2% considerably improved film flexibility. Moreover, it was found that damping of the mixture with only small amounts of water (2–5%) produced increases in film flexibility and strength.

The results of strength testing of some films are presented in Figures 9.3–9.7 and Table 9.1.

During the film extrusion and blowing, film sleeves of different parameters were obtained. Depending on the processed granulate composition they were flexible to greater or lesser extents. In the first stage of research, mixtures composed only of starch and glycerol were applied. The initial investigations confirmed potential for TPS application in foil manufacture and at the same time they directed further studies. The films obtained from pure mixtures with differing glycerol contents became less flexible and broke after cooling, even though good flexibility param-

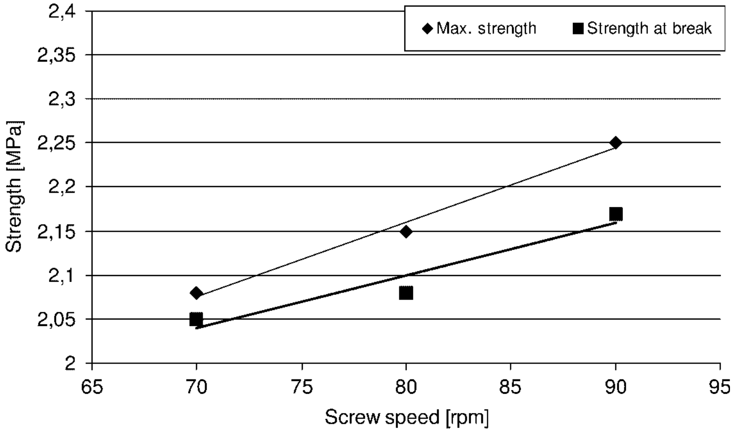

Figure 9.3 Strength as a function of extruder screw rotation speed for the sample A77B22M1 (notation as in Table 9.1).

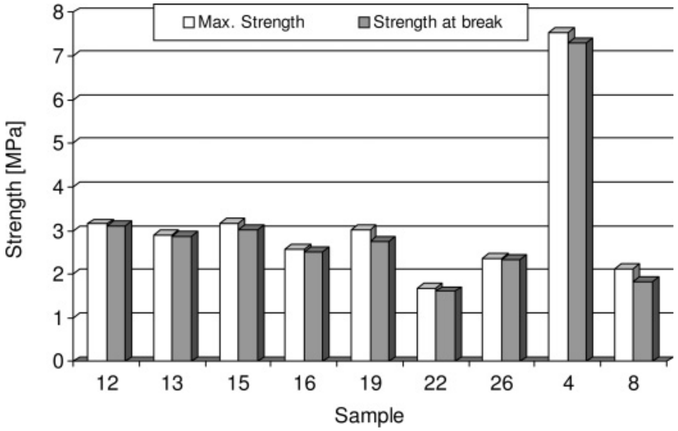

Figure 9.4 Strength comparison of film samples obtained with extruder screw rotation of 60 rpm (notation as in Table 9.1).

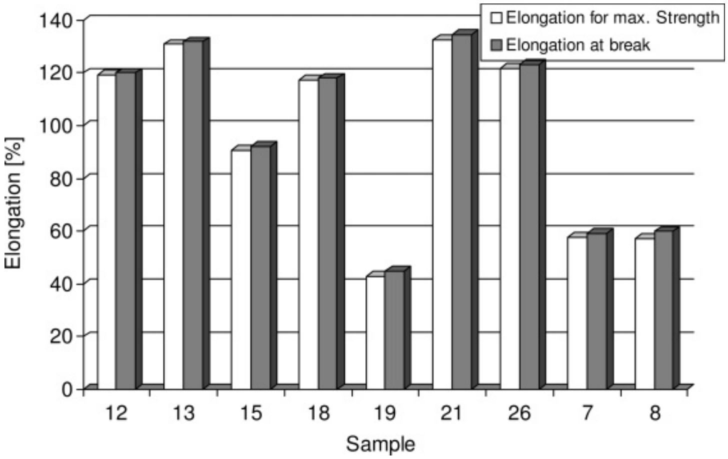

Figure 9.5 Comparison of elongation susceptibilities of film samples obtained at 60 rpm extruder screw speed (notation as in Table 9.1).

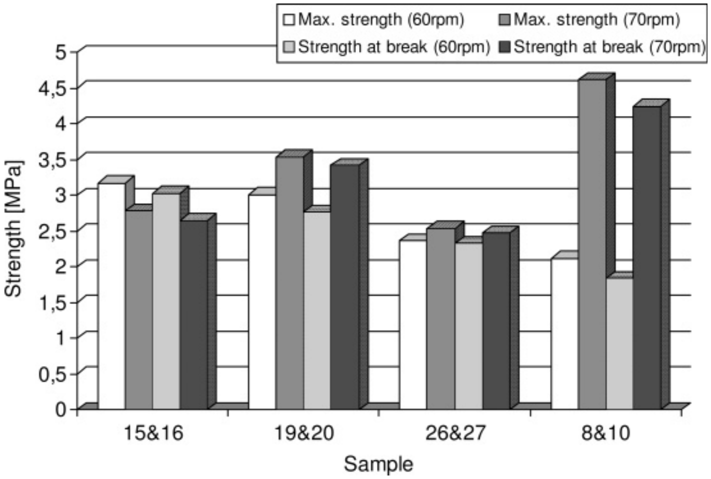

Figure 9.6 Strength comparison of film samples obtained at 60 and 70 rpm extruder screw speeds (notation as in Table 9.1).

eters were shown throughout the blowing time. Our work therefore became directed towards improvement of film flexibility after cooling as well as maintenance of suitable mechanical properties for longer periods.

Some new mixtures with 22% glycerol were used. Moreover, the mixtures I and II (notation as in Table 9.2) were supplemented with 1% emulsifier BRIJ 35, whereas the mixtures III–VI had only water as additive in amounts of 5% and 10%

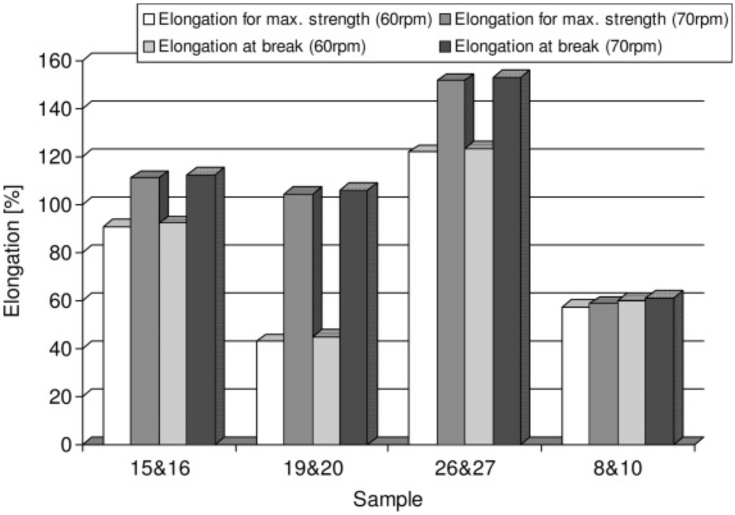

Figure 9.7 Comparison of elongation susceptibilities of film samples obtained at 60 and 70 rpm extruder screw speeds (notation as in Table 9.1).

of the dry mass. The mixtures VII and VIII, apart from 10% water, contained a different emulsifier – Tween 20 – at an amount of 2%.

Although quite satisfactory effects were recorded for application of mixture 2, better results were obtained with a screw of higher compression ratio (c.r. – 3.5) equipped with mixing elements. The obtained film showed very high flexibility at blowing, whereas after cooling it maintained substantial flexibility and did not become brittle. However, the film required the use of higher blowing temperatures.

The films originating from granulates No III, IV, V, and VI were fairly flexible and transparent despite great thickness, but could not be blown sufficiently. Because of the considerable water contents, the extrusion process needs higher temperatures to be employed.

The film produced from the mixtures IX and X at 1 : 1 ratio demonstrated unexpectedly good effects – a sleeve was flexible and easily blown. On cooling, the film did not become brittle and remained flexible. More advantageous results, however, were observed when a screw of 3.5 c.r. was used.

The film obtained from granulates VII and VIII could not be blown to an appropriate degree because of a high water content; it remained very thick.

Employment of different screws did not always have a significant influence on the final product, as is demonstrated by the film extruded from granulates XI and XII. In both cases, irrespective of screw rotation and geometry, it was impossible to obtain a film of satisfactory parameters. Under the influence of temperature the TPS granulate fed into the machine became sticky and difficult for further treatment (Table 9.2).

Table 9.1 Selected results of mechanical tests (screw compression ratio: 2.0).

No	Sample A/B/M/S (%)	Screw rotation (rpm)	Die Temp. (°C)	Max. strength (MPa)	Max. elongation (%)	Strength at break (MPa)	Elongation at break (%)	Thickness (μm)
1	A80B20	70	95	8.86	13.89	8.21	46.54	500
2	A75B25	70	90	5.43	74.49	5.40	79.28	610
3	A75B25	70	85	6.47	66.17	5.40	79.28	545
4	A80B20	60	95	7.54	41.50	7.29	53.50	400
5	A80B20	60	90	6.79	37.21	6.49	38.34	330
6	A80B20	60	85	4.27	64.99	4.04	67.42	140
7	A77B23	60	85	6.03	57.57	5.76	58.99	600
8	A77B23	60	80	2.12	57.22	1.84	59.92	150
9	A77B23	60	90	2.82	71.79	2.85	75.26	250
10	A77B23	70	80	4.62	58.77	4.25	61.25	420
11	A77B23	90	90	3.95	58.49	3.85	59.95	235
12	A78B21S1	60	85	3.15	119.13	3.11	120.00	340
13	A78B21S1	60	80	2.91	130.87	2.87	131.85	410
14	A77B23	50	75	2.66	104.90	2.57	106.34	390
15	A77B21S2	60	85	3.17	90.88	3.03	92.17	300
16	A77B21S2	70	90	2.78	111.12	2.65	112.52	390
17	A77B21S2	80	95	2.84	99.57	2.71	100.58	350
18	A77B21S2	60	85	2.57	117.25	2.52	118.05	330
19	A77B22S1	60	85	3.01	42.96	2.76	44.86	210
20	A77B22S1	70	90	3.54	104.39	3.42	105.94	280
21	A74B25S1	60	75	1.39	132.56	1.31	134.60	330
22	A74B25S1	60	80	1.68	130.66	1.61	133.56	320
23	A77B22M1	70	90	2.08	124.38	2.05	125.23	310
24	A77B22M1	80	90	2.11	131.54	2.08	132.30	360
25	A77B22M1	90	95	2.30	116.75	2.17	118.48	340
26	A77B22M1[a]	60	100	2.36	121.84	2.33	123.13	290
27	A77B22M1[a]	70	105	2.54	151.54	2.47	152.91	320

[a] Double extrusion-cooking of TPS.

Notation: **A** – potato starch, **B** – glycerol, **S** – polyoxyethylenesorbitan monolaurate (Tween 20), **M** – glycerol monostearate.

Samples of the film processed under the conditions presented in Table 9.2 were tested for stress and elongation. The main results are shown in Figures 9.8–9.13.

The effects observed in the strength tests confirmed good parameters of film from granulates I and II despite the screws used. The percentage elongation of the tested film ranged from 40% to 130% relative to film thickness varying from 0.15 mm to 0.42 mm. This film demonstrated good breaking strength and max

Table 9.2 Process conditions for film-blowing with use of different screws at 80 rpm.

No	Sample A/B/E/S/W (%)	Motor load (A)	Temperature (°C)					Screw compression ratio (–)
			barrel's sections				die	
			I	II	III	IV		
I	A77/B22/E1	8.4	101	102	136	116	117	3.5
II	A77/B22/E1	7.9	100	100	136	119	116	2.0
III	A73/B22/W5	12.5	112	101	136	117	121	3.5
IV	A73/B22/W5	8.6	103	101	137	115	118	2.0
V	A68/B22/W10	8.4	100	102	136	115	118	3.5
VI	A68/B22/W10	7.8	97	97	133	125	106	2.0
VII	A66/B22/S2/W10	8.4	98	90	138	114	135	3.5
VIII	A66/B22/S2/W10	8.1	99	92	139	114	137	2.0
IX	A76/B22/E2+A80/B20	7.8	91	90	137	123	124	3.5
X	A76/B22/E2+A80/B20	7.2	91	90	136	123	121	2.0
XI	A76/B22/E2	8.5	100	101	135	115	116	3.5
XII	A76/B22/E2	8.0	100	101	134	114	112	2.0

Notation: A – potato starch, B – glycerol, E – ether BRIJ 35, S – emulsifier Tween 20, W – H_2O addition.

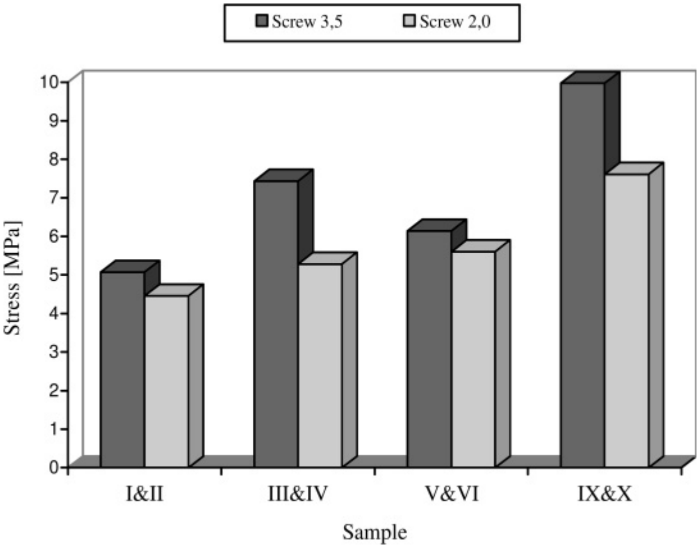

Figure 9.8 Mechanical strength comparison of film specimens (screw rotational speed 80 rpm, notation as in Table 9.2).

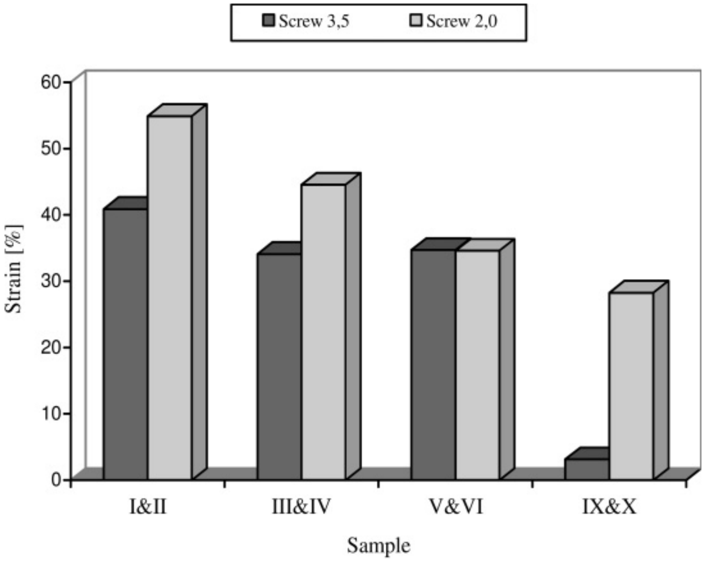

Figure 9.9 Elongation comparison of film specimens (screw rotational speed 80 rpm, notation as in Table 9.2).

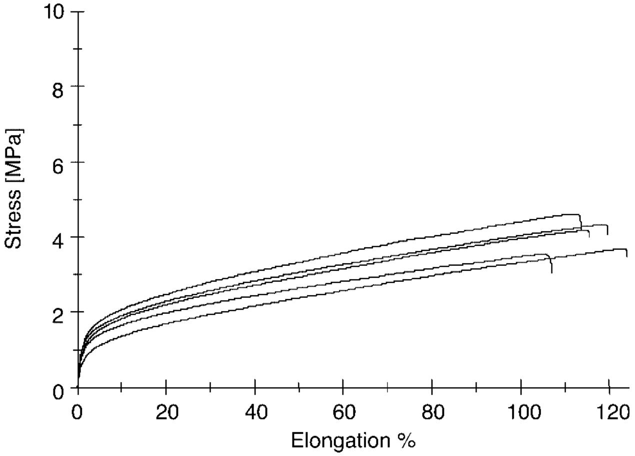

Figure 9.10 Test display sample: elongation against strength of foil made from mixture No. I (screw c.r. – 3.5; screw speed – 80 rpm).

force that reached 3.12 MPa to 6.11 MPa; the maximum tensile strain (εM) in the measurements was on average 40.88–114.6%, whereas tensile at break (εB) was 42.69–116.01%.

The films produced from granulates No III – VI, despite good transparency at 0.39 mm–0.52 mm thickness, turned out to be poorly flexible and their elongations

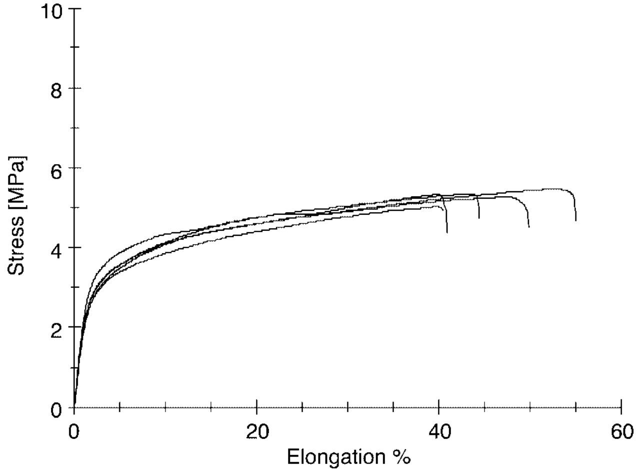

Figure 9.11 Test display sample: elongation against strength of foil made from mixture No. III (screw c.r.–3.5; screw speed–80 rpm).

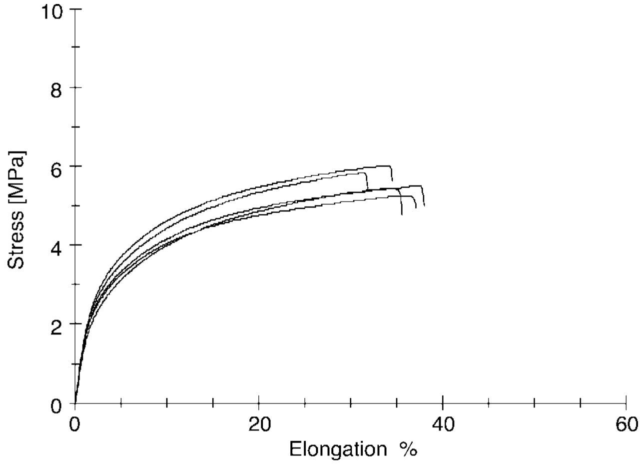

Figure 9.12 Test display sample: elongation against strength of foil made from mixture No. V (screw c.r.–3.5; screw speed–80 rpm).

were 38%–98%. Their tensile strengths were from 4.06 MPa to 7.43 MPa, whereas the maximum stress (σM) varied from 3.33 MPa to 6.61 MPa.

The film obtained from granulates IX and X showed that in spite of its slight elongation (up to 40%) it demonstrated very good strength parameters. The max tensile stress (σM) was from 7.61 MPa to 9.97 MPa, whereas the max tensile at break varied from 6.16 MPa to 8.77 MPa.

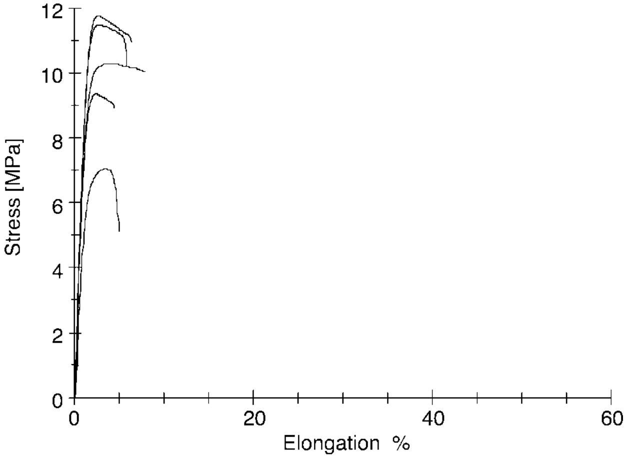

Figure 9.13 Test display sample: elongation against strength of foil made from mixture No. IX (screw c.r.–3.5; screw speed–80 rpm).

Microscopic analysis of the sampled foils under polarized light at most cases confirmed the appropriate material processing, and only in a few samples were very fine single grains of unprocessed starch recorded. Their presence did not substantially affect the produced foil quality.

9.2
Concluding Remarks

The most advantageous strength properties were recorded for the films with 20–25% glycerol contents. Polyoxyethylenesorbitan monolaurate (Tween 20) and glycerol monostearate in amounts up to 2% substantially improved (even by over 50%) film tensile susceptibility. Unfortunately, film strength then decreased. With increasing extruder screw rotational speed it was observed that strength and tensile stress of foil with additions increased in the 50–80 rpm range, but that film tensile stress fell when 80 rpm was surpassed. Therefore, it seems to be favorable to apply extruder screw rotations from 70–80 rpm.

Analysis of mechanical property measurements for films extruded from TPS showed that the extrusion processing parameters, the presence of emulsifier, and the water content in the material have a critical impact on film strength and elongation. The use of a screw of 3.5 compression ratio with an extra mixing section affected the film strength more, whereas a screw of 2.0 compression ratio influenced film elongation to a greater extent. According to expectations, the former screw application induced an increase in the energy consumption of the extrusion process. The best effects were reported when film was extruded from the mixtures Nos I and II with 22% glycerol and 1 % of BRIJ 35 emulsifier.

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10
Injection-Molding

Tomasz Oniszczuk, Leon P.B.M. Janssen

One of the principal methods for shaping synthetic polymers is injection-molding. The thermoplastic is melted in a cylinder or in a screw device and is subsequently pressed into a cavity with a specific shape. After that, cooling and solidification occur under sustained pressure to compensate for shrinkage of the material, and after complete solidification the object can be ejected [1] (Figure 10.1). Important factors in the injection-molding process are the temperature of the material upon injection and the temperature of the mold. Temperatures that are too high increase the cycle time and therefore they decrease the process efficiency, whereas temperatures that are too low result in a so called short shot, when the material solidifies before the mold is completely filled. A second important factor is the so called "clamp force", which indicates the maximum force that can be exerted on the mold before it starts leaking. This clamp force in turn, together with the area of the cavity in the mold, determines the maximum injection pressure that can be used. The injection technique enables objects varying from grams to kilograms to be obtained. Subject to the plasticizing system, injection-molding machines are divided into two types:

- ***Ram injection,*** in which a piston pushes the material into the mold. This machine is only used for relatively simple and small objects. Melting in the cylinder is often the time-limiting factor.
- ***Screw injection,*** in which a small extruder produces the melt, while the screw moves backwards and the melt collects before the screw. Once enough melt has been collected the screw moves forward, pushing the melt into the cavity. Because of its faster melting process and better mixing this type of machine is used for bigger or more complicated objects and if a high cycle time is required.

The brothers J.W. and J.S. Hyatt in the USA patented the first piston injection mold press in 1872, when they solved the problem of plasticizing a mixture of nitrocellulose and camphor. Much later a screw-injecting molding machine was designed. Nowadays screw injection molding is the most commonly used method for thermoplastic materials.

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Figure 10.1 Injection-molding machine (ARBURG 220H90-350).

In Poland, A. Smorawiński made a substantial contribution to the dissemination and development of injection-molding, publishing the first book on this subject [2, 3].

10.1
Screw Injection Molding

Unlike in normal extrusion, the screw can move in the axial direction. The material is extruded while the screw is rotating, and this causes the screw to be pushed far enough back that the space in front of the screw remains completely filled with the material. If enough material has collected in front of the screw, the screw is pushed forward by means of a hydraulic system, causing the material to be expelled. The molten material now enters into small ducts (called runners) and is let into the cavities through a narrowed section (the gate). The runners have to be big enough for the drop in pressure to be acceptable and for the material in the runners not to solidify before the injection is complete, and they also have to be small enough to assure that the amount of scrap material from the runners is minimal.

Three thermal effects can affect injection-molding:

- ***To obtain a short cycle time,*** the hot polymer is injected into a relatively cold mold. As a result, the polymer will already be starting to solidify on the wall of the mold while it is still being injected. This will cause an additional resistance to the flow. In extreme cases, the resistance to the flow may become so great that the mold will not fill completely. This is described as a “short shot”.
- ***Because injection-molding is a cyclic process,*** temperature variations in the polymer flow and in the temperature of the mold may occur.
- ***Viscous dissipation in the runners*** may lead to a considerable increase in temperature in the polymer flow.

Injection-molding can be done under conditions of constant throughput or constant pressure. Most processes, however, are carried out with constant throughput while the pressure increases during filling of the mold. As a result of the cooling and solidification of the material in the cavity, shrinkage will occur. To ensure that the object being injection-molded has the right shape, it is kept under high secondary pressure during solidification, with the mold remaining filled as a result. After solidification of the material in the gate, the pressure can be released. At this point the pressure in the mold should be so high that compression of the material will compensate for further shrinking due to solidification. When the object has cooled down sufficiently, the mold can be opened and the object can be ejected. These three stages are termed filling, packing, and cooling, respectively. The time required for the cooling can (if the objects are thick-walled, for example) determine the cycle time. In that case it may be worth considering use of a number of different molds for simultaneous filling by a machine.

The advantage of injection-molding with constant throughput is that once the volume of the mass that is to be injected (the so-called shot volume) is known, the injection time is easy to calculate and is not a function of process parameters such as viscosity. A disadvantage of injection with a constant throughput is that the pressure in the mold can become so high that the closing mechanism is no longer sufficiently rigid, and the mold will buckle away. This will cause frayed edges along the injection-molded article. Injection-molding machines are often described in terms of the maximum shot volume, the maximum injection throughput, and the maximum closing force or clamp force of the mold.

10.2
Injection-Molding Parameters

For the process of injection-molding the major thermal process parameters are:

- injection temperature,
- injection pressure, and
- mold temperature.

Optimal values of these parameters are of great importance for the time between two consecutive injections, the so-called cycle time, which in turn determines the economic feasibility of the process.

The injection process temperature is the temperature (or sometimes a range of temperatures), at which the mass is plasticized to such a degree that it may easily be injected from the heating cylinder into the mold. The choice of this temperature can depend on several factors, such as the type of polymer, the size and shape of the injected object, the maximum attainable pressure, and the mold temperature. The plasticizing of the material takes place in an electrically heated cylinder, where a certain temperature profile of the wall can be imposed. This temperature range is generally determined experimentally for the type of material, the kind of product, and the type of the injection-molding machine [4].

The injection pressure (p_w) is the pressure generated by the screw or the ram in the heating cylinder and it should be sufficiently high to press the plasticized mass from the cylinder into the mold, to fill the cooled mold completely before the material solidifies. The maximum injection pressure is determined on the basis of the diameter (D) of screw or ram, an external diameter (d) of the hydraulic piston in the shove and retract system of the screw or ram, the pressure in the hydraulic system (p_h), and the friction force (F) at screw shove [3]:

$$p_w * \frac{\pi D^2}{4} + F = p_h \frac{\pi d^2}{4} \tag{10.1}$$

from which:

$$p_w = p_h \left(\frac{d}{D}\right)^2 * \frac{4F}{\pi D^2} \tag{10.2}$$

The friction forces can be redefined in terms of frictional pressure by:

$$\Delta p_F = \frac{4F}{\pi D^2} \tag{10.3}$$

$$p_w = p_h \left(\frac{d}{D}\right)^2 - \Delta p_F \tag{10.4}$$

During the filling process the pressure in the mold itself (p_g), called the inner pressure, equals the injection pressure (p_w) minus the pressure decreases in the cylinder (Δp_c) the injection nozzle (Δp_d), and the runners (injection channels, Δp_k), respectively [3]:

$$p_g = p_w - \Delta p_c - \Delta p_d - \Delta p_k \tag{10.5}$$

The pressure required to pack the cavities in the mold mainly depends on the temperature of the mass at the nozzle and on the temperature increase due to viscous dissipation. This dissipation is proportional to the viscosity and quadratically proportional to the injection speed. Increased temperatures and the resulting decreases in viscosity improve the flow into the cavities, thus decreasing filling time, but they increase the cooling time needed before the object has solidified sufficiently to be ejected. A balanced choice of melt temperature and mold temperature is important for optimal production. Determination of these parameters is generally done experimentally.

Injection-molding machines are generally characterized by two different parameters: the maximum injection volume and the clamp force. The maximum injection volume determines the maximum volume of the object or of several objects in a single mold. The maximum clamp force is defined as the maximum force available to keep the mold closed without occurrence of leaking at the contact areas where the mold closes.

At the end of the injection cycle, when the flow has stopped no friction losses occur and Equation 10.4 degenerates into $p_g = p_w$. Because the maximum clamp force (F_K) equals the pressure in the cavity (p_g) times the projected area (A) the maximum projected size of an object that can be made on a particular machine is determined by:

$$A_{\max} = \frac{F_K}{p_W} = \frac{F_K}{p_h}\left(\frac{D}{d}\right)^2 \tag{10.6}$$

Injection process cycle: The injection-molding process is cyclic. This means that each process phase proceeds in definite, repeated periods of time. The cycle time is the time between closing of the mold at the beginning and the mold closing again after ejection of the object. This cycle time is mainly dependant on the efficiency of the plasticizing system of the injection machine and the cooling of the object before it can be ejected. For a given material these times are related to the structure of the object and its size; they vary usually between a few seconds and some minutes. This period of time comprises the times of each cycle phase. For maximum injection performance, the cycle time should be optimized [3].

Mold temperature: In the mold the final stage of the injection process – that is, the shape development and fixing through the cooling of the material – takes place. The coolant is generally water. The mold temperature ranges from 25–80 °C, subject to product requirements, material type, and shape of the cavity. The mold temperature can affect the product properties and appearance. Especially if the material can crystallize upon solidification, like various synthetic polymers, the mold temperature influences the nucleation and crystallization speed, which in turn have an impact on the physical properties of the end product. A second effect, dependent on the cooling speed, is the molecular relaxation of the material. During the injection process the molecules will be stretched and oriented, resulting in internal stresses in the material. Fast cooling will result in these stresses being "frozen in", and the deterioration of the mechanical properties of an object will be much faster than in cases in which the molecules have been able to relax and to lose their orientation because of slow cooling.

The plasticizing performance is, as stated before, another important parameter characterizing the injection process. It is defined as the maximum mass flow ( ) through a special nozzle at the end of the plasticizing system into the open space at the optimal rotary speed of screw. For practical application this value is taken as a standard for processing polystyrene (G_n) and other materials are related to it. In this way, the plasticizing performance for thermoplastic starches (or for other polymers) can be expressed as:

$$\dot{G} = k_{p1} * \dot{G}_n \tag{10.7}$$

where k_{pl} stands for a coefficient of relative plasticibility of material in relation to polystyrene. The k_{pl} coefficient values are the results only of the thermal properties of the material, and so they may differ slightly between samples or varieties of the same material [3, 4].

10.3
Injection Technology Use and Development Trends

Although the injection-molding of thermoplastic starches is still in its first stages of development, injection-molding is one of the most common shaping methods for synthetic polymers. In everyday life we encounter various types of packages, ready-to-use products, and household equipment manufactured with this technology. The most pronounced examples of this trend can be found in the car industry.

Products made by conventional injection-molding include the combined rear lights produced by the injection of many colors simultaneously. In special injection processes, suction manifolds for combustion engines are produced with the shell-forming technique, which combines injection and linking. Further examples from cars are jetting films for front panels of electrical equipment and spraying of lacquered components of the car body. The process depicted above must proceed under monitored conditions of the surroundings, and it is not only spotless surfaces that matter. For many applications optical quality is important, which requires a perfectly clean alloy, absolutely free from any inclusions. Such examples include optical data carriers, reflector glass, car windows, mirrors, prisms, car body interiors, and medical and pharmaceutical products [19, 20].

Because many injection-molding processes involve mass production, the future of this technique is closely connected to the use of readily available raw materials [2]. Extensive research into the introduction of biodegradable materials for the production of various objects is being performed all over the world; one of the most promising areas is the production of packaging. In this area, biopolymers, mostly based on various starches blended with plasticizers and natural fibers, represent good alternatives to synthetic plastics. The production parameters and the optimal mixture compositions having been established, it can be expected that thermoplastic starches will compete successfully with the conventional plastics in many areas of packaging.

There are several areas in which techniques used for synthetic polymers could be extended to thermoplastic starches. Combinations of material to form a product can be used in co-molding, for instance. At present in the plastics industry, co-molding is used to obtain cores made from recycled materials and skins that consist of virgin plastics. This technique could be extended to TPS: a core made out of thermoplastic starch in combination with a thin protective outer layer made from a synthetic polymer can be envisioned. After the life cycle of the product the outer layer would break during composting and the core would become free for biodegradation. A second example is the addition of a gas to form a foamed object, which is very common both in plastics processing and in snack technology. Equally, ready-foamed packaging material could be produced by injection-molding.

10.4
Reinforced Injection-Molding

In order to improve the physical properties of biopolymers or to reduce the price of a ready product, various types of fillers and carriers can be added. The fillers can affect the mechanical, physical, and chemical properties of a final product. Fillers can be divided by source or by morphology: by source we can distinguish between organic or inorganic fillers and by morphology between powdered, fibrous, and lamellar shape. They include emulsifiers, cellulose, plant fibers, bark, kaolin, pectin, etc. Extenders have a considerable influence on the technological properties of materials and these supplements enable the primary shrinkage of test bars to be reduced.

It is most logical to add equally degradable fillers to biodegradable thermoplastic starch. Natural fibers may be added to biopolymers at amounts of 1% or even up to 20–45%, depending on the kind of fibers used. The most common fibers have proven to be flax, hemp, coconut, jute, or cotton fibers. To achieve better adhesion between the fiber and the matrix material, the fibers are often modified in acid solutions or in acetone for degreasing and to produce structural changes in the fiber surface [5–9].

In the production of objects from synthetic plastics, two kind of fiber reinforcements can in general be found: short fibers and structured fibers. In short-fiber reinforcement, chopped fibers of 6 mm to 1 cm are mixed with the polymers and injected as a more or less homogeneous mass. In objects reinforced with structured fibers a woven or non-woven fiber mat is placed in the mold before the mass is injected. At present only the short-fiber reinforcement has an analogue in biopolymers.

For the injection-molding process the use of short-fiber-filled materials has some consequences:

- The fibers can increase the viscosity considerably, leading to higher injection pressures and larger temperature increases due to viscous dissipation.
- The runners should be straight without sharp bends to prevent the fibers from clogging up. Also, the gate design has to be modified.
- Because a slight obstruction has the tendency to filter out fibers and to form a tight clog, safety measures to prevent too-high pressure build-up have to be build in, especially in machines with constant throughput.
- Because many fibers show abrasive action, molds for reinforced injection-molding should generally have higher hardness to prevent excessive wear.

10.5
Application of Natural Fibers in Processing of Biopolymers

Natural fibers were already being used as reinforcement materials in ancient Egypt. House walls there used a mixture of clay, sand, and chopped straw, which after being dried provided the first construction composite material [7]. More recently, many materials for manufacturing have contained various fibers. Obvious examples are textiles, linen, and paper, made from commonly available fibers such as hemp, cotton, and jute. Some of these fibers have been successfully applied ever since. It was as early as in 1986 that the first aircraft tanks and seats were made from a compound of synthetic resin and natural fibers.

Concerns about our natural environment, protection of natural resources, and the opportunity to re-use old packaging all contribute to the growing interest in environmentally friendly materials obtained from renewable sources. At present, we are witnessing a dynamic increase in the use of natural fibers in the processing of thermoplastic polymers. Elevated pro-ecological awareness and new legal regulations have caused a turnabout in the design of composite products in which traditional fibers were being replaced by artificial ones [10–12].

The application of composites containing natural fibers depends on the production cost of off-the-shelf articles and their functional properties. Natural fibers are claimed to be more cost-effective than fibers traditionally used for the production of composites, such as carbon fiber or glass fiber, in terms of their procurement and also to have lower density, high hardness, coherence, acceptable rigidity, and mechanical properties, to be easy machined, and, first and foremost, to be biodegradable [6, 9].

It is necessary to maintain a balance between economy and ecology. This results in the application of biocomposites in some specific areas, such as the automotive industry, furniture, construction materials, and packaging. Car manufacturers aiming at the reduction of vehicle weight replace steel parts with aluminium, plastics, and composites. It is forecast that in the near future polymers and polymer composites will account for about 20% of vehicle weight. Car makers are also introducing materials containing natural fibers in order to economize in the manufacturing and on the weight of vehicles. Fiat and Daimler–Chrysler, for example, use linen and hemp fiber to make some selected car parts such as engine guards. In India, jute fiber is primarily used to produce composites. When combined with a polyester matrix, the mixture can be used to produce pipes, molds, slabs, and panels. The Indian government promotes large projects related to the use of jute fiber in the construction industry [7]. It is estimated that in the USA the demand for natural fiber in the automobile industry will rise annually by 30% and that in the construction sector by as much as 60% [9].

In recent years a new generation of biocomposites, made of biodegradable polymers as the matrix and natural fibers as strengthening components, has been emerging. Despite higher costs of manufacture, these materials should eventually compete with traditional composites because of their degradability. It is estimated that the increase in sales of biocomposite products will rise by 20–30% annually. What is more, the use of different biopolymer mixes with cheaper plastics may enable a balance between cost and biodegradability to be achieved. The trend is to replace traditional polymers as much as possible with biodegradable materials displaying high stability when used and having no negative effect on environment after their life cycle [9, 13–15].

The most common fibers in biocomposites come from linen, hemp, cotton, jute, coconut, banana, and leaves of various kinds of agave. The basic problem with the proper application of natural fibers is their great variation in quality and mechanical properties. Synthetic fibers such as glass fiber and carbon fiber have very specific physical characteristics, but the features of natural fiber depend on many factors, such as their origin, the age of the plant, whether the material comes from leaves or stem, and on the process of obtaining the fiber and its preparation.

Natural fibers should be subject to certain preparatory operations and modifications of their surface. After this process, they should display the following features:

- good adhesion between the fiber and matrix,
- suitable degree of polymerization and crystallization,
- resistance to humidity,
- non-inflammability, and
- homogenous physical properties.

10.6
Chemical Modification of Fibers

The chemical makeup and structure of a fiber depends on numerous factors such as climatic and cultivation conditions, age, and whether the fiber comes from leaves or stems. Natural fibers consist of more or less desirable components such as cellulose, hemicelluloses, pectin, lignin, wax, and water-dissolvable substances, all of which affect the fibers' physical characteristics.

Cellulose is a natural, fibrous polysaccharide and a basic component of cell walls of higher plants as well as algae, fungi, and bacteria. Its molecule consists of 3000–14 000 linearly combined β-D-glucopyranose units joined through β-1-4-glucoside bonds. A disaccharide unit incorporated in cellulose is cellobiose. The extended linear structure and numerous hydrogen bonds between glucose molecules create the opportunity for the development of the structures known as fibrils. In their vicinity, crystal structures of cellulose, the so-called micelles, are created. These are bordered by amorphous cellulose and free inter-micelle zones. The β bond contributes to the development of long, rigid threads of molecular weights of ca. 570 000. The highest cellulose content is found in cotton fibers [16, 17].

The results in Table 10.1 show considerable differences in the chemical makeup of different fibers. The lowest cellulose content and highest lignin content is observed in coconut fiber. The quantity of lignin and cellulose depends in the first place on the age and species of plants that provided the fiber [9].

Hemicellulose is a hydrophilic polymer; it therefore largely determines the water absorption by vegetable fibers [6].

Waxes influence the quality of fiber-polymer bond and hence the durability of obtained composite.

Both the quality and the properties of fibers depend on their length, size, maturity, and methods of processing. Table 10.2 compares the mechanical characteristics of selected natural fibers and synthetic fibers.

Table 10.1 Chemical compositions and structural parameters of some fibers [18].

Types of fiber	Cellulose	Lignin	Hemicellulose	Pectin	Wax	Microfibrillar/ spiral angle (Deg.)	Moisture content
jute (*Corchorus capsularis*)	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0	12.6
flax (*Linum usitatissimum*)	71	2.2	18.6–20.6	2.3	1.7	10.0	10
hemp (*Cannabis sativa*)	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8
ramie (*Boehmeria nivea*)	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0
kenafu (*Hibiscus cannabinus*)	31–39	15–19	21.5	–	–	–	–
sisal (*Agave sisalana*)	67–78	8.0–11.0	10.0–14.2	10	2.0	20.0	11.0
henequen (*Agave fourcroydes*)	77.6	13.1	4–8	–	–	14.0	–
cotton (*Gossypium* L.)	82.7	–	5.7	–	0.6	–	–
coir	36–43	41–45	0.15–0.25	3–4	–	41–45	8.0

Table 10.2 Comparative properties of some natural fibers and conventional man-made fibers [9].

Types of fiber	Density ($\mathrm{g\,cm^{-3}}$)	Diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
jute (*Corchorus capsularis*)	1.3–1.45	25–200	393–773	13–26.5	1.16–1.5
flax (*Linum usitatissimum*)	1.50	–	345–1100	27.6	2.7–3.2
hemp (*Cannabis sativa*)	–	–	690	–	1.6
ramie (*Boehmeria nivea*)	1.50	–	400–938	61.4–128	1.2–3.8
sisal (*Agave sisalana*)	1.45	50–20	468–640	9.4–22.0	3–7
cotton (*Gossypium* L.)	1.5–1.6	–	287–800	5.5–12.6	7.0–8.0
coir	1.15	100–450	131–175	4–6	15–40
E-glass	2.5	–	2000–3500	70	2.5
S-glass	2.5	–	4570	86	2.8
aramid	1.4	–	3000–3150	63–67	3.3–3.7
carbon	1.7	–	4000	230–240	1.4–1.8

Properties such as density, lack of electric conductivity, maximum tension, etc. depend on the internal structure and chemical makeup of fibers. Durability and rigidity is strictly related to the angle between the axis and fibril of the fiber. If the angle is smaller, the durability is better. Coconut fibers display the lowest durability (Table 10.2). They contain little cellulose and have a large fibril twisting angle (Table 10.1). On the other hand, the high level of maximum tension of linen fibers may be connected to high cellulose content and a relatively small twisting angle of microfibrils (Table 10.1). Some mechanical properties of natural fiber (durability, elasticity, rigidity) can be comparable to those of glass fiber. In some cases, natural fiber shows better parameters than glass fiber; hemp fibers, for example, are more rigid.

Both in the designing stage of a biocomposite and during its application, natural fibers have to be selected for the best mechanical properties combined with good processability. Low thermal resistances of natural fibers can cause many problems in the selection of polymers as matrix material. The processing temperature should not exceed 200 °C for more than 10 minutes. Higher temperatures and longer process times may result in weakening of the fiber and as a result the sturdiness of the composite. Fibers possess different thermal durabilities; ramie fiber, for example, loses 10% of its tear resistance after 10 minutes at a production temperature of 200 °C [18].

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11

Influence of Addition of Fiber on the Mechanical Properties of TPS Moldings

Tomasz Oniszczuk, Leon P.B.M. Janssen

Reinforcement by the addition of fibers is common practice in the field of synthetic polymers. When the material is stressed, part of the load will be absorbed by strong fibers, and in this way the strength of the reinforced object can be increased considerably. In the case of biodegradable materials such as thermoplastic starches, it is obvious that the use of biodegradable fibers should be strongly preferable. Fibers for use in common processes such as extrusion and injection-molding are of limited length because of processability. Fibers that were too long would excessively increase the viscosity and moreover would introduce rheopect behavior. The resulting extra increase in viscosity at elevated stresses is unwanted in processing. For the same reason the concentration of fibers is generally limited to 30%. An important parameter in fiber-reinforced materials is the strength of bonding between the fibers and the matrix material. If this bonding is too weak the fiber cannot take up the full force but will be pulled out of the object. This results in a sub-optimal strength.

11.1

Theory of Reinforcements

Optimal biocomposite materials can be processed on standard machines and devices as used in plastics processing [1–4].

The testing of these materials is through test samples: so-called “blades”. These blades are subjected to physical and microscopic examination in order to determine the influence of storage, manufacture, and morphology on the quality of a material and its use in packaging production [5, 6]. The microscopic examination is connected with the degree of fiber bonding with the biopolymeric matrix in the vicinity of the area where the sample breaks (Figure 11.1).

The evaluation of the fracture areas consists of evaluating the number of broken fibers and the number of fibers that are pulled out of the matrix. For broken fibers it can be concluded that the bonding is stronger than the fibers themselves, whereas for fibers that are pulled out the fiber strength is superior to the bond strength (Figure 11.2).

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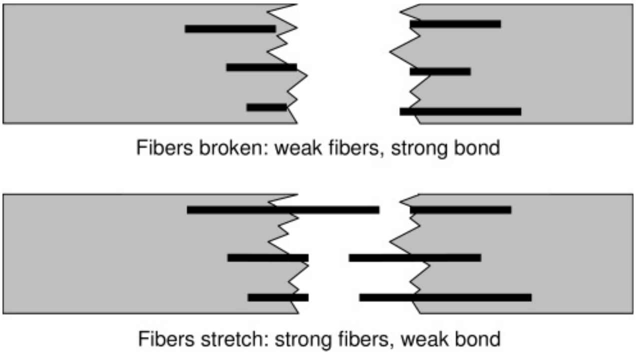

Figure 11.1 The area of biopolymer breakage depends on the degree of fiber and matrix bonding.

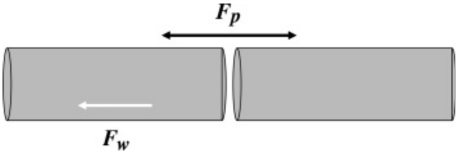

Figure 11.2 Forces acting on fiber during material breakage.

The bond strength between fibers and the thermoplastic starch matrix can be determined as the shear stress (τ) at the interface multiplied by the surface upon which it acts:

$$F_w = \tau\pi\frac{d}{2}l \tag{11.1}$$

where d is the fiber diameter and l is the fiber length.

The force at which the fiber breaks equals the tensile strength of the fiber material (σ_f) times the perpendicular surface:

$$F_p = \sigma_f\frac{\pi}{4}d^2\cdot[\mathrm{N}] \tag{11.2}$$

Because the fiber will break if $F_w > F_p$ it is possible to define a critical fiber length:

$$l_c = \frac{\sigma_f d}{2\tau} \tag{11.3}$$

In the simplest model it can be stated that if the fibers are longer than the critical length, then fiber breakage will occur, but fibers shorter than the critical length will be pulled out.

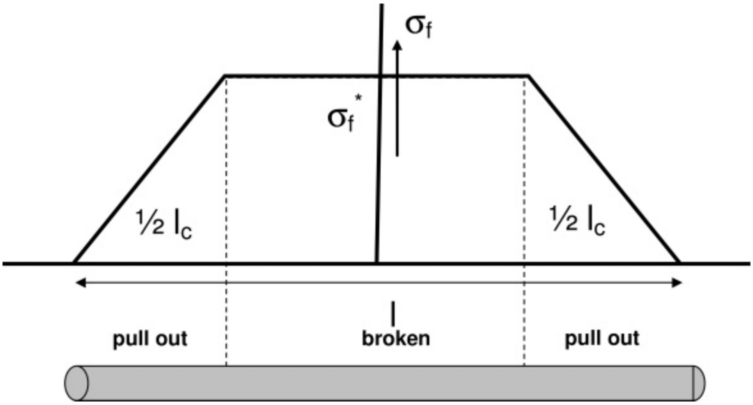

Figure 11.3 Minimal length of pull-out of the long fibers.

In reality, not all fibers will break exactly in the middle. If a fracture in the matrix material encounters the fiber close to one end, pull-out will always occur. If a failure in the matrix material reaches the fiber in the middle region the fiber will break in this middle part, but if it reaches the fiber close to the tip, pull-out will occur if the distance to the tip is in the range smaller than the pull-out length. The total reinforcement of a fiber can now be determined by addition of the contributions of the three regions.

Knowledge of the critical fiber length allows the determination of the number of broken fibers and pull-out fibers in the examined sample. In the case of application of fibers of more than l_c in length, fibers of $1/2l_c$ or more can be pulled out from the starch matrix (Figure 11.3). By macroscopic examination, it is possible to define the number of pull-out fibers versus broken fibers. By determining the pull-out length an indication of the bonding strength between fiber and matrix material can be obtained [7, 8]. For practical situations it can be generalized that if the relative amount of pulled-out fibers is large, improvement of the composite material can be achieved by improving the bonding and by increasing the lengths of the fibers. If, on the other hand, most of the fibers are broken, improvement of strength can only be achieved by using stronger fibers.

11.2
Experimental Data on Fiber-Reinforced TPS

When tests on the strength and bonding of fiber-reinforced composites need to be performed, firstly test bars have to be prepared. The total process consists of two steps. In the first step, starch is gelatinized and mixed with glycerol in an extruder and pelleted. For the experiments with fiber reinforcement the flax or cellulose fibers have to be mixed into the starch during the first process step. The pellets are then very similar to the pellets used in plastic processing and they can

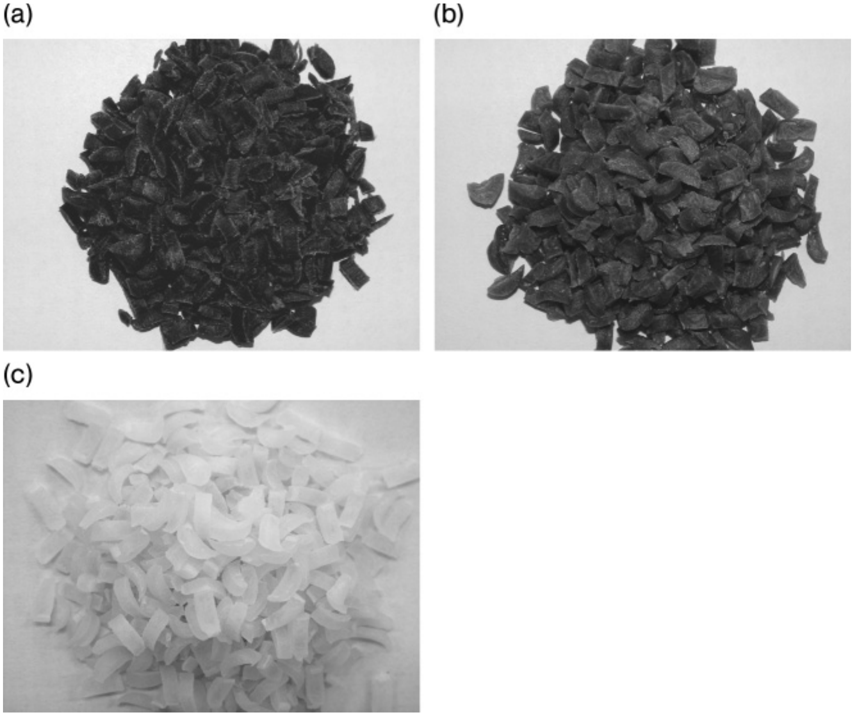

Figure 11.4 Granulates with a) 10% and b) 5% flax fiber content, and c) 5% cellulose fiber content.

be readily fed into the second step, where the product obtains its final shape [6, 13]. This second step is injection-molding (to form three-dimensional objects). Moisture adjustment occurs in the first step, and storage between the first and second production step should be such that this moisture content does not change.

It is advisable that, after mixing, the samples are left in airtight plastic bags for 24 hours in order to allow the intensification of the glycerol penetration into the starch granules. Directly before the extrusion, the mixtures must be stirred again for 10 minutes in order to guarantee a loose and slack mixture structure and to assure a regular feed into the subsequent mixing process.

After extrusion the obtained granulates should be dried in a vacuum laboratory drier at a temperature of 50 °C for 6 hours until a humidity of 4–6% is achieved (Figure 11.4).

As a next step, test bars should be obtained by injection-molding. Production of test bars in the form of a 'spade' is convenient for further examination of mechanical properties. Figure 11.5 shows a mold for the production of various test samples: from top to bottom for notched and unnotched impact strength, for bending tests, and for tensile testing.

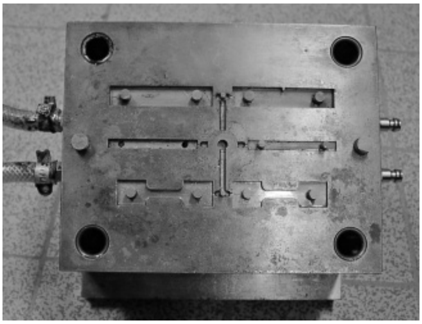

Figure 11.5 Injection mold for the ARBURG 220H90-350 injection machine.

11.3
Critical Fiber Length

In order to define the critical fiber length, it is necessary to know the shear stress (τ) between the fibers and thermoplastic starch. Unfortunately, independent measurement of the value of τ is impossible because of the lack of suitable measurement equipment. Because the problem of determining the value of steady stress between fibers and thermoplastic starch has only recently begun to attract interest, the scientific literature does not provide any definite data; the approximate value of τ was adopted from measurements reported by Morlin and Czigány [8]. In their research, they established that the shear stress between flax fibers and Mater-Bi (which is a variety of thermoplastic starch) amounts to 4.18 MPa.

The mechanical strength of flax fibers varies from 254 to 1100 MPa, depending on the type [9]. From measurements of mechanical features of flax fibers determined on a Wick tester, their breakage strength was established at 663 MPa. Microscopic measurement of the thickness of flax fibers (Figures 11.6 and 11.7) showed an average thickness of 12 μm.

Oniszczuk [6] determined from these results that the critical fiber length for the flax fiber/thermoplastic starch combination is 951 μm.

When performing microscopic examination of the breaking area of a molding, counting the number of the fibers present and measuring their lengths, it is possible to determine the number of broken fibers and the number of fibers that have been pulled out (provided that all the fibers are homogeneous distributed). Because thermoplastic starch with added flax fibers of 4 mm was used during the injection-molding process, the fibers in the breakage areas that have been pulled out are longer than half of the value of l_c: that is, at least 475 μm. Pictures of these fiber measurements are shown in Figures 11.8 and 11.9.

On examination of the samples with 5% flax fiber content, it can be noted that samples with higher glycerol content show shorter pull-out lengths and more breakage. Therefore it can be argued that an increase in glycerol content does not

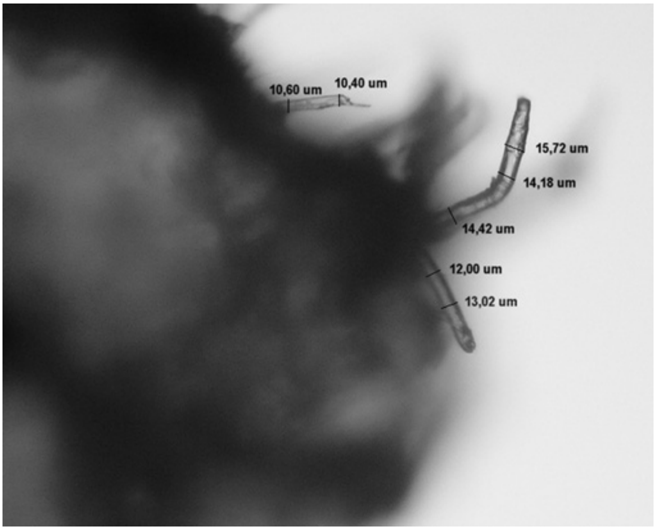

Figure 11.6 The area of breakage of biopolymer molding containing 20% glycerol and 10% flax fibers (fiber diameters).

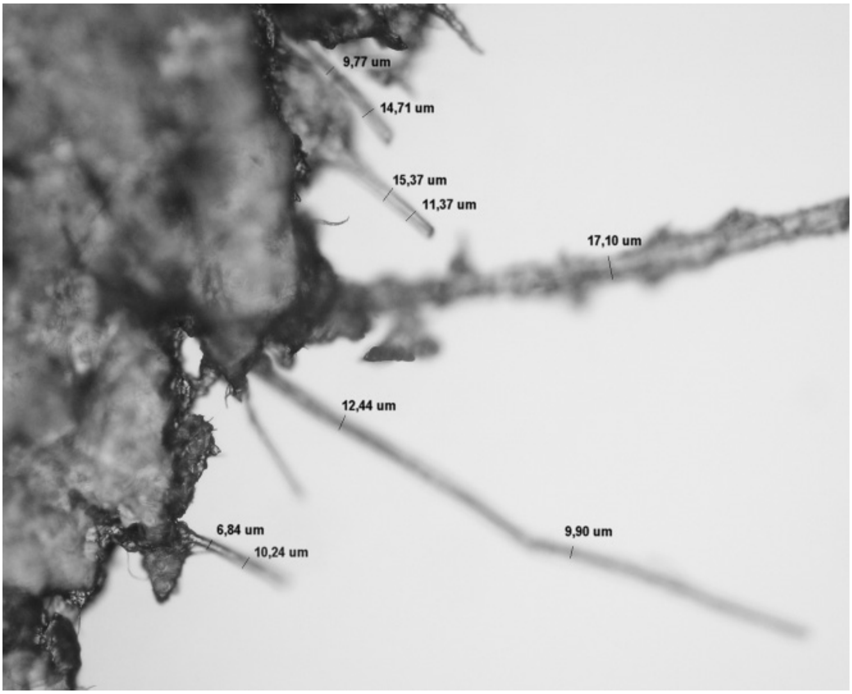

Figure 11.7 The area of breakage of biopolymer molding containing 25% glycerol and 10% flax fibers (fiber diameters).

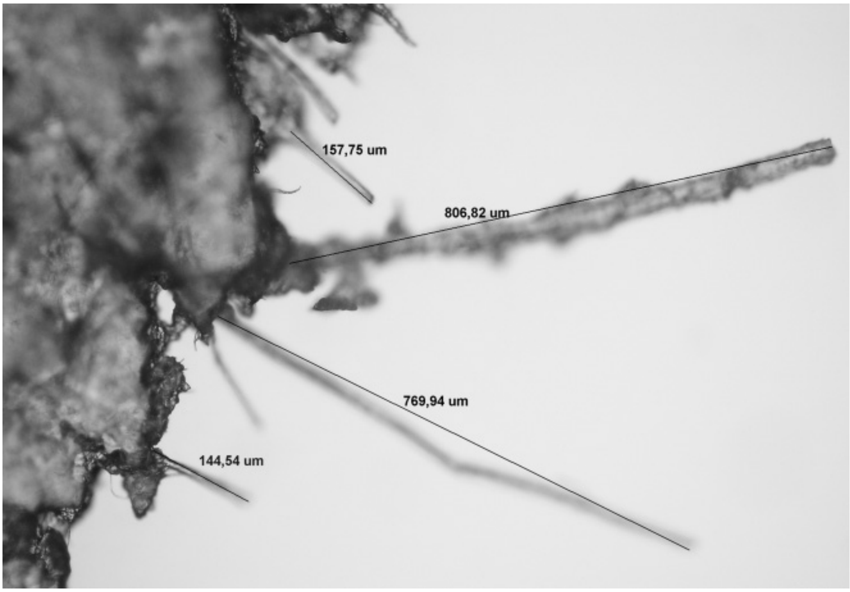

Figure 11.8 The area of breakage of biopolymer molding containing 25% glycerol and 10% flax fibers (fiber lengths).

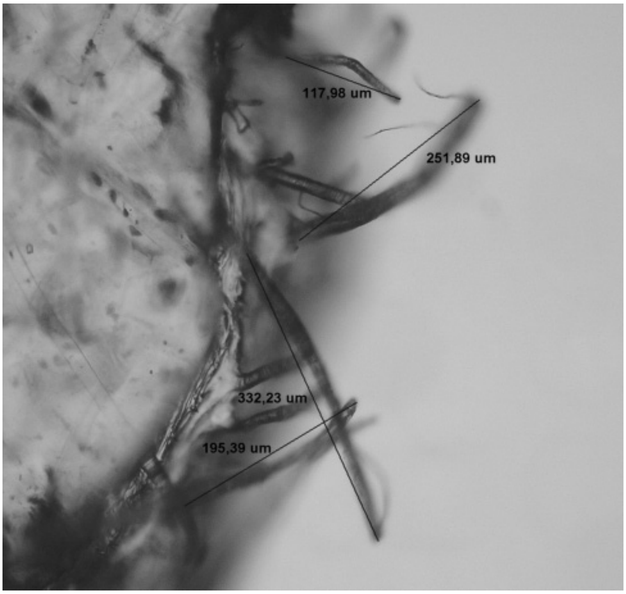

Figure 11.9 The area of breakage of biopolymer molding containing 22% glycerol and 5% flax fibers (length measurement).

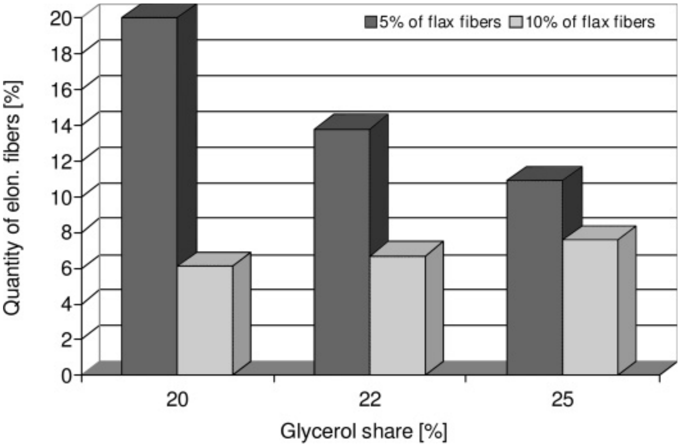

Figure 11.10 Influence of proportion of glycerol on the number of extended flax fibers.

decrease bonding between fiber and matrix material and that a higher plasticity of the starch improves the bonding and the reduced number of pull-out fibers is clearly visible (Figure 11.10). Increasing the glycerol content causes better plasticization of thermoplastic starch, which possibly improves the fiber bonding to the starch matrix through intensified adhesion. An increase in the percentage of flax fibers in the moldings to 10% resulted in enhanced mechanical strength. This might be associated with better fiber bonding with the thermoplastic starch, which is confirmed by the reduced number of fibers extending from the matrix. Nevertheless, the samples displayed a slightly increased number of extending fibers together with the increased glycerol concentration. Probably, despite its improved plasticity due to the presence of the large number of fibers, some proportion of the thermoplastic starch is not involved in the biopolymer matrix structure, which results in the extension of the fibers from the matrix [6].

11.4
Mechanical Properties

The mechanical properties of biocomposites depend on a number of factors. Firstly, these are the quantity and type of fiber added to the material, but the type and amount of plasticizers and the production temperature are also important parameters [14]. One of the parameters with a dominating influence on the mechanical properties of biocomposites is the quantity of both natural fiber and plasticizer [3, 4, 6]. It has been observed that the addition of fiber enhances the mechanical strength. The addition of extra plasticizer causes a decline in the maximum sample stress.

Figures 11.11 show the relationship between maximum stress and flax fiber content in samples containing 20, 22, and 25% of glycerol produced at a material

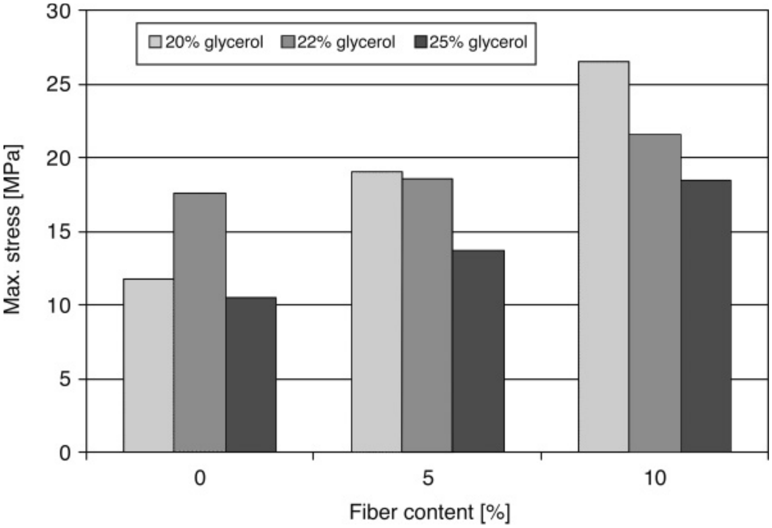

Figure 11.11 Relationship between the maximum stress and the fiber content in samples (sample injection temperature 120 °C) [6].

injection temperature of 120 °C. It is clear that the mechanical strengths of the samples improved together with increasing fiber content.

The samples with 20% glycerol content and 10% of flax fibers showed the highest strength (26.5 MPa). In the case of moldings obtained from granulate containing 22% glycerol, the addition of 5% or 10% of fibers improved the strength slightly. It was noted that in the moldings containing flax fibers the mechanical strength dropped with increasing glycerol content. Glycerol acts as a diluent and weakens the intermolecular bonds between flax fibers and starch [3]. The lowest mechanical strengths were observed with moldings produced from granulates containing 25% glycerol.

The same tendency can be seen in the case of samples obtained at different production temperatures. The highest mechanical strengths were displayed by moldings produced at a material injection temperature of 140 °C (maximal stress 27.8 MPa), whereas the lowest mechanical strengths were noted for moldings obtained at a temperature of 180 °C (10.8 MPa).

Wollerdorfer *et al.* [9] conducted research into the addition of fibers from different sources. They came to the conclusion that there is a considerable influence of the fiber content on the mechanical and strength features of moldings produced from maize and wheat starch in the high-pressure injection process. The use of flax fibers at levels from 10 to 20% considerably improved the mechanical strengths of samples relative to thermoplastic starch without additives. The value of the maximum stress with the addition of 10% of flax fibers was about 20 MPa, the addition of 15% of fibers increased the maximum stress up to 26 MPa, and in the samples with 20% flax fibers the stress was more than 36 MPa.

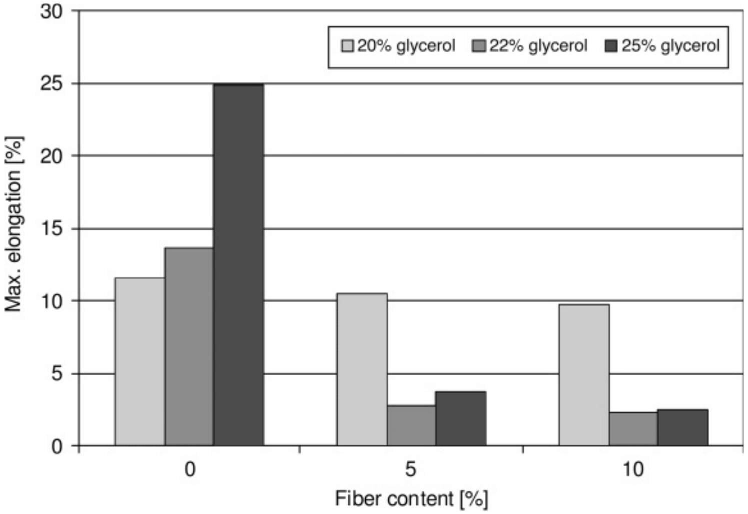

Figure 11.12 Relationship between the maximum elongation and the flax fiber content in samples (injection temperature 120 °C) [6].

Research carried out by Singleton *et al.* [10] into the influence of flax fibers on the properties of HDPE showed that addition of fibers also increases the stress at break in the case of synthetic polymers. The maximum stress was much larger than in the case of thermoplastic starches, due to the different properties of the polyethylene. Without the addition of fibers the maximum stress reached a value of about 27 MPa, and this value could be increased up to 40 MPa by the addition of 30% of flax fibers [10].

In addition, Oksman *et al.* [11] examined the impact of flax fiber on polypropylene (PP) and poly(lactic acid) (PLA), using press-molded stiff forms. The maximum stresses for pure materials amounted to 28 MPa for PP and 50 MPa for PLA. After addition of 30 and 40% of fibers there were slight increases in the stress values, varying from 2 to 5 MPa. This shows that flax fibers have only a minute impact on stresses in PP and PLA [11].

Another important parameter is the maximal elongation of the samples during stretching. For TPS without added fibers, it can be stated that the maximum elongation coincides with increasing injection temperature and with increasing glycerol content in the sample for the full spectrum of injection temperatures and for all glycerol concentrations investigated. The addition of fibers affected the elongation behavior of the material considerably.

Figure 11.12 shows some peculiar behavior. In the TPS with 20% glycerol content the addition of fibers hardly influences the stretching behavior, and the maximum elongation decreases slightly from 10.5 to 9.7%, approximately 10%. In the case of samples with higher glycerol contents of 22 and 25%, the addition of fibers decreases the maximum elongation considerably, although the differences

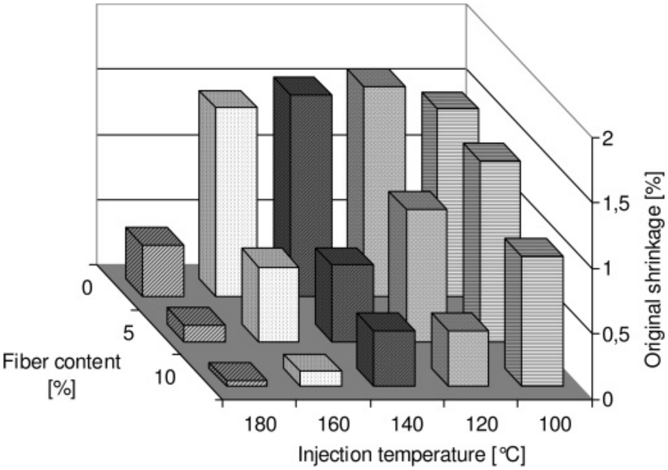

Figure 11.13 Influence of flax fiber content on the magnitude of original shrinkage of moldings (glycerol content 22%) [6].

between addition of 5% and 10% fibers are marginal. When an injection temperature of 180 °C was used instead of 120 °C, the largest maximum elongation (17.1%) was observed with the samples containing 25% glycerol and 5% flax fibers. The lowest maximum elongation (3%) was observed with moldings produced from granulate containing 22% glycerol and 10% flax fibers. Although the underlying mechanism is not yet completely clear, these findings indicate a negative impact of fibers on the flexibility of biopolymer composites.

Similar results were obtained by Wollerdorfer *et al.* [9] when examining starch moldings with the addition of flax fibers, and also by Ma *et al.* [12], who scrutinized moldings enriched with cotton starch.

Besides improving durability, the fibers used for biocomposite manufacture stabilize the shapes and reduce the original shrinkages of ready products. Oniszczuk [6] has reported that an increased linen fiber content will decrease original shrinkage values. The addition of plasticizer (glycerol) had an adverse effect on the original shrinkage.

A very significant parameter determining original shrinkage is the production temperature of the biocomposite. The lowest value of original shrinkage (0.04%) can be observed in samples produced at an injection temperature of 180 °C with granulates containing 10% linen fiber (Figure 11.13). A similar trend is evident in samples produced with 20% and 25% glycerol and 5% and 10% linen fiber.

11.5
Conclusions

Addition of plant fibers to thermoplastic starch granulates positively influences the mechanical strengths of moldings over the entire range of glycerol concentrations. The test bars produced from the granulate containing 10% flax fibers exhibited the greatest mechanical stress.

Examination of the surfaces of moldings with an optical microscope confirmed the lack of changes on their surfaces (cracks, scratches). On analysis of the areas of breakage on moldings, good bonding between fibers and biopolymer was observed in bars with higher glycerol contents, processed at up to 140 °C. Increased fiber content also improves form stability by decreasing shrinkage of the material through the release of internal stresses.

Biocomposites based on matrixes made from biodegradable polymer with reinforcement by natural fibers, such as thermoplastic starch with flax, have great potential as packaging materials of the future [6].

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12
Storage and Biodegradability of TPS Moldings

Tomasz Oniszczuk, Leszek Moscicki

Storage conditions are the most important factors determining the application and utility of packaging materials. Biopolymers are of special origin, so their behavior has to be taken into account during the design of packaging products.

12.1
The Influence of Low Temperatures on the Mechanical Properties of TPS Moldings

Starch biopolymers may be utilized in the packaging industry not only as protective wrappings for products stored under ambient conditions, but also at low temperatures and for frozen products. In connection with the possible applications of starch biopolymers as, for example, ice-cream sticks or stiff packaging for frozen food, selected mechanical features of starch moldings have been tested after storage under varied temperature conditions [1–4, 9, 10, 12].

In order to examine the behavior of products at low temperatures, the moldings were placed in a refrigerator (POLAR type CP 1116A, chilling) and a freezer (Whirlpool type AFG 6450 AP). Samples were put in single layers and stored at two different temperatures – +3 °C and −36 °C – for 24 hours at a given stage and for 30 days. Once taken out, the samples were placed in heat-insulating containers (in order to avoid molding temperature fluctuations) and were subsequently individually subjected to strength tests on a Zwick apparatus (type BDO-FBO 0.5 TH). These tests give an indication of the quality of the packaging under material cold-storage conditions [4].

12.1.1
Results of Measurements

The measurement results for the maximum stress of moldings produced at 140 °C and stored under different temperature conditions are presented in Figure 12.1. Moldings produced under such conditions had varied mechanical strengths depending on additives and storage conditions. Moldings produced without the addition of fibers displayed low stress values at below ambient temperatures.

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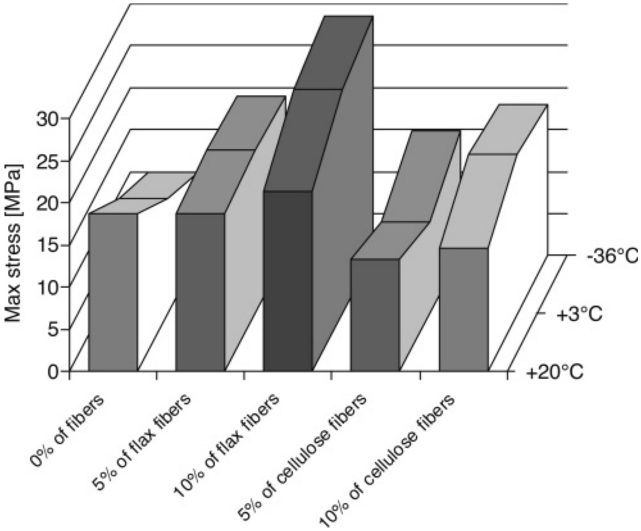

Figure 12.1 Influence of storage temperature and the quantity and type of natural fibers in moldings on the magnitude of maximum stress of moldings during tension test (glycerol content 22%, storage time 24 h, sample production temperature 140 °C).

Moldings with addition of various amounts of flax fibers had similar mechanical strengths at ambient temperature. Subjection to 24 hour storage at low temperatures, though, considerably changed the sample strengths. Surprisingly, the mechanical strength levels of moldings made with flax fibers were higher than those of the other tested moldings, which might be the effect of low temperature on the interaction between starch, glycerol, and flax fibers, and this in turn produced improvements in molding strength. Addition of larger quantities of flax fibers (10%) resulted in the most improved strengths out of all the tested moldings during break testing. For moldings with cellulose fibers, higher stress values – relative to moldings without additions – were also recorded after cool storage. However, the values of sample stress did not exceed 20 MPa, and the highest was observed at a storage temperature of –36 °C.

Extension of the preparation time to four weeks did not cause significant changes in the strengths of the tested products obtained at 140 °C, with or without the addition of plant fibers. In moldings with no fiber addition, lowered mechanical strengths were observed at the temperature of +3 °C, and storage at –36 °C did not have any impact on sample strength. During this examination the highest mechanical strengths were recorded for moldings with added flax fibers, regardless of storage temperature (Figure 12.2). Under freezing conditions, moldings with these fibers were the most stable on prolonged storage, and sample strengths remained unchanged (about 27 MPa). Almost identical values were observed with moldings with cellulose fibers, which, after long storage both in cool temperature conditions and frozen, exhibited high stability of the tested parameter.

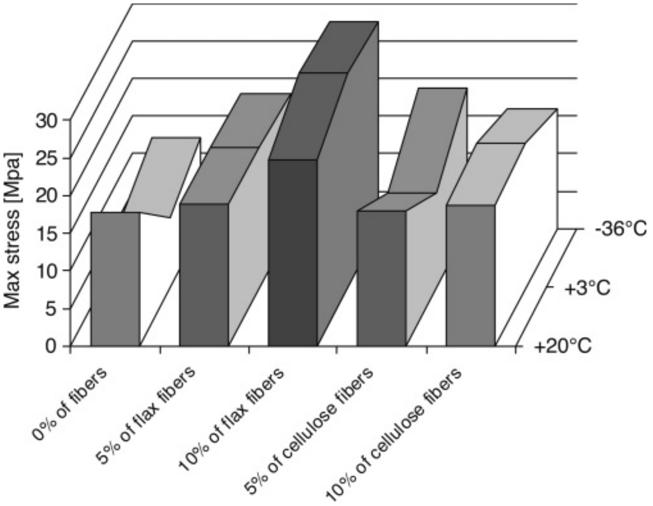

Figure 12.2 Influence of storage temperature and the quantity and type of natural fibers in moldings on the magnitude of maximum stress of moldings during break test (glycerol content 22%, storage time 4 weeks, sample production temperature 140 °C).

The results for measurement of plasticity, as the parameter of resistance to deformation during storage for 24 h, are shown in Figure 12.3. The top plasticity, regardless of storage temperature, was recorded for moldings produced without the addition of fibers over the full range of applied temperatures of production. When moldings with the addition of flax fibers were tested it was observed that the materials stored under cool conditions displayed better plasticity. Elongation values were reduced for samples containing 10% flax fibers. A reverse relationship was observed for moldings incorporating cellulose fibers. Lowest elongation and the next-best utilitarian features were displayed by moldings with 5% cellulose fiber content stored at +3 °C, both after 24 h and after four weeks (Figure 12.4). Generally, it can be concluded that the lengthening of storage time to four weeks did not particularly influence the elasticity of moldings, either those containing fibers or those free of them.

12.2
Evaluation of Biodegradability of TPS Moldings

Ranges and rates of biodegradation changes are subject to a number of factors, such as composition and activity of the bacterial flora, the presence of other compounds, temperature, pH, oxygen availability, pollutant "age", structure, polymer molecule structure, and MW, as well as sunlight. Biodegradation may occur under both aerobic and anaerobic conditions. The consequences of this process not only include the modification of some chemical groups, but mostly involve the

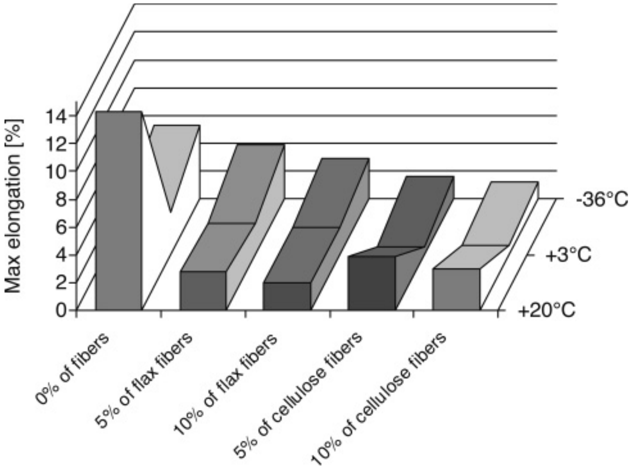

Figure 12.3 Influence of storage temperature and the quantity and type of fibers in moldings on the magnitude of maximum elongation of moldings during tension test (glycerol content 22%, storage time 24 h, sample production temperature 140 °C).

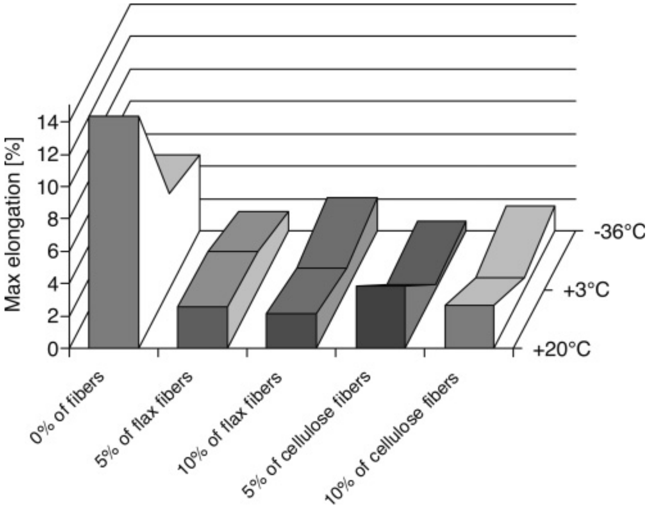

Figure 12.4 Influence of storage temperature and the quantity and type of fibers in moldings on the magnitude of maximum elongation of moldings during tension test (glycerol content 22%, storage time 4 weeks, sample production temperature 140 °C).

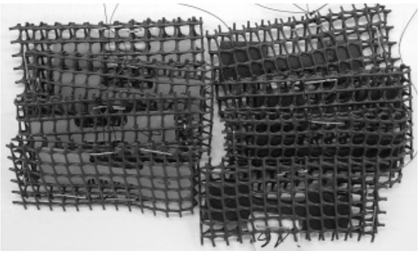

Figure 12.5 Samples of TPS moldings in plastic baskets.

Figure 12.6 Sample arrangement in boxes with soil.

decomposition of the basic structure of a compound, leading to its complete degradation into carbon dioxide, water, and inorganic soils [3, 5, 12, 13].

During our tests we wanted to check by how much and how quickly TPS moldings could decompose in a natural environment. Prepared test bars of molded potato starch, glycerol, and plant fibers (dry moisture contents of 4%) were placed in special baskets and stored in plastic boxes 15 cm underground, covered with garden soil of 70% humidity and pH 6.5 for 2, 4, 8 and 12 weeks. In order to assure stable soil humidity, the water loss indicated during the process was supplemented twice a week (Figures 12.5 and 12.6).

The boxes were stored in the fall season in a room without heating and with relatively stable humidity and temperature between 10 °C and 15 °C. After the storage period, the moldings were cleaned, weighed, and dried back to their original humidity of 4%. At the final stage, the samples were weighed again on an analytical balance in order to establish the weight loss [6, 7, 14, 15].

12.2.1
Results of Measurements

As already mentioned, in order to measure the degree of degradation, samples were checked after periods of 2, 4, 8 and 12 weeks. Results are presented in Table 12.1 and Figure 12.7.

Table 12.1 Mass decrement of moldings observed in biodegradability tests [4].

Content: starch/glycerol/ flax fbr./cellulose fbr. (%)	Mass decrement (%)			
	2 week	4 week	8 week	12 week
80/20/0/0	13.14	15.48	18.27	39.41
78/22/0/0	20.36	21.06	23.78	48.21
75/25/0/0	23.18	26.35	30.04	56.36
75/20/5/0	14.6	17.62	22.35	54.21
70/20/10/0	15.12	20.43	23.59	55.36
73/22/5/0	17.78	19.08	23.79	32.11
68/22/10/0	15.41	18.71	21.79	47.58
70/25/5/0	20.95	22.16	28.79	31.96
65/25/10/0	20.67	21.27	25.25	38.79
75/20/0/5	19.22	20.06	22.31	52.84
70/20/0/10	18	20.29	23.14	51.36
73/22/0/5	18.28	22.44	24.16	32.11
68/22/0/10	18.72	20.53	22.59	37.21
70/25/0/5	20.58	21.72	24.92	42.15
65/25/0/10	21.32	23.71	25.76	43.28

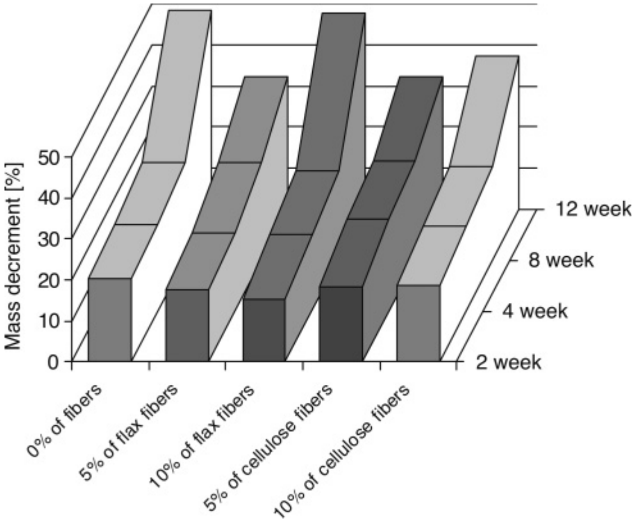

Figure 12.7 Influence of storage time and the quantity and type of fibers in moldings on mass decrement of moldings (glycerol content 22%, sample production temperature 160 °C).

All samples displayed the highest level of mass decrement after the first two weeks of storage: from about 13% (for samples containing 20% glycerol) to about 23% (for samples containing 25% glycerol). The surfaces of moldings were quickly exposed to decomposition after an encounter with humid soil, more quickly than their internal structures (molding cores).

It was observed that the mass decrement of the tested samples increased with increasing glycerol content in the moldings, whereas greater volumes of fiber content, on the other hand, limited the decomposition of moldings after a two-week storage period in soil. During further observations, it was noted that mass decrement of moldings over subsequent storage periods (4, 8, 12 weeks) was slower and amounted to 2–6% for all moldings (see Figures 12.8 and 12.9).

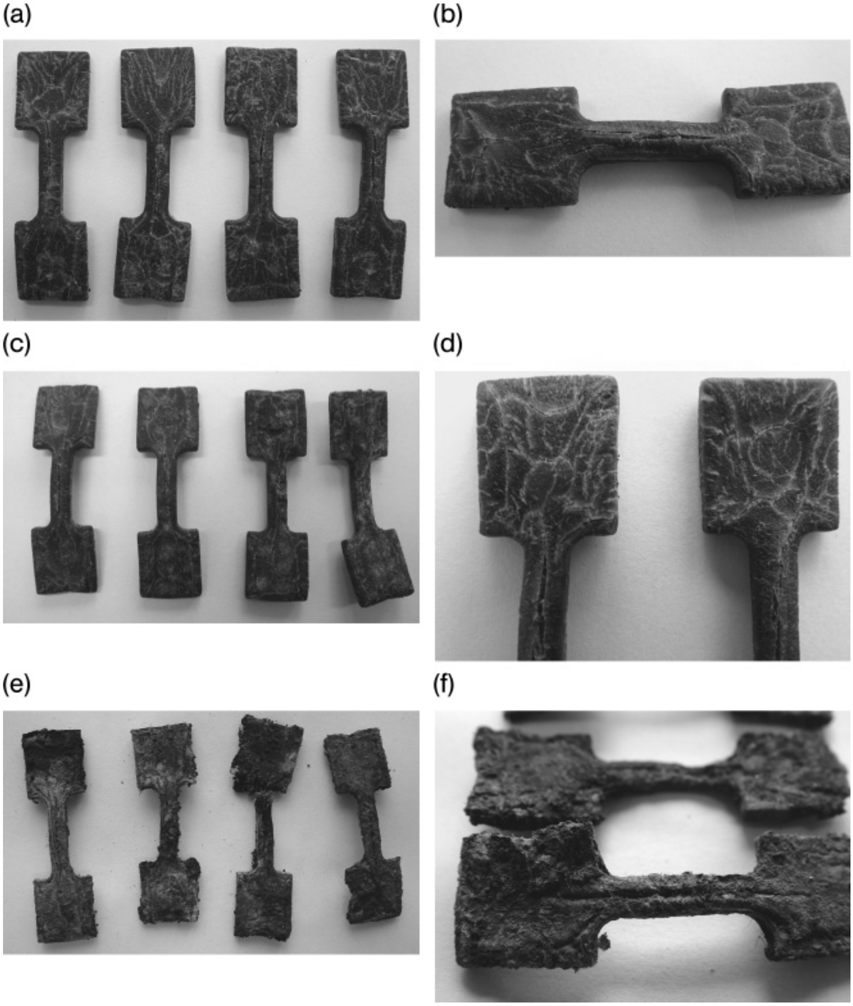

Figure 12.8 Biopolymer moldings containing flax fibers stored for different times: a), b) 2 weeks, c), d) 8 weeks, e), f) 12 weeks.

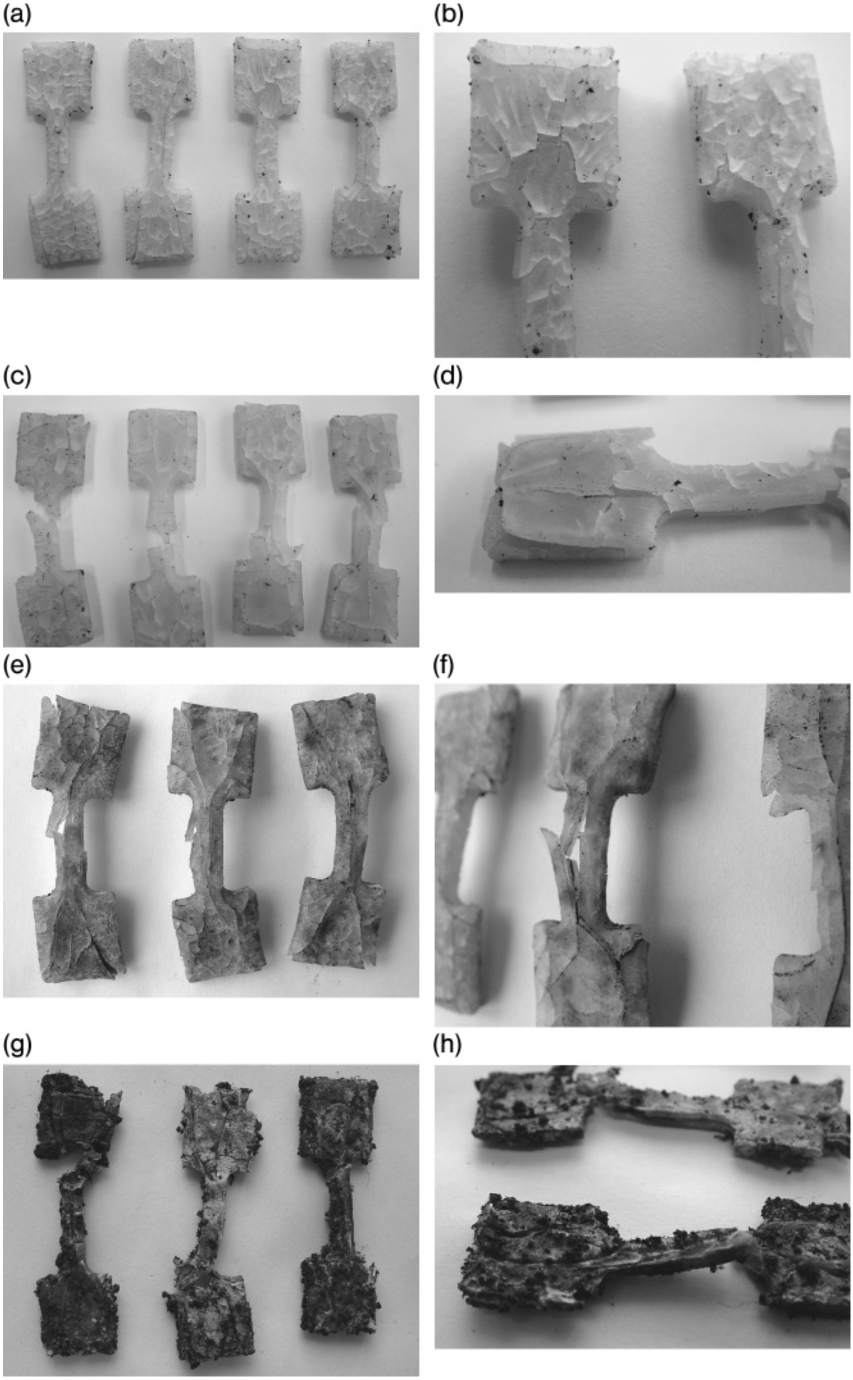

Figure 12.9 Biopolymer moldings containing cellulose fibers stored for different times: a), b) 2 weeks, c), d) 4 weeks, e), f) 8 weeks, g), h) 12 weeks.

Table 12.2 Strengths of moldings subjected to biodegradability testing[4].

Content: starch/glycerol/flax fibers (%)	Max stress (MPa)				Max elongation (%)			
	0 week	2 week	4 week	8 week	0 week	2 week	4 week	8 week
75/20/5	19.1 8	17.54	15.38	8.63	9.69	0.3	0.25	0.11
70/20/10	26.46	19.06	–	–	11.2	0.34	–	–
73/22/5	16.8	22.09	13.03	14.17	2.43	0.72	0.25	0.4
68/22/10	21.45	33.63	27.28	22.16	2.02	0.57	0.5	0.39
65/25/10	18.25	23.91	23.22	21.16	2.45	0.37	0.39	0.36

Strength tests of moldings kept in soil caused problems or were virtually unfeasible. After two-week periods of storage, some changes caused as a result of biodegradation (numerous cracks, lines) were noticeable on the moldings' surfaces.

Moldings produced with no addition of fibers and those produced with cellulose fibers fell to pieces and cracked during strength tests. The only samples suitable for use in testing were those containing flax fibers as additives. In the cases of moldings containing 22% glycerol and 5% and 10% flax fibers and of moldings with 25% glycerol and 10% flax fibers, increases in mechanical strength were observed even after two weeks of storage.

Table 12.1 presents the results for measurements of the maximum stresses and elongations of moldings in break tests after storage in soil for 2, 4, and 8 weeks. The results obtained can be explained in terms of the phenomenon of retrogradation of starch, which involves the recrystallization of amylose and amylopectin into an ordered crystalline network. Retrogradation takes place during the aging of starch, which is associated with the creation of intermolecular bonds in starch and leads to increased crystallinity. During the aging of starch, more extensive crystalline areas are formed; the gel shrinks, hardens, and releases water [8–11] (Table 12.2).

12.3
Concluding Remarks

The storage of different biopolymers at low temperatures differently and significantly influenced their mechanical properties (maximum stress, maximum elongation).

On the basis of the obtained results, it was concluded that biopolymers produced from starch might be successfully used for the manufacturing of packaging for food subject to cool storage. Temperatures (+3 °C, −36 °C) and sample storage times (24 h and 4 weeks) had no great influence on the quality parameters of biopolymers. The best usage parameters over the full range of cool storage temperatures were displayed by moldings containing 10% flax fibers. This biopolymer should find broad application in the packaging industry and, in particular, in the manufacture of disposable trays used in with food subject to low-temperature storage.

Biodegradability of TPS moldings exhibited a visible mass decrement during storage in soil. This decrement in the initial storage period was relatively rapid and then gradually reduced with the time of storage. The development of TPS biodegradability varies depending on the raw material used and on the chemical decomposition of starch that takes place during storage.

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13

Scaling-Up of Thermoplastic Starch Extrusion

Leon P.B.M. Janssen, Leszek Moscicki

13.1

Introduction

Scaling-up rules offer the potential to transfer knowledge obtained on small-scale laboratory equipment to large-scale production units. The principle of scaling-up is that equations describing the behavior of process equipment can be written in dimensionless form. If the resulting dimensionless groups are kept equal in the small-scale and in the large-scale equipment, the solutions of the various equations remain constant in dimensionless form.

Scaling-up of thermoplastic starch extrusion suffers from the same general problems that are encountered in many other processes in the process industry:

- on scaling up, the surface-to-volume ratio decreases and therefore the possibilities for heat transfer are limited in large-scale equipment,
- at equal temperature, differences in the temperature gradients, and therefore the heat fluxes, are smaller in large-scale equipment, and
- at equal shear fields in large-scale and small-scale equipment, diffusion limitations associated with distributive mixing can be more predominant in large extruders.

There are various theories on the scaling-up of single screw extruders. Because of the high viscosities involved, a considerable proportion of the process energy is transformed into heat by viscous dissipation. The thermal considerations will therefore dominate the scaling-up rules, and an important aspect is the extent to which the process is adiabatic or not. If the process can be considered to occur adiabatically, a sufficient condition for scaling-up will be that the energy input per unit throughput is constant and the average temperature of the end product will be the same in the small-scale and in the large-scale equipment. If this is not the case, similar temperature profiles in both types of equipment – called complete thermal similarity – are required.

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The degree to which a process is adiabatic can be estimated from the Brinkmann number (Br), which can be rewritten for extruders as:

$$Br = \frac{\mu v^2}{\lambda \Delta T} = \frac{\mu(\pi N D)^2}{\lambda \Delta T} \tag{13.1}$$

where λ is the thermal conductivity of the starch mass ($\mathrm{W\,m^{-2}\,K^{-1}}$) and ΔT is the temperature difference between the mass and the barrel wall. If this Brinkmann number is much larger than unity, adiabatic scaling-up is acceptable.

A particular dependency is the quadratic occurrence of the diameter. This implies that the Brinkmann number is generally large for production machines. It is generally not possible to keep the Brinkmann number constant for large-scale and small-scale machines. To obtain reliable predictions on a small-scale machine the Brinkmann number for this machine should at least be much larger than unity, which set its limitations to the minimum screw diameter of the small scale machine. If this number is smaller than unity for laboratory machines, reliable scaling-up is not possible.

In order to obtain complete thermal similarity, the screw rotation rate has to be decreased drastically, relative to the adiabatic case, with increasing screw diameter. As a result, the scale factor for the throughput is only 1.5 for Newtonian fluids (and decreases even further for fluids with pseudo-plastic behavior). This scaling-up factor (q) for the throughput is defined from:

$$\left[\frac{Q}{Q_0}\right] = \left[\frac{D}{D_0}\right]^q \tag{13.2}$$

where Q denotes the throughput, D the screw diameter, and the subscript 0 indicates the small extruder. In the case of adiabatic scaling-up a scaling-up factor of up to 3 can be achieved. For standard industrial extruder series it may be stated to a first approximation that:

$$\left[\frac{Q}{Q_0}\right] = \left[\frac{D}{D_0}\right]^{2.8}$$

When an extruder is scaled it is important to keep the process in the large machine as similar as possible to that in the small machine. Complete similarity is often not possible or it is impractical, so choices in similarity have to be made. Several types of similarities can play a role in the scaling-up of an extruder:

- ***Geometric similarity*** exists if the ratio between any two length parameters in the large-scale equipment is the same as the ratio between the corresponding lengths in the small-scale model. This is not necessarily the case, as will be seen later, but in general this condition can be very convenient.
- ***For hydrodynamic similarity*** two requirements should be fulfilled: the dimensionless flow profiles should be equal and, for twin-screw extruders, both

extruders should have the same (dimensionless) filled length. Equal dimensionless flow profiles lead to equal shear rates in corresponding locations, but not to equal velocities.

- ***Similarity in residence times*** means equal residence times in the small-scale and the large-scale equipment. This is not a requirement that is often fulfilled in extrusion processes, and in thermoplastic starch extrusion this can only be achieved if the scaling-up is adiabatic.
- ***Absolute thermal similarity*** is difficult to achieve, as stated before. This similarity indicates equal temperatures in all corresponding locations. A distinction has to be made between processes with small heat effects and those with large heat effects. For adiabatic processes in which the heat generation is far more important than heat removal to the wall, similarity based on overall energy balances is generally used. Although, strictly speaking, this does not lead to thermal similarity, equal average end temperatures of the product lead to far more favorable scaling-up rules.

13.2
Basic Analysis

To derive rules for scaling-up, all parameters are assumed to be related to the diameter ratio by a power relation. For this purpose, in this chapter all basic parameters are written in capitals, whereas the scaling-up factors are written in small print. This implies that all relevant parameters can be related to the screw diameter according to:

$$\left[\frac{N}{N_0}\right]=\left[\frac{D}{D_0}\right]^n;\left[\frac{P}{P_0}\right]=\left[\frac{D}{D_0}\right]^p;\left[\frac{\mu}{\mu_0}\right]=\left[\frac{D}{D_0}\right]^\upsilon;$$
$$\left[\frac{H}{H_0}\right]=\left[\frac{D}{D_0}\right]^h;\ \left[\frac{L}{L_0}\right]=\left[\frac{D}{D_0}\right]^l;\left[\frac{\tau}{\tau_0}\right]=\left[\frac{D}{D_0}\right]^t;\left[\frac{R}{R_0}\right]=\left[\frac{D}{D_0}\right]^r \tag{13.3}$$

where N is the rotation rate of the screws, P is the die pressure, and μ is the viscosity. The back flow (Q_b) is an important parameter in scaling up. For closely intermeshing twin-screw extruders it signifies the total amount of leakage flows, whereas for single-screw, self-wiping, and non-intermeshing extruders it signifies the pressure flow. H denotes the cannel depth, L the screw length, τ the residence time in the extruder, and R the pumping efficiency

For thermal scaling-up rules, two more parameters have to be used: the Greaz number (Gz), defined later, and the Brinkmann number (Br). The scaling-up notation for these dimensionless groups reads:

$$\left[\frac{Gz}{Gz_0}\right]=\left[\frac{D}{D_0}\right]^{gz}\ and\left[\frac{Br}{Br_0}\right]=\left[\frac{D}{D_0}\right]^{br} \tag{13.4}$$

13.3
Summary of Equations Used

Scaling-up rules are necessarily rather mathematical in nature. In this paragraph the extruder equations used are summarized.

The throughput of a single screw extruder can be written as:

$$Q = \frac{1}{2}\pi^2 N D^2 H(1-a)\sin\theta\cos\theta \tag{13.5}$$

θ is the flight angle and a is the throttle coefficient:

$$a = \frac{H^2 \Delta P \tan\theta}{6\mu(\pi N D)L} \tag{13.6}$$

The equation for the motor power in the pump zone can be written as:

$$E = \frac{(\pi N D)^2 WL}{H\sin\theta}(\cos^2\theta + 4\sin^2\theta + 3a\cos^2\theta) \tag{13.7}$$

where W is a channel width.

For use in scaling rules this equation can be simplified for screws with the same flight angle to:

$$E = const * \frac{\mu D^3 N^2 L}{H} \tag{13.8}$$

The pumping efficiency of the extruder is the ratio of energy used for pumping the material and the total energy input into the extruder.

$$R = \frac{QP}{E} \tag{13.9}$$

Thermal similarity yields from the energy balances:

$$\rho C_p\left(\frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y} + v_z\frac{\partial T}{\partial z}\right) = \lambda\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + q \tag{13.10}$$

In this equation q is the heat produced by viscous dissipation:

$$\begin{aligned} q = 2\mu&\left\{\left(\frac{\partial v_x}{\partial x}\right)^2 + \left(\frac{\partial v_y}{\partial y}\right)^2 + \left(\frac{\partial v_z}{\partial z}\right)^2\right\} + \\ &\mu\left\{\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right)^2 + \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right)^2 + \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right)^2\right\} \end{aligned} \tag{13.11}$$

If the equations above are made dimensionless there remain two important dimensionless numbers that govern the heat balances in the extruder: the Graez number and the Brinkmann number.

$$Gz = \frac{UH^2}{aL} \quad \text{and} \quad Br = \frac{\mu U^2}{\lambda \Delta T} \tag{13.12}$$

where λ is the thermal conductivity, T is the temperature, and $U = \pi ND$.

The Graez number accounts for the development of the temperature profile, whereas the Brinkmann number signifies the ratio between viscous dissipation and heat conduction to the wall.

13.4
Kinematic Similarity

Kinematic similarity means equal shear levels in the small and the large extruder. Its importance is coupled to the requirements for:

- equal mixing in small and large machines,
- equal distribution of viscous dissipation, and
- equal influence of non-Newtonian rheological effects.

For the throughput of the small laboratory extruder we can write:

$$Q_0 = \frac{1}{2}\pi^2 N_0 D_0^2 H_0 (1 - a_0) \sin\theta_0 \cos\theta_0 \tag{13.13}$$

and for the throughput of the production machine:

$$Q = \frac{1}{2}\pi^2 N D^2 H (1 - a) \sin\theta \cos\theta \tag{13.14}$$

If the screws of small and large machine have the same screw angle, which is the same as the same dimensionless pitch, we may write:

$$\frac{Q}{Q_0} = \frac{ND^2H}{N_0 D_0^2 H_0} \frac{(1-a)}{(1-a_0)} \tag{13.15}$$

and if we process both machines with the same throttle coefficient:

$$\frac{Q}{Q_0} = \frac{N}{N_0}\left(\frac{D}{D_0}\right)^2 \frac{H}{H_0} \tag{13.16}$$

Introduction of the diameter ratios as defined before:

$$\left(\frac{D}{D_0}\right)^q = \left(\frac{D}{D_0}\right)^n \left(\frac{D}{D_0}\right)^2 \left(\frac{D}{D_0}\right)^h = \left(\frac{D}{D_0}\right)^{n+2+h} \tag{13.17}$$

gives the exponent equation:

$$q = n + 2 + h \tag{13.18}$$

Because both machines operate with the same throttle coefficient:

$$a = a_0 \rightarrow \frac{H^2 \Delta P}{6\mu(\pi N D) L} \tan\theta = \frac{H_0^2 \Delta P_0}{6\mu_0(\pi N_0 D_0) L_0} \tan\theta_0 \tag{13.19}$$

and equal throttle coefficients lead to:

$$2h + p - \upsilon - 1 - n - l = 0 \tag{13.20}$$

For equal velocity gradients an extra equation is necessary:

$$\frac{\pi N D}{H} = \text{constant}$$

and therefore:

$$h = n + 1 \tag{13.21}$$

For kinematic similarity both (13.19) and (13.20) must be valid:

$$p = \ell - h + \upsilon \tag{13.22}$$

These results have to be combined with geometrical considerations of thermal scaling rules.

13.5
Geometrical Similarity

Geometrical similarity is often used for its simplicity, but it is not a strong requirement. Especially in processing thermoplastic starches, in which temperature and temperature homogeneity are very important, the principle of geometric similarity of small- and large-scale equipment cannot always be retained. Geometric similarity means that all dimensions scale in the same way, or:

$$l = 1 \text{ and } h = 1 \tag{13.23}$$

Geometric and kinematic similarity follows from a combination of this equation with Equations 13.1, 13.3 and 13.4, resulting in

$$n = 0;\, q = 3 \text{ and } p = \upsilon \tag{13.24}$$

This means for our process that:

- rotation speed must remain the same,
- throughput is proportional to D^3, and
- the die should be designed such that the pressure ratio equals the ratio between the end viscosities.

13.6
Motor Power and Torque

The motor power in the extruder can be approximated to:

$$E = const * \frac{\mu D^3 N^2 L}{H} \tag{13.25}$$

It should be realized that this equation does not include the power needed to transport the solid bed; however, this last item is not important for the thermal considerations in the next paragraphs.

The scale factor of the motor power can be defined as:

$$\frac{E}{E_0} = \left(\frac{D}{D_0}\right)^e \tag{13.26}$$

and we find:

$$e = 3 + 2n + \ell + \upsilon - h \tag{13.27}$$

and for the torque:

$$m = 3 + n + \ell + \upsilon - h \tag{13.28}$$

13.7
Equal Average End Temperature

Two types of thermal similarities can be used: equal average end temperatures and similar temperature profiles. The concept of equal average end temperatures can be applied if the extruder operates adiabatically or if $Br >> 1$. In this case scaling-up has to proceed according to equal motor power per unit throughput:

$$\frac{E}{Q} = const \quad or \quad e - q = 0 \tag{13.29}$$

With Equations 13.1 and 13.5 this leads for equal viscosities ($\psi = 0$) to

$$2h = 1 + n + l \tag{13.30}$$

In this case various degrees of freedom are still retained.

13.8
Similar Temperature Profiles

From the dimensionless energy equation it follows that thermal similarity can be attained if the dimensionless numbers of Graez and Brinkmann are the same for both sizes of machines.

Because:

$$Br = \frac{\mu(\pi ND)^2}{\lambda \Delta T} \tag{13.31}$$

we find for materials with the same heat conductivity (λ) that thermal similarity is attained if:

$$\upsilon + 2n + 2 = 0 \tag{13.32}$$

For materials with the same viscosity, this means: $n = -1$.

From:

$$Gz = \frac{\pi NDH^2}{aL} \tag{13.33}$$

it follows at equal heat diffusivity that:

$$1 + n + 2h - \ell = 0 \tag{13.34}$$

leading to thermal similarity (equal Br and Gz numbers) if:

$$2h = l \tag{13.35}$$

For extruders with equal length-to-diameter ratios ($\ell = 1$) this means that the channel depth must decrease according to $h = ½$, which together with Equation 13.18 gives:

$$q = 2 + n + h = 1.5 \tag{13.36}$$

or:

$$\frac{Q}{Q_0} = \left[\frac{D}{D_0}\right]^{1.5} \tag{13.37}$$

From the economical point of view this is very unfavorable, and should only be applied in very special situations.

13.9
Similarity in Residence Times

Equal residence time can be achieved if the volume divided by the throughput remains constant, or, if we define Z as the average residence time:

$$Z = const\frac{HLW}{Q} \tag{13.38}$$

which for screws with equal helix angle gives:

$$z = h + 1 + l - q \tag{13.39}$$

or with:

$$q = 2 + n + h \tag{13.40}$$

we find that:

$$z = l - n - 1 \tag{13.41}$$

For screws with geometric similarity – this means that ($l = -1$, $h = 1$ and $z = -n$) – equal residence times are only possible if the rotation speed is constant. In other cases equal residence times can only be obtained by changing the screw length, according to:

$$l = 1 + n \tag{13.42}$$

13.10
Guidelines for Scaling

In extrusion of thermoplastic starches, both heat of conduction and heat of dissipation are generally important in the process. In small machines the Brinkmann number is relatively small, but in larger machines the dissipation becomes more dominant and the process becomes more adiabatic. Because the thermal problems

Table 13.1 Application of Equation 13.30, giving a variety of possibilities for scaling rules.

n	*h*	*q*
–1.0	0.5	1.5
–0.6	0.7	2.1
–0.4	0.8	2.4
0.0	1.0	3.0

are predominant, the basis for the guide lines is Equation 13.30, which can be combined with various other (less strict) requirements. Application of Equation 13.30 gives a variety of possibilities for scaling rules, which give for screws with equal length to diameter ratio, for instance (Table 13.1):

Equal end temperatures with adiabatic operation still leave the degrees of freedom to scale according to similar temperature profiles (of course!) with $q = 1.5$ or to scale kinematically with $q = 3$ and with values in between. For the design of extruders for thermoplastic starches this means that the thermal stability of the material and of the process are important. For the compounding process for the preparation of the starch it can be envisioned that kinematic scaling-up should be preferred because temperature effects are still mildly important but kinematic similarity is important to achieve the same mixing mechanism (and therefore the same material) in the small- and the large-scale processes. For processes such as film blowing, on the other hand, thermal similarity is extremely important, leading to thermal scaling-up. Profile extrusion and sheet extrusion are "in-between" processes and could be designed with $n = -0.4$ and $h = 0.8$, leading to $q = 2.4$.

In the examples above the L/D ratio remains constant but the screw length can also be changed to retain extra degrees of freedom. This leads to a three-dimensional matrix of parameters, but that is outside the scope of this work.

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Summary

Synthetic polymers, also often called plastics, are the base materials for many new and beneficial products that meet our current and future needs. Many of the physical and chemical properties of plastics make them ideal materials for a wide variety of products and applications. However, because of their excellent mechanical properties, their increased use, mainly as packaging materials, leads to substantial environmental pollution. Although they are useful and desirable for many purposes, the indestructibility of petroleum-based plastics is a growing concern because of their accumulation in the environment. Polymer recycling has unfortunately not been successful, and it is estimated that only a few percent of the produced plastics are recycled worldwide. This is because recycling is expensive and the commingled waste is difficult to sort according to origin, color, and contained additives.

The plastics that are most widely used have poor biodegradability and may have lifetimes of hundreds of years when buried in typical solid-waste sites. Various approaches to render synthetic polymers degradable have been considered. In order to replace common synthetic thermoplastics by polymers of natural origin in commodity application, the biopolymers must be processable in existing, standard equipment and must have mechanical properties and stability comparable with those of the non-degradable thermoplastics. In addition to this, the biodegradability of the products may open avenues for increased use of farm commodities and other renewable resources. These materials could be used as substitutes for products made from non-renewable synthetic polymers. Degradable biopolymers can provide us with an increased flexibility in the design of materials, not only to suit desired product properties, but also to minimize any detrimental impact on the environment when the intended use of the product has ended.

In the last decades there has been significant interest in developing materials from blends of natural and synthetic polymers. These blends can be processed into useful disposable end-products that could alleviate the disposal problem by degrading in selective environments. Partially biodegradable polymers, obtained by blending biodegradable and non-biodegradable commercial polymers, can effectively reduce the volume of plastic waste by partial degradation. In many applications they can be more useful than completely biodegradable ones, due to the economic advantages and superior properties imparted by the commercial

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polymer used as a blending component. In order to obtain a cost-effective partly biodegradable plastic, starch-filled polyethylene (PE) is still the best alternative. Starch and PE blends are incompatible at a molecular level, however, and the resulting segregation often leads to poor performance. In order to overcome this drawback, either PE or starch should be modified. Nevertheless, the resulting products are not easily (read: fully) biodegradable.

In recent years great efforts have been made to produce suitable alternatives to replace non-degradable plastics with biodegradable polymers. Research into the development of biodegradable polymers derived from renewable resources gained considerable momentum in the 1990s, although the use of starch to produce biodegradable plastics began in the 1970s. In the temperature range from 90 °C to 180 °C, in the presence of plasticizers such as polyols or acrylamide, and under pressure and shear, starch can easily be molten. This allows starch to be processed by injection-molding, extrusion, and blow-molding, similarly to most synthetic thermoplastic polymers. Different extrusion processing conditions alter the transformation of the starch during the preparation of the thermoplastic starch resin, which ultimately affects the mechanical properties of the finished product.

Starch has been viewed as an important candidate in certain thermoplastic applications because of its known biodegradability, availability, and low cost. Agricultural crops provide different sources of biopolymers (starch, protein, and cellulose) which can readily be used to make biodegradable plastics. When biodegradability is required, thermoplastic starch (TPS) can be an alternative material for replacement of many petroleum-based products and it has gained much attention. Development of practical thermoplastic starch resins includes the addition of processing aids and plasticizers to aid gelatinization during processing, thus producing suitable mechanical properties in the finished product.

There are two approaches to overcome starch's drawbacks. One method is to blend starch with other biodegradable polymers. Another method to modify the properties of starch is the preparation of starch derivatives by replacing the hydrophilic –OH groups by hydrophobic groups, by esterification and etherification, for example. However, the prices of these modified starches are higher than those of other polymers. One of the simplest methods to reduce product hygroscopicity is the application of a coating with a paraffin-like material by spraying or other coating techniques.

With regard to the production of biodegradable thermoplastic material in an extruder, the base material consists of a natural polymer, a plasticizer, and an inorganic or organic compound such as a filler or fiber. The presence of fillers keeps the plasticizer in the material, and so the mechanical properties of the composite TPS are more stable than those in other biodegradable thermoplastic materials. Studies with biodegradable starch-based polymers have recently demonstrated that these materials have a range of properties, which make them suitable not only for agricultural films and coatings but also for use in several biomedical applications. These may range from bone plates and screws to drug delivery carriers and tissue engineering scaffolds. TPS is useful to make commercial articles either by injection-molding or film-blowing. TPS can be used in the form of biodegradable foams widely employed as cushioning materials for the protection of fragile products during transportation and handling. TPS films display low oxygen permeability and so also become attractive materials for food packaging.

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