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Biodegradable starch-based polymeric materials

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Abstract. The effects of low-molecular-weight additives, temperature and mechanical action on the structure and properties of starch are discussed. Special attention is given to mixtures of starch with synthetic polymers, *e.g.*, co-polymers of ethylene with vinyl acetate, vinyl alcohol, acrylic acid, cellulose derivatives and other natural polymers. These mixtures can be used in the development of novel environmentally safe materials (films, coatings, packaging materials) and various articles for short-term use. The bibliography includes 105 references.

I. Introduction

Modern-day technology calls for the development of polymeric materials the properties of which do not change even after long-term use. The effects of environmental factors (*e.g.*, water, atmospheric oxygen, sunlight and biological agents, such as microbes, fungi, insects, *etc.*) reduce the service life of many articles prepared from polymeric materials. All this raises the problem of creation and application of special-purpose stabilisers and bioprotectors.[1] However, the immense bulk of polymeric materials and articles made thereof puts forward a problem of their further destruction or disposal after the termination of their service life. Many polymers are decomposed in the environment over a relatively long period of time; therefore, the production of biodegradable materials is as important as their stabilisation. Polymers, particularly household plastics and films, must be rapidly decomposed after use under the influence of chemical (atmospheric oxygen, water), physical (sunlight, heat) and biological (bacteria, fungi, yeasts, insects, *etc.*) environmental factors.[2,3] These factors produce a synergistic effect, eventually resulting in the fragmentation of the polymer owing to the destruction of its macromolecules and their conversion into low-molecular-weight compounds that can be further involved in the natural circulation of substances. In the strict sense, the term 'biodegradation of a polymer' implies deterioration of its physical and chemical properties and a decrease of its molecular mass down to the formation of CO_2, H_2O, CH_4 and other low-molecular-weight products under the influence of microorganisms in both aerobic and anaerobic conditions.[4,5]

Microorganisms or enzymes produced by them cause the decomposition of natural polymers (*e.g.*, cellulose, starch, chitin, polypeptides, *etc.*) into low-molecular-weight compounds which are further involved in the metabolism of the elemental forms of life.[6] Enzymes play the role of catalysts favouring the degradation of the main polymeric chain. Specific enzymes evolved in the course of evolution can selectively destroy natural high-molecular-weight compounds, such as cellulose, proteins and other natural polymers. For example, amylase induces the degradation of the starch molecule. Enzymes causing the destruction of synthetic polymers, *e.g.*, polyalkenes or polyvinyl polymers, are absent in Nature. However, these classes of polymers are especially extensively used in the production of packaging materials and articles for short-term use. These wastes constitute the greater part of municipal garbage in all industrially developed countries.[2,7–9] The interest in materials based on natural polymers (*e.g.*, starch, chitin) has increased considerably in the recent years, because owing to their structural features these compounds can be involved in natural circulation and thus be environmentally safe.

The problem of development of biodegradable polymeric materials has been considered in detail in reviews.[10–13] It was shown that the use of natural renewable polymers is the most promising and economically advantageous approach. The synthesis of novel biodegradable polymers and chemical modification of natural polymers were described by Vasnev.[14] The methods for estimating the biodegradability of polymeric materials based mainly on the analysis of products of the activity of bacteria which decompose polymers have been developed and standardised in many countries.[4,15–17]

Here we survey the most recent data concerning the properties of materials prepared from starch or its mixtures with synthetic polymers.

II. The structure of starch

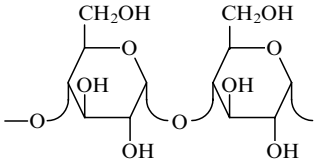
Starch is a natural polysaccharide which is accumulated in plant tubers, seeds, stalks and leaves in the course of their vital activity. The main sources for the commercial production of starch are potatoes, wheat, corn and rice. Starch comprises two polymeric components, *viz.*, amylose and amylopectin, they are built of α-D-glucopyranose residues but differ in both structure and function. The amylose content in native starch usually varies from 20 mass % to 30 mass %, while amylopectin constitutes the greater part (70%) of the starch molecule. At the same time, the

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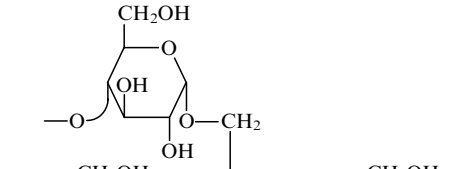
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amylose content in high-amylose starch can reach 50 mass % to 70 mass %.[18]

Amylose (**1**) is a linear polymer, which consists of α-(1,4)-D-glucopyranoside residues with the average molecular mass of $\sim 10^2$ to 10^3 kg mol^{-1}. In cellular starch, the helical chains of amylose form complexes with lipids. Amylopectin (**2**) contains α-(1,4)- and α-(1,6)-linked glucose residues. Extended linear chains involve α-(1,4)-bonds and a great number of shorter branchings are linked through α-(1.6)-bonds.



1



2

The molecular mass of amylopectin is approximately 10^5 kg mol^{-1}. The branchings in the starch molecule may contain, on the average, up to twenty glucose residues. Amylopectin molecules also form helices; it is noteworthy that shorter side chains form double helices.[19, 20]

The spatial structure of amylopectin has not been clearly understood yet. A number of models have been proposed[21] in order to establish a correlation between the character of branchings in the chains of amylopectin and its ability to form regular crystalline regions. The Robin–Mercier scheme[22] (Fig. 1) provides an example of such models. This model takes account of the presence of amorphous regions in the amylopectin molecule formed by chain branchings and of crystalline regions consisting of linear, parallelly stacked fragments.

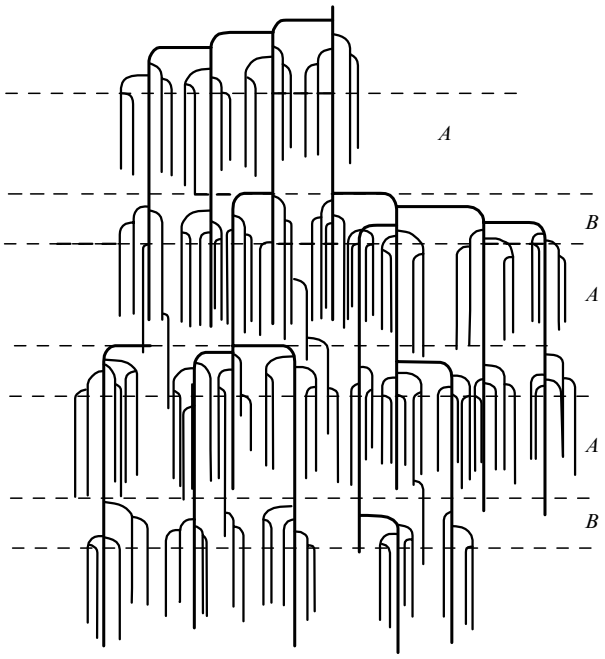


Figure 1. A structural model of amylopectin; *A* are crystalline regions, *B* are amorphous regions.[22]

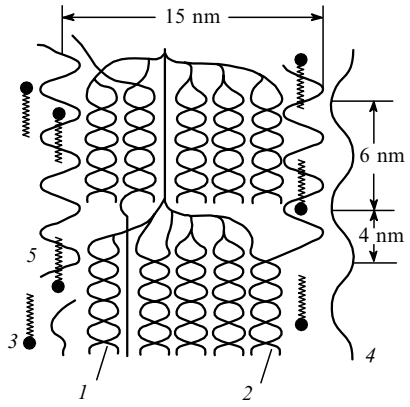


Figure 2. The structure of native starch;[20] (*1*) helices of amylopectin, (*2*) hybrid helices of amylose and amylopectin, (*3*) free lipids, (*4*) free amylose, (*5*) V-structures of amylose.

The degree of crystallinity of natural starch depends on its origin and varies from 15% to 45%. The structure of starch formed by regular stacking of the double chains of amylose and amylopectin and incorporating lipid molecules which form complexes with them is schematically represented in Fig. 2. Using wide-angle X-ray scattering,[19, 23] it was shown that the crystalline structures of starch isolated from different parts of plants differ considerably. This polysaccharide was found to exist in three polymorphous modifications. Starch from gramineous seeds has the so-called A-structure, tuber starch has the B-structure, while starch extracted from roots and stalks of plants has the C-structure. The crystalline structures of the A- and B-types are associated with the amylose fragment and consist of parallel coiled right double helices with anti-parallel packing. Each turn of the helix comprises six α-D-glucose residues. The conformations of the double helices of amylose in A- and B-structures are identical, but the A-structure is represented by a unit cell of the orthorhombic type (a = 1.190 nm, b = 1.770 nm, c = 1.052 nm), whereas the B-structure is represented by a hexagonal unit cell ($a = b$ = 1.85 nm, c = 1.04 nm). Besides, in natural starch amylose complexes with lipids form structures of the V-type. The content of crystalline structures of the A- and B-type in starch samples of different origin was found to be 56% and 44%, respectively.[24] The presence of these structures was confirmed by IR spectroscopy.[25]

Starch contains a large proportion of amorphous regions. However, the glass-transition temperature (T_g) of dry starch cannot be measured because it lies above the temperature at which the decomposition of the polymer occurs; its calculation is based on the estimation of the plasticising effect of water which penetrates into the amorphous regions of the starch molecule and decreases T_g. The concentration dependence of T_g of the starch–water system can be described by the equation[26]

$$T_c = 244.9 - 1565\,\omega + 2640\,\omega^2,$$

where ω is the content of water (w/w) in swollen starch. Extrapolation of these data for T_g of the starch samples plasticised with water to various degrees gave T_g values ranging from 230 to 250 °C.[20, 26]

Starch is present in plants in the form of granules having the diameter from 2 to 100 μm.[27] The structure of these supramolecular granules is complex and has not yet been finally elucidated. It is known that starch granules comprise both crystalline and amorphous regions. The amorphous regions form a continuous phase and incorporate crystals of a lamellar type.[27] Microscopic analysis of the supramolecular structure of starch granules[28]

revealed that the lamellae predominantly consist of amylopectin. Their sizes depend on the origin of starch and their localisation in the granules and vary from 20 to 500 nm.

Starches isolated from different natural sources differ in their sensitivities to destructive factors, such as temperature and enzymic hydrolysis. Thermolysis of starch granules isolated from potatoes, wheat, barley, rice, corn and tapioca was studied at fixed temperatures (170–325 °C).[29] It was found that corn starch exhibits the highest resistance to heating, whereas barley starch is the least thermostable. This may be due to the differences in the molecular masses and ratios of linear and branched components of starches having different biological origin.

III. Effects of water and plasticisers on the properties of starch

Starch is a typical hydrophilic polymer; it may contain up to 30 mass % – 40 mass % of bound water. It is known [23] that different structures of starches of the A- and B-types bind differently to water. In structures of the B-type, water is mobile and can easily enter and leave the complex (Fig. 3). In crystallites of the A-type, water of hydration forms a layered structure and is firmly bound to the surrounding double helices of amylose. Therefore, A-structures are less sensitive to the atmospheric moisture than B-structures.

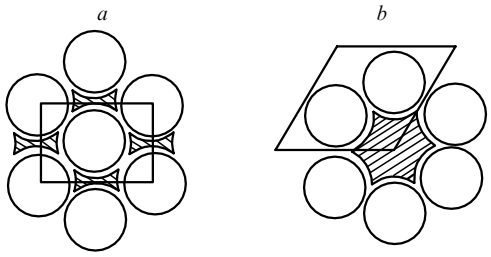


Figure 3. The schematic representations of the crystalline structures of amylose with water. (*a*) A-amylose complex, (*b*) B-amylose complex. The hatched areas designate absorbed water.

Studies of the effect of water on starch provide additional information about the structure of this polymer. Dissolution of starch in water is a complex process, which strongly depends on temperature. Swelling of starch in saturated water vapour at room temperature results in the formation of a gel which retains the predominant polymer-to-polymer contacts.[30] This process does not result in complete dissolution of starch as is evidenced by the shape of the isotherm of water vapour sorption [31] characteristic of systems with limited swelling of a polymer. However, the mobility of starch molecules increases with an increase in the amount of absorbed water as a result of which the linear component of the polymer, *viz*., amylose, forms a true solution with water. This is accompanied by the formation of a two-phase swollen gel–solution system.

A high-energy interaction with water of several samples of amylose starch having a crystalline structure of the B-type and the chain length of 12–55 residues was established by scanning calorimetry and sorption.[32] However, at room temperature the energy of the interaction of the components is too low to compensate for the oppositely directed entropic contribution. Therefore, complete destruction of the polymer-to-polymer contacts and solubilisation of starch do not occur. Water is a poor solvent for amylose starch at room temperature.

The solubility of starch increases with temperature. The swelling of dispersions (2.6 mass %) of corn and pea starches in water was studied by laser diffractometry.[33] It was found that heating above gelatinisation temperatures significantly changes both the sizes of starch granules and their distribution according to size. The maximum increase in the diameter of starch granules is ~ 3.5-fold.[33] The behaviour of the starch–water system at a wide range of temperatures was studied by differential scanning calorimetry (DSC), dilatometry, rheology and polarisation microscopy using rice,[34] potato [26,35] and wheat [35] starches as examples. The sizes of starch granules first increase slightly in excess of water at 35 to 55 °C and then increase sharply (by 55%) at 65 °C, reaching the maximum at 75 °C. At temperatures above 75 °C, starch granules are destroyed and crystallinity disappears. The viscosity of the system kept at the temperatures indicated above increases until the gelatinisation step is reached. At higher temperatures, amylose is separated from amylopectin due to partial destruction of the physical lattice nodes after which starch dissolution begins. Cooling of aqueous solutions of starch again results in the formation of gels which contain swollen granules consisting predominantly of amylopectin; the amylose component of starch is predominantly localised in the intergranular space.

The dissolution of rice starch was studied by DSC and was interpreted [34] as a phase transition, since the thermograms displayed a peak of heat absorption at 75 °C corresponding to the gel transition. Using DSC, it was shown that the increase in the water content in wheat starch from 2.8 mass % to 90 mass % and subsequent heating induced several structural transitions due to melting of amylopectin crystallites and its complexes with lipids as well as due to melting of amylose in the swollen samples.[36]

The content of amylose and amylopectin, their molecular masses and the content of lipids depend on the origin of starch. These factors affect the interaction of starch with water. The gel-forming abilities of starches isolated from the grains of hard and soft corn,[37] hard wheat and potatoes grown in different geographical zones, from rice [34] and green herbs [38] have been studied. It was shown that starches isolated from gramineous plant seeds contain less amylose than potato starch and have lower values of the temperature and enthalpy of gelatinisation. In contrast, starches isolated from green herbs, which contain more amylose (up to 30 mass %) of high molecular mass (up to 4.5×10^3 kg mol^{-1}) and highly branched amylopectin, have higher values of these parameters.

Studies on the structure and gelatinisation of amylopectin samples ($M_w = 0.2 \times 10^3 - 1 \times 10^3$ kg mol^{-1}) specially prepared from yellow corn revealed [21] that the gels kept at constant temperature (4 °C) are typical representatives of thermoreversible gels formed by physical lattice nodes. The crystallinity of such gels increases upon storage as can be evidenced from wide-angle X-ray scattering data [21] and the increase in the area of the endothermal peak on the DSC curves [21,39] resulting from the increase in the enthalpies of melting of starch crystallites. Apparently, water which plays the role of a plasticiser by increasing the mobility of starch granules increases the crystallinity as in the case of the synthetic polymers.[40] It was also shown [21] that the structural perfection of amylopectin crystallites depends on the conditions of gel crystallisation.

The interaction of starch samples differing in the amylose content with water was studied by Shogren and Jasberg.[18] The behaviour of corn starch containing 28 mass % of amylose in the swelling and subsequent gelatinisation differs considerably from the behaviour of starch with the amylose content of 50 mass % to 70 mass % at equal molecular masses of the polymers. These differences affect starch concentrations at which gelatinisation begins, enthalpies of gelatinisation and the syneresis rates of the gels.

The effect of the molecular mass of the amylose starch on its solubility was studied by Moates *et al*.[32] With a change in the molecular masses from 2 to 10 kg mol^{-1} in systems with the same degree of swelling (0.8), the dissolution temperature of starch increases from 57 to 119 °C. Extrapolation to infinitely high molecular mass gives a dissolution temperature of 147 °C.

It was found [41,42] that homogenisation of wheat or potato starch in water is facilitated by mechanical action on the system, *e.g*., by extrusional stirring of the components. It was shown [42]

that the threshold of a twin-screw extruder of the mixer driver is 120 – 150 kW h^{-1} below which the system cannot pass into the fluid state. This limiting value depends on the viscosity of the mixture, which is proportional to the molecular masses of amylose and amylopectin.

Plasticisation of starch with water and its simultaneous exposure at elevated temperature and under mechanical stress makes it possible to change considerably the physical and mechanical properties of the starch – water system. The reason for these changes is in irreversible destruction of starch granules, mechanical stress being the crucial factor in this process. Reprocessing of plasticised starch on standard technological equipment for moulding of plastic materials (*e.g.*, extruders, casting machines, *etc.*) permits one to obtain materials possessing different physical properties.

Glycerol and oligomeric polyglycols can also exert a plasticising effect on starch. These plasticisers are generally used in combination with water. The thermoplastic properties of materials obtained by extrusion of mixtures of potato starch with glycerol and water were studied by van Soest *et al*.[43] Two specimens were studied based on the native starch, *viz*., that with M_w = 37 000 kg mol^{-1} and that with M_w = 1900 kg mol^{-1} prepared by partial acid hydrolysis. The specimens containing less than 9 mass % of water were glass-like and had elasticity moduli from 400 to 1000 MPa. If the water content in these materials was from 9 mass % to 15 mass %, they acquired elastic properties but became soft and fragile with an increase in the water content above 15 mass %. The differences in the thermoplastic properties of these materials are due to the presence of water rather than to the differences in the molecular weights of the starches. Thermomechanical analysis revealed that T_g of the extruded samples decreased appreciably with an increase in the water content (Table 1). It was assumed[43,44] that the properties of starch-based thermoplastic materials are determined by the formation of a complex network consisting of linear chains of amylose and branched molecules of amylopectin in which hydrogen bonds play a crucial role. A lower value of the fracture energy of an elastic material prepared from low-molecular-weight starch can be attributed both to the shorter length of the amylose chain and to smaller molecular mass and branching of the amylopectin molecules.

Table 1. The changes in T_g of extruded samples of potato starch plasticised with water.[43]

Water content (mass %)	T_g /°C	
	material prepared from native starch	material prepared from hydrolysed starch
14	5	–
11	25	–
8	42	–
5	59	58

The effects of glycerol (14 mass % – 39 mass %) and water (1 mass % – 28 mass %) on the phase behaviour of barley starch were studied using DSC and dynamic thermomechanical analysis.[45] Samples with low content of water and glycerol formed homogenous monophasic systems. Strong interaction of starch with glycerol in samples containing less than 20% of water presumably impedes crystallisation of amylopectin as a result of which the system remains amorphous and monophasic. With an increase in the concentration of the plasticising agents, the mixture separates into a starch-enriched and a starch-depleted phases as evidenced from the appearance of mechanical loss peaks corresponding to T_g of the individual phases.

Simultaneous use of water and glycerol as plasticisers makes it possible to obtain flexible starch-based thermoplastic materials by compression moulding[46] and extrusion.[47] The materials prepared from corn, potato and wheat starches were characterised by constant (with respect to starch) content of glycerol (1 : 0.3), contained from 8 mass % to 25 mass % of water and were elastic (T_g < 20 °C). Studies of mechanical properties of such materials established a dependence of the elasticity modulus and breaking stress (σ_p) both on the content of the plasticising agents and on the origin of starch.[46,47] The difference in mechanical properties is presumably due to the higher content of amylopectin in corn starch, which is plasticised with water more readily than potato starch enriched with high-molecular-weight amylose.[47]

The mechanical properties of plasticised starch depend on the storage time prior to testing.[48,49] Storage of thermoplastic materials prepared from corn[48] and potato[49] starch at high relative humidity (up to 90%) results in an increase in their breaking stress, while their elongation at disruption decreases. The reason for this phenomenon is the time-dependent post-crystallisation of starch in the presence of water and glycerol; the degree of crystallinity of B-type structures in the tested samples increases from 5% to 30%.

The amylose and amylopectin components of starch plasticised with water and glycerol manifest different abilities for structural rearrangements.[50] Analysis of extrusion samples of specially prepared high-amylose and high-amylopectin starches (the amylose content varied from 0% to 70%) revealed[50] that in amylose-enriched materials further crystallisation occurs much faster than in amylopectin-enriched ones.

The higher ability of plasticised amylose for post-crystallisation was also established in samples of the amylose starch obtained by compression moulding.[51] The elasticity moduli of plasticised, partially crystallised samples comprising structures of the V- and B-types were practically the same immediately after moulding. After storage, the elasticity moduli of the samples prepared from normal corn starch was ~ 100 MPa, whereas those of the high-amylose starch were of about 700 MPa. These differences seem to be due to the fact that high-amylose starches contain more amorphous structures capable of additional crystallisation.[51]

Storage of samples also causes certain changes in T_g due to the condensation of amorphous regions of starch as a result of formation of additional nodes on the physical lattice and conformational rearrangement of the macromolecules, leading to the formation of molecular and intramolecular double helices of amylose and amylopectin.[39]

In addition to glycerol and polyglycols, other substances can exert a plasticising effects on starch. Calorimetric determination of T_g of starch films containing water and additives (10% – 20%) of glycerol, sorbitol, sodium lactate, urea, ethyleneglycol, diethyleneglycol, polyethyleneglycol (PEG-200) and glycerol diacetate was carried out by Lourdin et *al*.[52] All these compounds, with the exception of glycerol diacetate, formed homogeneous systems with starch; their T_g decreased monotonically with an increase in the concentration of the plasticisers. The glycerol acetate – starch system was characterised by phase separation; the value of T_g did not change in the presence of the plasticiser.

The water in the starch not only transfers the system into a thermoplastic state upon extrusion, but also partly protects the polymer from destruction. For example, sage starch which contained from 34% to 47% of water was incapable of dextrinisation (*i.e.*, degradation leading to low-molecular-weight and oligomeric carbohydrates) but was easily gelatinised, if the extrusion was carried out under drastic conditions (150 °C, high screw speeds).[53] According to other investigators, the processing of this polysaccharide into a thermoplastic material is always accompanied by destruction. Thus, mixing of yellow corn starch[54] with water (18 mass % or 23 mass %) in a two-screw extruder decreases its molecular mass from 3.36×10^5 to 4×10^4 kg mol^{-1}. After repeated extrusion in a single-screw extruder at 110 or 130 °C, the decrease in the molecular mass is less pronounced. It was proposed[54] to use the value of specific mechanical energy applied to the polymer on moulding for the calculation of the expected

decrease in the molecular mass when choosing the type of the extruder and the regime of moulding of thermoplastic materials.

Water and other agents containing hydroxy groups are used as additives in the preparation of thermoplastic materials for single or short-term use. A significant drawback of these materials is their low resistance to water. Therefore, in recent years starch mixtures with synthetic polymers have acquired increasing importance together with thermoplastic materials prepared from starch without additives. These materials combine characteristic properties of their synthetic component with biodegradability owing to the presence of a natural biodegradable component, *viz*., starch.

IV. Mixtures of starch with synthetic polymers

Composite starch mixtures with various synthetic polymers were first proposed in the 1970–1980's.[55–59] Most often, starch is used for the modification of polyethylene (PE), a film material designed for short-term use (*e.g*., packaging of food stuffs, agriculture and medicine, *etc*.). In these mixtures, starch usually plays the role of a filling agent, which ensures the biodegradation of the polymeric item after its service life is over.[60] Thermoplastic mixtures of synthetic polymers with starch are typically prepared from starch plasticised with glycerol and water. The components are mixed in an extruder at ~ 150 °C, which temperature ensures good gelatinisation of the polysaccharide[61] and leads to the formation of two-phase mixtures the biodegradation of which begins from the surface of a starch-enriched film. Small amounts of pro-oxidants favour biodegradation by inducing oxidative decomposition of the material under natural conditions.[62] A PE–starch–vegetable oil mixture is an example of such a composition.[63] Vegetable oil plays the role of a pro-oxidant and simultaneously facilitates the mixing of the natural and synthetic polymers in the course of moulding.

Starch is poorly compatible with non-polar PE; therefore, investigations into improvement of the affinity of the natural and synthetic polymers should be aimed at preparing starch mixtures with co-polymers of ethylene with other more polar monomers as well as at producing modified starches with enhanced affinity for PE.

1. Mixtures of starch with ethylene co-polymers

Co-polymers of ethylene with vinyl acetate (EVAc) or the products of saponification of acetate groups in these co-polymers are most commonly used as components of starch mixtures. These mixtures are prepared from yellow or native corn as well as from high-amylose starch Hylon VII by extrusion with the ethylene–vinyl alcohol co-polymer [EVAl, 56% of $CH_2CH(OH)$ units]. Their structural characteristics were studied by wide-angle X-ray scattering, scanning and transmission electron microscopy and DSC.[64] Heterogeneous mixtures of EVAl with yellow corn starch displayed a clearly defined boundary between the phases; the sizes of the domains were proportional to the extrusion time. In heterogeneous mixtures of EVAl with native corn and Hylon starches, the inhomogeneities decreased faster than in the case of yellow corn starch; the boundaries between the phases as seen in the electron micrographs were diffuse. There was a decrease in the melting temperature of the synthetic polymer, which testified to partial miscibility of the components at the interphaces. Simmons and Thomas[65] prepared phase-separated mixtures of various compositions, which contained domains (0.1–3 μm) enriched either with starch or with EVAl depending on the composition. At the starch content of 55 mass %–60 mass %, the phase reversal was accompanied by drastic changes in the domain sizes. An analysis of the phase compositions of starch mixtures revealed that the compatibility of the components increased with an increase in the amylose content in the starch.

Fibres cast from these mixtures manifested reduced sensitivity to moisture and low initial rates of enzymic biodegradation even in starch-enriched systems. The surface of these fibres was coated with a layer of a synthetic co-polymer, since the matrix phase of the system was EVAl with the starch content of up to 70 mass %.[64,65]

The water resistance and mechanical properties of starch mixtures are determined by the ratio of their constituents. Absorption of moisture by films[66] prepared by blowing of mixtures of native corn starch pre-plasticised with glycerol and water and EVAl [1 : 1 (mixture A); 2 : 1 (mixture B)] varied from 2% to 11% and was greater in the films prepared from mixture B. The breaking strength of the films prepared from mixture A was one-third of that for films prepared from pure EVAl and even less for films prepared from mixture B.

The use of electron irradiation (flux energy 2.5 MeV, 2500 Gray s^{-1}) in the formation of thermoplastic EVAl–starch mixtures makes it possible to modify the structure and rheological properties of these compositions.[67,68] EVAl was shown to be resistant to irradiation, which causes predominantly destruction of starch macromolecules by changing their supramolecular organisation and thus facilitating the mixing of starch with EVAl. The mechanical and rheological properties of irradiated mixtures differ substantially from those of the original samples. The mixtures containing high-amylose starch appeared to be the most resistant to irradiation, which can be attributed[68] to chemical reactions of the linear molecules of the amylose starch with the synthetic polymer under the influence of irradiation.

The conditions for moulding of starch mixtures with EVAl strongly influence their degradability. The favourable effect of the structural anisotropy of starch–EVAl mixtures which appears in the injection moulding on the resistance of the mixtures to the action of physiological solutions (estimated from the mass loss and changes in the mechanical properties upon ageing for 80 days) and ethylene oxide used for the sterilisation of materials in clinical practice was demonstrated by Reis *et al*.[69]

In-depth studies into the properties of starch mixtures with EVAc and with EVAc modified with maleic anhydride (EVAMA) were carried out by Ramkumar *et al*.[70–74] Mixtures of commercial corn starch (25 mass % of amylose, 75 mass % of amylopectin) with co-polymers containing 18 mass % (EVAMA-18) and 28 mass % (EVAMA-28) of CH_2CHOAc units and about 0.8 mass % of anhydride fragments were prepared by extrusion carried out at different temperatures, screw speeds and mixing times. A dynamic mechanical analysis[72] performed at different shear rates (0.005–0.5 s^{-1}) and frequencies (0.1–100 s^{-1}) in a broad range of temperatures revealed that all the mixtures under study displayed two regions of relaxation transition temperatures, *i.e*., -30 °C for the synthetic polymer and 40 °C for starch, which testifies that these systems are heterogeneous. The introduction of anhydride fragments into the co-polymer macromolecule causes a shift in the transition temperatures, which suggests improved compatibility of the components.

The changes in the crystallinity of starch granules in the course of mixing were demonstrated by DSC.[72] The starch–EVAMA mixtures are characterised by lower values of heats of melting (Table 2), *i.e*., the structure of starch granules in these mixtures changes to a greater degree. Repeated compression moulding of the mixtures also decreases the heat of melting.

With an increase in the starch content in the mixtures, the viscosity of the systems changes, reaching a maximum level at 70 mass % of starch. The absolute viscosities of the mixtures containing EVAMA-18 are higher than those of starch–EVAMA-28 mixtures. It is noteworthy that the viscosities of starch mixtures of any composition exceed the additive values.[72,73]

The ability of starch mixtures to absorb water strongly depends on the moulding conditions, *e.g*., temperature, screw speed and injection pressure. Starch–EVAMA mixtures absorb water more readily than starch–EVAc mixtures (22 mass %–37 mass % or 20 mass %–27 mass % of water, respectively). Contrariwise, in the presence of water the values of diffusion coefficients and structural relaxation times calculated from the anomalous sorption model were higher for starch–EVA mixtures. These differences were attributed to the different degree of

Table 2. The heats of melting of starch mixtures with ethylene co-polymers.[70]

Sample	Heats of melting[a] of samples /J g^{-1}	
	following extrusion	following additional compression moulding
Starch – EVA[b]		
20 : 80	–	75.8
40 : 60	101.0	95.5
Starch – EVAMA-18[b]		
40 : 60	46.9	19.7
70 : 30	–	98.0
Starch – EVAMA-28[b]		
40 : 60	56.6	26.0
70 : 30	–	68.7

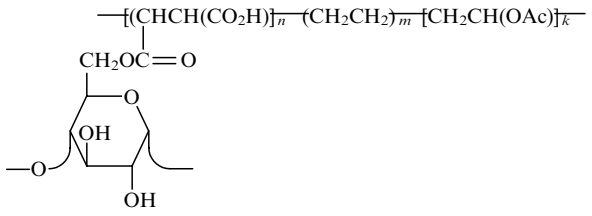
[a] The heat of melting of dry starch is 35.9 J g^{-1}; [b] The figures in parentheses designate the starch : co-polymer ratios.

starch destruction during the formation of mixtures with EVAc and EVAMA rather than to the presence of anhydride groups in the co-polymer.[70]

Using wide-angle X-ray scattering, it was shown[73] that 20-week storage of starch mixtures with a synthetic polymer leads to structural rearrangements resulting in the restoration of the crystalline structure of starch, which was completely lost in the course of moulding. The changes in crystallinity are especially well-pronounced during the first five weeks following moulding; as a result, the resistance of starch samples to rupture increases. After storage of the samples at 10 °C, the structural changes become less apparent, but are manifested on storage at 50 °C, since relaxation transitions in starch occur around this temperature.[72]

From the data taken altogether, Ramkumar *et al.*[70–74] concluded that the presence of anhydride fragments in the co-polymer chain is favourable for the improvement of compatibility of the starch mixture constituents. Mixtures of co-polymers of EVAc and EVAMA with the starch content of 70 mass % manifest good mechanical and moulding properties and are fairly resistant to water.

Mixtures of starch with an ethylene – propylene co-polymer (EP), polystyrene (PS), an ethylene – propylene – maleic anhydride co-polymer (0.8 mass %, EPMA) as well as with a styrene – maleic anhydride co-polymer (8 mass %, SMA) obtained by extrusion at 120 – 180 °C were studied at different effective mechanical moulding energies.[75–79] In these studies, the effects of the composition (40 mass % – 70 mass % of starch) and moulding conditions on the structure and properties of starch mixtures were analysed. As in the case of starch – EVAMA mixtures,[70,72] the miscibility of components improved in the presence of anhydride fragments in the synthetic polymer chain. This phenomenon was interpreted[75–79] as the chemical reaction between starch and the synthetic polymer under the influence of high temperatures and shear stress in the extruder on moulding. This reaction results in the formation of ester bonds between the carboxy groups in the co-polymer chain and the primary hydroxy groups of starch.



Comparison of mechanical characteristics of the mixtures suggests that the co-polymers containing anhydride fragments react more strongly with starch (Table 3).[76] The breaking strength of starch – SMA mixtures is lower than that of pure SMA or PS but higher than that of starch – PS mixtures. In EPMA-containing compositions, the increase in the starch content up to 70 mass % increases the breaking strength of the systems. The increased resistance of starch mixtures with polymers containing anhydride groups is a result of enhanced interphasic adhesion at the boundary between the structural inhomogeneities caused by the reaction of the anhydride groups of the synthetic polymer with the hydroxy groups of starch.

Table 3. The breaking strengths of polymers and polymer – starch mixtures.[76]

Sample	Starch : co-polymer ratio	σ_p /MPa
SMA		33.2
Starch – SMA	60 : 40	18.4
	70 : 30	17.7
PS		31.0
Starch – PS	60 : 40	9.6
EPMA		6.2
Starch – EPMA	60 : 40	6.4
	70 : 30	8.3
EP		> 8.9
Starch – EP	70 : 30	2.8

Starch mixtures with EPMA and SMA are easy to mould, display satisfactory mechanical characteristics and are biodegradable by spores of the fungus *Penicillium funiculogum*, which is facilitated with an increase in the starch content. At low starch content, starch granules remain encapsulated within the synthetic polymer and are thus hardly accessible to microorganisms.[76]

Starch – EPMA and starch – SMA films are highly hydrophilic. Adsorption of water by these specimens depends on the method for the preparation of the mixtures and the moulding regime, since mechanical action induces decomposition of starch granules. Both compositions are rather resistant to water at room temperature despite high starch content (50 mass % – 80 mass %); after keeping in water for two months, they absorb as little as 10 mass % – 30 mass % of H_2O. The resistance of starch mixtures with EPMA to water under conditions mimicking sterilisation (121 °C, 10 min) is higher than that of starch mixtures with SMA.[76]

Using scanning electron microscopy, it was shown[78] that a material possessing good mechanical properties can be prepared by varying the compositions of three-component mixtures (starch – SMA – EPMA) and moulding conditions. Starch granules in this material have a size of 1 to 5 μm.

A thermoplastic material was obtained[80] by extrusion of a mixture of wheat, potato, corn or rice starch (36 mass %) with an ethylene – acrylic acid co-polymer (used as ammonium salt, EAA, 41 mass %), water (12.5 mass %), urea (8.4 mass %) and polyethylene glycol (PEG, 2,1 mass %). Mechanical characteristics of films depended on the origin of starch as well as on the contents of water and PEG. The films based on wheat starch possessed the highest values of the elasticity modulus (~ 180 MPa). The mechanical characteristics deteriorate with an increase in the concentration of the plasticiser.

Thermooxidation resistance of mixtures of low-pressure polyethylene (LPPE) with a methyl methacrylate – butadiene – styrene co-polymer (MBS), with EAA and plasticised starch at 190 °C was studied[81–83] using thermogravimetry, DSC and IR spectroscopy both upon continuous heating and in the isothermal regime. It was shown that MBS and EAC accelerate, whereas starch

decelerates thermooxidation of LPPE. A ternary LPPE – EAA – starch system appeared to be the most resistant to temperature, apparently due to the stabilising effect of the co-polymer at the PE – starch interface.

2. Mixtures of starch with cellulose derivatives and other natural polymers

A great number of investigations of the past decade[84–92] were devoted to studies of starch mixtures with other natural polymers, such as pectins, cellulose, *etc*., or products of their chemical modification. The feasibility of production of biodegradable packaging films for food stuffs as well as for biomedical purposes from starch – gutta-percha mixtures was studied by Arvanitoyannis *et al*.[84]

Biodegradable starch mixtures with natural water-soluble polysaccharides, *viz*., pectins, were studied[85–87] using dynamic mechanical analysis, dilatometry, scanning electron microscopy and IR spectroscopy. Plant cell wall pectins contain esterified polygalacturonic acid residues, the degree of esterification depending on the origin of pectin. The pectins studied were isolated from citrus plants, sugar beet, almonds and water-melon rinds.[85–87] The rupture strength and elasticity modulus of films cast from aqueous solutions practically do not depend on the origin of pectin. The rupture strengths of glycerol-plasticised films of pectin – starch mixtures change only slightly with an increase in the plasticiser content up to 45 mass %. Further increase in the glycerol content up to 75% sharply decreases the rupture strength and increases 10-fold the chain elongation at break. The increase in the starch content in the mixtures attenuates the plasticising effect of glycerol and thus makes the films more rigid. The level of mechanical properties of pectin – starch – glycerol films correspond to the mean values of the mechanical characteristics of films prepared from ordinary synthetic polymers (σ_p = 27 MPa, elasticity modulus $2\times10^3-3\times10^3$ MPa). A change in the dynamic strain at a constant frequency of 1.6 Hz over a broad range of temperatures (from -100 to -200 °C) causes the appearance of three regions of mechanical relaxation, *viz*., at -50, 25 and ~ 100 °C. The position of mechanical losses peaks depends on the amount of the plasticiser (glycerol) added, *viz*., the transition temperature decreases with an increase in the glycerol concentration. Using IR spectroscopy, it was shown[83] that the position of the band corresponding to the carboxy group of pectin changes noticeably after addition of glycerol, whereas the positions of the absorption bands characteristic of starch change to a lesser degree. The results of spectral studies[83] suggest that plasticised films prepared from starch mixtures are highly compatible with pectin. However, phase homogeneities of the systems under study were not proved.

Extrusion of corn starch mixtures with microcrystalline cellulose and methyl cellulose (MC) in the presence of additives, *e.g*., plasticisers (polyols), or without them was used to produce edible films.[88] The increase in the concentration of the cellulose component increases the rupture strength and decreases the elongation at break and the permeability of films for water vapour.

Thermoplastic films plasticised with triacetylglycerol were obtained by hot moulding of mixtures of potato or corn starch with cellulose diacetate (CDA).[89] The ratio of the polymeric components in the mixtures was varied at a constant concentration of triacetylglycerol (35 mass %) relative to the total polymer mass. It was shown that the effective viscosity of the mixture decreases with an increase in the starch content from 10 mass % to 80 mass %, while the fluidity index of the melt increases from 2 to 70 g within 10 min, which was interpreted as an increase in the plasticiser content relative to CDA with a rise in the starch content in the system. Potato starch forms more viscous compositions with CDA than corn starch.

Commercial plasticised films were prepared from starch – CDA mixtures by injection moulding.[90] In their mechanical properties, these films are similar to polystyrene films but are additionally biodegradable. In these mixtures, biodegradation first affects starch and the plasticiser and only afterwards involves CDA. The compositions containing starch and cellulose acetate are unstable in sea water but can be used as biodegradable nontoxic plastics for short-term use in air.

Using static sorption of water vapour, it was shown[91,92] that water-soluble starch forms mixtures with MC and carboxymethylcellulose (CMC), which are thermodynamically compatible if the starch content is below 25 mass %; with an increase in the starch content, the systems become microheterogenous. The rate of biodegradation of such films by microorganisms in water – soil suspensions as determined by the evolution of carbon dioxide depends on the degree of swelling and solubility of the components of the polymeric mixture in water, which facilitates their biodegradation. The rate of biodegradation of MC and CMC mixtures with starch in aqueous media does not depend on the phase state of the system and increases with an increase in the starch content.

Starch mixtures with ternary co-polymers based on caprolactam, dodecalactam and salts of adipic or sebacic acids with hexamethylene diamine were obtained by compression moulding.[93] The mixtures of components containing up to 30 mass % of starch are compatible as evidenced from the negative iodine test and the presence of a single relaxation dielectric loss peak around 50 °C. The resistance of these mixtures to water depends on the number of non-polar methylene groups between the amide bonds of the co-polymer. In systems with the same content of starch, the stability of the mixture containing a dodecalactam-based co-polymer is higher. The biodegradation of these films in water, as in the majority of starch-containing mixtures, is facilitated with an increase in its concentration in the system.

Extrusion of a mixture of starch, EVAl and inorganic compounds, *e.g*., hydroxyapatite, was used to obtain biodegradable materials.[94] These compositions contain more than 30 mass % of natural or synthetic hydroxyapatite and resemble bone both in exterior and in mechanical properties. Scanning electron microscopy and X-ray diffractometry data testify to the homogeneity of their microstructure.

All the polymeric mixtures mentioned above could find practical application in the future. The thermoplastic materials (*e.g*., Mater Bi, Novon, Bioflex) manufactured in Italy, USA, Canada and Germany (predominantly for 'fast food' enterprises) provide examples of commercial compositions based on starch.[7,95–97]

Novon, a thermoplastic material prepared from plasticised starch, usually contains modified derivatives of polysaccharides.

Mater Bi represents a mixture of starch with polycaprolactone or EVAl and usually contains glycerol as the plasticiser.

The materials prepared from these compositions are highly stable and compete favourably with PE films in mechanical properties.[96,97] The films prepared by extrusion and blowing can be used in the production of plastic bags for carrying small loads ($\sim$ 3 to 5 kg).

The biodegradability of Mater Bi materials under aerobic and anaerobic conditions in water and in compost has been studied in detail.[95] It was shown that the plasticiser is washed out rapidly in aqueous media. The starch : polycaprolactone ratio remains constant (54 : 46) under aerobic conditions during biodegradation with bacteria; under anaerobic conditions, the biodegradation predominantly affects starch.

3. Chemical modification of starch

Yet another method for the preparation of starch-based materials is chemical modification of starch, which consists in polymer-analogous transformations (most commonly, by esterification of the hydroxy groups) or introduction of fragments of different chemical origin into the polysaccharide macromolecule (*e.g*., the synthesis of the so-called graft co-polymers). In this review, we shall consider the properties of the compositions containing the products of polymer-analogous conversions of starch and their mixtures with other polymers.

Starch acetates differing in the degree of substitution (from 1.5 to 2.5) were obtained from high-amylose corn starch.[98] According to DSC data, their T_g values changed from 165 to 185 °C; after plasticisation with water, T_g decreased to 35–95 °C. Extrusion of highly substituted starch acetate containing 15 mass % of water was used to obtain foamed materials, which surpassed foamed polystyrenes in plasticity and stability on compression. It is assumed[98] that such materials can be used in the production of packaging materials for agricultural and food industries.

Mechanical properties of films prepared from acetylated starch are determined by the origin of starch,[99] being dependent on the content of amylose and amylopectin in the original polymer.[100] The films with a high content of branched amylopectin acetate display high rupture strengths but are fragile.[100]

Starch acetates are much less hygroscopic than non-modified starch.[100] Using four samples of acetylated corn starch with a fixed (from 3.3 mass % to 66 mass %) content of amylose as examples, it was shown that esterification increases the solubility and swelling capacity of starch in organic media.[99] Acetylated starch gels are less rigid and more elastic and transparent than the gels formed by the original starch. The low-amylose starch acetate is an exception. However, in contrast to native starch, the acetylated products are less biodegradable, since esterification prevents the action of enzymes on starch.[99]

Mixtures of acyl derivatives of starch with yet another biodegradable polymer, *viz*., poly-3-hydroxybutyrate (PHB), are highly recommended as candidates for starch compositions.[101] The components of the polymeric composition are incompatible as evidenced from the independence of the positions of their characteristic absorption bands in the IR spectra on their ratio. However, the temperature and enthalpy of melting of partially crystallised PHB decrease after the addition of starch acetate, which affects the morphological properties of PHB crystallites and increases its ability for crystallisation.

Carboxymethyl starch was obtained by treatment of yellow corn starch and pigweed starch (the degree of substitution = 0.1–0.2) with chloroacetic acid.[102] Small additions of carboxymethyl starch were used for the extrusion of various food stuffs derived from semolina. It was found that modified starch improves processing of these products.

Elastic edible films were prepared from hydroxypropyl starch mixed with gelatine and plasticised with polyols and water (up to 25 mass %) by Arvanitoyannis *et al*.[103] The permeability of these films for oxygen and CO_2 increases with an increase in the content of the plasticiser in the system, which deteriorates the quality of packaging materials for food stuffs.

Higher fatty acid esters of starch are promising reagents for mixing with non-polar polymers, such as PE and polypropylene.[104] The reaction of starch with the corresponding acid chlorides in DMSO gave starch octanoates and dodecanoates with the degree of substitution of 1.8 and 2.7. The ester groups containing higher alkyl radicals improve the affinity of starch for the non-polar synthetic polymer and act as internal plasticisers. The compatibility of starch dodecanoate with PE is higher than that of starch octanoate. The starch dodecanoate–PE mixtures manifest higher thermal stabilities, greater elongation at break upon rupture and lower moisture absorption than starch octanoate–PE mixtures. However, being introduced into PE at any ratios, these substances decrease the rate of biodegradation of the mixture in comparison with starch–PE mixtures.

Starches modified by the introduction of cholesterol residues[105] and mixed with high-pressure PE were used for the production of blown films. In comparison with non-modified starch, these materials are more homogenous and more stable. Biodegradation in a compost of films prepared from these mixtures occurs even faster than that of non-modified starch–PE mixtures, apparently due to the loosening of the starch structure caused by bulky cholesterol fragments.

The preparation and investigation of properties of the systems based on chemically modified starch has found lesser application than the preparation of systems from mixtures of native starch with other polymers.

V. Conclusion

Studies carried out in the past decades have demonstrated that biodegradable materials should combine high mechanical and other essential operational and technological properties (*e.g*., stability, low gas permeability, environmental safety, easy moulding, *etc*.) with biodegradability. Biodegradable materials based on starch or starch mixtures with synthetic polymers are the most readily available and have found wide practical application.

The properties of starch-based polymeric materials including their biodegradability depend on the compatibility of the mixture components and the structure of the systems thus prepared. However, the thermodynamic and energetic characteristics of the interaction of starch with synthetic polymers within the mixtures and the structure of such systems are still poorly known. It is these properties of starch mixtures with synthetic polymers that must be subject of comprehensive analysis in order to establish the general regularities with the ultimate goal to select the components and technologies for the preparation of polymeric materials, which are stable in various media and biodegradable.

The widening of the range of biodegradable polymeric systems is very important for future studies; therefore it is hoped that the results described in this review will be useful for further studies based on the use of this environmentally important scientific approach.

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