Understanding the Processing of Thermoplastic Starch

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Summary: The thermoplastics processing of native starch in the presence of water is a recent development with very wide possible applications. Eventually, oil-based polymer materials have to be replaced in many applications by sustainable, inexpensive, natural materials from renewable resources. The present contribution focuses on the injection moulding of starch. The bases of the processing and the thermal and molecular changes occurring are described. In addition, the rheological behaviour of starch-water melts during processing is analysed quantitatively to give apparent melt viscosities. The dimensional, thermal and mechanical properties of moulded thermoplastic starch polymer (TSP) materials and the products presently being produced from them are discussed.

Keywords: injection moulding; native starch; thermoplastic starch polymer (TSP)

Introduction

The thermoplastics processing of natural hydrophilic polymers in the presence of water is a recent development with very wide possible applications.[1–10] Eventually, oil-based polymer materials could be replaced in many applications by inexpensive, natural products from renewable sources. Such products have a useful life and properties and are biodegradable with natural degradation products.

It has been found that by heating hydrophilic polymers in closed volumes in the presence of given amounts of water, homogeneous melts may be formed. If such melts are produced in injection-moulding machines and extruders then they may be processed like thermoplastics. The processing of various starches and of gelatin and other hydrophilic polymers and blends to useful thermoplastics materials has been achieved in this way.[1–10] An essential feature is that a confined volume must be maintained throughout the process if a solid rather than a foamed product is to be achieved.

The present contribution focuses on the injection moulding of potato starch. The basis of the process is described. In addition, the rheological behaviour of starch-water melts during the refill part of the injection-moulding cycle is analysed quantitatively to give apparent melt viscosities. Finally, the dimensional, thermal and mechanical properties of moulded thermoplastic starch polymer (TSP) materials and emerging TSP-based products are discussed.

The Bases of Thermoplastic Starch Melt Formation

Comparison with the Processing of Cellulose and Cellulose Derivatives and Conventional Starch Processing

In polymeric terms, a main distinction between starch and cellulose is that the former contains highly branched molecules, whereas the latter contains only linear molecules. The branching means that crystalline sequences are shorter in starch and fibres do not form. Accordingly, native

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starch is more readily destructured than native cellulose in the presence of water. Indeed, native cellulose cannot be processed as a thermoplastic and it has to be converted to derivatives, e.g., esters and ethers, to reduce the strength of intermolecular forces so that molecular flow can occur under the action of heat and shear. The thermoplastics processing of cellulose derivatives is well-established and well-understood and does not involve water as an integral part of the processes.

The destructuring of starch under the action of heat, water and shear is, of course, the basis of much food preparation and the processing of starch for food and adhesives dates back several millennia into human history. Such conventional processing of starch is in the presence of heat and *excess* water. Initially, a process occurs that is termed gelatinisation,[11,12] resulting in a breaking down of the structures in the starch granules to different extents, depending on the starch and the processing conditions. The structure of the starch granule is very complex and hierarchical, and it is partly crystalline. Importantly, the crystallinity and the supramolecular structure are based on the amylopectin component, and not on the amylose. The initial granules can be up to 100 μm in diameter. In excess water, the amylopectin crystallinity is lost, some hydrolytic degradation occurs, granules swell and eventually disappear, and the linear amylose molecules diffuse into solution. On aging, the starch solution or suspension undergoes so-called retrogradation to a swollen network material with a structure now based principally on associations between sections of amylose molecules.

From a structural polymer materials point of view, the preceding, conventional processing of starch uses too much plasticiser (water) and eventually lays emphasis on the wrong component, namely, the lower molar mass amylose, of $M_n < 10^6$ g mol^{-1}. Native amylopectins, on the other hand, can have M_n and M_w in excess of 10^6 g mol^{-1} and 10^8 g mol^{-1}, respectively. Superior mechanical properties of amorphous materials will be obtained if the molecular, solid or network structure is formed at lower water contents and is based on the branched component of higher molar mass. In this respect, important breakthroughs occurred in the 1980s,[1,2,13] culminating in the thermoplastics processing of starch at approximately its natural water content (≈15%), in a closed volume at temperatures above 100 °C. Using conventional injection moulding, glassy, amorphous, thermoplastic starch polymers (TSPs) were obtained. An important characteristic of thermoplastic starch formation is the thermal and mechanical (shear) destructuring of the starch granules to form a homogeneous melt, unaccompanied by swelling.

Compatibility with Water

Starch is a hydrophilic polymer, that is, for present purposes, a polymer whose uptake of water in equilibrium with pure water is unlimited. Hydrophilic polymers are characterised by water-vapour adsorption isotherms of sigmoidal shape, indicating the presence of bound and unbound water, tending to an infinite amount of water adsorbed in the presence of pure water.[2] Such behaviour ensures no phase separation will occur during processing. As illustrated in Fig. 1, both gelatin and starch show the

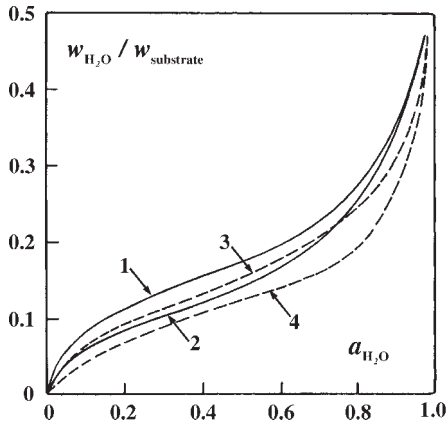

Figure 1.
Adsorption isotherms of gelatin and starch in equilibrium with water vapour of activity a_{H_2O}. Curves: 1 – gelatin 20 °C; 2 – gelatin 60 °C; 3 – starch 20 °C; 4 – starch 67 °C.

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required form of adsorption isotherm and both can be successfully injection moulded in the presence of water.[1,2]

Thermal Changes During Processing

The thermal changes occurring on heating starch-water mixtures can be followed using differential scanning calorimetry (DSC) employing completely filled pans with seals designed to withstand the pressure generated by the sample (up to 30 bar). Fig. 2 shows examples of the endothermic changes in a potato starch at two water contents. The endotherm for the higher water content occurs at les than 100 °C and is characteristic of the gelatinisation of conventional starch processing, in which the starch granules become swollen and destructured and lose amylose by diffusion. The endotherm for the lower water content is characteristic of melt formation, namely, a thermal and aqueous destructuring of the amylopectin crystallites and molecular order in the granule without the mass diffusion of water.[1–3,14,15] At 12% water, there are only about 1.2 molecules of water per anhydroglucose unit. A similar variation in the temperature of the destructurisation endotherm with water content also occurs in gelatin-water mixtures.[2]

The temperature range and size of the melt-formation endotherm for starch and water mixtures depend on the type of starch and also on the particular batch of starch. For example, different trace amounts of metallic ions in potato starches can affect the temperature range and, hence, the processing conditions.[16] In general, the temperature range of the endotherm has to be exceeded before destructuring is complete and a homogeneous melt can be achieved.[13]

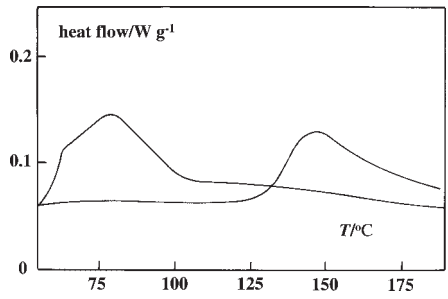

Figure 2.
Examples of DSC endotherms for a potato starch at 42% and 12% water content ($=100W_{H_2O}/(W_{H_2O}+W_{starch})$).

Molecular Changes on Heating Starch-Water Mixtures[9,10]

Figs. 3 and 4 illustrate the molecular changes that occur on heating potato starch-water mixtures in closed glass ampoules for various lengths of time at 140–160 °C. Generally, due to hydrolysis, molar mass reduces as the length of time of heating increases. Fig. 3 shows the logarithmic (Mark-Houwink) plot of intrinsic viscosity ($[\eta]$) versus mass-average molar mass (M_w), as determined by Rayleigh light scattering. The low Mark-Houwink exponent of 0.39 is due to the hydrodynamic dominance of the highly branched amylopectin species. The intrinsic viscosity of the native starch was found to be about 280 $cm^3\ g^{-1}$ consistent with $M_w > 10^8$ g mol^{-1}.

Fig. 4 gives the logarithmic plot of number-average molar mass (M_n) versus M_w. The values of M_n were determined from assays of the numbers of reducing end-groups per unit mass of sample. There is only one reducing end-group per molecule, hence, the number of reducing end-groups present in a sample is equal to the number of molecules present and showing that M_w/M_n decreases rapidly as more hydrolysis occurs. At the highest molar mass shown in Fig. 4, $M_w \approx 1.5 \times 10^7$ g mol^{-1}, $M_w/M_n \approx 300$, whilst for the lowest molar mass shown, $M_w \approx 5 \times 10^4$ g mol^{-1}, $M_w/M_n \approx 6.2$. This large decrease in the polydispersity ratio is consistent with random chain scission through hydrolysis, with the larger molecules being the more likely to be attacked, causing M_w to be reduced more quickly than M_n. To obtain injection-moulded TSPs with satisfactory mechanical properties it is found that M_w should lie in the approximate range 10^6–10^7 g mol^{-1}, with Fig. 4 indicating that M_w/M_n then lies in the approximate range 100–300.

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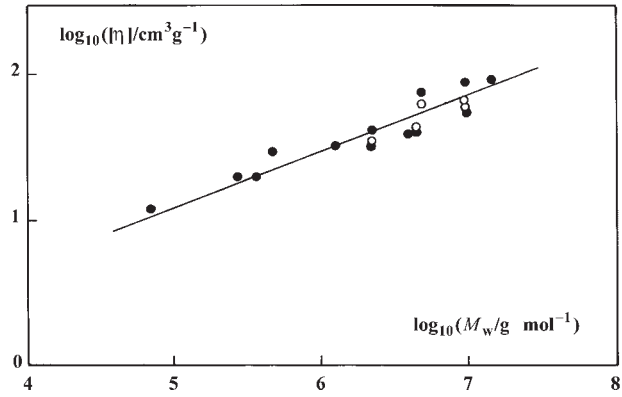

Figure 3.
$\log_{10}[\eta]$ versus $\log_{10}M_w$ (Mark-Houwink plot) for hydrolysed potato starches. • $[\eta]$ measured in dimethyl sulfoxide at 40 °C; ○ $[\eta]$ measured in dimethyl sulfoxide/6 M urea at 40 °C; M_w measured in dimethyl sulfoxide. Least-squares line gives $[\eta]/\text{cm}^3\ \text{g}^{-1} = 0.23(M_w/\text{g mol}^{-1})^{0.39}$.

Injection-Moulding Behaviour and Apparent Melt Viscosity

By carrying out injection moulding with a given mould (shot volume), given screw and given temperature profile, it is possible to measure the variation of refill times for material to feed in front of the screw at different screw-rotation speeds and under different applied back-pressures. The shear rate ($\dot{\gamma}$) is determined by the rotational speed of the screw and the back-pressure defines the reverse pressure drop along the metering zone of the screw.[15,16] As back-pressure is increased for a given screw speed, refill time increases as the backward (viscous) flow rate increases, detracting more from the forward, drag flow due to screw rotation, to give a lower net flow rate. In addition, assuming Newtonian behaviour, the backward flow rate is inversely proportional to the viscosity of the melt (η). Hence, η can be determined from the change of refill time (net flow rate) with back-pressure at a given $\dot{\gamma}$ (screw speed).

Fig. 5 shows apparent values of η for starch-water melts, determined from back-pressure experiments, plotted versus $\dot{\gamma}$ and compared with values of η for polyethylene melts, taken from a manufacturer's literature. From the similarity of the

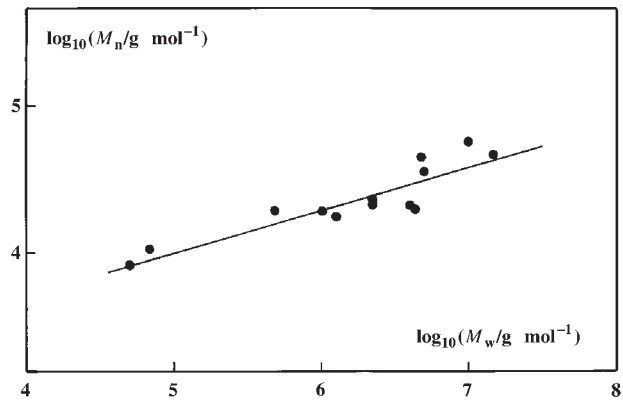

Figure 4.
$\log_{10}M_n$ versus $\log_{10}M_w$ for for hydrolysed potato starches. Least-squares line gives $M_n/\text{g mol}^{-1} = 405(M_w/\text{g mol}^{-1})^{0.28}$.

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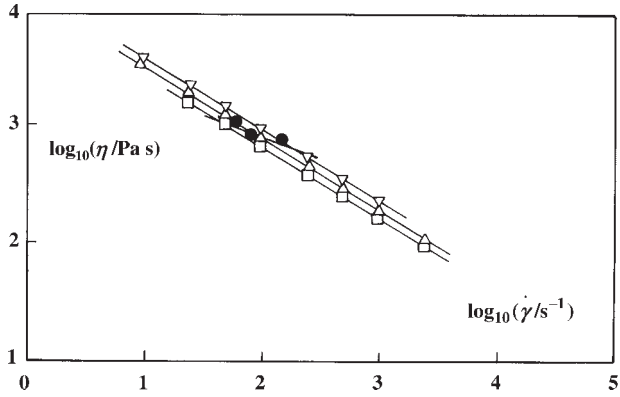

Figure 5.
Comparison of melt viscosities of a medium density polyethylene and a starch-water mixture. Polyethylene: □ 230 °C, △ 210 °C, ▽ 190 °C. • Starch-water, 17% water, 175 °C (metering zone); apparent melt viscosities from back-pressure experiments using a standard Arburg injection moulding machine.

values of η obtained for a given shear rate, it can be seen that, once the other processing parameters, such as water content, temperature profile and screw characteristics, are properly defined, starch processes like polyethylene. The similarity of the viscosity-shear rate behaviour of starch-water melts to that of polyethylene shown in Fig. 5 is corroborated by the measurements of viscosities of pre-processed corn starch-water melts by Willet, Jasberg and Swanson.[5]

Properties of Injection-Moulded TSPs

Dimensional Stability

Obviously, the dimensions of moulded objects from hydrophilic polymers depend on their water contents. If precise dimensions are required, processing should be carried out so that products are formed at approximately the equilibrium in-use water content. For potato starch, for example, this means water contents of around 14% for use under ambient conditions (50% relative humidity, 20–25 °C). If higher water contents are used in processing, distortion and shrinkage will occur as the equilibrium water content is naturally achieved after processing. In addition, higher water contents can induce more hydrolytic degradation of the starch chains during processing and also gelatinisation rather than melt formation. If lower water contents are used, thermal degradation can occur during processing, as well as swelling after processing.

Thermal Properties[2]

Fig. 6 shows the glass-transition temperatures of injection-moulded starch-water and gelation-water mixtures. Similar values of T_g (60 °C to 80 °C) are observed for the

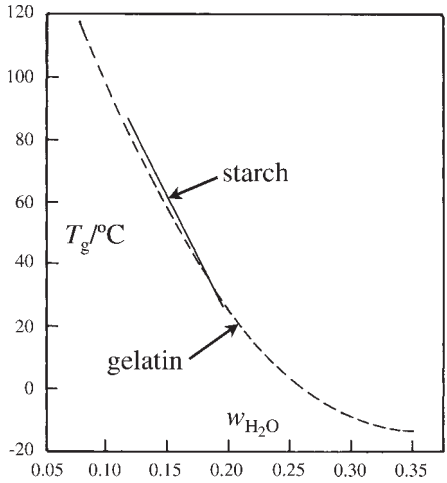

Figure 6.
Glass-transition temperature (T_g) versus weight fraction of water (w_{H_2O}) for injection-moulded gelatin-water and starch-water mixtures.

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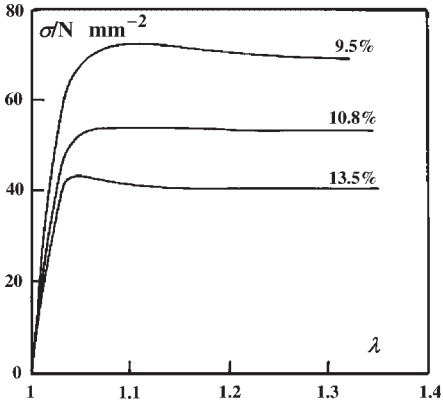

Figure 7.
Tensile stress (σ) versus deformation ratio (λ) of injection-moulded potato starch at ambient temperature and the water contents specified with the curves.

two materials under normal ambient conditions, when values of w_{H_2O} are in the range 0.12 to 0.14. The materials are then in their glassy states.

Stress-Strain Behaviour

Fig. 7 illustrates the stress-strain behaviour at ambient temperature of tensile test-pieces moulded from potato starch at 17% water and conditioned to the water contents shown. Accordingly, the glass-transition temperatures (see Fig. 6) vary from about 60 °C to 100 °C and the behaviour shown in Fig. 7 is typical of that of glassy thermoplastics. The initial moduli are about 1.5 GPa, similar in value to those of glassy polyolefins, polypropylene and high-density polyethylene, and the materials show yield points at between 5 to 10% extension. The changes in properties with decrease in water content are consistent with the loss of free water, which has a plasticising action on the materials.

It should be noted that, to obtain optimal, reproducible stress-strain proerties, pre-extrusion of the starch-water mixtures needs to be used. The extrusion produces[10] a reduction in molar mass of at most a factor of about two, compared with the reduction by a factor of about twenty during the subsequent injection moulding. The latter, much larger reduction in molar mass is expected[10] because of the reverse shear flow that occurs during the refill part of the injection moulding cycle (see Fig. 5).

It is important that further systematic and fundamental studies on TSP processing and TSP materials are pursued in the future. In comparison with that of synthetic polymers, knowledge of the processing-structure-property relationships for TSP-based materials is still in its infancy. However, it is an exciting field with many possibilities for discoveries and developments.

TSP-Based Products

The first commercial product made of injection-moulded TSP was the drug-delivery capsule, Capill[1,14,19,20] and further products are gradually appearing, e.g., golf tees, cutlery, plates, food containers. In addition, extrusion has been applied to produce rigid foams, suitable for loose-fill packaging. Generally, the polymers are dimensionally and mechanically stable under ambient, indoor conditions and are completely biodegradable and compostable. They break-down in water. Hence, TSPs can be considered as a new class of inexpensive, green polymers that can be

Table 1.
Examples of TSP-based materials and products.

Product or Material Name	Product Type	Manufacturer
Capill	pharmaceutical capsules	Capsugel/Warner Lambert; West Pharmaceutical Services
Eco-Foam	foam packaging pellets	National Starch
Mater-Bi (starch and starch blends with hydrophilic polymers)	moulding & extrusion powders for flexible films, rigid packaging, moulded articles, etc.	Novamont, Italy

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returned to the natural cycle, with no pollution, after use.

Further developments include the thermoplastic processing of blends of starch with hydrophilic synthetic polymers,[21,22] e.g., poly(ε-caprolactone) and poly(ethylene-vinyl alcohol), to give the possibility of flexible films and materials with improved mechanical properties, lower water sensitivity, but also lower biodegradability. Table 1 summarises the TSP-based materials and types of products currently available.

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