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Thermoplastic starch

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SUMMARY: The thermoplastics processing of natural hydrophlic polymers in the presence of water is a recent development with very wide possible applications. Eventually, oil-based polymer materials could be replaced in many applications by inexpensive, natural products from renewable resources. As with conventional thermoplastics, hydrophilic polymer melts may be processed by injection moulding and extrusion. The present contribution focuses on the injection moulding of potato starch. The basis of the processing and the thermal changes occurring during processing are described. In addition, the rheological behaviour of the starch-water melts during processing is analysed quantitatively to give apparent melt viscosities. The thermal and mechanical properties of moulded starch materials and the drug delivery behaviour of starch capsules are discussed.

Introduction

The thermoplastics processing of natural hydrophilic polymers in the presence of water is a recent development with very wide possible applications[1-5]. 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. Injection-moulded starch and gelatin capsules have already been produced[1,2,6-8].

It has been found that by heating hydrophilic polymers in closed volumes in the presence of given amounts of water for given times, 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[2-5]. 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.

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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 thermal and mechanical properties of moulded starch materials and the drug-delivery behaviour of starch capsules[1,6,8] are discussed.

Basis of hydrophilic-polymer melt formation

Considerations of the formation of starch melts may be to some extent be generalised to embrace other hydrophilic polymers. For present purposes, such polymers may be considered as those in which the uptake of water by polymer in equilibrium with pure water is unlimited. They are characterised by water-vapour adsorption isotherms of sigmoidal shape, characteristic of 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. Both gelatin and starch show the required form of adsorption isotherm and both can be successfully injection moulded in the presence of water[1,2)].

In thermoplastics processing, the hydrophilic polymer/water mixtures start at room temperature and are subjected to thermal and mechanical energy (due to shear). Their temperatures must be increased sufficiently to allow the disordering of supramolecular structures to give homogeneous melts. In gelatin, the fibrillar structure must be destroyed and in native starch, the granular structure[2)]. The temperature of melt formation is dependent on the water content. It has to be sufficient for destructuring before degradation, but not so high as to give melts of low viscosity and materials of low modulus, as, for example, in the processing of starch for foods.

The melt formation in starch/water and gelatin/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. 1 shows examples of the endothermic changes in a potato starch at two water contents. The endotherm for the higher water content occurs at a lower temperature and characterises gelatinisation, in which the starch granules become swollen and destructured and lose amylose by diffusion. The endotherm for the lower water content characterises melt formation, which is a thermal and aqueous destructuring of the crystallites and molecular order in the granule without the mass diffusion of water[1,3,6,9)]. 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)].

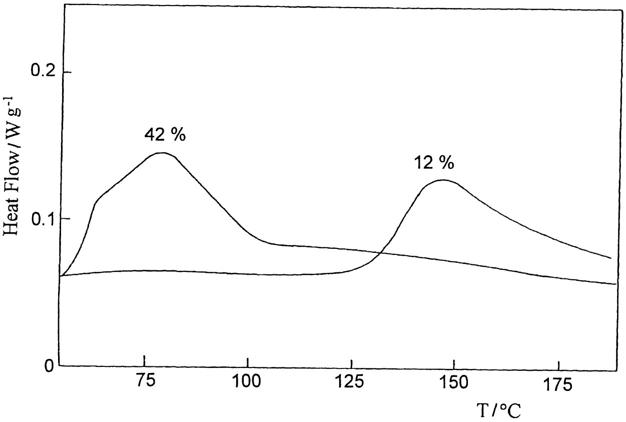

Fig. 1: Examples of DSC endotherms for a potato starch at 42% and 12% water content $100 W_{H_2O} / (W_{H_2O} + W_{starch})$

Fig. 2 shows the results of Donovan[9)] on the enthalpy of denaturation of potato starch determined using DSC endotherms. The occurrence of a high-temperature, melt-formation endotherm at low water contents is immediately apparent. However, when the water content exceeds approximately 3 molecules of H_2O per anhydroglucose unit (1 molecule of H_2O per OH group) the low-temperature endotherm becomes significant, reflecting the thermal changes of gelatinisation, characterised by free water rather than by bound water. The thermoplastic processing of starch occurs at between 1 and 2 molecules of H_2O per anhydroglucose unit and only the upper, melt-formation endotherm is operative. (Donovan in fact never reached such low water contents in his measurements because his DSC sample pans exploded).

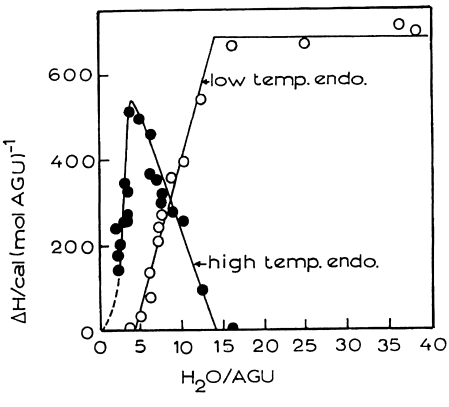

Fig. 2: Enthalpy of denaturation of potato starch determined from DSC endotherms as a function of molar ratio of water to starch. AGU = anhydroglucose unit. O low-temperature endotherm; ● high-temperature endotherm (after Donovan[9)])

For starch and water mixtures, the temperature range and size of the upper melt-formation endotherm depends 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[10)]. In general, the temperature range of the endotherm has to be exceeded before destructuring is complete and a homogeneous melt can be achieved[11)].

Obviously, the dimensions of moulded objects from hydrophilic polymers depend on their water content. If precise dimensions are required, processing should be carried out 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. If higher water contents are used in processing, distortion and shrinkage will occur as the equilibrium water content is achieved after moulding. In addition, higher water contents can induce 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 moulding.

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[12,13]. 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. In addition, as the backward flow rate is inversely proportional to the viscosity of the melt (η), assuming Newtonian behaviour, η can be determined from the change of refill time (total flow rate) with back-pressure at a given ($\dot{\gamma}$) (screw speed).

Fig. 3 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 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.

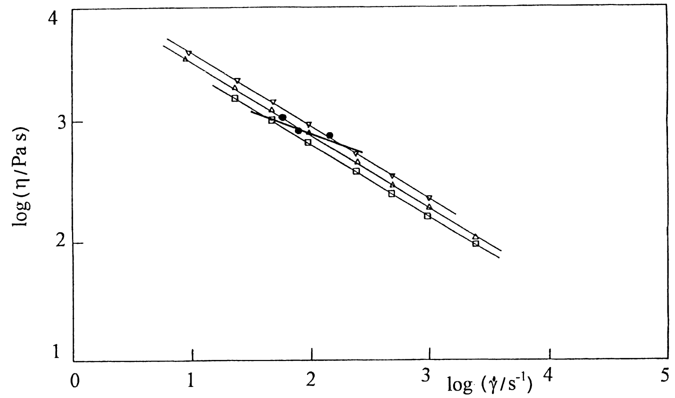

Fig. 3: Comparison of melt viscosities of a medium density polyethylene and a starch-water mixture. Polyethylene: 230°C, Δ 210°C, ∇ 190°C. Starch-water, 17% water, • 175°C (metering zone); apparent melt viscosities from back-pressure experiments using a standard Arburg injection moulding machine

The viscosity-shear rate behaviour of potato starch-water melts shown in Fig. 3 is corroborated by the measurements of viscosities of pre-processed corn starch-water melts by Willet, Jasberg and Swanson[5)]. Their results are illustrated in Fig. 4 where similar viscosities in relation to those of a polyethylene are apparent.

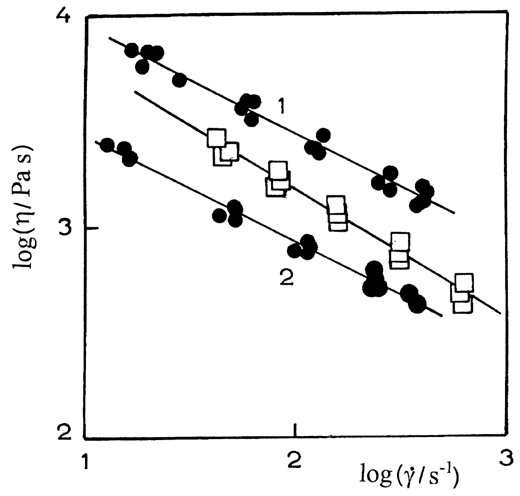

Fig. 4: Comparison of the melt viscosities at 160°C of pre-processed thermoplastic corn starches and low density polyethylene. Starch-water: ● curve 1-15 % water; curve 2-20 % water. Polyethylene:$\dot{\gamma}$(after Willett, Jasberg and Swanson[5)]).

Thermal behaviour

Fig. 5 shows the glass-transition temperatures of injection-moulded starch-water and gelatin-water mixtures. Similar values of T_g are observed for the two materials under normal ambient conditions of w_{H_2O} in the range 0.12 to 0.14. The materials are then in the glassy state.

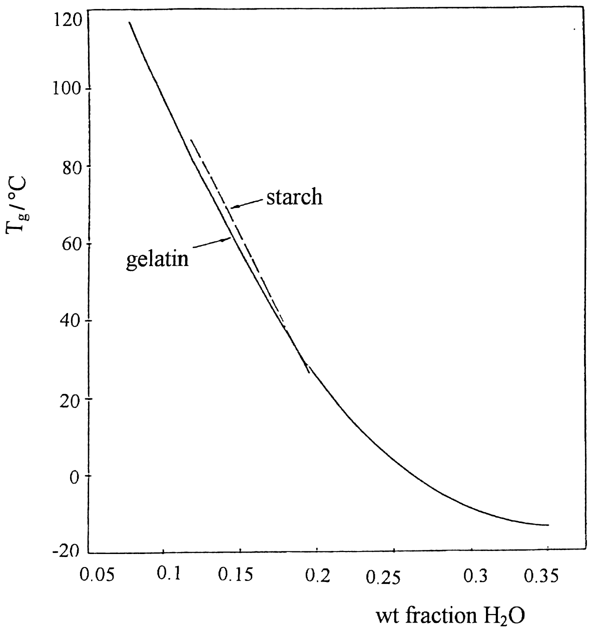

Fig. 5: Glass-transition temperature versus weight fraction of water (w_{H_2O}) for injection-moulded gelatin-water and starch-water mixtures (after Stepto and Tomka[2])

Stress-strain behaviour

Fig. 6 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. Their behaviour is typical of that of glassy thermoplastics. The glass-transition temperatures (see Fig. 5) vary from about 60°C to 100°C over the range of water contents shown. 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.

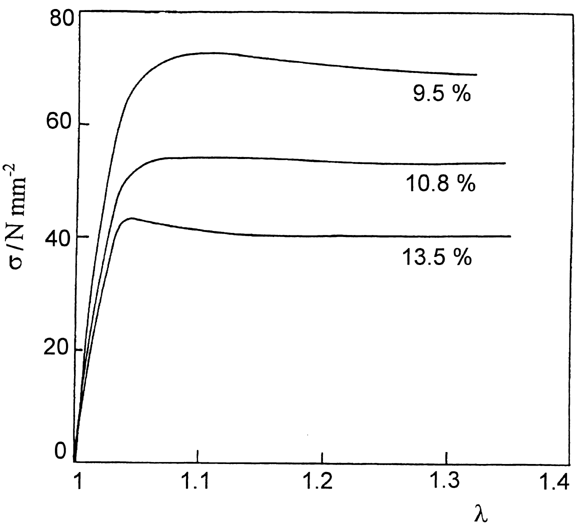

Fig. 6: Tensile stress (σ) versus deformation ratio (λ) of injection-moulded potato starch at ambient temperature and the water contents specified with the curves.

Drug-delivery capsules

The first commercial product made of injection-moulded thermoplastic starch was the drug-delivery capsule, Capill[1,6,7)]. It is illustrated in fig. 7 in comparison with a conventional, dip-moulded hard gelatin capsule (HGC). It is immediately apparent that a smaller closure area can be used with the injection-moulded product. This is because the dimensions can be much more closely controlled in injection moulding than in dip moulding. External, linear dimensions of caps and bodies of the starch capsule are constant to better than 0.1 mm and wall thicknesses to even less. Cap and body can be joined by a tamper-resistant, snap connection to give a smooth surface to the capsule. In addition, the same-sized cap can be used with different lengths of body to produce, for example, size 1 and size 4 capsules. Finally, in contrast to dip moulding, the injection-moulding process is not restricted to particular shapes of article and other products applicable to drug and food delivery can be produced just as easily.

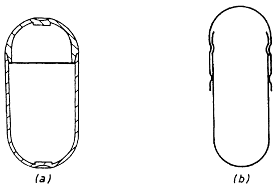

Fig. 7: (a) Injection-moulded starch capsule (Capill) in comparison with (b) a dip-moulded hard gelatin capsule (HGC) (Coni-Snap). The diameters are approximately 8 mm

The comparative in-vivo bioavailability of various substances in Capill and HGC have been studied[7)] and the two delivery systems have been shown to be bioequivalent. Fig. 8 illustrates the bioequivalence, showing the comparative delivery of Aspirin from Capill and HGC[7)].

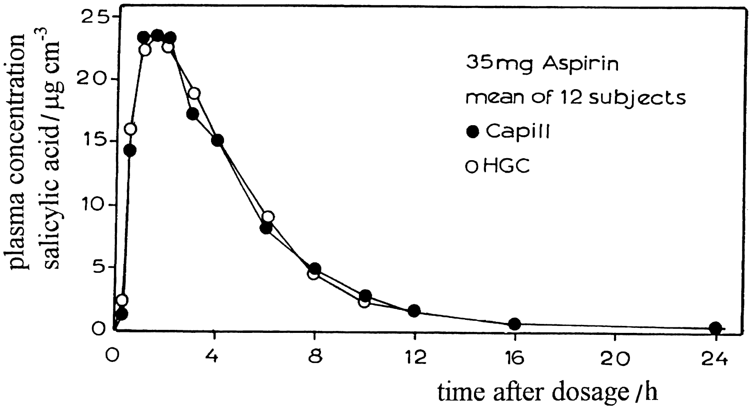

Fig. 8: Release of Aspirin from Capill and HGC

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