

Injection Moulding of Natural Hydrophilic Polymers in the Presence of Water

Robert F. T. Stepto* and Ivan Tomka*

Throughout history, natural polymers have been processed and used. The development of synthetic resins started in the last century. In recent decades, developments have almost exclusively been linked with polymer syntheses from petrochemicals and the introduction of new processing techniques. The present contribution is the first description of the modern thermoplastics processing of unmodified or untransformed natural hydrophilic polymers. Such processing leads directly from the natural polymer to a thermoplastic material. It opens up a new future and basis for the economic, bulk production of polymer products which are no longer based on petrochemicals. The processed materials have a useful life and properties but are biodegradable with natural degradation products.

1. Introduction

Except for rubber, the conventional processing of natural polymers requires the dissolution of the polymer or chemically

modified polymer in water or other suitable solvent and the subsequent removal of the solvent to give the final material^[1]. Examples are the production of fibres, films, and thermoplastics from regenerated celluloses and cellulose derivatives^[2], and films from gelatin^[3]. Chemical modification means that the material formed is no longer a natural polymer, and the use of a solvent with unmodified polymers seriously limits processing speed and flexibility. The solvent must finally be removed from the polymer and the shapes of prod-

uct which can be formed, e.g. fibres and films, are strongly process-dependent.

With aqueous processing, drying may be avoided if the water content of the starting material and the end-product are the same and remain constant during the process. In principle, the constancy of water content can be achieved by using a technique which keeps the material within a confined volume. Injection moulding is an obvious choice provided the natural polymer plus water can be transformed into homogeneous melt without excessive oxidative and thermal degradation. Recent investigations have shown that it is possible to produce drug containers from starch and gelatin in the presence of water by injection moulding^[4]. The resulting injection-moulded drug-delivery devices are not only a step-forward in drug-delivery technology, but also in polymer processing technology. It is the first use of elevated temperatures to injection mould native, unmodified polymeric materials having high water contents into articles of stable shape.

The injection moulding process uses the compatibility of water and the hydrophilic polymer and the transformation of the native structure of the polymer in the presence of water into a homogeneous melt.

2. Injection Moulding

Injection moulding is widely used for processing thermoplastic polymers and is sometimes used for processing thermosetting materials^[5]. Fig. 1 illustrates the essential parts of a conventional injection-moulding machine and Fig. 2 the stages of a cycle in the (continuous) injection moulding process. The state of the polymer

*Correspondence: Dr. I. Tomka
Institut für Polymere
Eidgenössische Technische Hochschule Zürich
ETH-Zentrum, Universitätstrasse 2
CH-8092 Zürich

Dr. R. F. T. Stepto
Capsugel AG
Äussere Baselstrasse 303
CH-4125 Riehen

in Fig. 1 corresponds to stage IV in Fig. 2 and the time for a complete cycle (stages I→IV) is usually a few seconds.

Solid polymer in the form of a powder, or, more usually, granules or pellets is fed through the hopper into a rotating, reciprocating screw. The feed material moves

along the screw towards the tip. During this process, its temperature is increased by means of external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. Notice that, over the compression zone, the diameter of the core of the screw increases towards the tip. Thus, the feed is compressed as it is transported. The compression is important for providing friction, to aid melting, and for the exclusion of air from the particulate feed in order to obtain a homogeneous melt.

Whilst the screw is rotating, (stage I, Fig. 2), the material in the mould is cooling and the exit from the barrel to the mould is closed, either through a shut-off nozzle or by solidified, previously injected material. Hence, melt transported to the end of the screw must be accommodated within the barrel beyond the non-return valve. To enable this to occur the screw moves backwards as it rotates. This «reciprocating», axial movement takes place against a pre-determined, hydraulic back-pressure which also aids the uniformity of feed and homogeneity of melt.

When sufficient melt has collected in front of the screw for injection of the next shot, rotation of the screw stops whilst the polymer in the mould finally cools suffi-



Robert Frederick Thomas Stepto (born 1937 in Moredon, England) studied Chemistry at The University of Bristol from 1955–1961. He then carried out postdoctoral research at The University of Manchester Institute of Science and Technology, where he is Reader in Polymer Science and Technology. He is presently working as Vice-Director, Research and Development, Polymer Processing at Capsugel AG, Basel. His research interests cover the solution properties of polymers, computational studies of polymers, polymerization statistics, polymer networks, and the processing of hydrophilic polymers. He is the author or coauthor of numerous scientific papers in journals and books and is the current Chairman of the Polymer Networks Group.



Ivan Tomka (born 1936 in Szeged, Hungary) studied Chemistry, Physics, and Mathematics in Budapest, Cambridge, and Bern from 1954–1966. He carried out postdoctoral research at the Universität Bern. In 1966, he joined the central research laboratories of Ciba-Geigy AG to work on the characterization and industrial applications of polymers. In 1976, he was awarded an ETH prize for his work on photographic gelatin. Since 1980 he has been Reader and Senior Research Scientist at the Polymer Institute of the ETH Zürich. He is the author of numerous patents, and scientific papers in journals and books. His research interests cover the solution and bulk properties of polymers, and the structure and properties of hydrophilic polymers.

Joint work on the injection moulding of starch drug containers involving Dr. Tomka and Dr. Stepto's research group at Capsugel recently gained the Interphex Award for Innovation in Production in the Pharmaceutical Industry.

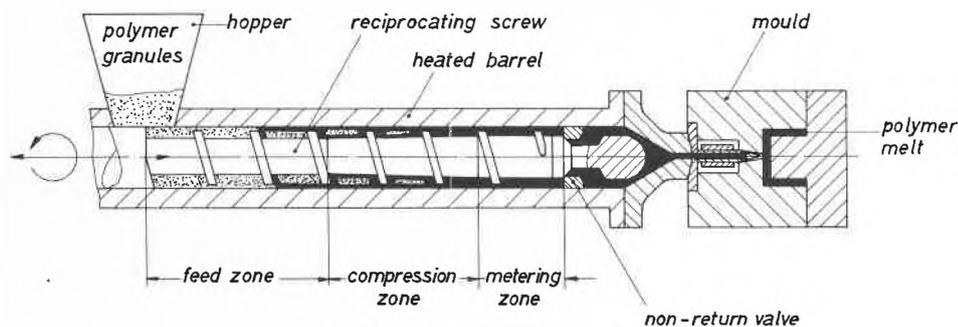


Fig. 1. Schematic representation of the polymer-processing parts of an injection-moulding machine. As indicated, the screw undergoes reciprocating action (axial translation) as well as rotation.

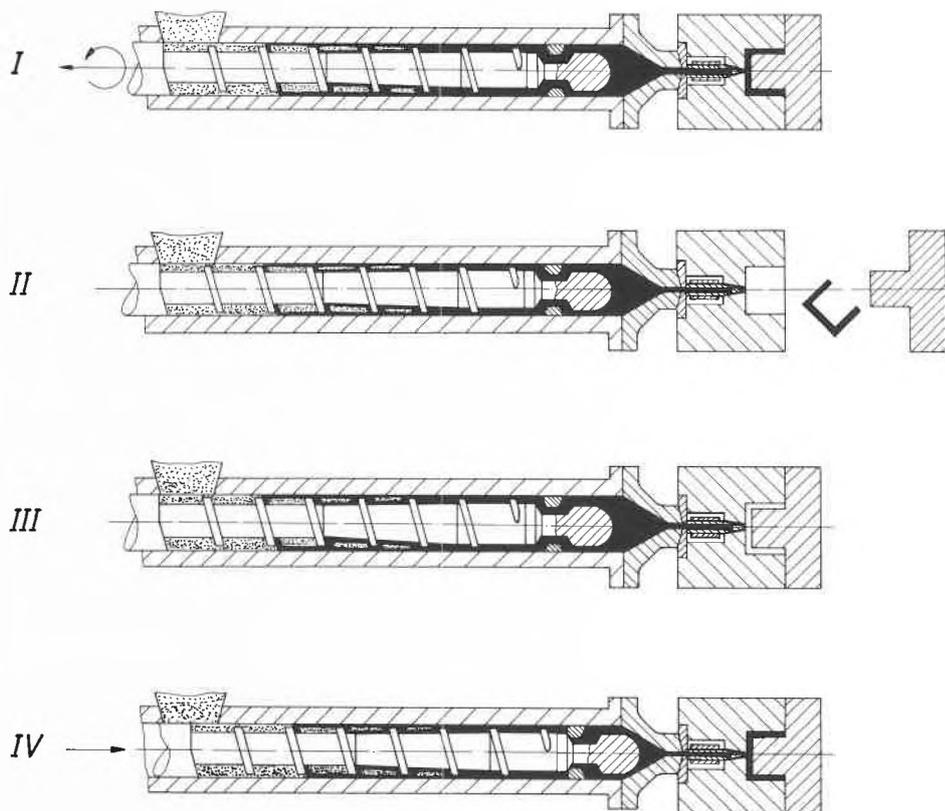


Fig. 2. Stages of a cycle in the injection-moulding process. (Fig. 1 corresponds to stage IV).

ciently for the mould to be opened and the moulded part or parts to be ejected (stage II, Fig. 2). The mould then closes (stage III, Fig. 2) and the screw moves forward quickly under high pressure, injecting molten polymer and refilling the mould cavities (stage IV, Fig. 2). Pressures between 700 and 2000 bar are used in the injection part of the cycle and the non-return valve at the end of the screw ensures that melt does not flow back along the screw during injection.

Throughout the process, the mould is kept below the glass-transition or melting temperature of the polymer. As polymer is cooling in the mould, the gate or entrance to the mould contains melt which is kept under a holding pressure (within stage IV, Fig. 2). Thus, the melt in the mould contracts and becomes compressed by the relatively slow injection of a small volume of melt. Injection continues until the material in the gate has solidified. The screw then commences rotation and backward axial movement to start the next cycle (stage I, Fig. 2). The conditions of secondary injection are so arranged that the mould is finally filled with the correct amount of solid material.

2.1. Injection Moulding Conditions

Table 1 gives examples of the temperatures used for the injection moulding of some common thermoplastics in relation to their melting and glass-transition temperatures (T_m and T_g). The temperature of the melt in the barrel is always higher than T_m for crystallizable polymers and higher than T_g for non-crystallizable polymers (e. g. polystyrene). The higher the temperature of the melt, the lower is its viscosity and the easier is flow and mould filling. However, the temperature is limited, as degradation of the polymer must be avoided and solidification in the mould should not take too long. Antioxidants are sometimes added against degradation and plasticizers to aid flow. The temperature in the mould dictates the rate of cooling and complete filling should be achieved before solidification starts. In addition, the structure of the material formed is affected by the cooling rate. To aid ejection of the moulded part, mould-release agents are sometimes used as additives to the feed or are sprayed onto the surfaces of the mould cavities. They reduce adhesion between the moulded part and the mould.

Table 1. Typical temperatures used for the injection moulding of thermoplastics.

Polymer ^{a)}	Melt Temp. [°C]	Mould Temp. [°C]	T_g [°C]	T_m [°C]
LDPE	180–250	20–40	–110	115
HDPE	220–300	20–60	–100	134
PP	230–280	20–60	–10	165
PS	170–280	10–60	90–100	—
Nylon 6.6	260–290	40–90	50	240

^{a)} LDPE: low-density (branched) polyethylene
 HDPE: high-density polyethylene
 PP: polypropylene
 PS: polystyrene

3. Injection Moulding of Hydrophilic Polymers

Basically, the requirements for the injection moulding of hydrophilic polymers are the same as those for conventional thermoplastics, namely:

- melt formation at the processing temperature without the onset of thermal and oxidative degradation;
- the melt should have a viscosity which allows the mould to be filled at the injection pressure used;
- mould release should occur without plastic deformation or rupture of the product;
- the moulded material must have suitable physical properties.

With hydrophilic polymers, the amount of water present markedly affects processing and materials properties. Hence, to assess the suitability of a hydrophilic polymer/water system for injection moulding it is important to investigate:

- the sorption isotherms at various temperatures;
- the compatibility of the polymer with water;
- the process of melt formation;
- the development of material homogeneity during processing;
- physical properties of the resulting processed material.

The following sections describe investigations which have been carried out using starch and gelatin, with particular emphasis on starch.

3.1. Sorption Behaviour

Fig. 3 shows that the gelatin/water^[6,7] and starch/water systems^[8] have similar adsorption isotherms. For both systems in fixed volumes, the phase separation of pure water does not occur on raising the temperature.

The shape of the isotherms has been shown to be characteristic of systems with strong polymer-polymer and polymer-solvent interactions^[9,10]. In the case of water as solvent, the occurrence of this shape

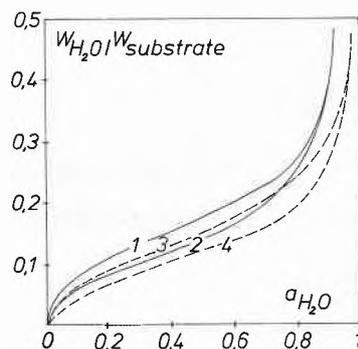


Fig. 3. Adsorption isotherms of the gelatin/water^[6,7] and starch/water systems^[8]; weight of water per unit weight of starch ($W_{H_2O}/W_{substrate}$) versus water-vapour activity (a_{H_2O}). Curves: 1 gelatin, 20°C; 2 gelatin, 60°C; 3 starch, 20°C; 4 starch; 67°C.

of isotherm, where the uptake of water by polymer in equilibrium with pure water is unlimited, may be taken for present purposes as the definition of a hydrophilic polymer. The shape arises from the partial replacement of polymer-polymer hydrogen bonds by polymer-water hydrogen bonds, giving equilibria involving two states of the water (bound and unbound) and two states of the polymer (free and associated). In some cases, limited swelling in pure water may occur because the polymer-polymer interactions are too strong, e. g. for gelatin at 20°C. However, as the temperature is raised to above 40°C unlimited swelling occurs and the gelatin dissolves in pure water^[9]. This change in behaviour infers that isotherms 1 and 2 in Fig. 3 cross at high water activities. The 20°C isotherm (curve 1) reaches a value of $W_{H_2O}/W_{gelatin} = 10$ at $a_{H_2O} = 1$, whereas isotherms at 40°C and above lead to asymptotic behaviour at $a_{H_2O} = 1$.

In the context of the processing of polymer/water systems at defined initial water contents in closed volumes, the temperature dependences and shapes of the adsorption isotherms determine whether phase separation, giving a pure water phase ($a_{H_2O} = 1$) will occur. Irrespective of the initial water content, the increase of temperature during processing should not result in phase separation. The asymptotic behaviour of the isotherms as $a_{H_2O} \rightarrow 1$ assures this does not occur.

3.2. Characterization of Compatibility

The properties of the hydrophilic polymer/water system above 100°C are important for processing, unless high water contents are used. Adsorption isotherms cannot easily be measured above 100°C. However, compatibility may be characterized through cohesive energy density (*c.e.d.*) differences between polymer and solvent. For native starch and for gelatin these differences cannot be calculated using the tables of group contributions normally employed for linear polymers having only van der Waals interactions^[11]. To overcome this difficulty, the temperature and pressure dependences of the specific volume were measured using an apparatus developed and built by Zoller^[12]. From data obtained over the temperature range 80–150°C, the reduced equation of state for polymer melts developed by Simha^[13] allowed calculation of the *c.e.d.* of starch (484 cal cm³) and of gelatin (400 cal cm³). The values are close to those of water (529 cal cm³), indicating the continuing compatibilities of starch and gelatin with water above the maximum temperatures of the measured isotherms.

3.3. Melt Formation

In thermoplastics processing, the hydrophilic polymer/water mixtures will start at

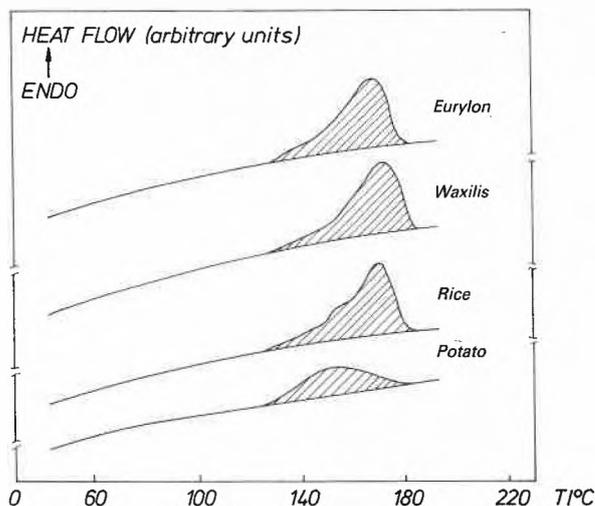


Fig. 4. Melt formation of native starches. DSC thermograms at 17% water content.

room temperature and be 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^[14] must be destroyed and in native starch, the granular structure^[15]. The temperature of melt formation is dependent on the water content. This 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 in the processing of starch for foods.

The melt formation in starch/water and gelatin/water mixtures was followed using differential scanning calorimetry (DSC) using completely filled pans with seals designed to withstand the pressure generated by the sample (up to 30 bar). Fig. 4 shows the endothermic transitions which characterize the melt formation of various native starches at 17% water content (weight of water/[weight of water + weight of starch]). Table 2 shows the enthalpies associated with the transformations. Although the temperature of melt formation is dependent on the water content, it is distinct from the gelatinization of the granules which occurs at lower temperatures and higher water contents^[16]. A similar transformation occurs in gelatin/water mixtures and the mid-point against water content in Fig. 5.

Table 2. Melt formation of various starches at 17–19% water content.

Starch	Melt Formation Range [°C]	Heat of Melt Formation [cal·g ⁻¹]
Eurylon	120–180	3.90
Waxilis	120–180	4.00
Rice	120–180	3.20
Potato	120–180	1.65

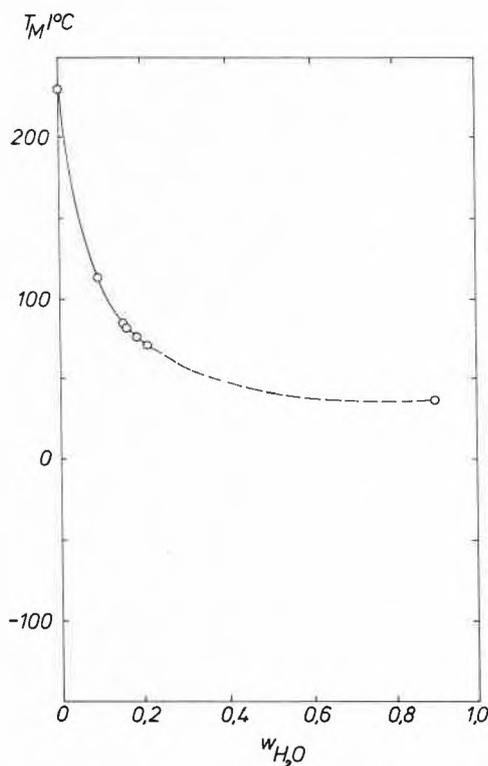


Fig. 5. Melt formation in the gelatin/water system. Mid-temperature of melt formation (T_M) versus weight fraction of water (w_{H_2O}).

3.4. Melt Formation on Injection Moulding

The injection moulding of starch/water and gelatin/water mixtures at less than 20% water content was found to be possible^[4]. The temperature along the screw was increased from room temperature to the melt formation temperature at the metering zone and nozzle. Fig. 6 (see p. 80) shows a series of photomicrographs for the starch/water system, using polarized light microscopy (a) and scanning electron microscopy (b), of samples of material taken from the feed zone (1), the compression zone (2), and the metering zone (3) of the screw. The tendency to homogeneous melt along the screw is apparent. Similar condi-

tions are sometimes employed in the extrusion cooking of starch^[17]. However, a homogeneous product is not then obtained because the material is not kept in a confined volume throughout the process.

4. Properties of Injection Moulded Starch and Gelatin

Fig. 7 shows the T_g of the processed starch and gelatin materials as a function of water content. Under normal ambient conditions the weight fraction of water in both materials is 0.12 to 0.14. The figure shows that the materials are then in the glassy state.

The weight average molar masses of processed potato starch measured by light scattering in dimethyl sulfoxide (DMSO) solution were found to be about 2×10^6 g mol⁻¹. A similar value has been deduced for native potato starch from gradient-field, pulsed NMR measurements in DMSO^[18]. The results indicate that melt formation is not accompanied by significant degradation.

Fig. 8 shows samples of injection-moulded starch. The opaque sample contained a small percentage of additive to aid powder flow during injection moulding. The circular moulding is still stable after 2 years.

The mechanical properties of injection moulded starch materials are at present under study. Preliminary tensile tests under ambient temperature/humidity conditions show brittle fracture, as expected from Fig. 7. The breaking stress is about 3×10^7 N m⁻² with an elongation at break of about 4%.

The first commercial product to be made from injection moulded starch is CapillTM, a capsule-shaped drug delivery device^[4]. It has been found to have satisfactory mechanical properties for use with automatic

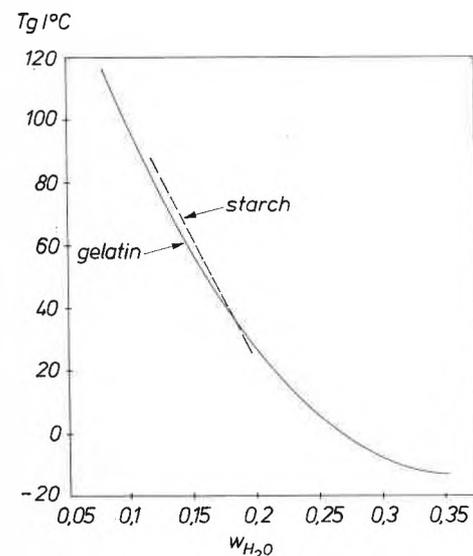


Fig. 7. Glass-transition temperature (T_g) versus weight fraction of water (w_{H_2O}) for processed gelatin/water^[7] and starch/water mixtures.

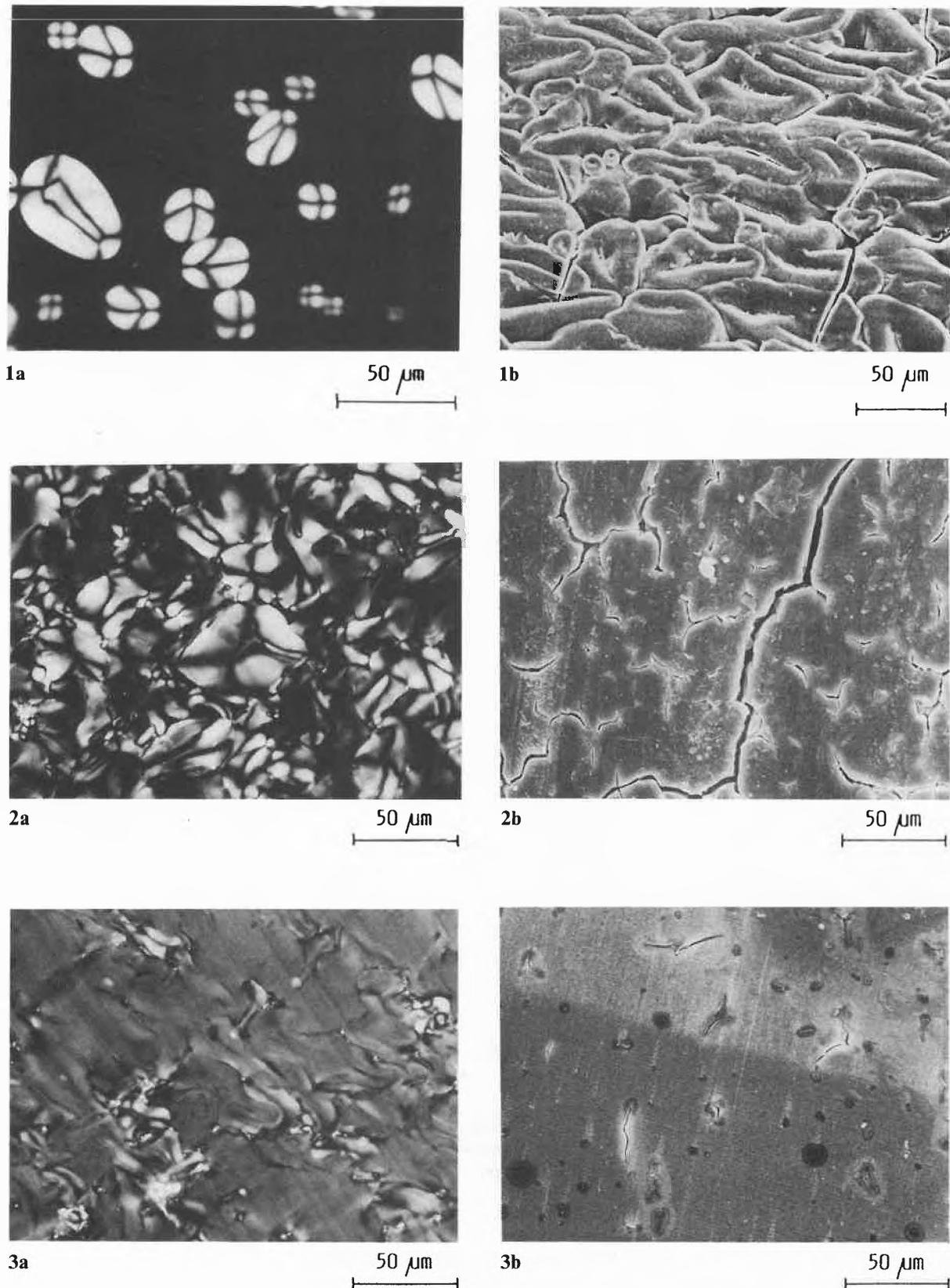


Fig. 6. Starch/water melt formation along the screw during injection moulding. Photomicrography using (a) polarized light microscopy and (b) scanning electron microscopy. Samples from: (1) feed zone, (2) compression zone, and (3) melting zone.

filling machines. In this application of injection-moulded starch, the physiological acceptance and biodegradability of the processed material are essential.

5. Discussion and Outlook

The processing of natural, hydrophilic polymers has wide implications for the fu-

ture production and use of polymeric materials. The processed materials are still biodegradable to natural products and, with development, the disadvantages of the present-day dependence on petrochemicals, e. g. limited supply and environmental pollution, could be avoided. Further, starch is the cheapest polymer available today. The raw material and processing costs are much less than the total costs

of producing synthetic polymers from petrochemicals.

The processing by injection moulding of hydrophilic polymers of defined water contents should be of general applicability. It depends on the complete compatibility of the polymer/water mixture under the conditions used for processing and the constancy of the water content during processing. For gelatin and starch, the changes

occurring during processing include the denaturation or destructuring of the polymer to form homogeneous melts. The processed starch and gelatin material described in this paper are brittle below the temperature of glassy solidification (T_g). This follows from the adsorption isotherms (Fig. 3) and the dependences of T_g on water content (Fig. 7). Current investigations show that, if desired, the brittleness can be reduced by mixing the gelatin and starch with other hydrophilic polymers before processing. It may also be reduced by chemical modification and/or crosslinking, possibly during processing.

The properties of the processed starch and gelatin are sensitive to atmospheric moisture. The sensitivity can be reduced by the blending or reactive processing already mentioned. In addition, hydrophobic coatings may be employed. The type and extent of the modification to be used will depend on the desired balance between properties, retention of properties, and eventual biodegradation.

This account has given only preliminary results, but has presented the possibility of injection moulding natural, hydrophilic polymers at fixed water contents. The systematic investigation of the processing of melts of starch, gelatin, and other hydrophilic polymers is underway. The development of other techniques based on extrusion, reaction injection moulding, and melt spinning will also be investigated. Enormous potential now exists for the development and processing of non-oil-based polymeric materials.

Acknowledgements: The authors wish to thank the Riehen R + D Group of Capsugel for carrying out much of the work described in this paper in the course of the development of «Capill», the Swiss National Research Council for support through National Project 19, Dr. Po Len Yeh and Dr. M. Müller (ETH) for the photomicrographs and Dipl. Ing. B. Gut (ETH) for help with the physical measurements.

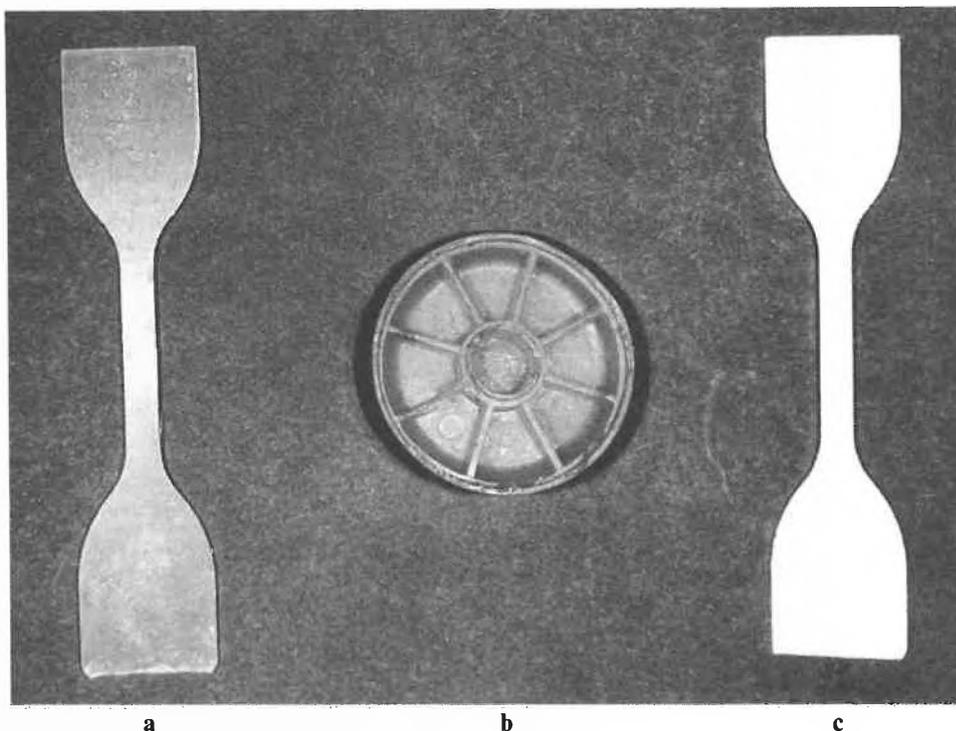


Fig. 8. Photographs of injection-mouldings: (a) opaque tensile test-piece, (b) circular moulding, (c) clear tensile test-piece.

Received: January 7, 1987 [TR 16]

- [1] N. M. Bikales (Ed.): *Encyclopedia of Polymer Science and Technology*, Wiley-Interscience, New York (1964).
- [2] N. M. Bikales, L. Segal (Ed.): *Cellulose and Cellulose Derivatives*, Vol. V, Wiley-Interscience, New York (1971).
- [3] A. G. Ward, A. Courts (Ed.): *The Science and Technology of Gelatin*, Academic Press, New York (1977).
- [4] a) L. Eith, R. F. T. Stepto, I. Tomka, F. Wittwer, *Proc. 5th Pharmaceutical Technology Conference, Harrogate* (1986), p. 178; b) *Drug Dev. Ind. Pharm.* 12 (1986) 2113; c) *Interphex '86, Brighton, Conference Reports*, Cahnners Ltd., Twickenham, UK (1986), p. 2-22.
- [5] S. Middleman: *Fundamentals of Polymer Processing*, McGraw-Hill, New York (1977).
- [6] D. Gehrmann, Dissertation, Technische Hochschule Darmstadt (1979).
- [7] I. Tomka, *Chimia* 37 (1983) 33.
- [8] C. van den Bergen, Ph. D. Thesis, Landbouwhogeschool Wageningen (1981).
- [9] S. Gal., I. Tomka, R. Signer, «Zur mathematischen Behandlung der Wasserdampfsorptionsisothermen quellbarer Stoffe», *Chimia* 30 (1976) 65.
- [10] I. Tomka, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 27 (1986) 129.
- [11] J. Brandrup, E. H. Immergut (Ed.): *Polymer Handbook*, 2nd Ed., Wiley-Interscience, New York (1975).
- [12] P. Zoller, *J. Polym. Sci.* 16 (1978) 1491.
- [13] V. S. Nanda, R. Simha, T. Somcynsky, *J. Polym. Sci. C* 12 (1966) 277.
- [14] I. Tomka, H. Bohonek, A. Spühler, M. Ribeaud, «Structure and Formation of the Gelatin Gel», *J. Photogr. Sci.* 23 (1975) 97.
- [15] R. L. Whistler, J. N. BeMiller, E. F. Paschall (Ed.): *Starch: Chemistry and Technology*, 2nd Ed., Academic Press, New York (1984).
- [16] J. W. Donovan, *Biopolymers* 18 (1979) 263.
- [17] P. Colonna, J. P. Melcron, B. Vergnes, C. Mercier, *J. Cereal Sci.* 1 (1983) 115.
- [18] P. T. Callaghan, J. Lelièvre, *Biopolymers* 24 (1984) 441.