

INFLUENCE OF PROCESSING METHODS ON STARCH PROPERTIES

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Abstract

Native potato starch was prepared using different processing methods. The samples were characterised by means of wide angle x-ray scattering, optical microscopy, differential scanning calorimetry and microhardness. Compression moulding of the starch granules leads to sintered relatively brittle materials. Here the amylopectin crystals of the native powder remain grossly preserved. Preparation of dry films from aqueous gels results in a disintegration of the native starch granules structure and in the formation of a new semicrystalline structure comprising crystallized amylose molecules. Injection moulding of native starch is found to be a processing method giving rise to amorphous materials with superior mechanical properties.

Key words: Starch, injection molding, microhardness, crystallinity, calorimetry

Introduction

In recent years starch, the polysaccharide of cereals, legumes and tubers, has acquired relevance as a biodegradable polymer and is gaining increasing importance as an industrial material [1]. Starch is a thermoplastic polymer and, therefore, it can be extruded or injection moulded. It can also be processed by application of pressure and heat. Lately starch has been used successfully as a matrix in composites of natural fibers (flax, jute etc.) [1]. The use of starch in these composites could be of value in potential applications such as the development of inner parts of automobiles. An advantage of this biopolymer is that its preparation as well as its destruction do not act negatively upon the environment. A further advantage of starch is its low price as compared with conventional synthetic thermoplastics (polyethylene, polypropylene).

All starches are biosynthesized as semicrystalline granules containing densely packed polysaccharides (amylose and amylopectin) and relatively little water [2,3]. The granules that have dimensions typically ranging from 1 to 100 μm , are often compared to positive polymer spherulites with radial orientation of the starch polymer chains. It is commonly accepted that amylopectin, the high molecular weight (10^8 g/mol), highly branched constituent of starch granule, is predominantly responsible for the crystalline structure of native starch. Recent studies show, in addition, that the microstructure of native starch grains is characterised by the alternation of semicrystalline amylopectin shell shaped zones and amorphous amylose regions[4].

The interpretation of the x-ray diffraction patterns of native starch is often difficult because of the low crystallinity, small size, defects and the multiple orientations of the amylopectin crystallites [5]. Two main distinct types of X-ray scattering patterns are

commonly observed (A and B) characteristic of cereal and tuber starches respectively. Potato starch has been shown to crystallize in a hexagonal unit cell in which the amylopectin molecules twist in a double helix (B-structure) [6]. Between adjacent helices a channel is formed in which 36 water molecules can be located within the crystal unit cell. By means of heat treatment this structure can be transformed into a more compact monoclinic unit cell (A-structure) [7]. Amylose (the linear and minor component of starch) can be crystallized from solution in the A, B or V types [8] yielding diffraction patterns similar to those of amylopectin but with higher resolution and orientation. V-amylose is the term used for crystalline amyloses co-crystallized with compounds such as alcohols or fatty acids [9,10].

Starch is still at an initial stage as far as its applicability as a polymeric material is concerned. Preliminary experiments have been reported on the development of high-strength and high-modulus polyethylene-starch composite films and the degree of biodegradability has been examined [11]. Nevertheless, the correlation between structure and properties of pure starch is not yet fully understood and the investigation of different processing methods has not yet been fully examined.

The objectives of the present work are:

- to modify the structure of native potato starch using different processing methods aiming at new materials with enhanced properties
- to analyse the water content of the processed samples as evidenced by differential scanning calorimetry
- to examine the surface mechanical properties as a function of processing conditions and water content.

Experimental Part

Materials and Samples preparation

Potato starch (Avebe) was examined in five different forms: 1) in native powder form as received, 2) after compression moulding with and without additives at 140°C, 3) in the form of dry films (30 µm thick) from aqueous gels, 4) by compression moulding the latter films and 5) by injection moulding at various temperatures using different moulds. Bar shaped mouldings were prepared using both a conventional dumb-bell mould and an elongational flow mould described elsewhere [12].

It is well known that every starch processing method is facilitated by the presence of water. Water depresses the melting point of amylopectin crystallites and lowers starch melt viscosity. Native potato starch contains about 18% water when stored at room atmosphere (room humidity about 55%). If one does not add more than about 10% water the melt processed starch will solidify when cooling down. If more water is given to the starch, its glass transition falls below room temperature [13]. The molding then exhibits a rubbery state and solidifies later when the excess water evaporates.

Compression and injection molding was carried out with native potato starch dried at room temperature and then mixed with 7% water. After processing, the samples were subjected to ambient atmosphere and investigated after a storage time of at least 4 weeks.

Techniques

The samples were investigated by X-ray scattering, differential scanning calorimetry (DSC) and microhardness techniques. Wide angle x-ray scattering (WAXS) patterns of the various samples were taken at room temperature using a powder diffractometer with Ni filtered Cu K α radiation from a rotating anode generator (40 kV and 140 mA). The

calorimetric measurements of the samples were obtained at a heating rate of 10°C/min using a Perkin Elmer DSC-4 differential scanning calorimeter. Microhardness (H) was measured at room temperature using a Leitz tester adapted with a square based diamond indenter. The H-value was derived from the projected area of indentation. A loading cycle of 6 seconds was used and loads of 0.15, 0.25 and 1N were applied.

Results and Discussion

Influence of processing on the structure

Figure 1 shows the X-ray diffractograms of the different starch samples before and after processing by various methods. Potato starch in powder form shows an X-ray scattering pattern which is typical for the crystalline B-modification (diffraction peaks at 5.6°, 15° (broad), 17° (strong) and a doublet at 22-24° (2 θ)) (see Fig. 1a). After compression moulding at 140°C the degree of crystallinity decreases and the structure of amylopectin seems to transform into the A-modification showing just the characteristic peaks at 15,2° 17° and 23.4° (2 θ) (Fig. 1b). Figure 2 shows an optical micrograph under polarized light of a thin section cut from a compression moulded sample. One observes the starch granules as globular white zones exhibiting the typical Maltese cross. By adding a mineral additive (Lafarge clay cement (25wt%)) to the starch powder (7% water) and preparing a compression moulded sample at 140°C, the crystalline peaks of the WAXS pattern of the native starch disappear. One observes only an amorphous halo together with the crystalline reflections from the mineral (Fig. 1c). The addition of the cement particles not only improves the compressing molding process but also leads to the disappearance of the initial crystalline structure.

Another way to modify the structure of native starch is by preparing an aqueous gel at about 50-60°C (gelatinization) and then by drying out the solvent in such a way that thin solid films are obtained. The morphology of the native starch granules is not detectable under the optical microscope. Figure 1d shows the WAXS pattern of the gel dried film. In this case a crystalline structure reappears, which can be also associated to the B-modification. While in the native structure the crystallites are attributed to the ordering of amylopectin molecules, the crystals appearing in the gel films are mainly related to the crystallization of the short amylose chains [14]. The melting of these short chain crystals contributes to the asymmetry of the DSC melting endotherm in the 140-180°C range [7]. Through compression of the gel films (dried always at room temperature, then milled and wetted by 7% water) at 140°C the crystalline peaks corresponding to amylose crystals tend to disappear.

A further route to prepare a new material is by means of injection moulding the initial native powder. Figure 1e shows the WAXS diffractogram of the injection moulded sample using an elongational flow mould and a processing temperature of 120°C. In this case the X-ray pattern corresponds to an amorphous halo, indicating the complete disappearance of the original native structure. The yield strength of these materials exhibit values of the order of 55 MPa, which are larger than those found in injection moulded materials using conventional moulds (~20 MPa). Since the WAXS pattern of these latter mouldings also shows an amorphous halo, similar to that of figure 1e, one has to look for an explanation for the different mechanical properties obtained based on the different microstructural behaviour from the amylopectin and amylose regions respectively. As the X-ray diffraction patterns show no orientation, one may speculate that the higher mechanical strength values obtained with the elongational flow mould are due to a

stretching of the amylose network which finally relaxes in the mould. The stretching may activate the gelatinization of the amylose network. It was shown by Lai and Kokini [15] that mechanical activation during processing favours gelatinization. On the other hand, the brittle behaviour of the conventional mouldings might be connected to a possible cleavage between segregated subparticles of the initial granular structure. Furthermore a stronger thermal contraction might be responsible for an embrittlement of the moldings. [7]

Calorimetry

DSC measurements of the processed samples in the temperature range 3-250°C were also carried out. Due to water evaporation from the starch the thermal transitions of the starch were masked. A typical thermogram of an injection moulded sample is shown in figure 3. One sees a very broad maximum at about 100°C which is related with the evaporation of water. However the high temperature tail suggests the presence of water molecules which are strongly bound to the starch molecules. Figure 4 illustrates the clear correlation of the enthalpy derived from the area of the DSC-endotherm to the weight loss due to the evaporation of water in the starch samples. Most interesting is the fact that the slope of the plot (2440 J/g) corresponds to the heat of evaporation of the water [16] in agreement with the above contention.

Mechanical Properties: influence of water

The surface mechanical properties, particularly those of the injection moulded samples were measured using the microindentation hardness technique. This property has been shown to be related to the yield stress through the well known Tabor relation, which also applies for polymers [17]. Figure 5 shows the hardness values for several samples

processed at different temperatures with different initial water content. Results show an increase of H with the injection temperature, from 120 MPa up to 140 MPa, in the range between 80°C and 110°C. These hardness values are notably higher than those found for conventional injection moulded thermoplastic polymers like polyethylene (50-60 MPa) [18,19]. This first increase of microhardness with temperature might be connected with the gradual disappearance of defects and grain boundaries. For processing temperatures higher than 110°C a decrease in hardness is observed. The H-variation with temperature is linearly related with the corresponding changes observed in the density of the samples [20]. The decrease in H observed for $T > 110^{\circ}\text{C}$ is probably related to some degradation of the material occurring at higher temperatures [21].

We have also observed that the microhardness of the mouldings notably rises after removing the water from the sample. Water is the usual plasticizer in starch processing and mechanical properties are greatly influenced by the amount of water [2,22]. Figure 6 illustrates the variation of the hardness after storing the dry sample at ambient atmosphere. The hardness of the dry sample shows a value of about 210 MPa which is already comparable to that of some metals (Al, Cu, Ag, etc) [23]. However, the hardness value rapidly decreases with storage time and after 1 day it reaches again those values corresponding to the air stored sample.

Conclusions

The transformation of the original native structure of starch through compression moulding is not substantial. The preservation of the native structure results in a sintered material of granules separated by weak zones which lead to brittle behaviour. By preparation of gels from aqueous dispersions the native structure is destroyed. After drying

the gel in the form of films, no memory of the native granules is preserved. In this case, during the drying out process, the amylose molecules can build up a crystalline structure, similar to that of the native powder. Differential scanning calorimetry measurements furnish information about the evaporation of water from the samples. Only through the thermomechanical processing of starch by means of injection moulding can the initial semicrystalline granule structure be destroyed and a homogeneous amorphous high performance material is obtained. This material showed better performance when processed by using an elongational flow mould. Microhardness measurements of the injection mouldings evidence mechanical properties which are close to those typical for some metals.

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Figure Captions

- Fig.1 Wide angle X-ray diffraction profiles of potato starch samples before and after processing: a) native starch, b) compression moulded sample at 140°C, c) compression moulded starch-cement composite, d) starch gel dried film, e) elongational -flow injection moulded starch.
- Fig.2 Optical micrograph under polarised light of a compression moulded starch thin film (x 40).
- Fig.3 First and second DSC run for an injection moulded starch sample.
- Fig.4 Enthalpy variation for injection moulded starch as a function of weight-loss (water evaporation) during heating up.
- Fig.5 Microhardness dependence of starch samples as a function of injection temperature.
- Fig.6 Hardness dependence on storage time of dry starch samples at ambient atmosphere.

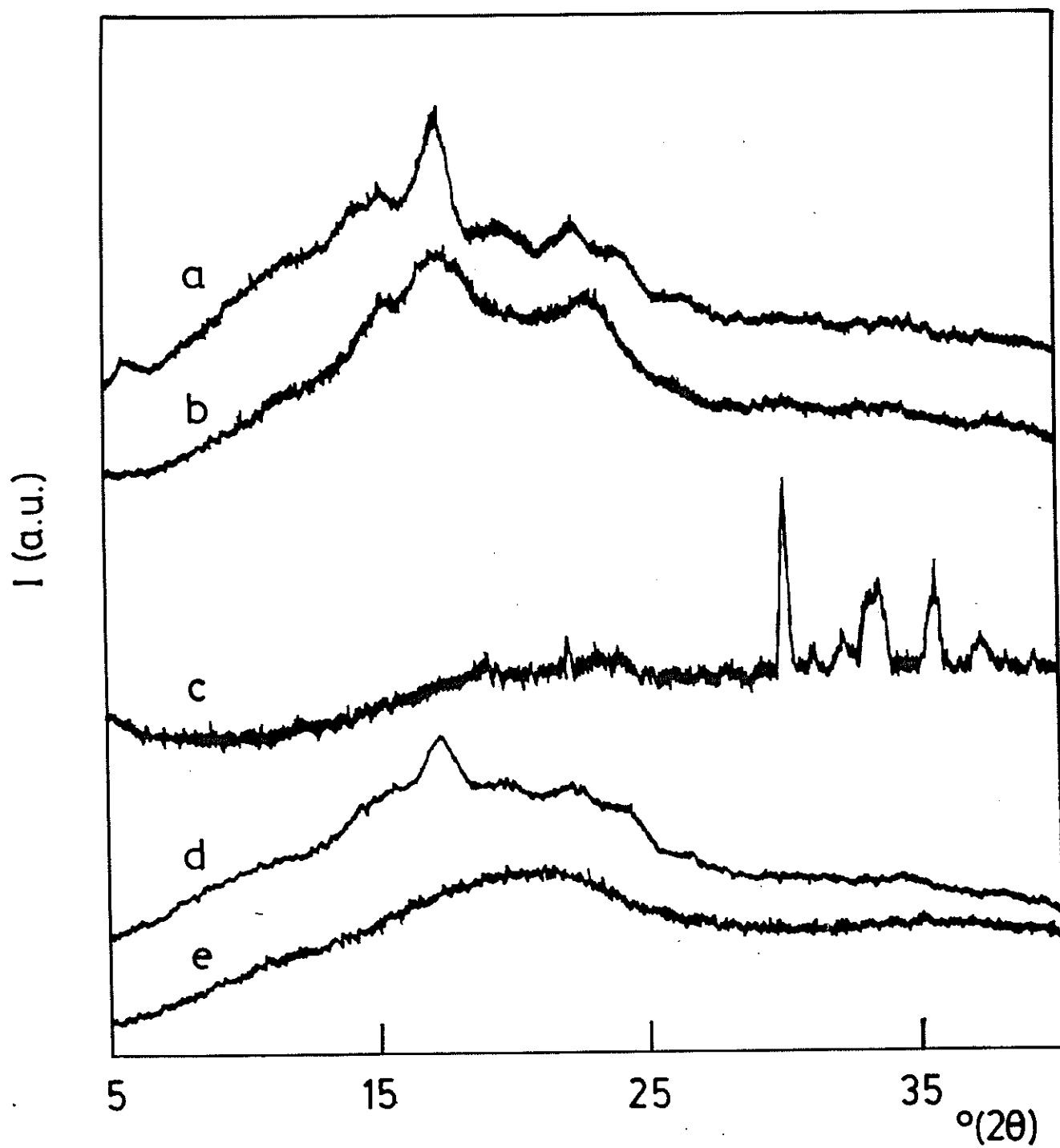
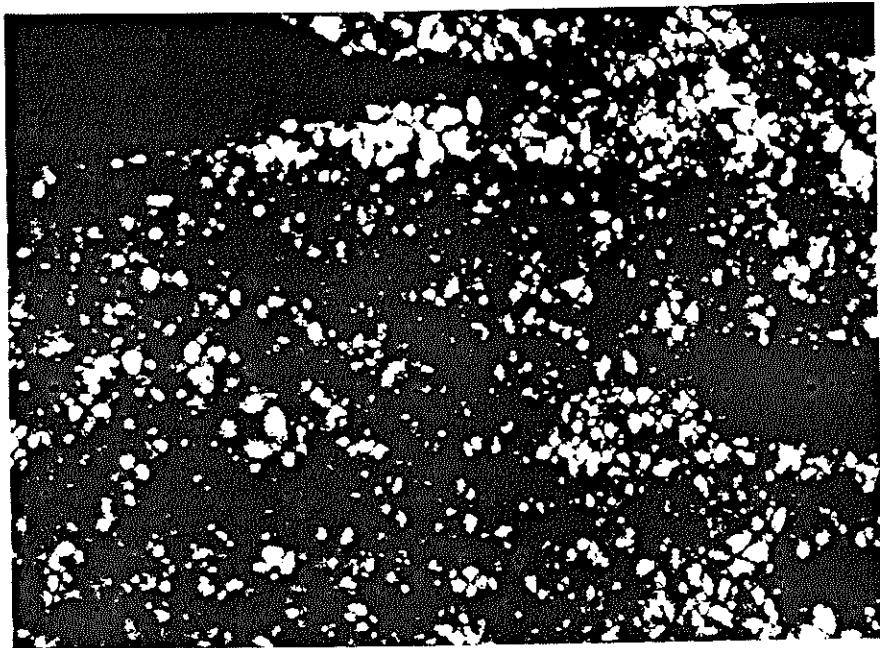


Fig 1



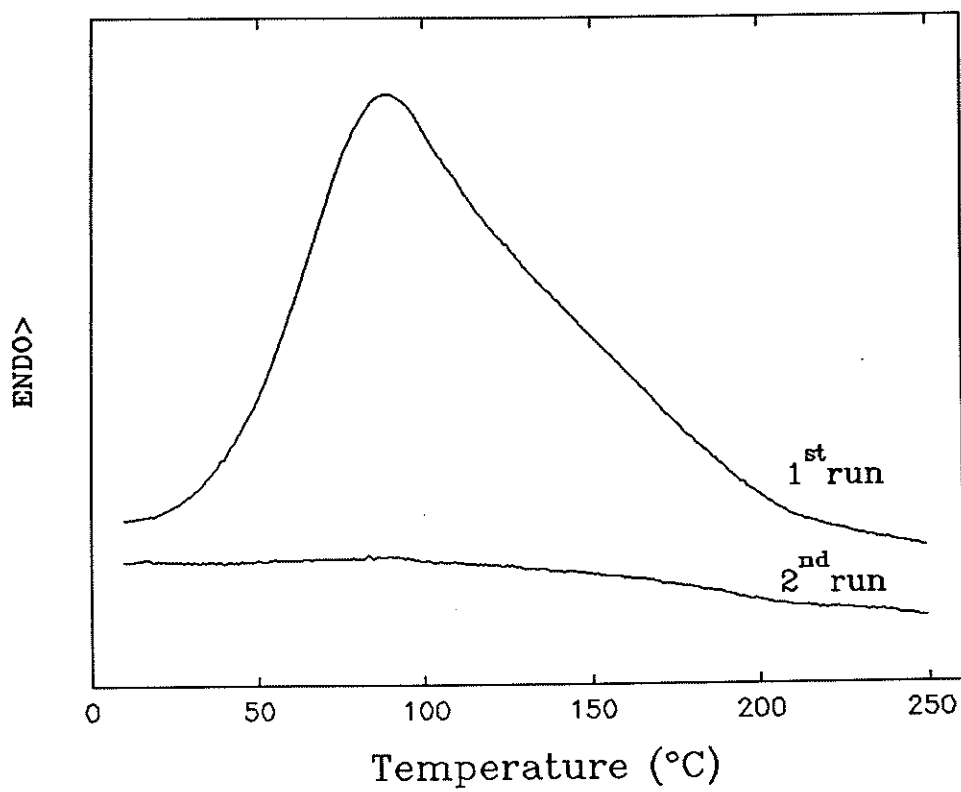


Fig 3

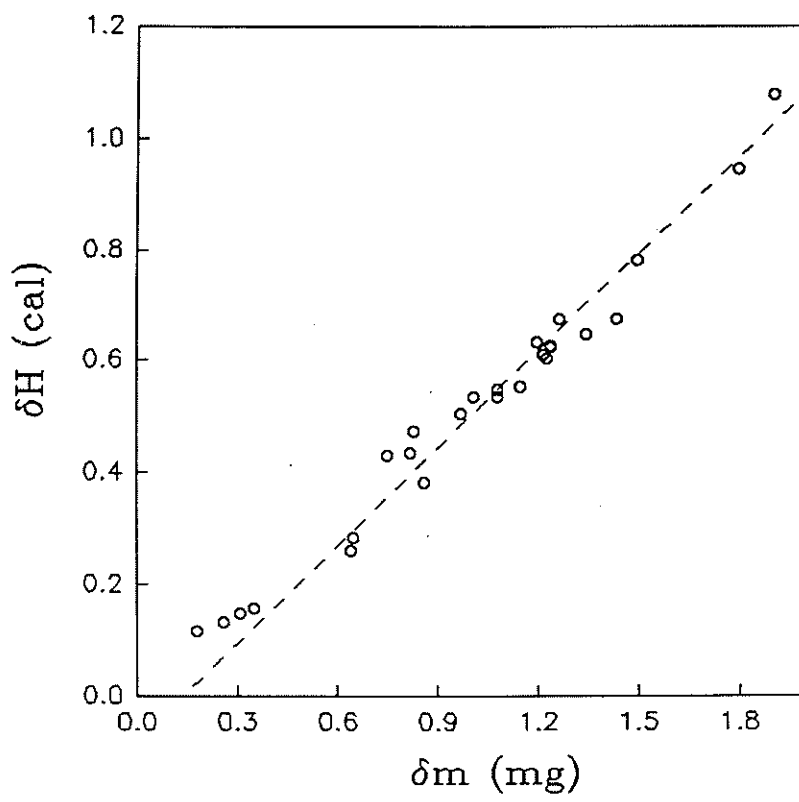


Fig. 4

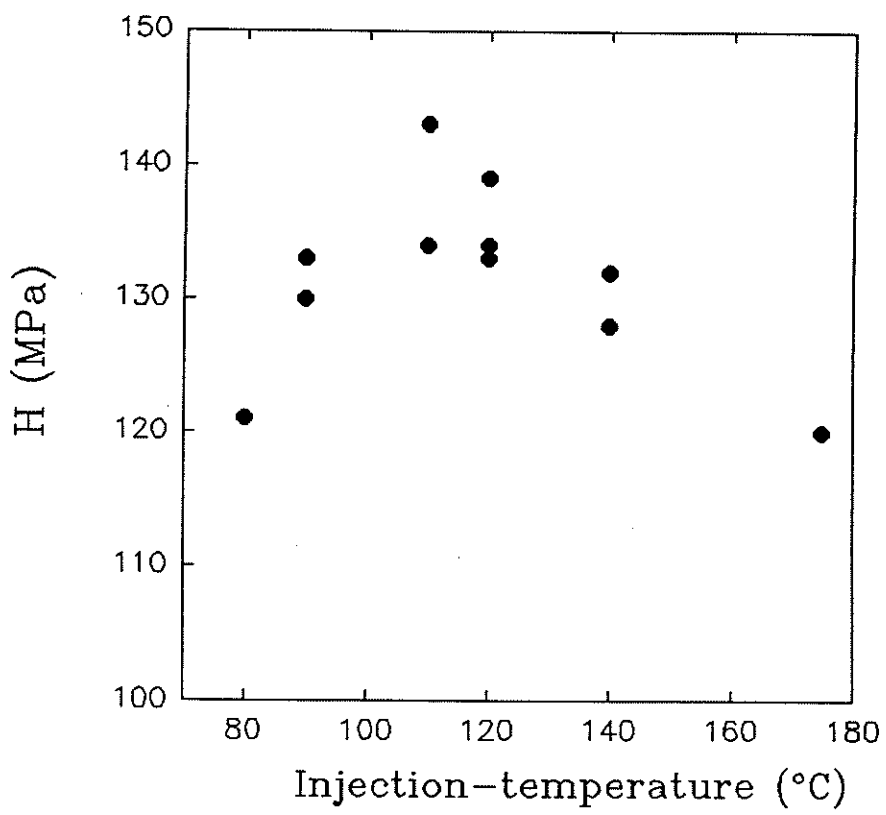


Fig. 5

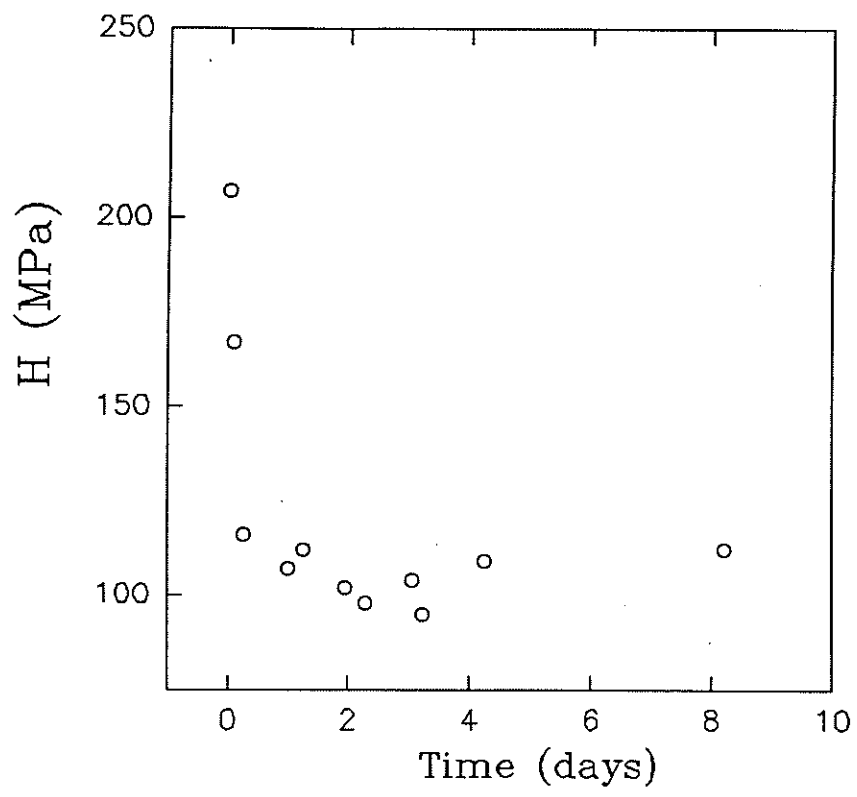


Fig 6