MICROHARDNESS AND WATER SORPTION IN INJECTION MOLDED STARCH.

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ABSTRACT: The microhardness of injection molded potato starch was investigated in relation to the water sorption mechanism. The creep behaviour under the indenter and the temperature dependence of the microhardness are reported. The influence of the drying time upon microhardness, weight-loss and density changes for materials with different injection molding temperatures is highlighted. Results reveal the role of the various mechanisms of water evaporation involved. The occurring structural mechanisms are discussed in terms of the gradual transformation of single helices of amylose and amylopectin into a network structure of double helices and the partial destruction of this structure. Experiments on starch samples, heated at 200°C, suggest the occurrence of an extreme densification of the network hindering the water adsorption in a humid atmosphere.

Key words: starch, microhardness, water diffusion

INTRODUCTION

With the increasing tendency nowadays to use renewable resources, attention is focusing on the possibility of using natural polymers to replace synthetic ones. Starch is a polysaccharide which is produced by photosynthesis in many plants as a form of food storage. Furthermore, starch is a thermoplastic biopolymer that can be transformed by means of conventional thermomechanical treatments using a suitable plasticiser (typically water) ¹. The possibility of using starch films in the packaging industry gave rise to early studies on their mechanical properties ^{2,3}. More recently, the deformation of thin films from extruded starch was investigated ⁴. These studies indicated that extrusion at low temperatures yields non-homogeneous films showing granule remnants which affect the mechanical performance. The influence of the processing methods on starch properties

has been the object of a preceding investigation ⁵. Thus, compression molding of starch granules leads to sintered brittle materials. In the compression molded samples the majority of amylopectin crystals remains preserved as revealed by x-ray diffraction and optical microscopy. The preparation of starch films from gels results in a disintegration of the structure of native starch granules and in the formation of a new structure formed by the crystallisation of the linear amylose molecules ⁵. On the other hand, injection molding of native starch at temperatures above 80°C is shown to give rise to amorphous materials with excellent mechanical properties. The elastoplastic properties of injection molded starch based materials show a clear hardening upon thermal treatment ⁶. The hardness increase has been associated with a water decrease detected in these materials. The concept of micromechanical characterisation of polymer materials has enjoyed steady growth and popularity in recent years ⁷. Particular attention has been given to the microhardness as a technique capable of detecting morphological and textural changes in polymers.

The purpose of the present study is to extend the above studies and examine the influence of the water content on the microhardness of injection molded starch materials exposed to the influence of different thermal treatments and relative humidities.

EXPERIMENTAL

Native potato starch granules (Emsland Superior) were used for the preparation of the samples. The granules were mixed with 5% wt. water for the injection molding process. It is known that starch processing is enhanced by the presence of water which depresses the melting point of the amylopectin crystallites and lowers the starch melt viscosity ⁸. By using an appropriate temperature, the obtained melt can be injected into a mold at a given pressure. Molded specimens of the usual dumb-bell shape for mechanical testing show a 35mm central bar with rectangular cross-section of 4×5.2 mm. In order to perform microhardness measurements, 2mm thick sections were cut with a microtome from the centre of the samples. 45 μ m slides were also used for water sorption experiments and for the recording of transmission infrared spectra. Processing parameters such as melt

temperature T_m and type of mold (elongational, intermediate or normal flow) during injection were varied. Preliminary studies showed that a 10°C step variation of the melt temperature from 130 up to 180°C does not significantly change the average microhardness H of the samples, which yields an approximate value of 120 MPa. Hence only two melt temperatures were chosen for the present study: a low temperature of 100°C and a higher one of 140°C with nozzle temperatures of 100 and 120°C respectively. The next question was to determine whether a change of melt flow during the injection process could affect the microhardness values and/or create any type of anisotropy within the samples. Among all the studied samples only one, produced under an elongational flow regime, shows a certain increase of the H -values at about 1mm from both surfaces. However, no hardness difference was found between the flow and the perpendicular directions (no traces of indentation anisotropy). In order to improve the smoothness of the samples surface and obtain well defined indentations, diamond paste with a particle size of 1 μ m was used to polish the surfaces. It was found that this method temporarily raises the humidity of the sample, producing a decrease in microhardness. Conventional H -values were recovered after 24 hours. Macroscopic density values of 2mm thick samples were obtained by means of a density gradient column with a mixture of carbon tetrachloride and dioxane. Transmission infrared spectra of 45 μ m films were recorded using a Perkin-Elmer FTIR spectrometer with a resolution of 2 cm^{-1} after five accumulated scans.

RESULTS

In order to compare the mechanical properties of two samples, one processed at low temperature ($T_m = 100^\circ\text{C}$) and the other one injection molded at high temperature (140°C), microhardness was analysed as a function of loading time (Fig. 1). It is observed that the microhardness values and the hardness rate of decrease with time (creep constant) are lower for the material processed at low T_m , which means that creep is slower for the low temperature sample. This result suggests that there must be some kind of variation in the amorphous structure of both materials to account for the strong differences in mechanical

properties observed.

The next arising question is to determine the temperature dependence of H for the two above mentioned materials. In what follows we shall use a constant loading time of 0.1 min, which has been commonly used as a compromise between reproducible hardness measurements and a minimum creep of the material ⁷. Measurements were performed at room conditions, i.e. at 25°C and an average relative humidity of 50%. Fig. 2 shows that H -values are always higher for the high temperature material. In addition, at least four temperature intervals can be defined for both injection temperatures where significant microhardness changes are detected:

- 1.- An H -increase from room temperature up to roughly 40°C.
- 2.- A "plateau" in the range 40–55°C.
- 3.- A new hardness increase from 55°C to 70°C.
- 4.- Finally, for $T > 70^\circ\text{C}$, a clear microhardness decrease for both samples.

The latter H -decrease could eventually be associated to the presence of the glass transition for potato starch. However, it is known ^{9,10} that the glass transition of partially dried starch occurs at a higher temperature. A possible explanation for the observed results could be related to a modification of the structure which leads to a degradation of the mechanical properties ¹¹.

Fig. 3 illustrates for the high temperature sample ($T_m = 140^\circ\text{C}$) the H -increase as a function of the square root of time t at 70°C. This temperature is the highest reachable one that can be used without the occurrence of any structural degradation (Fig. 2). Therefore, it has been chosen to analyse the total water evaporation from the studied injection molded samples. From this plot one may attempt to distinguish three different regimes of H -behaviour which can be associated to the first three regions in Fig. 2.

Another technique, which also provides information about the water content within starch, is the determination of the macroscopic density. The obtained results are summarised in Fig. 4, where density has been plotted against the square root of the condi-

tioning time at 70°C. The final experimental density value of the dry injected sample is found to be $1520 \pm 5 \text{ kg/m}^3$. On the other hand, the wet density values could be slightly overestimated with increasing water content in the gradient density column because of the existing solubility between water and dioxane. Dioxane acts as a drying agent in contact with starch because this solvent, although not capable to penetrate into the material due to its large molecular size, produces a certain extraction of water molecules. This effect should explain the large deviation observed for the untreated sample ($t=0$), which yields a density value of 1490 kg/m^3 in contrast to typical values of 1460 kg/m^3 found in the literature ¹². The change in the slope observed in Fig. 4 in the 6–8h time interval could again be related to the above mentioned time intervals in Figs. 2 and 3.

DISCUSSION

Hardness variation upon water removal: temperature and time dependence

The different regimes, observed as a function of temperature in Figs. 2 and 3 could be addressed in terms of different degrees of bound water present in the samples. A concept which has been often used to account for the different NMR relaxation times of water molecules found with increasing amount of adsorbed water in starch ¹³. However, according to calculations performed on an atomistic model for amorphous starch with different water content ⁸ it was found that the binding energy of water is constant with increasing water content. This means that each water molecule tends to form four hydrogen bonds, irrespective of whether the surrounding partner is starch or other water molecules. A result which seems to rule out the existence of especially bound water. However, as an excess-energy of evaporation is actually observed to increase with decreasing water content, this excess has been attributed to changes in the starch matrix upon addition or removal of water molecules ⁸. In preceding studies ^{14,15} the analysis of x-ray diffraction patterns of processed starch offered a possible explanation about the structural changes

occurring on injection molded material as a function of temperature. Accordingly, the first interval (H -increase) can be associated to a transformation of the majority of single helices into a network structure of double helices. The "plateau", showing a constant microhardness, could be due to the combination of two opposing effects: a densification of hard elements, which are the double helices and the partial destruction of some of these elements. Finally, the second H -increase found between 55°C and 70°C could be associated to the end of the plasticising effect of water and the increasing amount of contacts among starch molecules.

Weight loss analysis: influence of sample thickness

Having in mind that the microhardness increase, observed in Figs. 2 and 3, is mainly related to the water evaporation from the sample, we wish to discuss next the weight decrease as a function of time which is achieved by conditioning the material at 70°C. It is evident that the thickness of the sample plays here an important role in the water content evolution. Figs. 5a and 5b illustrate the weight-loss evolution for two samples of 45 μ m and 2mm thickness respectively. As expected, the thinner sample (prepared at both processing temperatures) loses a large amount of water in the first two minutes (Fig. 5a). The whole drying process is completed a few minutes later. On the contrary, the 2mm thick sample shows a rather continuous weight loss behaviour, that makes difficult to distinguish between the different mechanisms due to their mutual superposition (Fig. 5b).

Table 1 summarises the different adsorption/desorption limits of the thicker and thinner samples for the two investigated materials. A set of samples stored for 24 hours at room conditions were weighted. Thereafter, half of the samples were dried at 70°C and the other half were stored again in a humid atmosphere till weight constancy was reached. The differences between the initial weight values at room conditions and the final, dry or humid, values are collected in Table 1. According to these data, although the 2mm thick samples seem to contain a higher proportion of water than the thinner counterparts

under normal conditions, this is a clear artifact due to the instant uptake of water of the dry samples during the weight measurement. Both type of samples should contain similar relative amounts of water provided the same initial state of equilibrium. On the other hand after the measured time, thick samples show a lower relative capture of water in a humid atmosphere. The total weight difference (from dry to humid) is always lower for the thick samples, owing to the more difficult access to the inner regions. From the viewpoint of processing, it is noteworthy that the structure developed by the sample injected at high temperature seems to be able to accommodate a smaller amount of water than the low temperature one (last line in Table 1).

Most interesting is to plot the microhardness increase (Fig.3) as a function of the weight decrease measured shown in Fig. 5b. Fig. 6 reveals that the strongest increase (2/3) of microhardness does not correspond to the initial 7% weight loss, but rather to the final 3%. In accordance with Fig. 2, this would mean that the more pronounced H -enhancement corresponds to the interval where the last traces of water are evaporating and cannot act any more as a material softener. This notorious H -increase probably can be associated to the third mechanism of evaporation proposed in ref. ¹⁵.

High temperature treatment

In view of the higher H -values obtained for the higher injection molding temperature ($T_m=140^\circ\text{C}$) (see Fig. 2), we have tested a simple method of structure modification at still a higher temperature (200°C), for a very short time to prevent degradation. Our aim is here to attempt to stabilise the microhardness increase of starch by hindering the water penetration. The detailed weight loss of water due to treatment at 200°C can be studied by FTIR spectroscopy by following the band corresponding to the O-H deformation modes at 1640cm^{-1} (Fig. 7) ¹⁶. A Fickian diffusion, typical for high temperature treatments ¹⁵, is observed. Practically all the water is lost after the first 30 seconds of thermal treatment, without any appreciable changes in the other IR bands. Fig. 8 shows the different behaviour of the two injection molded samples ($T_m = 100^\circ\text{C}$ and $T_m = 140^\circ\text{C}$),

heated at 200°C for various times, with reference to the adsorption of water in a humid atmosphere. Fig. 8 also illustrates the excess of water increase in relation to a reference sample which was kept in a normal atmosphere. For $t = 0$, samples adsorb more than 15% excess water than the initial state. It is noteworthy that the adsorption capacity is hindered with increasing treatment time at 200°C. It is seen that the samples that were dried at 200°C, despite the drastic decrease in water content, show a considerable resistance against water adsorption in a humid atmosphere. In the extreme case of a fully dried sample (100s at 200°C) no more water is adsorbed in a humid atmosphere (see Fig. 7). This finding could be discussed as an extreme densification of the network of double helices that hinders the penetration of water molecules within the material.

CONCLUSIONS

1.- The dependence of the microhardness upon annealing temperature of injection molded starch can be discussed in terms of three different temperature intervals, corresponding to characteristic structural changes.

2.- These three regimes can be also characterised in an isothermal experiment as a function of diffusion time.

3.- The first regime involves a microhardness increase correlated to a strong weight loss of water. The second regime corresponds to a constancy of the H -value which is associated to a lower evaporation rate. The third regime is revealed by a very sharp H -increase which is associated to the evaporation of the small amount of remaining water.

4.- The first mechanism is associated to a structural transformation of the majority of single helices into double helices of amylopectin. This is followed by a second mechanism where densification of hard elements (double helices), as well as a partial destruction of some of these elements take place simultaneously. Finally, the third mechanism might be correlated to the end of the plasticising effect of water and the increasing amount of intermolecular contacts among starch molecules.

5.- The temperature of injection modifies the amorphous structure of injection molded

starch, which results in a higher microhardness for the higher injection temperature ($T_m=140^{\circ}\text{C}$). Starch samples annealed for short times at still higher temperatures (200°C) exhibit an enhanced resistance to water penetration.

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LEGEND TO THE FIGURES

Fig. 1: Log-log plot of microhardness as a function of loading time for the two materials processed at: $T_m = 100^\circ\text{C}$ (■) and $T_m = 140^\circ\text{C}$ (●).

Fig. 2: Microhardness as a function of temperature for the two investigated materials: $T_m = 100^\circ\text{C}$ (■) and $T_m = 140^\circ\text{C}$ (●). Vertical lines denote the proposed temperature intervals (see text).

Fig. 3: Microhardness as a function of the square root of drying time at 70°C for the higher temperature sample ($T_m = 140^\circ\text{C}$).

Fig. 4: Density variation as a function of the square root of drying time at 70°C for the higher temperature sample ($T_m = 140^\circ\text{C}$; thickness = 2 mm).

Fig. 5: Weight loss as a function of the square root of drying time at 70°C for two different sample thickness: a) $45\ \mu\text{m}$ and b) 2 mm.

Fig. 6: Microhardness data of Fig. 3 plotted as a function of weight loss of Fig. 5b.

Fig. 7: Weight loss in real time as a function of the square root of treatment time at 200°C followed by FTIR for $45\ \mu\text{m}$ samples. Same symbols as in Fig. 1.

Fig. 8: Relative water weight uptake for the two injection molded materials treated at 200°C (same symbols as in Fig. 1) for different times and thereafter exposed to a humid atmosphere for 24h.

Table 1: Relative weight variation (%) as compared with ambient conditions of two samples, both dry and humid, with different thickness.

T_m	140°C		100°C	
thickness	45 μ m	2mm	45 μ m	2mm
dry	-6.2	-7.6	-9.2	-12.2
humid	11.5	5.9	11.1	3.9
difference	17.7	13.5	20.3	16.1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8