Micromechanical properties of injection molded starch/wood-particle composites

A. Ueberschaer^{1*}, M. E. Cagiao¹, R. K. Bayer^{1*}, S. Henning², F. J. Baltá Calleja^{1}**

¹Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, Serrano 119, E-28006 Madrid, Spain

²Institute of Materials Science, Martin-Luther University Halle-Wittenberg, D-06099 Halle/Saale, Germany

ABSTRACT

The micromechanical properties of injection-molded starch/wood-particle composites were investigated as a function of particle content and humidity conditions. The composite materials were characterized by scanning electron microscopy and X-ray diffraction methods. The microhardness of the composites is shown to increase notably with the concentration of wood particles. In addition, the creep behavior under the indenter and the temperature dependence are discussed in terms of the independent contribution of the starch matrix and the wood microparticles to the hardness value. The influence of the drying time on the density and weight uptake of the injection-molded composites is highlighted. Results reveal the role of the mechanism of water evaporation involved, showing that the dependence of water uptake and temperature is higher for the starch/wood composites than for the pure starch sample. Experiments performed during the drying process at 70°C indicate that the wood present in starch composites does not prevent the water loss from the samples.

Key words: Potato starch; wood-powder; composites; microhardness; creep.

^{*}) Permanent Address: Institut für Werkstofftechnik, Universität Kassel, Mönchebergstrasse 3, D-34125 Kassel, Germany

****)** Correspondence to: F.J. Baltá Calleja (e-mail: embalta@iem.cfmac.csic.es)

INTRODUCTION

Polymer composites are a key component of current polymer research and technology [1]. This is due in part to the ease of production of new materials by mixing and the diversity of properties that result. Most important advantages are that both, their mechanical and their physical properties can be monitored in different ways by adding additives [2]. However, one negative aspect is their recycling ability. Due to the high amount of different polymers available, recycling of synthetic polymers is always complex and involves a high expenditure. For this reason, industry and science are dealing with the problem of substituting synthetic polymers by natural ones. Natural polymers can be conveniently recycled without harming the environment. Starch is one of the most interesting natural materials according to its physical and structure-forming properties as well as its high availability [3].

The research on starch-based polymers is already in progress for several years with the aim to modify its physical and mechanical structure to make it more resistant against humidity and flexible against external forces. The structure of starch in its native state and during gelatinization has been studied in recent years using small and wide-angle X-ray diffraction methods [4,5]. The processing of starch can be done by means of injection-molding, being nowadays a very common and efficient method [6]. Starch based materials will be interesting candidates in the near future, especially for packaging and car industry. Another tendency in this area has been the development of high strength synthetic polymer-starch composites aiming to the development of biodegradable materials [7].

Despite the fact, that wood flour has been known as an inexpensive filler in plastic compounds for many years, and that commercial wood-filled plastics are more and more common, the remaining problem is the low mechanical properties of wood-filled

composites [8]. The injection molding process for wood-filled thermoplastic materials opens up a new field for research and innovative applications.

The purpose of the present study is to examine the influence of wood-microparticles added to the starch samples into the resulting micromechanical properties of the injection-molded composites. Preceding microhardness studies have shown that microindentation is a promising technique for the nanostructural characterization of semicrystalline polymers and multicomponent systems [9]. This work also attempts to improve the starch resistance against the humidity. In recent years, the interaction of water with starch films and the influence of the processing methods on the structure and micromechanical properties of potato starch and its clay cement composites have been object of study [6, 10-12]. In addition, the structural changes induced on injection molded potato starch by heat treatment in water atmosphere have been also investigated [13].

EXPERIMENTAL

Materials

Native potato starch granules (Emsland Superior Stärke GmbH, Emlichheim, Germany) were used as basic material for the preparation of different injection-molded samples. After adding 10 wt% of water to the potato starch granules, the composite was stored in an air-tight box for 24 hours at room temperature to allow the water molecules to draw into the cores of the granules. It is known that the addition of water to starch leads to an improvement of the sample preparation. Thus, the water content depresses the melting point of the amylopectin crystallites and lowers the starch melt viscosity [11]. Wood powder (Lignocel Type RK 400, Faserstoff-Werke J. Rettenmaier & Söhne GmbH + Co, Rosenberg, Germany) was, then, added to the potato starch granules to obtain composites with varying wood content from: 0 up to 60 [wt %]. The composites were finally

processed by using an injection-molding machine (“Arburg Allrounder S250”, Arburg, Germany). The injection-molded parameters used for the different composites are listed in table 1. The mould used was dumbbell shaped with the usual size for mechanical testing. After injection molding, the specimens were stored in an air-tight box at room conditions (approx. average: 25°C, 47% humidity).

Techniques

For the microhardness measurements, a Leitz Tester (Wetzel, Germany) adapted with a Vickers (square-based) diamond was used with a loading time of 6s to minimize the creep of the material [9]. Before the measurements, the central bar of each sample was cut from its endings and divided into two pieces. All the microhardness measurements were performed on the outer surface of these pieces. Samples were previously polished with sandpaper with a granulation up to 4000 to improve the surface contrast properties. This treatment was done carefully to avoid heating up the samples at the surface and influencing its mechanical properties. Four different loads (15g, 25g, 50g, 100g) were used to analyze the microhardness dependence upon load. At least 10 different impressions for each load were made on the central part of the bar surface for each composite. For each composite two specimens were used to derive a representative average of the results. Both diagonals of each impression were measured to check whether there was any kind of indentation anisotropy due to the injection process. The microhardness values H were derived from the linear regression of P vs d^2 , following $H=1.85 P/d^2$, where d is the mean diagonal length of the indentation in meters and p the applied force in Newtons [9]. The microhardness was determined within $\Delta H/H \sim 0.03$. Figure 1 shows, as an example the plot of load vs d^2 for pure starch and for the 60%

composite, respectively. For the largest load used very large impressions were obtained (120-135 μm).

To determine the dependence of the microhardness upon the temperature, two different composites (0 wt %, 60 wt % wood content) were examined. Samples were fixed on a heating plate, which could be controlled by an external device. During the operation, the temperature was gradually increased from room temperature (25°C) up to 85°C within intervals of 5°C. Microhardness impressions with a load of 100 g and a loading time of 6 s were taken at each temperature interval. Before performing the microindentation experiment the temperature calibration was done by placing some crystalline chemicals with very precise melting points on the upper surface of the composite sample.

For the determination of the creep constant, (microhardness as a function of loading time), we have used a constant load of 25g and four different loading times (0.1, 1, 10, and 100 min).

Two mm thick samples were prepared for measuring their weight and density changes under different conditions. Samples with a wood content of 0 and 30wt % were studied. The samples were cut from the central bar immediately before the beginning of the experiment to avoid structural changes, especially those due to the drying process. Weight and density values were determined on every sample before and after subjecting them to different thermal treatments, i.e., a drying process at 70°C, and two wetting processes in a humid atmosphere at 40°C and 80°C, respectively, during selected time intervals. All these thermal treatments were performed in an oven previously heated at the selected temperature. In case of treatments made in a humid atmosphere, samples were introduced in the upper plate of an exiccator that contained some amount of water in its lower part. The exiccator was closed, leaving a very small opening in the closing valve, just enough to avoid the development of an excessive pressure inside the container.

Samples were weighted with a precision balance (Genius ME, Sartorius, Germany). For measuring the density, a density gradient column was prepared by using the pair of solvents CCl₄-n-hexane. During the filling process of this column, both solutions were mixed slowly. Hence a linear gradient with increasing density from the top to the bottom was established.

RESULTS

Structure and morphology

Scanning electron microscopy of the original starch injection molded samples and of the 60% wood composites are shown in Fig. 2. The surface of the injection molded composites is clearly covered by patches of irregular wood particles of widely varying sizes. Inspection of the films indicates that the larger particles (having average sizes between 50-100 μm) are surrounded by much smaller grains (1-20 μm). Wide angle X-ray diffraction patterns of the composites reveal the appearance of the X-ray diffraction reflections of wood, indicating that the amorphous structure of the starch matrix is not affected by the addition of the wood particles. In summary, from the X-ray diffraction results together with the microscopy observations one concludes that wood particles do not induce crystallization of starch. However, there may be hydrogen bonding between starch and wood particles because both are polar and hydrophilic and chemically similar.

Microindentation hardness measurements: dependence of wood-particle content, humidity and heat treatment.

The addition of wood microparticles to the starch samples leads to an increase in the microhardness as shown in Fig. 3. It is noteworthy that none of the examined samples showed any elastic recovery (see Fig. 1).

The temperature dependence of the composites hardness values is shown in Fig. 4. It is seen that both samples (wood-content 0% and 60%) exhibit the same tendency, showing a gradual hardness increase with increasing temperature, the H values for the sample containing the highest amount of wood-powder been notably higher than those for pure starch. These results are in agreement with the data obtained previously on injection molded pure starch samples [12].

From the plot of $\log H$ vs $\log t$ for the series of studied composites the creep constant k was derived as:

$$H(t) = H_0 t^{-k} \quad (1)$$

Fig. 5 shows the decrease of the creep constant k with increasing wood content. This result indicates that creep is slower for the samples with a high amount of wood-powder.

Density and weight changes upon drying and treatment in humid atmosphere

The drying experiment at 70°C leads to a weight loss of both samples (0 and 30% of wood content) (see Fig. 6a). Both samples show similar slopes, except during the first 4 hours. Furthermore, the weight loss of the starch/wood composite appears to be higher than for pure starch. The density of the examined samples (see Fig. 6b) shows an initial increase upon drying, followed by leveling-off tendency. It is to be noted that the addition of wood reduces the density of the starch sample. The density increase of the starch sample reaches a constant level 9 hours after the start of the treatment whereas the density of the starch/wood composite is almost constant after 4 hours. It is noteworthy that the density reaches a constant level whereas the weight loss continues up to the end of the treatment (after 30 hours).

Furthermore, the weight of the samples increases during their treatment in a humid atmosphere. We obtained an increase of 10.1% for the starch/wood composite and

8.9% for pure starch after 30 hours at 40°C (see fig. 7a). With 6.2% (0% wood) and 5% (30% wood), the measured increase was smaller for the samples treated at 80°C (compare Fig. 7b to Fig. 7a). At the end of each measurement the weight uptake seems to reach a limiting value.

In contrast to the drying process, the density of the samples decreases under the treatment in humid atmosphere (Figs. 8a and b). This corresponds to the weight uptake under these conditions. In both experiments (40°C, 80°C) we also obtained an initial change of density down to a constant level. For the 40°C treatment we observe a constant density level after approximately 16 hours that is almost similar for both samples. In case of 80°C, we observed a constant density level after 4 hours for the starch/wood composite and after 9 hours for pure starch.

DISCUSSION

Fig. 3 emphasizes the fact that H is a linear increasing function of the wood-particle content, w . Although we did not measure the hardness value of pure wood, it is possible to extrapolate the linear regression of Fig. 3 up to 100% of wood content. According to the plot of H vs. w (Fig. 3) the hardness of starch-wood composites can be described by the linear relationship:

$$H = w H_{St} + (1 - w) H_w \quad (2)$$

where, $H_{St} = 99,5 \text{ MPa}$ and $H_w = 153.5 \text{ MPa}$. Wu et al [14] and Curvelo et al [15] have shown that wood content induce a similar increase in flexural and tensile strength, and elastic modulus of the starch/wood fiber composites.

It is remarkable, that wood inspite of its lower density as compared to starch (as evidenced from Figures 6b and 8a, and b) shows higher hardness values. Equation 2

implies, that starch is not structurally influenced by the interaction with wood, H_{St} being constant throughout the whole concentration range. On the other hand, from eq. 2 it can be concluded that there must be a good contact between the starch matrix and the wood particles, probably due to hydrogen bonding formation. Fig. 2 confirms indeed the existing good interaction between the starch matrix and the microadditive. This might be understood from the mixing process of the two components in a rotating drum, which obviously produces electrical charges on the surfaces of the wood particles. The good contact between wood fibers and a thermoplastic starch matrix has been also pointed out by Curvelo et al [15].

The results shown in Fig. 5 show that the creep constant gradually decreases with increasing wood content of the samples, confirming that the addition of wood powder to the starch improves its mechanical properties. The fact that pure starch is the more flexible component in comparison to the stiffer one (wood) is reflected in the lower creep constant found for wood. In other words, the presence of wood particles influences the mechanical properties of the matrix.

The temperature dependence of microhardness yields a more or less a similar behavior for the two examined materials (pure starch and 60% of wood-content). The increase of the hardness values as a function of the temperature can be related to the amount of water within the samples. In a preceding study we showed that the hardness of starch is influenced by the amount of water present in the sample, the hardness values increasing with decreasing water content [10]. The water disrupts the hydrogen bonds between the starch molecules, diminishing the intermolecular forces and, hence, reduces the hardness of the material.

It is noteworthy the local maximum shown by both samples at about 70°C which is correlated to the occurrence of structural degradation [12]. One may think that, perhaps,

degradation is the reason why the indentations cannot be clearly seen at temperatures beyond 70°C.

The behavior of the samples subjected to the drying process at 70°C (Fig. 6) can be easily explained as due to the water removal from the samples. Taking into account the weight loss and density evolution for both series of samples, it seems apparent that the water content is higher in the starch-30% wood composite than in pure starch. In fact, the wood powder used to prepare the starch composites also contains some inherent humidity (see Table 2). This is probably the reason for the smaller density- and the higher weight-loss values found for the composites during all the drying process, as compared to those for the pure starch sample. According to the density evolution (Fig. 6b), the water-loss process seems to be completed after 4 hours of heating in the starch-30% wood composite, whereas it takes a longer time (about 9 hours) in case of pure starch. On the other hand, the rate of water loss is also initially higher in the composite samples. Therefore, it seems that the starch-wood composites contain a higher amount of water, though this water is easier to remove than in case of pure starch. For treatment times longer than 4 or 9 h, samples are still losing weight, whereas the density becomes constant. Due to the relation between density, weight and volume ($\rho = m/V$), we suggest that, beyond the treatment time in which density keeps constant, there must be some microvoid formation within the samples.

Conversely to the results obtained during the drying process, during thermal treatment in humid atmosphere, both at 40 and 80°C, the weight of the composites clearly increases (Fig. 7). The density evolution of the samples agrees well with the weight uptake under these conditions (see Fig. 8). Both effects are thought as due to the water absorption from the samples, favored by the high temperature and the humid atmosphere.

We assume that the lower water uptake for the samples treated at the higher temperature, in contrast to that for the samples at lower temperatures, is caused by the equilibrium between the evaporation and penetration of the water. At lower temperatures the evaporation of water is smaller leading to a higher water uptake.

CONCLUSIONS

- Results show that the hardness of the starch-wood particle composites notably increases with the wood-particle content.
- The dependence of the water uptake and temperature for, both, the starch/wood composites and the pure starch sample is higher at lower temperatures.
- The weight loss and uptake ability of the wood-starch composite is higher than for starch alone, in agreement with the results obtained during the drying process at 70°C.
- The presence of wood particles in the starch composites seems not to prevent the water loss of the samples.

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FIGURE CAPTIONS

- Fig. 1. Applied load as a function of squared indentation diagonal for injection-molded pure starch (white symbols) and 60% wood composite (dark symbols). Squares and circles correspond to measurements performed on two different specimens for each composite.
- Fig. 2. Scanning electron micrographs: (a) injection molded starch and (b) 60% wood composite
- Fig. 3. Plot of microhardness (H) as a function of wood-particle content (%) for the composites investigated
- Fig. 4. Variation of H as a function of T for pure starch and the 60% wood composite
- Fig. 5. Variation of the creep constant as a function of wood-particle content for the various composites.
- Fig. 6. Changes in weight loss (a) and density (b) after drying the pure starch sample and the 30% wood composite at 70°C
- Fig. 7. Weight uptake after wetting pure starch and 30% wood composite at: (a) 40°C and (b) 80°C
- Fig. 8. Density changes of pure starch and the 30% wood composite in a humid atmosphere at: (a) 40°C and (b) 80°C

Tab. 1: Parameters of the injection-molding process for different composites

Parameter	Unit	Pure starch				Starch and wood-powder			
Injection Pressure	bar	1300				1300			
Holding pressure	bar	800	200	50	25	350	200	50	25
Time of holding pressure	s	1	5	2	0,5	1	5	1	0,5
Cooling time	s	80				60			
Injection speed	mm/s	45				45			

Tab. 2: Weight changes [%] of the wood particles under different conditions

Conditions	Sample 1	Sample 2
Drying (250C, 95s)	-3.66	-3.68
Wetting (25C, 21h)	+14.20	+16.22

Fig. 1

a)

b)

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6a.

Fig. 6b.

Fig. 7a.

Fig. 7b.

Fig. 8a.

Fig. 8b.