

Micromechanical Properties of Injection-Molded Starch–Wood Particle Composites

A. Ueberschaer,¹ M. E. Cagiao,¹ R. K. Bayer,¹ S. Henning,² F. J. Baltá Calleja^{1,*}

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

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

Received 21 March 2005; accepted 8 July 2005

DOI 10.1002/app.23304

Published online in Wiley InterScience (www.interscience.wiley.com).

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 was shown to increase notably with the concentration of the wood particles. In addition, creep behavior under the indenter and temperature dependence were evaluated in terms of the independent contribution of the starch matrix and the wood microparticles to the hardness value. The influence of drying time on the density

and weight uptake of the injection-molded composites was highlighted. The results revealed the role of the mechanism of water evaporation, showing that the dependence of water uptake and temperature was greater for the starch–wood composites than for the pure starch sample. Experiments performed during the drying process at 70°C indicated that the wood in the starch composites did not prevent water loss from the samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4893–4899, 2006

Key words: polysaccharides/hardness composites; creep

INTRODUCTION

Polymer composites are a key component of current polymer research and technology.¹ This is in part because of the ease of production of new materials by mixing and the diversity of properties that result. The 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. Because of the high amounts of different polymers available, recycling of synthetic polymers is always complex and involves high expenditures. For this reason, industry and science are tackling this problem by investigating the substitution of synthetic polymers

for 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

Research on starch-based polymers has already been in progress for several years, with the aim of modifying the physical and mechanical structures of such polymers to make them more resistant to humidity and more 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} Processing of starch can be done by injection molding, which nowadays is a very common and efficient method.⁶ Starch-based materials will be interesting candidates in the near future, especially for the packaging and car industries. Another aspect of research in this area has been the development of high-strength synthetic polymer–starch composites with the aim of developing biodegradable materials.⁷

Despite that for many years wood flour has been known as an inexpensive filler in plastic compounds and that commercial wood-filled plastics are more and more common, low mechanical properties remain a problem with wood-filled composites.⁸ The injection-molding process for wood-filled thermoplastic materials opens a new field for research and innovative applications.

The purpose of the present study was to examine the influence of wood microparticles added to starch

*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)

Contract grant sponsor: MEC, Spain; contract grant number: FIS2004-01331).

Contract grant sponsor: Alexander von Humboldt Foundation, Bonn, Germany.

Contract grant sponsor: Secretaría de Estado de Universidades e Investigación, MEC, and European Social Fund (to R.K.B.); contract grant number: SAB2003-0131.

Contract grant sponsor: Deutsche Forschungsgemeinschaft, DFG (to R.K.B.).

Contract grant sponsor: “Leonardo” Programme (to A.U.).

TABLE I
Parameters of 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		

samples in the resulting micromechanical properties of the injection-molded composites. Previous microhardness studies have shown that microindentation is a promising technique for the nanostructural characterization of semicrystalline polymers and multicomponent systems.⁹ The present work also attempted to improve the resistance of starch to 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 objects of study.^{6,10-12} In addition, the structural changes induced in injection-molded potato starch by heat treatment in water atmosphere also have been investigated.¹³

EXPERIMENTAL

Materials

Native potato starch granules (Emsland Superior Stärke GmbH, Emlchheim, Germany) were used as the basic material for the preparation of different injection-molded samples. After adding 10 wt % water to the potato starch granules, the composite was stored in an airtight box for 24 h 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 improvement in sample preparation. Thus, the water content decreased the melting point of the amylopectin crystallites and lowered 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 in order to obtain composites whose wood content varied from 0 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 I. The mold used was dumbbell shaped and of the size usually used for mechanical testing. After injection molding, the specimens were stored in an airtight box at room conditions (approximate averages: 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 6 s to minimize the creep of the material.⁹ Before measuring, the central bar of each sample was cut from its endings and divided in two. All microhardness measurements were performed on the outer surface of these pieces. Samples previously had been polished with sandpaper with a granulation of 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 loads (15, 25, 50, and 100 g) were used to analyze the microhardness dependence upon load. At least 10 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 for any kind of indentation anisotropy from the injection process. Microhardness values (H) were derived from linear regression of P versus d^2 , following $H = 1.85 P/d^2$, where d is the mean diagonal length of the indentation in meters and P is the applied force in Newtons.⁹ Microhardness was determined within $\Delta H/H \sim 0.03$. Figure 1 shows, as an example, the plots of load versus d^2 for pure starch and for the 60% composite. For the largest load used, very large impressions were obtained (120–135 μm).

To determine the dependence of microhardness on temperature, two composites (0 and 60 wt % wood content) were examined. Samples were fixed on a heating plate that could be controlled by an external device. During the operation, the temperature was gradually increased from room temperature (25°C) to 85°C in 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, temperature calibration was done by placing some crystalline chemicals with very precise melting points on the upper surface of the composite sample.

For determination of the creep constant (microhardness as a function of loading time), we used a constant

load of 25 g and four loading times (0.1, 1, 10, and 100 min).

Two-millimeter-thick samples were prepared for measuring the changes in their weight and density under different conditions. Samples with a wood content of 0 and 30 wt % were studied. The samples were cut from the central bar immediately before the beginning of the experiment in order to avoid structural changes, especially those resulting from the drying process. The weight and density of sample were determined before and after their being subjected to different thermal treatments, that is, a drying process at 70°C and two wetting processes in a humid atmosphere at 40°C and 80°C during the selected time intervals. All these thermal treatments were performed in an oven previously heated at the selected temperature. For treatments done in a humid atmosphere, the samples were introduced into the upper plate of a dessicator 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 excessive pressure developing inside the container. Samples were weighted with a precision balance (Genius ME, Sartorius, Germany). To measure density, a density gradient column was prepared by using a pair of CCl_4 -*n*-hexane solvents. During the process of filling this column, both solutions were mixed slowly, establishing a linear gradient with density increasing from the top to the bottom.

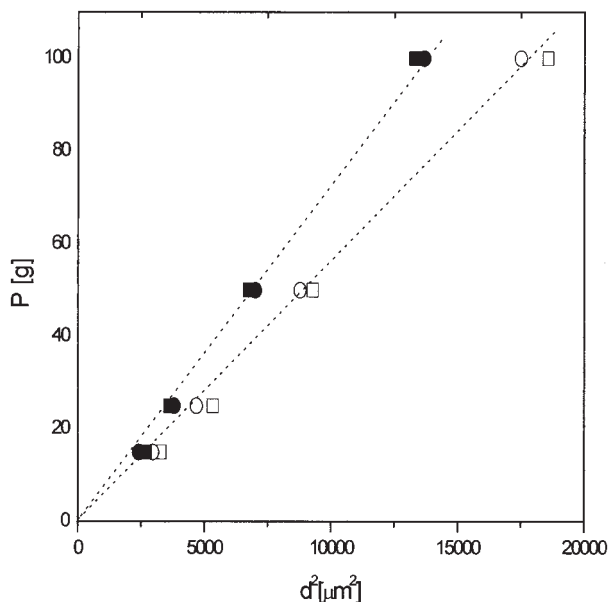
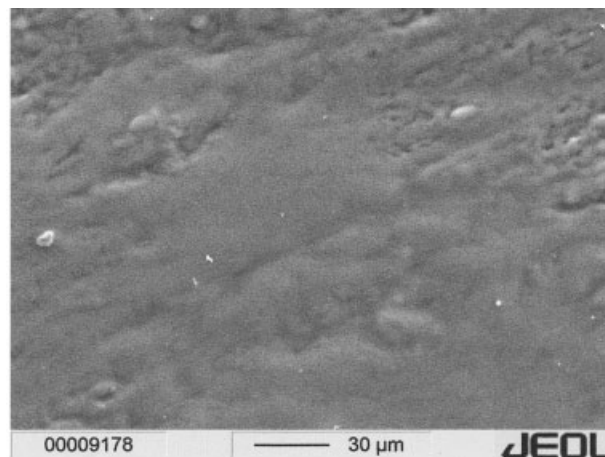
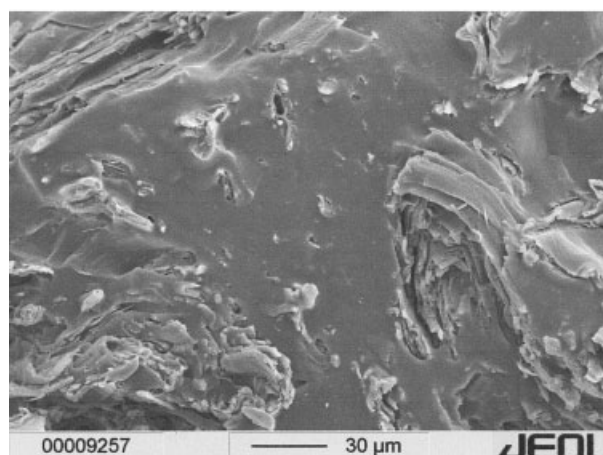


Figure 1 Applied load as a function of squared indentation diagonal for injection-molded pure starch (white symbols) and 60% wood composite (dark symbols). Squares and circles correspond to the measurements of two specimens for each composite.



a)



b)

Figure 2 Scanning electron micrographs of: (a) injection-molded starch and (b) 60% wood composite.

RESULTS

Structure and morphology

Scanning electron microscopy of the original starch injection-molded samples and of the 60% wood composites is shown in Figure 2. The surface of the injection-molded composites is clearly covered by patches of irregular wood particles of widely varying size. Inspection of the films indicated that the larger particles (having average sizes between 50 and 100 μm) were surrounded by much smaller grains (1–20 μm). The wide-angle X-ray diffraction patterns of the composites revealed the appearance of X-ray diffraction reflections of the wood, indicating that the amorphous structure of the starch matrix was not affected by the addition of the wood particles. In summary, from the X-ray diffraction results together with the microscopy observations, it can be concluded that wood particles

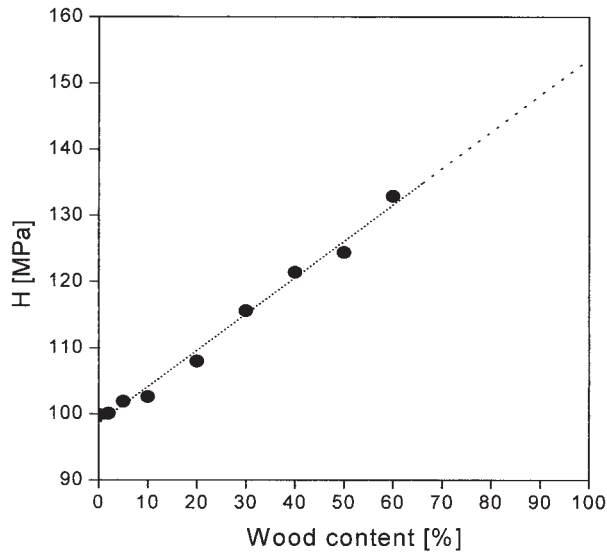


Figure 3 Plot of microhardness (H) as a function of wood-particle content (%) for the composites investigated.

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 led to an increase in microhardness, as shown in Figure 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 Figure 4. It can be seen that both samples (wood content 0% and 60%) exhibited the same tendency, showing a gradual increase in hardness with increasing temperature, with the H values of the sample containing the highest amount of wood-powder notably higher than those of pure starch. These results are in agreement with previous data on injection-molded pure starch samples.¹²

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

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

Figure 5 shows the decrease in the creep constant with increasing wood content. This result indicates that creep was slower for the samples with a high amount of wood powder.

Density and weight changes upon drying and treatment in a humid atmosphere

The drying experiment at 70°C led to a weight loss of both samples [0% and 30% wood content; see Fig.

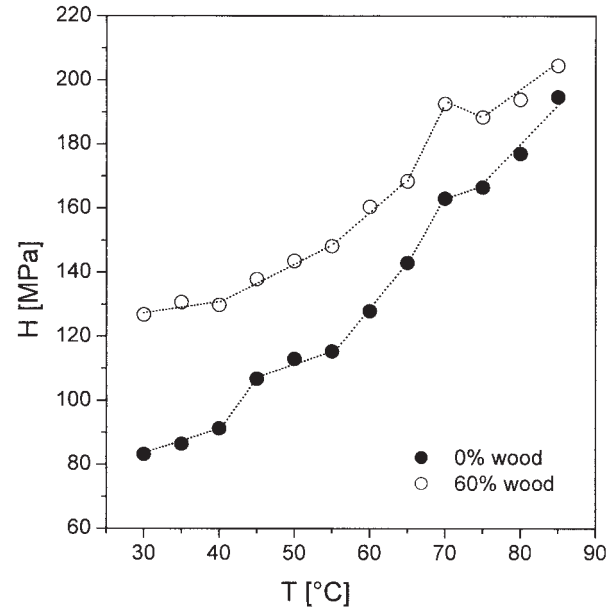


Figure 4 Variation in H as a function of T for pure starch and the 60% wood composite.

6(a)]. Both samples showed similar slopes, except during the first 4 h. Furthermore, the weight loss of the starch/wood composite appeared to be higher than that for pure starch. The density of the examined samples [see Fig. 6(b)] showed an initial increase upon drying, followed by a leveling-off tendency. It should be noted that the addition of wood reduces the density of the starch sample. The density increase of the starch sample reached a constant level 9 h after the start of the treatment, whereas the density of the starch/wood

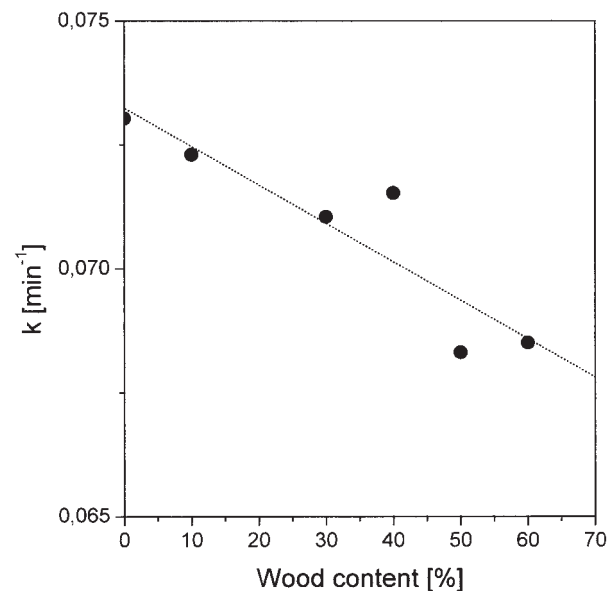


Figure 5 Variation in the creep constant as a function of wood-particle content for the various composites.

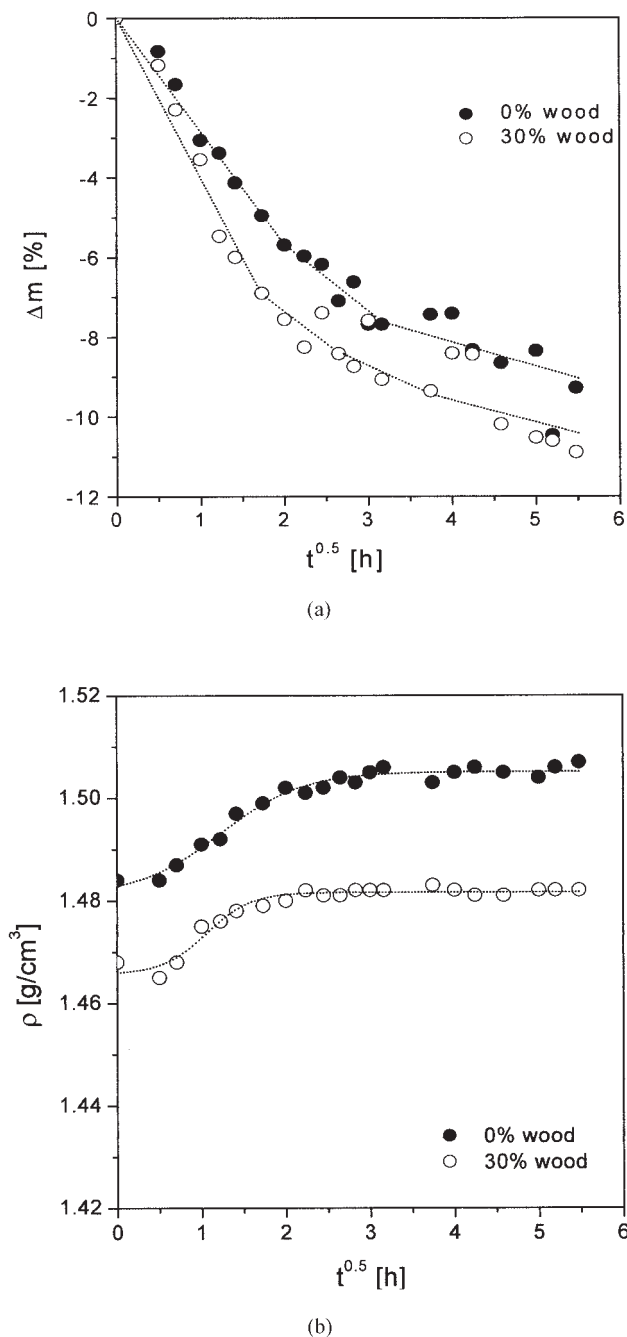


Figure 6 Changes in (a) weight loss and (b) density after drying the pure starch sample and the 30% wood composite at 70°C.

composite was almost constant after 4 h. It is noteworthy that the density reached a constant level, whereas the weight loss continued to the end of the treatment (after 30 h).

Furthermore, sample weight increased during the treatment in a humid atmosphere. We obtained an increase of 10.1% for the starch-wood composite and of 8.9% for pure starch after 30 h at 40°C [see Fig. 7(a)]. With 6.2% (0% wood) and 5% (30% wood), the measured increase was smaller for the samples treated at

80°C [compare Fig. 7(b) to Fig. 7(a)]. At the end of each measurement, the weight uptake seemed to reach a limiting value.

In contrast to the results from the drying process, the density of the samples decreased after the treatment in a humid atmosphere [Fig. 8(a,b)]. This corresponds to the weight uptake under these conditions. In both experiments (40°C and 80°C), we also obtained an initial change in density down to a constant level. For the 40°C treatment, we observed a constant den-

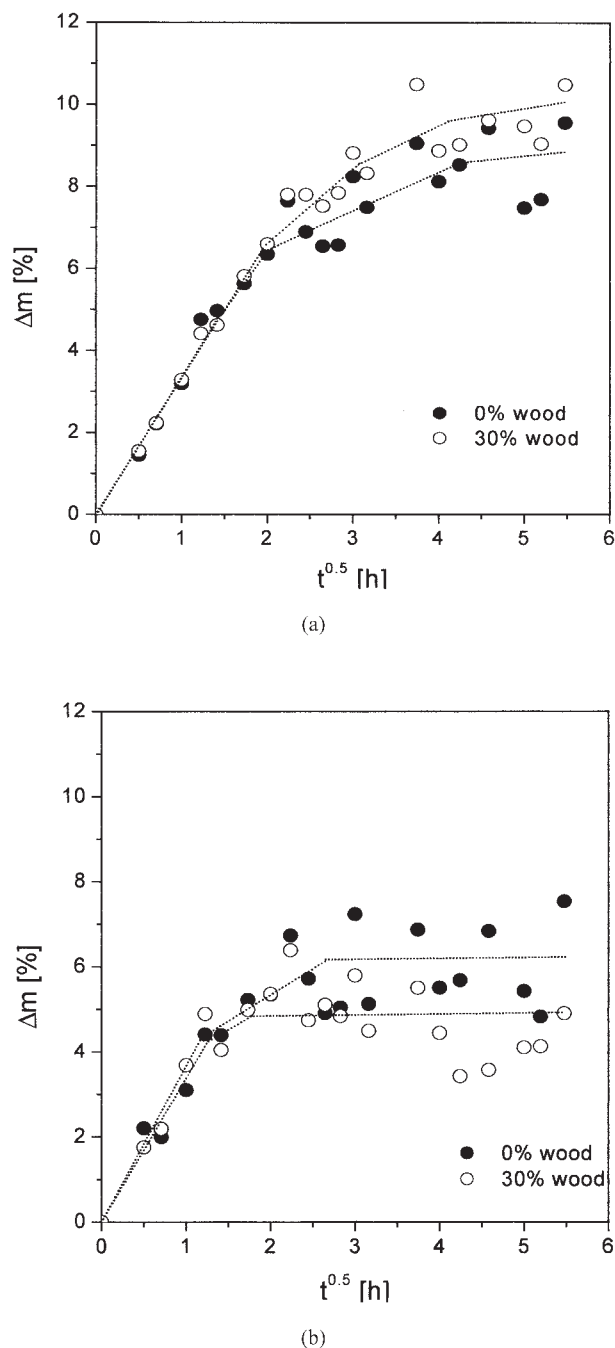


Figure 7 Weight uptake after wetting pure starch and the 30% wood composite at: (a) 40°C and (b) 80°C.

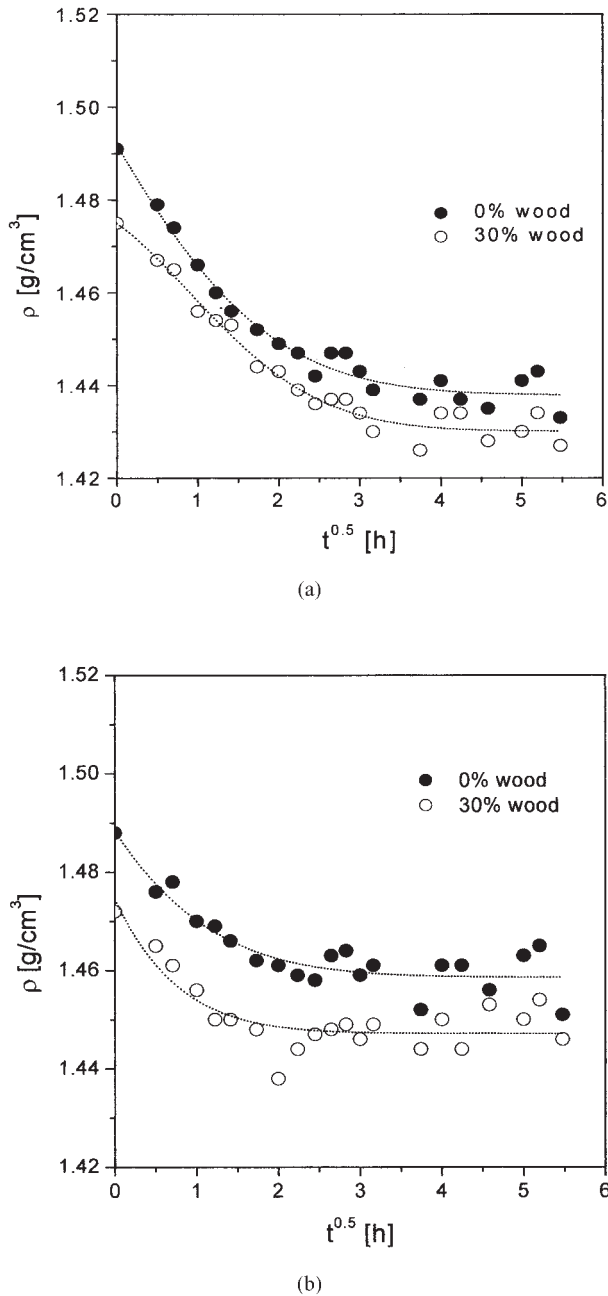


Figure 8 Density changes in pure starch and the 30% wood composite in a humid atmosphere at: (a) 40°C and (b) 80°C.

sity after approximately 16 h that was similar for both samples. For the 80°C treatment, we observed a constant density after 4 h for the starch/wood composite and after 9 h for the pure starch.

DISCUSSION

Figure 3 shows that H is an increasing linear function of the wood-particle content, w . Although we did not measure the hardness of the pure wood, it is possible to extrapolate the linear regression of Figure

3 up to a 100% wood content. According to the plot of H versus w (Fig. 3), the hardness of the starch-wood composites can be described by the linear relationship

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

where $H_{St} = 99.5$ MPa and $H_w = 153.5$ MPa. Wu et al.¹⁴ and Curvelo et al.¹⁵ showed that wood content induce a similar increase in the flexural and tensile strength and the elastic modulus of starch/wood fiber composites.

It is remarkable that the wood, despite being lower in density than the starch [as shown in Figs. 6(b) and 8(a,b)], showed higher hardness values. Eq. (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 good contact between the starch matrix and the wood particles, probably because hydrogen bonding formation. Indeed, Figure 2 confirms the existing good interaction between the starch matrix and the microadditive. This might be understood by 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 also was pointed out by Curvelo et al.¹⁵

The results shown in Figure 5 indicate that the creep constant gradually decreased with an increasing wood content of the samples, confirming that the addition of wood powder to the starch improved its mechanical properties. That the pure starch component is more flexible component than the stiffer one (wood) is reflected in the lower creep constant found for wood. In other words, the presence of wood particles influenced the mechanical properties of the matrix.

The temperature dependence of microhardness yielded more or less a similar behavior for the two examined materials (pure starch and 60% wood content). Increased hardness values as a function of 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 in the sample, with hardness increasing with decreasing water content.¹⁰ Water disrupts the hydrogen bonds between starch molecules, diminishing intermolecular forces and hence reducing the hardness of the material.

It is noteworthy that the local maximum shown by both samples, about 70°C, was correlated with structural degradation.¹² Perhaps degradation is the reason why indentations could not 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 resulting from removal of water from the samples.

TABLE II
Weight Changes (%) of Wood Particles under
Different Conditions

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

Taking into account the weight loss and density evolution for both series of samples, it seems apparent that water content was higher in the starch-30% wood composite than in the pure starch. In fact, the wood powder used to prepare the starch composites also contained some inherent humidity (see Table II). This is probably the reason for the lower density and higher weight loss found for the composites during the entire drying process, as compared to those for the pure starch sample. According to the density evolution [Fig. 6(b)], the water-loss process seemed to be completed after 4 h of heating in the starch-30% wood composite, whereas it took longer (about 9 h) in the pure starch. In contrast, the rate of water loss also was initially higher in the composite samples. Therefore, it seems that the starch-wood composites contained a greater amount of water, though this water was easier to remove than, than did the pure starch. With treatment times longer than 4 or 9 h, the samples continued to lose weight, whereas density became constant. Because of the relation between density, weight, and volume ($\rho = m/V$), we suggest that, beyond the treatment time in which density stays constant, there must be some microvoid formation within the samples.

In contrast to the results obtained during the drying process, during thermal treatment in a humid atmosphere both at 40°C and 80°C, the weight of the composites clearly increased (Fig. 7). The density evolution of the samples agreed well with the weight uptake results under these conditions (see Fig. 8). Both effects are thought to have been the result of water absorption from the samples, which was favored by the high temperature and the humid atmosphere.

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

CONCLUSIONS

- The results showed that the hardness of the starch/wood particle composites notably increased with the wood-particle content.
- Both the starch/wood composites and the pure starch sample were more water uptake and temperature dependent at lower temperatures.
- The weight loss and uptake ability of the wood-starch composite were higher than those of starch alone, in agreement with the results obtained during the drying process at 70°C.
- The presence of wood particles in the starch composites did not seem to prevent the water loss of the samples.

The Arburg Company in Lossburg, Germany, is acknowledged for the kind supply of the injection-molding machine used in this study.

References

1. Meyers, M. A.; Ritchie, R. O.; Sarikaya, M., Eds. *Nano and Microstructural Design of Advanced Materials*; Elsevier: Amsterdam and New York, 2003.
2. Shonaike, G. O.; Advani, S. G., Eds. *Advanced Polymeric Materials: Structure Property Relationships*; CRC Press: Boca Raton, FL, 2003.
3. Poutanen, K.; Forssell, P. *Trends Polym Sci* 1996, 4, 128.
4. Jenkins, P.J.; Donald, A. M. *Carbohydr Res* 1998, 308, 133.
5. Waigh, T. A.; Perry, P.; Riekkel, C.; Gidley, M. J.; Donald, A. M. *Macromolecules* 1998, 31, 7980.
6. Flores, A.; Bayer, R. K.; Krawietz, K.; Baltá Calleja, F. J. *J Macromol Sci Phys* 2000, B38, 749.
7. Nakashima, T.; Matsuo, M. *J Macromol Sci Phys* 1996, B35, 659.
8. Rowel, R. M. In *Science and Technology of Polymers and Advanced Materials*; Prasad, P. N.; Mark, J. E.; Kandil, S. H.; Kafafi, Z. H. Plenum Press: New York, 1998; p 869.
9. Baltá Calleja, F. J.; Fakirov, S. *Microhardness of Polymers*; Cambridge University Press: Cambridge, UK, 2000.
10. Baltá Calleja, F. J.; Rueda, D. R.; Secall, T.; Bayer, R. K.; Schlimmer, M. *J Macromol Sci Phys* 1999, B38, 461.
11. Benczédi, D.; Tomka, I.; Escher, F.; *Macromolecules* 1998, 31, 3055.
12. Ania, F.; Dunkel, M.; Bayer, R. K.; Baltá Calleja, F. J. *J Appl Polym Sci* 2002, 85, 1246.
13. Cagiao, M. E.; Rueda, D. R.; Bayer, R. K.; Baltá Calleja, F. J. *J App Polym Sci* 2004, 93, 301.
14. Wu, Q. X.; Sakabe, H.; Isobe, S. *Ind Eng Chem Res* 2003, 2, 6765.
15. Curvelo, A. A. S.; de Carvalho, A. J. F.; Agnelli, J. A. M. *Carbohydr Polym* 2001, 45, 183.