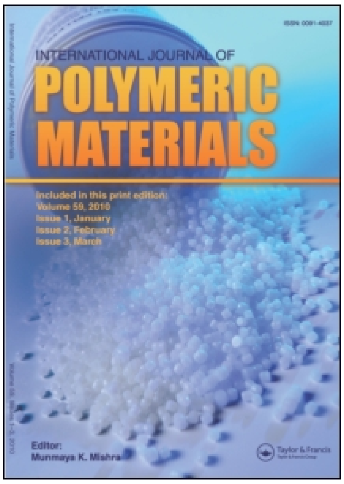

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Wood pulp reinforced thermoplastic starch composites

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WOOD PULP REINFORCED THERMOPLASTIC STARCH COMPOSITES

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Thermoplastic starch is potentially a low cost alternative biodegradable plastic that is readily available material, but owing to its poor mechanical properties and high susceptibility to water, its actual replacement of the polymers currently in use is limited. In this study we investigated the employment of wood pulp as fiber reinforcement for thermoplastic starch. The composites were prepared with regular cornstarch plasticized with glycerol in the presence of fiber. The matrix compositions were starch/glycerol 70/30, 80/20 and 90/10 (w/w). The wood pulp fiber content was varied from 5 to 15% by weight. The composites were characterized by mechanical tests, scanning electron microscope and water absorption experiments at 97% relative humidity. It was found that the addition of fiber led to a large increase in the elastic modulus and tensile strength and that these effects are very dependent on the glycerol content. The water absorbed by the composites was sharply reduced by the addition of pulp, and seems to be independent of the amount of glycerol and pulp content. Scanning electron microscopy of fracture surfaces revealed that fibers were well dispersed in the matrix and were strongly bonded to it.

Keywords: thermoplastic starch, composite, cellulose, wood pulp, mechanical properties, water absorption

1. INTRODUCTION

The widespread use of synthetic plastics verified over the past half century become these materials the best candidate for replacement of everything from packaging to construction material in the aerospace industry. The production of plastic still continues to grow and for example in the packaging industry, it is growing at a rate of about 25 per cent per year [1]. Nowadays the total volume of plastic produced worldwide exceeds that of steel [2]. One of the

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Address correspondence to A. A. S. Curvelo, Instituto de Química de São Carlos – CP 780 – CEP 13560-750 – São Carlos – Brasil. E-mail: aprigio@iqsc.sc.usp.br main uses for plastics is in packaging, where they are used as a substitute for paper, aluminum, steel and, recently, for products made traditionally of glass. This success is due to the ease with which polymers are processed, low energy consumption during fabrication [2] and their inertness, that makes them suitable to be used in all areas. However, this rapid expansion in plastic material consumption is causing a huge problem in waste management. Several alternative waste treatment methods have been considered, such as reusing, recycling, incineration, pyrolysis and substitution by biodegradable or compostable materials.

Many efforts have been made in recent years to develop biodegradable materials, particularly compostable plastics, *i.e.*, plastics that degrade easily under well-defined environmental conditions [3]. These materials may be synthetic, natural, or a combination of both. One of the most studied and promising raw materials for the production of biodegradable plastics is starch, which is a natural renewable polysaccharide obtained from a great variety of crops, that is readily available and of low cost, especially when compared to synthetic plastics.

The use of starch to produce biodegradable plastics began in the 1970s. In the granular state, it was used as filler for polyolefins [4, 5] and as a component in synthetic polymer blends with a totally disrupted starch granule structure [6, 7]. Starch has also been modified by grafting vinyl monomers (*e.g.*, methyl acrylate) onto the starch backbone, yielding thermoplastic materials that can be injection-molded or extruded into films with properties similar to low density polyethylene [8]. Thermoplastic starch [9–11] is a relatively new material for application as a biodegradable plastic and is one of the main polymers studied today in this field. It is used alone or compounded, usually, with polar synthetic polymers, in contents that usually exceed 50%.

Starch is not a true thermoplastic but, in the presence of plasticizers, (water, glycerin, sorbitol, *etc.*) at high temperatures (90–180°C) and under shear, it readily melts and flows, enabling its use as an injection, extrusion or blow-molding material, similarly to most conventional synthetic thermoplastic polymers.

Thermoplastic starch has two main disadvantages in comparison with most plastics currently in use, namely it is mostly water-soluble and has poor mechanical properties. Its water resistance may be improved by mixing it with certain synthetic polymers [11], adding crosslinking agents such as Ca and Zr salts [12] and lignin [13]. Their mechanical properties have usually been improved by adding synthetic polymers, such as EAA (ethylene-acrylic acid copolymer) and EVOH (ethylene-vinyl alcohol copolymer) [11, 14]. Another approach that has been considered for this purpose is the use of fibers as reinforcement for thermoplastic starch. In general, fiber reinforced polymers are used whenever there is a need to combine high mechanical properties with low weight. Glass, carbon and aramide fibers are of high importance in industry in technical applications such as in the automotive and aerospace sectors. The use of natural fibers as a reinforcing component for thermoplastic and injection moldable materials has been much studied for polymers such as polypropylene [15, 16], polyethylene [17] and polystyrene [18], and for thermosetting resins such as epoxy, polyester and phenolic resins [19, 20]. Natural fibers, compared to the widely used glass fiber, afford these composites their low weight and high specific strength and the possibility of combination with polar matrix, without the need for compatibilizing agents. During processing, the natural fibers have a low abrasion effect, thus preserve the fabricating equipments for longer. Finally, natural fibers are renewable resource with a low cost, compared to glass or other synthetic fibers. However, when natural fiber is used with synthetic matrix, they are protected from the environment, and could not be biodegraded. Also they can impede recycling because of their sensitivity to the severe reprocessing conditions. The use of natural fibers to reinforce biodegradable polymers, such as thermoplastic starch, is a new approach. This is also a very new subject in the literature and few publications about it are available. The fibers that have been described for this purpose are cellulose microfibrils [21], natural fibers such as flax, ramie, jute, *etc*. [22, 23], commercial regenerated cellulose fibers [23, 24] and recently bleached wood pulp [25]. Hydroxyapatite [26] and Kaolin [27] were already reported as reinforcing agents for thermoplastic starch.

This paper reports the properties of thermoplastic starch composites prepared with glycerol as plasticizer and kraft bleached and thermomechanical wood pulp from *Eucalyptus urograndis* and *Eucalyptus grandis* respectively, as reinforcement. Wood pulp is the raw material for the production of many products, the main product in importance and volume being paper. Both bleached and thermomechanical wood pulp are standardized raw materials readily available at a low price and specified by international standards, aspects that make these short fibers very attractive sources for thermoplastic reinforced composites production.

2. MATERIALS AND METHODS

2.1. Materials

In this study, two different pulps were evaluated as reinforcing agent in thermoplastic starch (TPS). The first one was bleached kraft pulp from *Eucalyptus urograndis* supplied by Aracruz Celulose S.A. (Brazil), having 8 to 10% moisture and an average fiber length of 1 mm. The second was unbleached thermomechanical pulp of *Eucalyptus grandis* (TMP) supplied by Melhoramentos S.A. (Brazil), having 65% moisture and an average fiber length of 0.75 mm. The sizes of fibers were determined by optical light microscopy at 50 X magnification of a 2% water suspension.

The kraft pulp was previously dispersed in a Turrax by the following procedure. Ten grams of pulp was suspended in 1500 cm^3 of water and dispersed in the Turrax mixer operated at approximately 20,000 rpm for 3 minutes. Dispersion efficiency was checked by observation of a sample under 20X magnification lens. The dispersed fibers were filtered through a 0.088 mm aperture sieve and pressed until approximately 200% excess of water (w/w) was achieved. The TMP pulp was used directly as received.

2.2. Matrix and Composites

Regular cornstarch (28% amylose) supplied by Corn Products Brasil Ltd. and reagent grade glycerol was used to prepare the thermoplastic starch. Starch and glycerol were pre-mixed in polyethylene bags until a homogeneous mass or powder was obtained. The amount of fiber in the composite was calculated as a percentage of the total dry weight of starch plus glycerin.

The composites were prepared in a Haake Rheomix 600 batch mixer equipped with roller rotors. The starch, glycerol and fiber mixture was loaded into the pre-heated mixer chamber at 150°C. The rotors were operated at 50 rpm and the mixing time was 6 minutes. The compositions of prepared materials are presented in Table 1.

2.3. Specimen Preparation and Mechanical Tests

The mass taken from the mixer was hot pressed at 160°C to produce 100 × 100 mm plates with 2.5 mm thickness. The stress-strain tests were performed with an Instron model 5500 R testing machine, operated at a

TABLE 1 Non-reinforced TPS and composites formulations (percentage by weight)

Formulation code	*Starch/glycerol ratio*	*Fiber content (wt. %) (with respect to the matrix)*
G30	70/30	–
G40	60/40	–
G50	50/50	–
G30F5	70/30	5
G30F10	70/30	10
G30F15	70/30	15
G40F10	60/40	10
G50F5	50/50	5
G50F10	50/50	10
G50F15	50/50	15

Note: The number after the letter "G" denotes the glycerol concentration in the matrix and the number after the letter "F" denotes the content of fiber.

velocity of 50 mm/min. From the stress-strain curves were determined the ultimate tensile strength (UTS), the secant elastic modulus at 1% strain ($E_{1\%}$) and strain at break (ε_r). Five specimens for each composition were cut with a dumb-bell shape and were tested after a four-week period of conditioning at 25°C and 53% relative humidity (RH). The specimen shapes and the general conditions were in accordance with ASTM D 638M [28].

2.4. Scanning Electron Microscopy (SEM)

Fragile fractured surfaces of composite samples, fractured in liquid nitrogen, were studied with a LEO 440 scanning electron microscope, with a tungsten filament operated at 8 to 15 kV. The samples were coated with 200 Å of gold.

2.5. Water Absorption Experiments

The specimens (10 mm × 20 mm × 2.5 mm) were dried overnight at 105°C before the absorption experiments. The samples were conditioned in hermetic containers with 97% relative humidity at 25 ± 2°C using saturated K_2SO_4 salt solution, as specified in ASTM E 104 [29]. The amount of water absorbed by the samples was determined by weighting the samples periodically until constant weights were reached. The water uptake of the samples was calculated as follows:

$$\text{water uptake } (\%) = \frac{M - M_o}{M_o} \times 100$$

where M is the weight at time t and M_o is the weight before exposure to 97% RH and corresponds to the weight of dry sample.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties

The data obtained from the mechanical tests for the modulus, ultimate tensile strength and elongation at break are presented in Table 2.

The data for tensile strength (UTS) and modulus ($E_{1\%}$) are plotted respectively in Figures 1 and 2 as a function of glycerol and fiber contents, for (a) kraft pulp and (b) thermomechanical pulp composites.

When the glycerol content in the matrix is increased, both the tensile strength and the modulus drop sharply. The presence of fibers increases the tensile strength and the modulus in all cases, but this effect is especially noticeable in the less plasticized composites. This interdependence between the glycerol and the fiber content shows clearly the interaction of these variables. The plasticization causes a softening of the matrix, and so its tensile strength and modulus fall. The fiber, even in quantities as small as

TABLE 2 Tensile modulus, tensile strength, and elongation of the starch reinforced thermoplastics

Glycerin content (*wt* %)	Fiber content (*wt* %)	Kraft wood pulp composites $E_{1\%}$ (*MPa*)	Kraft wood pulp composites *UTS* (*MPa*)	Kraft wood pulp composites ε_r (%)	TMP wood pulp composites $E_{1\%}$ (*MPa*)	TMP wood pulp composites *UTS* (*MPa*)	TMP wood pulp composites ε_r (%)
30	0	63	4	52	63	4	52
	5	119	6	13	175	6	15
	10	197	10	12	265	7	8
	15	341	10	9	387	9	5
40	0	19	2	29	19	2	29
	10	75	3	7	149	4	5
50	0	4	1	24	4	1	24
	5	43	3	8	48	2	8
	10	25	2	10	87	2	4
	15	106	6	9	92	2	5

5%, causes a pronounced increase in the modulus and in the tensile strength, but this effect is more evident in the modulus. It is possible to see in Figures 1 and 2, that for the same composition of the matrix, the modulus drops monotonically, as the fiber content falls to 5%, dropping sharply in the absence of fiber. These results show that even with small addition of fiber it is possible to change dramatically the mechanical properties of thermoplastic starch. This may be attributed to the high efficiency of the reinforcement promoted by the pulp fibers, which in turn is due to its high compatibility with the matrix and the low specific density of the pulp, which makes even low mass contents important, as it corresponds to high volume fraction.

The tensile strain decreases with the addition of fiber or glycerol to raw matrix. For the samples prepared with 30% glycerin the elongation at break drops from 52% for the raw matrix to values ranging from 5 to 15% for the composites. The decrease in tensile strain due to the inclusion of fiber is expected, whereas, in general the addition of plasticizer increases the tensile strain. In the case of thermoplastic starch the increase in the glycerol content increases the fragility of the matrix, so that it becomes more susceptible to the propagation of fissures.

3.2. Scanning Electron Microscopy

SEM micrographs (at 1000X magnification) of fractured surfaces for some composites are shown in Figures 3 and 4 for kraft and TMP reinforced wood pulp composites, respectively.

The observation of SEM micrographs shows that the fibers are uniformly dispersed in the thermoplastic starch matrix. This aspect confirms the visual observation of the composites. However, the composites made with

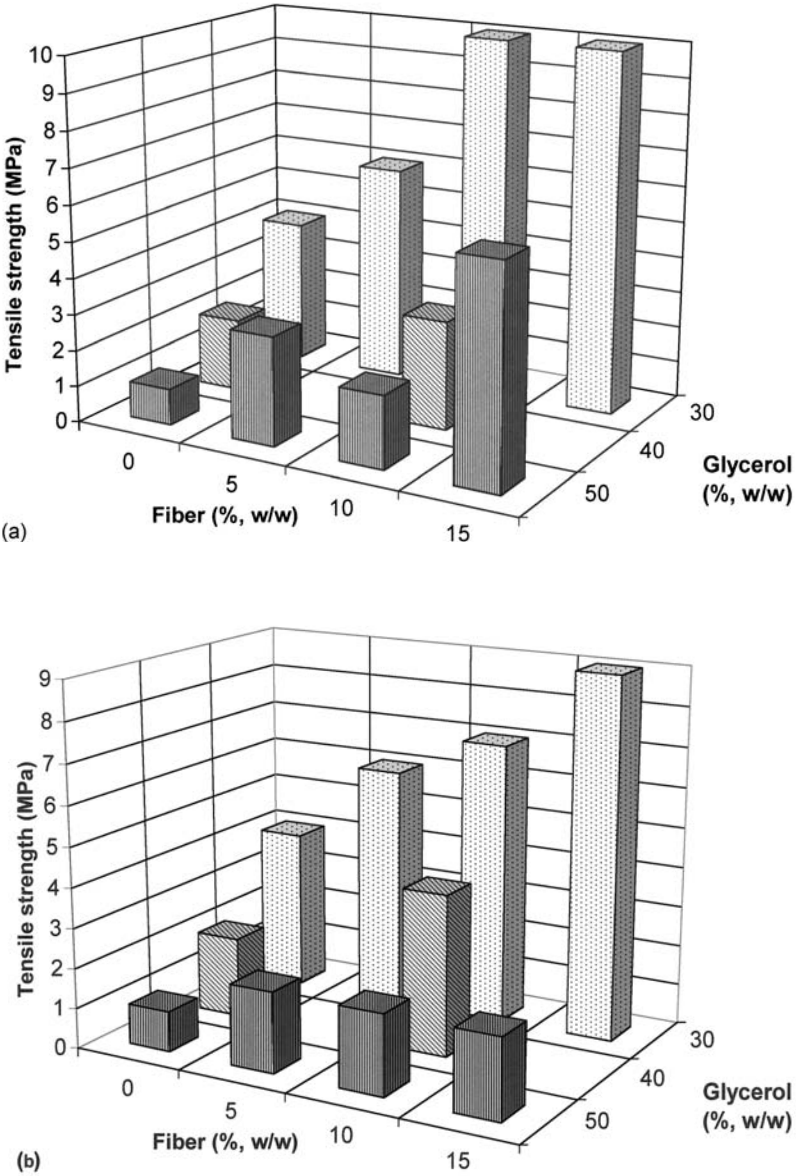

FIGURE 1 Tensile strength as a function of glycerol and fiber content of (a) kraft wood pulp composites and (b) TMP wood pulp composites.

bleached kraft pulps exhibit some small fiber agglomerations, which were eliminated prior to the preparation of the plates from which the specimens were cut. In all fractures fiber breakage was seen, while fiber pullout was

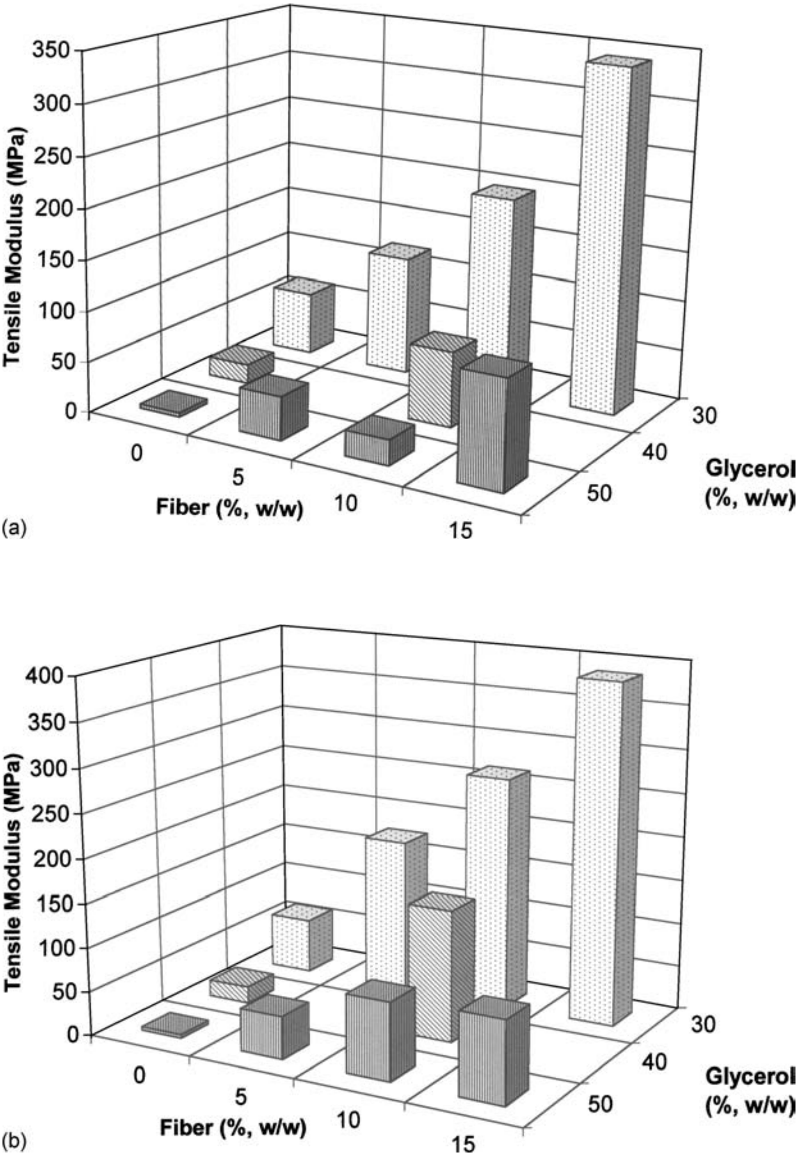

FIGURE 2 Tensile modulus as a function of glycerol and fiber content of (a) kraft wood pulp composites and (b) TMP wood pulp composites.

absent, indicating a strong interfacial adhesion. This result is interesting because an increase of glycerol content in the matrix, which causes its softening, seems not to affect the adhesion between the matrix and the fibers.

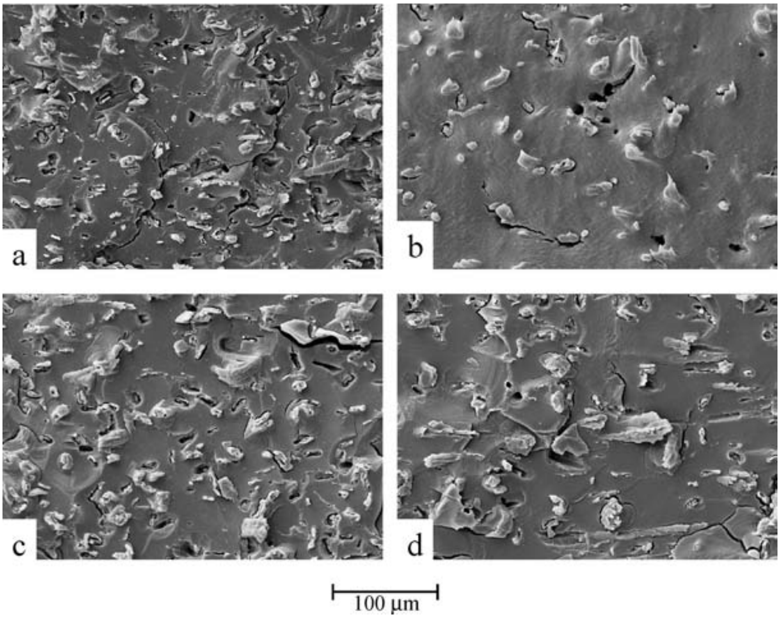

FIGURE 3 SEM micrographs of the specimens: (a) G30F5, (b) G30F15, (c) G50F5, and (d) G50F15, for kraft wood pulp composites.

The morphologies of the fractures in the kraft and thermomechanical pulp reinforced composites are almost similar.

3.3. Water Absorption Experiments

The results of water absorption experiments measured as a function of time in 97% relative humidity (RH) are plotted in Figures 5a and 5b, for the composites with kraft and TMP wood pulp, respectively.

At shorter times the kinetics of absorption is fast, leading to a plateau at later times. This plateau corresponds to the maximum water absorption, or water absorption at equilibrium. The data for water absorption at equilibrium in function of glycerol and fiber content, for the matrix and the composites with kraft and TMP wood pulps are plotted in Figures 6a and 6b, respectively.

As is possible to see in Figures 6a and 6b, the water absorption at equilibrium for the raw matrix increases with the content of glycerol and is higher than that of the composites. All the composites have water absorption at equilibrium of the same order (33 to 43%), which indicates that this property is independent of the glycerol and fiber contents. This is a

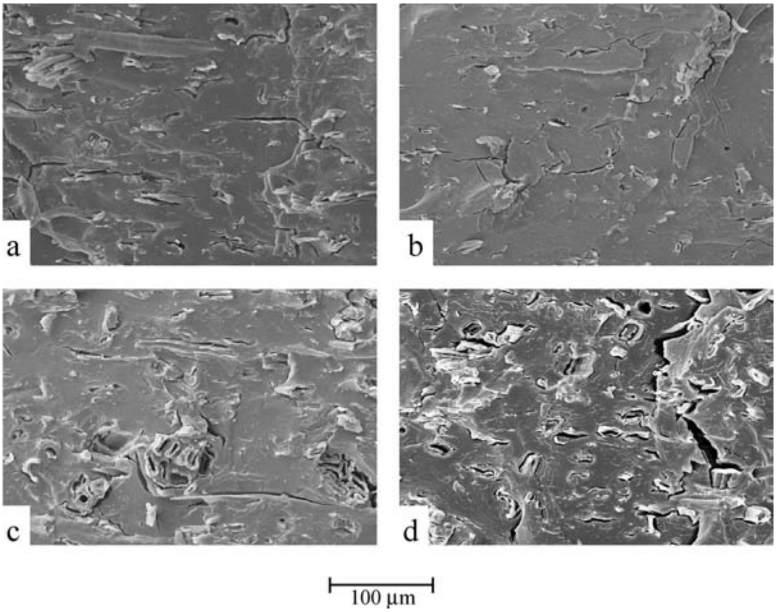

FIGURE 4 SEM micrographs of the specimens: (a) G30F5, (b) G30F15, (c) G50F5, and (d) G50F15, for TMP wood pulp composites.

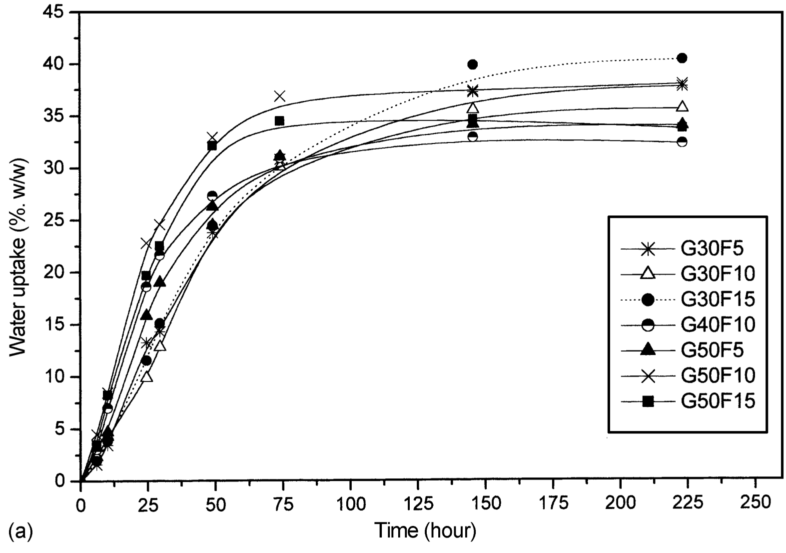

FIGURE 5 Water uptake as a function of time in 97% RH for (a) kraft and (b) TMP wood pulp composites.

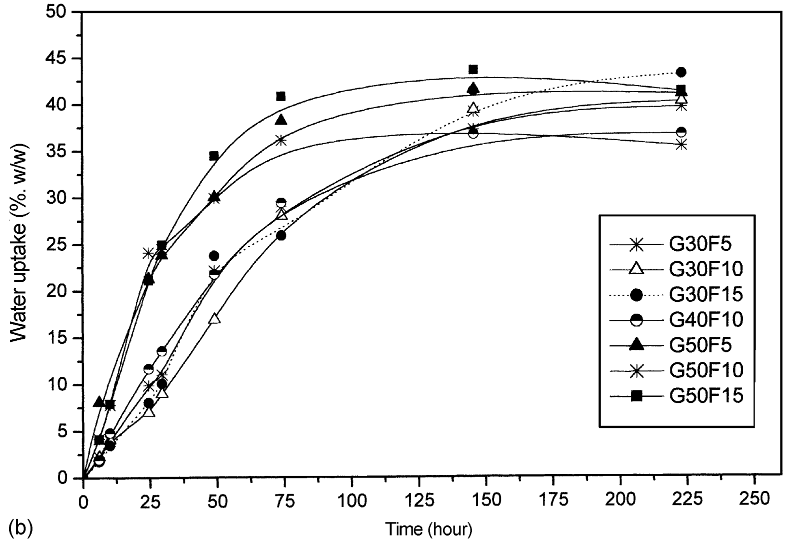

FIGURE 5 (Continued).

surprising result and the fiber seems to operate as a buffer, that not only decreases the tendency of the thermoplastic starch to absorb water but also makes the composites almost insensitive to water absorption, irrespective of

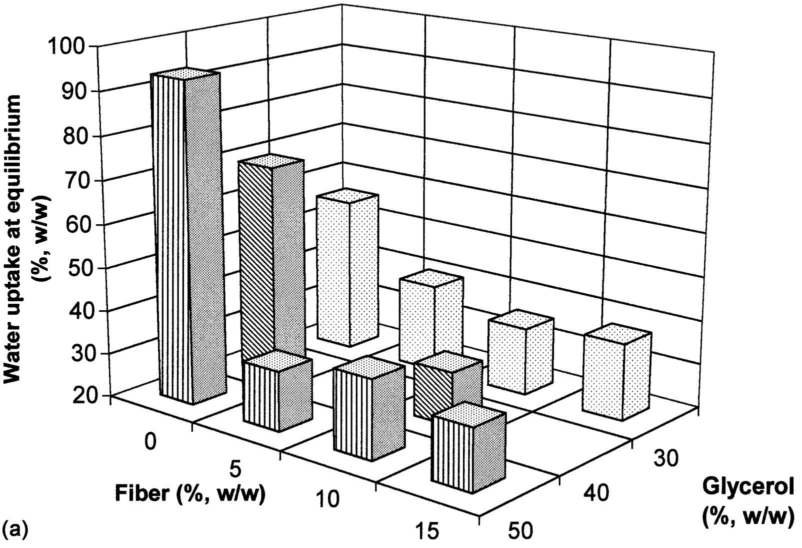

FIGURE 6 Water uptake at equilibrium, as a function of glycerol and fiber contents for (a) kraft and (b) thermomechanical wood pulp composites.

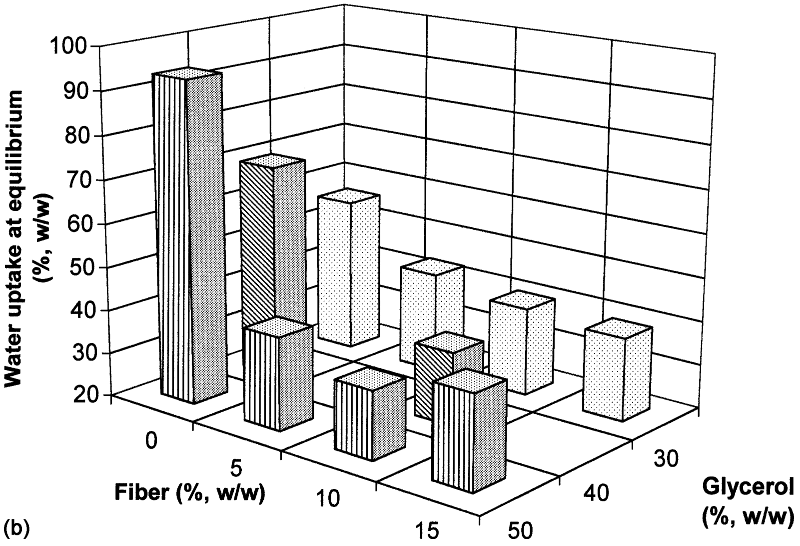

FIGURE 6 (Continued).

the proportion of glycerol and fiber present. These effects could be attributed to two main factors:

(a) The fiber could absorb the excess of glycerol in the different matrices, making them similar in terms of available glycerol content, despite the total glycerol content. It is important to note that, the amount of water absorbed increases with an increase in glycerol content (see Figs. 6a and 6b).

(b) The fibers produce a network that hinders the swelling of the matrix, consequently obstructing the absorption of water. If the quantity of fiber decreased to a point where the network is broken, the water absorption increases.

These two effects probably occur at the same time, both having the same effect on the character of water absorption, so the relative influence of each one on this property is difficult to determine.

The pulp fiber proves to be not only an efficient reinforcing material, but also a hydrophilic modifier, making the composites less hydrophilic and more resistant to the effects of moisture.

4. CONCLUSIONS

The results reported in this study describe the utilization of bleached kraft and unbleached thermomechanical wood pulp fibers as reinforcement materials for thermoplastic starch based matrix. Wood pulp fiber, when added in the range of 5 to 15% by weight, is effective in improving the mechanical properties of thermoplastic starch. The modulus increases more than 5 times in the 30% glycerol plasticized composites and more than 20 times in 50% glycerol plasticized composites. The effect of fiber on the modulus is more pronounced for the composites with more plasticizer and the increase in modulus for the composites plasticized with 50% glycerol is almost four times greater than for the 30% glycerol plasticized composites. The tensile strength increases more than twice in all composites and its highest value was found in the composites plasticized with 30% glycerol and reinforced with 10 and 15% fiber, reaching values up to 10 MPa. These values may be compared with low density polyethylene, and made these materials viable for several uses for which the unreinforced material can not be used.

The presence of fibers causes a large reduction in the water absorption at equilibrium (97% RH) for the composites. Apparently, the water absorption behavior of the composites are not affected by the fiber content, nor by the content of plasticizer, in the range investigated, making all the composites similar with respect to water absorption at equilibrium.

The use of kraft or thermomechanical pulps caused some differences in the processing of the composites. The thermomechanical pulp is easily dispersed in the matrix, giving a more homogeneous material. With respect to the mechanical and water absorption properties the use of both kinds of fiber seems to be equivalent.

The utilization of wood pulps as reinforcement for thermoplastic starch was very successful, as they not only improved its mechanical properties but also led to a decrease in the moisture sensitivity. In this way, the wood pulp reinforced starch composites eliminated (at least in part) the two main weaknesses of thermoplastic starch matrix.

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