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Thermoplastic starch–cellulosic fibers composites: preliminary results

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Abstract

In this work we use cellulosic fibers from *Eucalyptus urograndis* pulp as reinforcement for thermoplastic starch in order to improve its mechanical properties. The composites were prepared with regular cornstarch plasticized with glycerin and reinforced with short cellulosic fibers (16% w/w) from bleached pulp. The fibers were added to the thermoplasticized starch directly in an intensive batch mixer at 170°C. The mixture was hot pressed in 2–3 mm-thick plates and then cut to prepare the specimens for mechanical tests. The composite was analyzed by thermal analysis (DSC and TGA) and water absorption experiments. The composite shows an increase of 100% in tensile strength and more than 50% in modulus with respect to non-reinforced thermoplastic starch. Scanning electron microscopy of fractured surfaces revealed a very good adhesion between the fibers and the matrix. The results obtained show clearly the advantages in the use of thermoplastic starch reinforced with cellulosic fibers, a natural, cheap and abundant material.

Keywords: Thermoplastic cornstarch; Composite; Cellulose; Eucalyptus wood pulp

1. Introduction

Much effort has been made in recent years to develop biodegradable materials, particularly compostable plastics, i.e. plastics that degrade easily under well-defined environmental conditions (Gatenholm & Mathiasson, 1994). 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. Starch is a low cost material (about US$0.25 per kilogram) in comparison to most synthetic plastics and is readily available.

The use of starch to produce biodegradable plastics began in the 1970's. In the granular state, it was used as a filler for polyolefins (Griffin, 1977, 1978) and as a component in synthetic polymer blends with a totally disrupted starch granule structure (Otey & Westhoff, 1979, 1982). Starch has also been modified by grafting with 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 (Willett, Jasberg & Swanson, 1994).

Thermoplastic starch (Shogren, Fanta & Doane, 1993) 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, allowing for its use as an injection, extrusion or blow molding material, similar to most conventional synthetic thermoplastic polymers.

Thermoplastic starch has two main disadvantages when compared to most plastics currently in use, i.e. it is mostly water-soluble and has poor mechanical properties. Its water resistance may be improved by mixing it with certain synthetic polymers (Bastioli, 1995), adding crosslinking agents such as Ca and Zr salts (Shogren, Lawton, Tiefenbacher & Chen, 1998) or adding lignin (Baumberg, Lapierre, Monties & Della Valle, 1998). Several synthetic polymers have been used to improve the mechanical properties of thermoplastic starch, such as ethylene–acrylic acid copolymer (EAA), ethylene–vinyl alcohol copolymer (EVOH) (Bastioli, 1995; Pierre, Favis, Ramsay, Ramsay & Verhoogt, 1997). Another approach that has been considered to achieve this objective is the use of fibers as reinforcement for thermoplastic starch. The use of natural fibers to reinforce thermoplastic starch and other biodegradable

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materials is a new approach; thus, few publications are available on the subject. The fibers described in the literature for this purpose are cellulose microfibrils (Dufresne & Vignon, 1998), natural fibers such as flax, ramie, jute, etc. (Mittenzwey, Seidenstücker, Fritz & Süßmuth, 1998; Wollerdorfer & Bader, 1998) and commercial regenerated cellulose fibers (Funke, Bergthaller & Lindhauer, 1998; Wollerdorfer & Bader, 1998).

Unlike biodegradable polyesters, when natural fibers are mixed with polysaccharides (thermoplastic starch and its blends or cellulose derivatives) their mechanical properties become notably improved. This fact has been attributed to the chemical similarity of polysaccharides and plant fibers, providing good compatibility between them (Wollerdorfer & Bader, 1998).

This paper reports on the properties of thermoplastic starch composites prepared with glycerin as plasticizer and bleached *Eucalyptus urograndis* pulp fibers as reinforcement.

2. Materials and methods

The preparation of the thermoplastic starch (matrix) and fiber composites, as well as the materials used are described below. The composites were characterized by thermal analysis, water absorption, scanning electron microscopy (SEM) and by mechanical tests.

2.1. Fibers

Bleached *E. urograndis* pulp was supplied by Aracruz Celulose S.A. with 8–10% moisture content. Average fiber length was 1 mm and aspect ratio was 60. The fiber dimensions were determined by optical light microscopy with a 50X magnification from 2% water suspension.

Fiber dispersion directly into the thermoplastic starch did not produce satisfactory results, since it left several fiber agglomerations in the matrix; pre-dispersion of the fibers was therefore necessary. The pulp (10 g), suspended in 1500 cm^3 of water, was dispersed in a Turrax mixer operated at approximately 20,000 rpm for 3 min. Dispersion efficiency was checked by observation of a sample under a Carl Zeiss Jena Plastival 50 magnifying glass with 20× and 32× magnification. The dispersed fibers were filtered through a 75-mesh sieve and pressed until approximately 200% excess of water (w/w) was achieved.

2.2. Matrix and composites

Regular cornstarch (28% amylose), supplied by Corn Products Brasil Ltda., and reagent grade glycerin were used to prepare the thermoplastic starch. Starch and glycerin, 30% w/w of glycerin to starch (dry bases), were pre-mixed in polyethylene bags until a powder was obtained. Preliminary experiments performed in our laboratories indicated that the glycerin content should be in the range of 20–40% (without added water). Lower amounts produces difficulties in the processing and higher amounts lead to glycerin's exudation. The amount of fiber in the composite was calculated as a percentage of the total dry weight of starch plus glycerin. The utilization of 16% of fibers (by weight) corresponds to the higher amount that could be homogeneously dispersed in our experimental conditions.

The composites were prepared in a Haake Rheomix 600 batch mixer connected to a torque rheometer equipped with roller rotors. The starch, glycerin and fiber mixture was loaded into the pre-heated mixer chamber at 170°C. This temperature represents the optimization between melt viscosity with minor degradation. The chamber was opened to release water vapor at 1 min intervals or less. The rotors operated at 80 rpm and the discharge was done after 8 min of mixing.

2.3. Specimen preparation and mechanical tests

The mass taken from the mixer was hot pressed at 160°C to produce 10 × 10 cm plates with a 2.5 mm thickness, which were then stored at 22–25°C and a relative humidity of 60–70%.

Tensile tests were carried out to determine the ultimate tensile strength (UTS), the secant modulus at 1% strain ($E_{1\%}$) and strain at break (ε_r). The tests were performed according to ASTM D-638M (1990) on six specimens that were cut with a dumb bell shape cutter and stored for 14 days at 22–25°C and a 43% relative humidity. The stress–strain test was performed using an Instron model 5500 R testing machine operated at a velocity of 50 mm/min.

The moisture content of the samples was determined by drying the samples at 105°C to a constant weight.

2.4. Scanning electron microscopy

The fragile fracture surface of the composite samples produced in liquid nitrogen were studied with a LEO 440 scanning electron microscope with a tungsten filament operated at 15 kV. The samples were coated with 250 Å of gold.

2.5. Water sorption

Newly prepared samples were dried at 105–110°C for 12 h and then stored at 43 and 100% relative humidity at 25 ± 2°C. The 43% relatively humidity was obtained using a saturated solution of K_2CO_3, according to ASTM E-104 (1985), while the 100% relative humidity (saturated) was reached by using a closed vessel containing water. The K_2CO_3 used was laboratory reagent grade. The amount of water absorbed by the samples was measured until constant weight was reached (at least one week).

2.6. Thermal analysis

Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC 50. Samples of approximately 25–40 mg were placed in aluminum pans. The analyses were

Table 1
Tensile test results of thermoplastic starch and its composite with 16% of fiber

Sample	$E_{1\%}$ (MPa)	ε_r (%)	Ultimate tensile strength (MPa)
Thermoplastic starch 30% glycerin	125 ± 4	31 ± 11	5 ± 1
Composite 16% fiber	320 ± 70	11 ± 0,2	11 ± 2

performed under a nitrogen flow of 20 ml/min, at a heating rate of 5°C/min. The samples were heated at temperatures above their T_g (120°C) and quenched in liquid nitrogen prior to the final analysis, allowing the thermoplastic starch to become frozen in the amorphous state. The graphic determination of glass transition temperature was done taking the temperature corresponding to the half-variation in calorific capacity during transition ($T_g^{1/2}$).

The thermogravimetric analysis was made in a Shimadzu TG-50, at a rate of 10°C/min from ambient temperature to 900°C. The analyses were performed in a nitrogen atmosphere with a 20 ml/min flow rate.

3. Results and discussion

3.1. Mechanical properties

Table 1 shows the modulus ($E_{1\%}$), elongation (ε_r) and the UTS for the composite prepared with 16% of fiber w/w and the pure matrix.

The $E_{1\%}$ and the tensile strength show 156% and 120% increases, respectively, while elongation was reduced from 31% to 11%. The moisture content of samples was 22% for the thermoplastic starch and 15% for the composite.

3.2. Scanning electron microscopy

SEM micrographs of the fragile fractured surface of 16% filled thermoplastic starch composite are shown in Figs. 1 and 2 at 250× and 2500× magnification, respectively. Fig. 1 shows clearly that the fibers were very well dispersed in the starch matrix. Fiber breakage can be clearly seen in both micrographs, particularly in Fig. 2. This effect and the absence of fiber pullout indicate good adhesion between the starch matrix and the cellulose fiber (Salilba & Snide, 1990). The fiber's surfaces appear to be covered by starch, attesting the strong adhesion between the composite components.

3.3. Water sorption

The results of water sorption experiments performed at 43 and 100% relative humidity are shown in Table 2.

Moisture sorption was dramatically reduced with the incorporation of fiber. These results are ascribed to the fact that starch is more hydrophilic than cellulose and the fibers absorb part of the glycerin. This results in a less hydrophilic matrix, since plasticized starch is increasingly sensitive to water uptake the higher the glycerin content is, as observed by Dufresne and Vignon (1998). They found a similar result for water absorption in starch thin films with cellulose microfibrils.

3.4. Thermal analysis

The DSC results, which show that the presence of fiber increases the T_g of the matrix, are in agreement with the water sorption experiments. Fig. 3 shows the DSC thermal

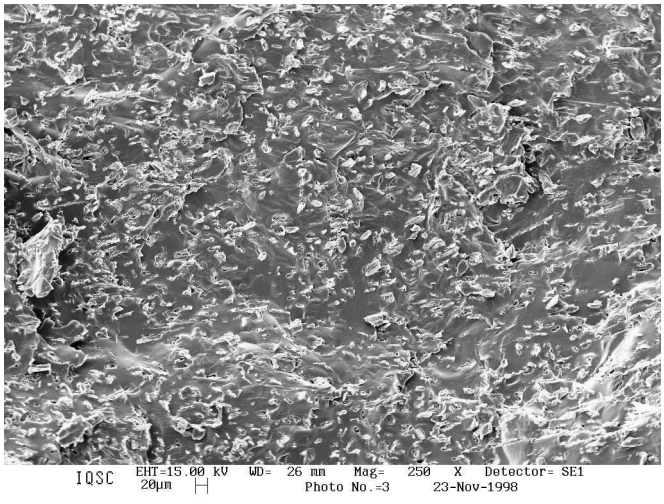

Fig. 1. SEM micrograph at 250× magnification of fragile fractured surface of 16% fiber filled thermoplastic starch (30% glycerin) composite.

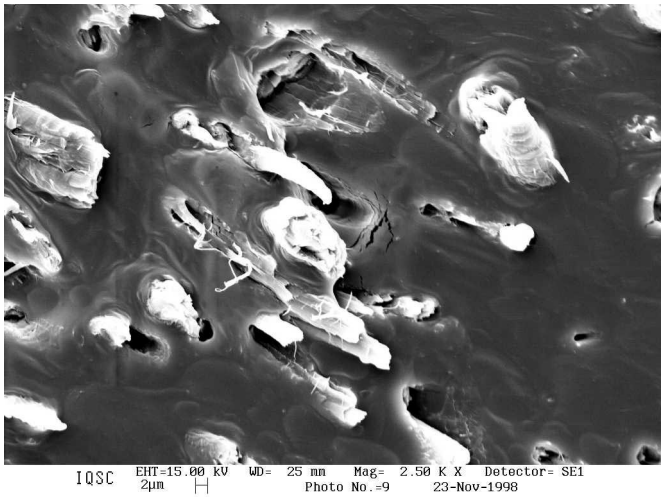

Fig. 2. SEM micrograph at 2500× magnification of fragile fractured surface of 16% fiber filled thermoplastic starch (30% glycerin) composite.

traces for the thermoplastic starch and the composite. Two transitions were detected in both materials. One of these transitions, at higher temperatures, occurs at 2°C for thermoplastic starch and at 17°C for its composite, while the lower temperature transition appears at −55 and −45°C, respectively, for thermoplastic starch and its composite. The high temperature transitions are the vitreous transition, determined as $T_g^{1/2}$. The difference in $T_g^{1/2}$ for the thermoplastic starch and the composite was attributed to fiber interaction with the plasticizer, since the matrix in the composite is less plasticized than the pure matrix.

The transition at lower temperatures, i.e. −55 and −45°C, was first detected by Lourdin, Bizot and Colonna (1997), by DMTA measurements, who found that these transitions are slightly dependent on the concentration of plasticizer. These transitions were attributed to the main plasticizer itself.

Fig. 4 presents the TG experimental results. The behavior of the mass loss curve is similar in the thermoplastic starch and the composite, while the onset of decomposition occurs at 320°C in both. Mass loss, at the onset temperature, is 30 and 23% for thermoplastic starch and its composite, respectively. This difference is due to the differences in equilibrium moisture content of each sample, i.e. 22% for thermoplastic starch and 15% for its composite.

4. Conclusions

This study provided an initial insight into the use and characteristics of pulp fibers in starch-based composites. Pulp readily works as reinforcement even in relatively low quantities, since 16% produced a significant increase in the modulus and tensile strength. The results of DSC experiments indicate an interaction between the fiber and the glycerin, causing the reduction of glass transition temperatures of the matrix in the composite and a reduction in the water sorption of the composites in comparison to the pure matrix.

Table 2
Sorption of moisture from samples conditioned in 43 and 100% relative humidity at 25 ± 2°C

Samples	43% Relative humidity	100% Relative humidity
Thermoplastic starch	9	65
16% Fiber composite	5	34

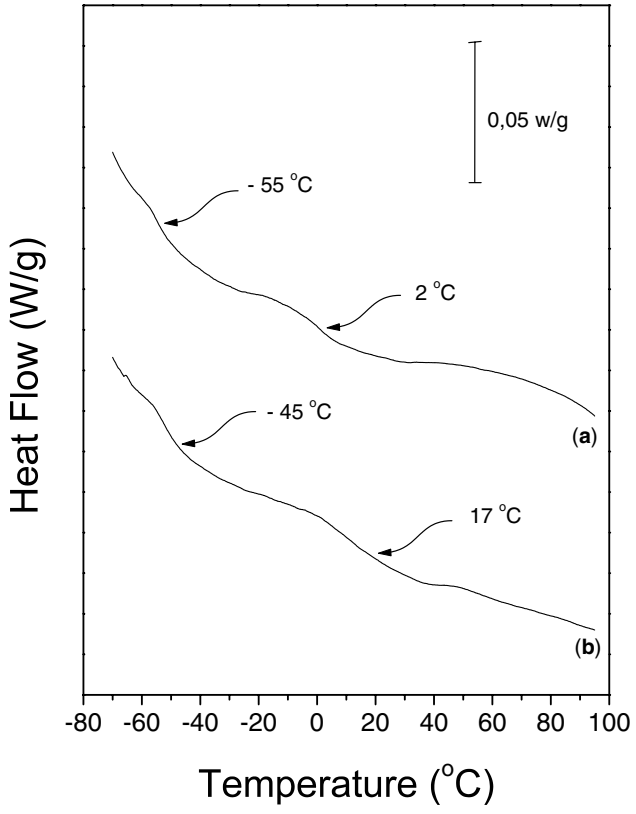

Fig. 3. DSC scans for: (a) thermoplastic starch with 30% glycerin; and for (b) 16% fiber filled thermoplastic starch composite.

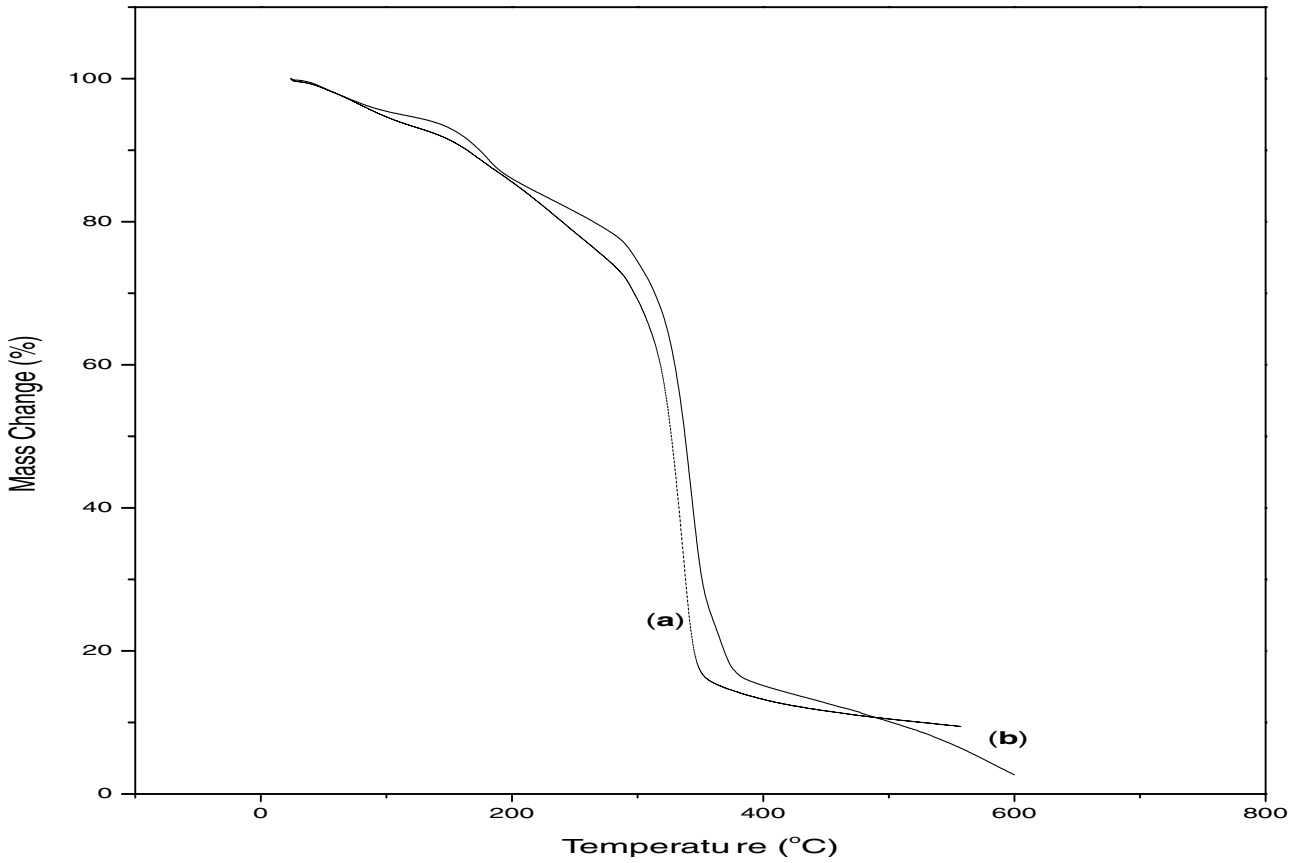

Fig. 4. TG scans for: (a) thermoplastic starch with 30% glycerin; and for (b) 16% fiber filled thermoplastic starch composite.

Pulp is a commercially available, low cost material specified by international standards and appears to be a promising source of fibers for the production of commodity materials.

The main drawback involved in the use of pulp as a fiber is the tendency of fibers to self-agglomerate, which makes it difficult for them to disperse in the matrix.

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