PROCESSING AND PROPERTIES OF BIODEGRADABLE COMPOSITES BASED ON MATER-BI AND SISAL FIBER

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SUMMARY: Relationship between processing conditions and properties were reported. Alkaline treatment was performed in order to improve the adhesion and/or compatibility of the fiber with the matrix. The effect of the treatment on the tensile properties and morphology was determined. Fiber content enhances the tensile properties of Mater-Bi. The experimentally and observed tensile properties (modulus and tensile strength) of short sisal fiber and Mater-Bi with different fiber loading have been compared with the existing theories of reinforcement. SEM photomicrographs of the fractured composite surfaces was analyzed.

KEYWORDS: biodegradable composites-natural fiber-mechanical properties processing

INTRODUCTION

Compounding thermoplastic polymers with natural fibers is a good approach to obtain special composites with useful properties [1-3]. Table 1 shows the mechanical properties obtained with thermoplastic and natural fibers.

Table 1. Tensile properties of natural fiber composite with 20%vol fiber

Composite	Modulus (MPa)	Elongation at break (%)	Strength (MPa)	Reference
PP/Bamboo	2500		16	[4]
MAPP/PP/Flax	2800	1.3	21	[5]
PP/Bagasse	≈600	8.0	17	[6]
LDPE/short sisal	453	10	12.5	[7]
LDPE/treat.sisal	926	12	16.5	[7]

Moreover, fully biodegradable composites are a particular class of materials obtained by the combination of a biodegradable polymer matrix with natural fibers. Although these materials can offer very interesting properties only few studies have been reported [8-9].

The aim of this work is the determination of the mechanical properties of a fully biodegradable composite using sisal fibers and an industrial biodegradable polymer. Effects of processing conditions and fiber content and treatment of fiber on mechanical properties will be studied

EXPERIMENTAL

Materials

Mater-Bi-Z ZF03 (Mater-Bi) kindly supplied by Novamont, Italy was used. Polycaprolactone (PCL) from Aldrich Chem. Co., USA, (Mn=42500) was also utilized as matrix composite. Brascorda, Brazil supplied the sisal fibers.

Fiber treatment

An alkaline fiber treatment was done to the fibers. The fibers were placed in a stainless steel vessel with a 10% p/v solution of NaOH and continuously stirred for 1 h at 80ºC. Afterwards, fibers were washed with distilled water and oven dried at 100ºC until constant weight was achieved.

Preparation of the composites

A twin-screw extruder (Haake Rheomex CTW 100) was used to disperse fibers in the polymer matrix. Different fiber contents were analyzed: 10, 20, 30 and 40%wt. A different residence time was used for each composition to guarantee a better fiber dispersion. After extrusion, samples were obtained by calendering.

Testing of fibers and composites

INSTRON 4204 was used for the tensile tests. A test length of 30 mm for the fibers and a crosshead speed of 10 mm/s were employed and an average of 50 test was taken for each sample (ASTM D 3379-75). Tensile test of bone-shaped composite specimens was carried out using a crosshead of 2 mm/s (ASTM D639-90). Fiber content was determined by dissolution of Mater-Bi in dioxane while fiber length and diameter were obtained by optical microscopy on 100 fibers. To determine the adhesion between fiber and matrix, fiber pullout specimens were prepared by aligning single fiber into the matrix. The analysis of the fractured surfaces of the sample was done by means of scanning electron microscopy (SEM).

RESULTS AND DISCUSSIONS

Tensile test for treated and untreated sisal fiber:

Mater-Bi and PCL are ductile materials with relative low modulus (37 MPa and 110 MPa, respectively). Sisal fiber tensile test was performed for treated and untreated fibers.
Modulus, stress and strain at break was determined for the fibers. Table 2 shows the obtained results.

The modulus has a slightly increases, may be due to the change from cellulose I to cellulose II and the partial extraction of lignin and hemicellulose [10]. The treated fiber shows a wider distribution of the strain, as consequence of the high fibrillation (Figure 1).

Table 2: Tensile Test of Sisal Fibers

Sisal Fiber	Untreated	Treated
Modulus (GPa)	7.5	12
Strength (MPa)	190	200
Elongation %	3.2	3.3

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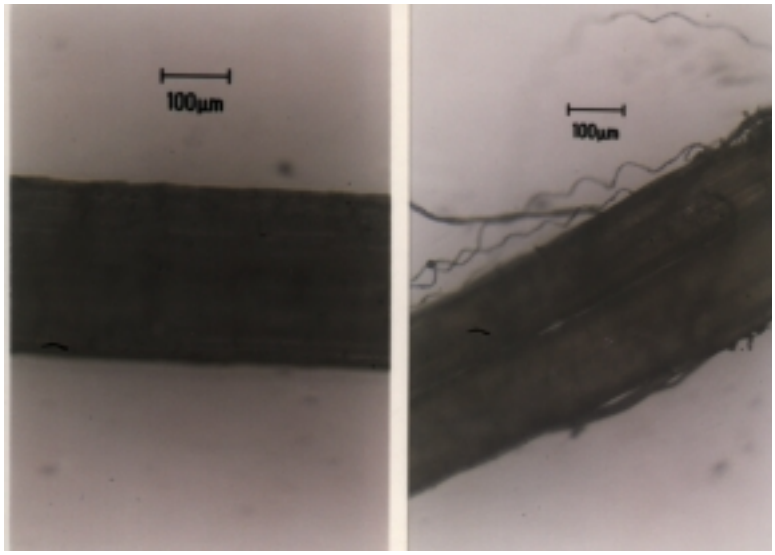

a b

Figure 1: Fiber before and after the alkali treatment: a) untreated, b) treated

Processing Conditions.

In order to obtain a well-mixed composite, the residence time and temperatures were changed for each fiber content. Table 3 shows the residence time and temperatures selected for each composite.

Table 3: Processing Conditions

% wt sisal fiber	Extruder Processing Conditions
10%	40, 70, 100 y 120^{0}C
20%	First extrusion 40, 70, 100 y 120^{0}C Second extrusion 40, 70, 100 y 120^{0}C
30%	First extrusion: 40, 70, 100 y 120^{0}C Second extrusion 40, 70, 100 y 120^{0}C Third extrusion 40, 70, 110 y 130^{0}C
40%	First extrusion: 40, 70, 100 y 120^{0}C Second extrusion 40, 70, 100 y 120^{0}C Third extrusion 40, 70, 110 y 130^{0}C Forth extrusion: 40, 70, 110 y 140^{0}C

The sample with 40%wt. was clearly degraded due to the high residence time into the extruder. The blended fiber and matrix are calendered after the extrusion with the following conditions: 40, 80, 100 and 120 ºC for each fiber content. The speed of the screw was 100 rpm and the pulling velocity was 85 rpm.

Figure 2 shows the photographs of the obtained fiber after the processing (extracting the fiber with dioxane from the composite). It is clear that the fiber suffers damaging during the processing. Fiber after processing has a rough surface morphology. Fibrillation, i.e. breaking down of the composite fiber bundle into smaller fibers, was produced during the processing. This effect increases the effective surface area available for contact with the matrix and reduce the fiber diameter. However, the aspect ratio does not increase (only from 13 to 16) with the high content of fiber, since they were shortened during processing. Results of the final fiber length and diameter as a function of fiber content and residence time in the extruder are shown in Table 4.

Table 4: Fiber Length as a function of Extruder Residence Time
Initial Sisal Length: 7.2±0.6mm

%wt sisal	Residence Time (s)	Diameter (mm)	l_{exp} (mm)	l (mm) modulus model	l(mm) strength model
10	85	0.33	4.4±0.8	5.7	5.9
20	170	0.26	3.1±0.5	3.8	4.6
30	250	0.16	2.6±0.6	4.4	4.0

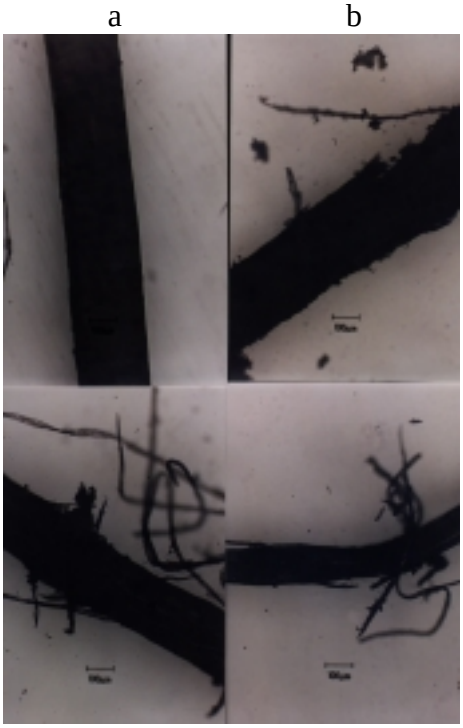

Figure 2:Photomicrograph of the sisal fiber: a) as received, b) from the composite of 10%wt, c) from the composite of 20%wt, d) from the composite of 30%wt

Composite tensile test

Figure 3 shows the tensile test result for the untreated fiber based composites. Fiber acts as reinforcement of the matrix and the mechanical strength increases with fiber concentration in spite of the damaging effect occurring during processing. Elastic modulus of composites also increases with fiber concentration (Table 5)

Table 5.: Tensile test result of the composite with different content of fibers

	Untreated fibers			Treated fibers		
% wt fiber	E (MPa)	$\sigma_{máx}$ (MPa)	$\varepsilon_{máx}$ (%)	E (MPa)	$\sigma_{máx}$ (MPa)	$\varepsilon_{máx}$ (%)
0	37±0.9	7.3±1.3	859±89	37±0.9	7.3±1.3	859±89
10	138±13	10.9±0.9	545±44	112±16	6.4±0.8	608±53
20	257±17	12.7±0.5	8.0±0.9	221±24	8.8±0.9	11.2±1.5
30	468±98	14.4±1.6	4.1±0.8	410±36	10.9±2.1	6.1±0.5

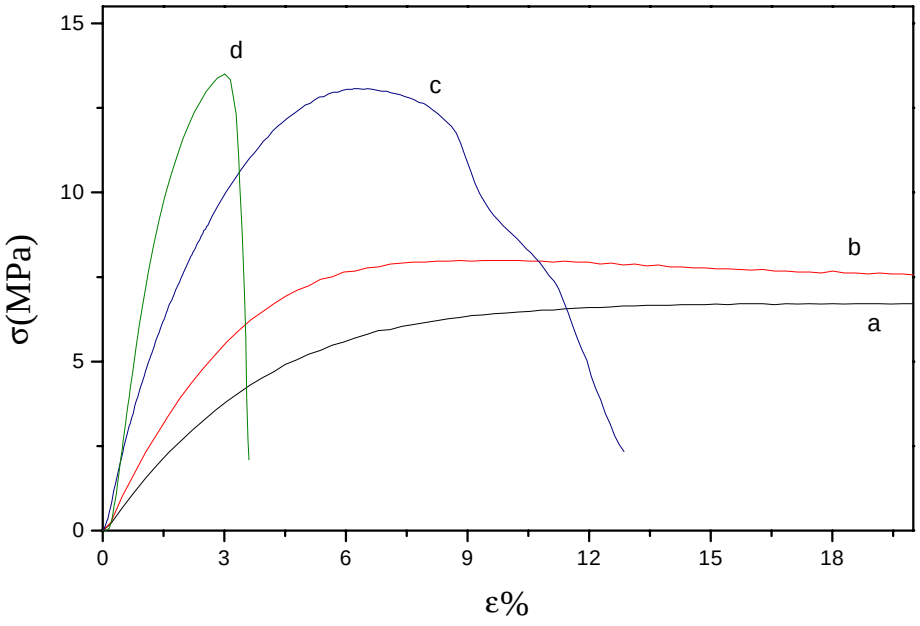

Figure 3: a) Mater-Bi, b) Mater-Bi/10wt.%Fiber, c) Mater-Bi/20wt.%Fiber, d)Mater-Bi/30%wt.Fiber

The modulus and strength slightly decreases after the fiber treatment. It is may be due to the higher damaging of treated fiber in comparison with untreated fiber during extrusion. If the fiber length decreases from the original length a decrease in the mechanical properties could be expected. Kuruvilla et al [7-11] suggested a critical sisal fiber length of approximately 6 mm for LDPE matrix.

The use of treated fibers results in composite with slightly higher elongation at break. It could be due to the formation of a natural mat with mechanical anchoring or agglomeration of fiber due to the higher OH content and hydrogen bonds between the fibers as consequence of the alkaline treatment [6]

Other important result is that in spite of that the density of the fiber decreases with the treatment and it was possible to introduce more quantity of sisal fiber without degradation (a sample of 40%wt was possible obtained).

Experimental modulus of composites based on untreated fiber were analyzed according to the modified Halpin-Tsai equation [12]:

$$E_c/E_m = (1+ A\ B\ \phi_2)/(1-B\ \psi\ \phi_2) \quad (1)$$

$$A = k_E - 1\ ,\ k_E = 1+2l/d \quad (2)$$

$$B = \frac{\frac{E_f}{E_m} - 1}{A + \frac{E_f}{E_m}} \quad (3)$$

$$\psi = 1 + (1 - \phi_{\max}) \frac{\phi_2}{\phi_{\max}^2} \quad (4)$$

where E_f ,E_c and E_m are the fiber, composite and matrix modulus respectively ϕ_2 is the fiber volume fraction, *l* is the length and *d* is the fiber diameter and ϕ_{max} is the maximum packaging volume (0.82 for random packaging). The length of the fiber was calculated with the model and it is shown in Table 4.

Strength increases when the fiber volume fraction increases. The model of Browyer-Bader was used for the fiber length calculation [13]:

$$\sigma_c = \sigma_f K_1 K_2 \phi_f + \sigma_m \phi_m \quad (5)$$

where σ_c and σ_f are the composite and fiber strength, respectively. K_1 and K_2 are two constants (K_1=0.2 and K_2=l/2 l_c , for the case that l > lc; where l_c is the critical length). The results are also shown in Table 4.

Both models predict a higher length or a higher aspect ratio, especially for the 30%wt of fiber composite. It is may be due to the effective diameter which acts into the composite is less than the calculated after the extraction with solvent. The other possibility is that the effective length (i.e., the act fiber length into the composite) is higher than the measured due to percolation effect.

In order to determine the fiber-matrix adhesion, pullout tests were carried out for Mater-Bi and PCL with sisal. PCL-sisal showed a better fiber-matrix adhesion than Mater-Bi whose formulation includes PCL and starch as main components, and plasticizer as minor one. The latter can be responsible of the less adhesion with fibers. SEM fractured surface also proof that there is not adhesion between untreated fiber and matrix of Mater-Bi. Pull out test on the treated fiber and SEM photomicrographs are performing.

CONCLUSIONS

Biodegradable composites based on sisal fiber and Mater-Bi have been investigated. The elastic modulus increases with the increase of fiber content. Also, the mechanical strength increases and it is an indication that the fiber acts as reinforcement material.

No adhesion was found between Mater-Bi and untreated sisal fiber, probably as consequence of the additive included in the formulation. Fibrillation of the fiber after treatment could acts as mechanical anchoring.

Length and diameter of the fiber decrease with the increase of the residence time, due to the intense shear stresses developed into the extruder

Improvement of mechanical properties could be obtained by optimizing the processing conditions, which determine a modification of the fiber aspect ratio, l/d, as consequence of the reduction of length and the separation of fibers into distinct fibrils. Finally, alkaline treatment should be optimized in order to improve fiber properties and fiber-matrix interactions.

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ACKNOWLEDGEMENTS

Financial support of Fundacion Antorchas, CNR (Italy) and CONICET (Argentina) are gratefully acknowledged.