

Effect of Processing Conditions on Mechanical and Viscoelastic Properties of Biocomposites

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ABSTRACT: To study the effects of processing conditions on the viscoelastic and mechanical properties of biodegradable composites, we prepared several composites based on sisal fibers and biodegradable polymers. The effects of processing conditions such as the speed of rotation, temperature, and time of mixing were investigated. The mechanical and viscoelastic properties of these composites were affected by the processing conditions. This was principally due to the

modification of the initial aspect ratio of the natural fibers as a result of the shear stresses that developed in the mixer during the compounding. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1637–1642, 2003

Key words: fibers; biodegradable; composites; mechanical properties; creep

INTRODUCTION

Recently, the production of biodegradable materials has received considerable attention because of environmental concerns. Biocomposites are materials obtained by the combination of biodegradable polymers with natural fibers. Because of the biodegradability of both components, the composite is expected to be biodegradable. Biodegradable polymers are used in biomedical applications, but their use in commodity applications is still limited because of economical reasons, difficulties related to their processing, and their poor thermal stability.¹ The use of natural fibers has several advantages over traditional reinforcing materials such as glass fibers, talc, and mica: low cost, low density, high toughness, acceptable specific strength properties, reduced tool wear, good thermal properties, enhanced energy recovery, and biodegradability.

Natural fibers are often employed to reduce the cost per unit volume and to improve the specific mechanical properties of biodegradable and nonbiodegradable polymers.^{2–10} However, because of their hydrophilic nature, their compatibility with hydrophobic matrices is low, and this affects the final performance of the composites. Chemical and physical treatments should, therefore, be employed to improve the properties of the natural fibers and to promote better adhesion between the natural reinforcement and the polymeric matrix.^{2,3,11–13}

Sisal fibers, used in this work, are natural fibers that are extracted from the agave plant, but their properties,

such as the density and diameter, are affected by the extraction method.¹⁴ These fibers have high tensile strength and modulus and can be used to produce reinforced polymers for several applications.¹⁵ Many workers have used sisal fibers as reinforcements in thermoplastic composites, and the factors affecting the mechanical properties of these composites have been studied.^{1,7–11}

We previously reported on the preparation and characterization of biocomposites composed of a biodegradable matrix and sisal fibers.^{9,16} Shear stresses that developed during mixing and extrusion processes were responsible for damage to the fibers, and these effects were correlated to the rheological properties of the thermoplastic matrices. The higher shear stresses that developed in a counterrotating, conical, and intermeshing twin-screw extruder, which was used to disperse the fibers, caused a great reduction in both the fiber diameter and length.¹ Similar effects were observed when fibers were dispersed in the polymeric melt with a Brabender mixer.¹⁶ The length and diameter of the initial fibers were reduced during mixing; this effect was correlated to the magnitude of the shear stress developed in the mixer. An increase in speed of rotation (SR) or a reduction in the temperature produced fibers of smaller dimensions but with higher aspect ratios [length/diameter (l/d)].

Because fibers can work as reinforcements or fillers, depending on several factors such as the fiber/matrix interaction, l/d , and the critical fiber length (l_c), the properties of composites are strongly dependent on the processing method and conditions.

The aim of this work was to study the effects of processing conditions on the mechanical and viscoelastic properties of biodegradable composites based on sisal fibers and mater Bi-Z ZF03 (Bi-Z) or mater Bi-Y 101 (Bi-Y).

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TABLE I
Processing Conditions of Biocomposites

Sample	Matrix	Sisal fibers	Temperature (°C)	Speed of rotation (rpm)	Time of mixing (min)
Z1	Mater Bi-Z	—	120	60	2
Z2	Mater Bi-Z	Untreated	120	110	6
Z3	Mater Bi-Z	Untreated	140	110	6
Z4	Mater Bi-Z	Untreated	120	60	6
Z5	Mater Bi-Z	Untreated	120	110	2
Z6	Mater Bi-Z	Treated	120	110	6
Y1	Mater Bi-Y	—	180	80	4
Y2	Mater Bi-Y	Untreated	180	20	2
Y3	Mater Bi-Y	Untreated	180	20	4
Y4	Mater Bi-Y	Untreated	180	20	6
Y5	Mater Bi-Y	Untreated	140	20	2
Y6	Mater Bi-Y	Untreated	160	20	2
Y7	Mater Bi-Y	Untreated	180	50	2
Y8	Mater Bi-Y	Treated	180	110	6

EXPERIMENTAL

Materials

Mater Bi-Z and mater Bi-Y, supplied by Novamont (Italy), were used as matrices. Sisal fibers, supplied by Brascordor (Brazil), were used either as received or after an alkaline treatment. The latter were prepared by being placed in a stainless steel vessel containing a 10% (w/v) solution of NaOH for 1 h at 80°C under continuous stirring. The fibers were then washed in distilled water and oven-dried at 100°C until a constant weight was achieved.

Mixing operation and sample preparation

A Haake model 9000 rheocorder was used to disperse sisal fibers in the polymeric melt. To evaluate the effect of the processing conditions, we prepared composites containing 20% (wt/wt) sisal fibers at different temperatures, SRs, and times of mixing. After the mixing process, composites based on mater Bi-Z were prepared by calendaring with a Haake TP1 Postex calendar machine. Composite samples based on mater Bi-Y were prepared with a Carver laboratory press at 160°C. Table I lists the experimental conditions used for preparation.

Tensile and creep properties

The tensile testing of the composites was carried out with an Instron model 4204 machine at a constant speed of 2 mm/min. Four dog-bone samples (20 mm × 5 mm) were tested for each composite. A DuPont 983 dynamic mechanical analyzer was used to analyze the creep behavior of the polymeric matrices and their composites at 30°C.

RESULTS AND DISCUSSION

Tensile properties

To study the effect of the processing conditions on the mechanical and viscoelastic properties of the biode-

gradable composites, we prepared several samples under different experimental conditions (see Table I). As reported and discussed in a previous work,¹⁶ the internal mixer used for the preparation of the composites had two geometric features: a narrow gap between the rotor wings and mixer wall and a larger space between the rotors. This space was assumed to be a well-mixed tank in which extensive mixing took place, whereas dispersive mixing occurred in the narrow gap under the wing. When a fiber entered the narrow gap (high shear zone), it was broken into smaller fibers if the hydrodynamic forces exceeded the fiber strength and/or the cohesive forces between the individual fibers. During each pass through the narrow gap, some of the fibers were broken; the amount depended on several factors, such as the fiber shape and size, the viscosity, the local shear rate, and the length and height of the narrow gap.

The final diameter (d) and l/d values of the fibers, extracted from the composites after their preparation, and the tensile properties of the produced composites are reported in Table II. Figures 1 and 2 show the stress-strain curves for the composites based on mater Bi-Z and mater Bi-Y, respectively.

Samples Z2 and Z4 were prepared at the same temperature and time of mixing but at different SRs. The tensile modulus and maximum tensile strength increased when SR increased from 60 (sample Z4) to 110 rpm (sample Z2), and this improvement was related to the increase in l/d . As a matter of fact, the increase in SR led to the increase in the shear stresses in the melt, and this resulted in a reduction of the fiber size and an increase in l/d , which varied from 72 mm/mm at 60 rpm to 120 mm/mm at 110 rpm (see Table II). Variations of the initial l/d values were obtained through changes in other processing parameters. Even though the volumetric fraction of the fibers was kept constant, the tensile properties of the composites were different because of the different l/d values of the fibers in the composites (Figs. 1 and 2).

TABLE II
Tensile Properties of Biocomposites and Geometrical Characteristics of Sisal Fibers

Sample	l/d (mm/mm)	d (mm)	Tensile strength (MPa)	Tensile modulus (MPa)
Z1	—	—	4.027 ± 0.679	27.5 ± 8.1
Z2	120.4	0.042	10.39 ± 1.444	222.0 ± 24.2
Z3	126.2	0.032	10.09 ± 2.323	275.8 ± 58.1
Z4	72.4	0.109	6.67 ± 1.651	116.7 ± 9.1
Z5	97.2	0.122	9.03 ± 0.493	198.6 ± 27.0
Z6	136.7	0.043	13.03 ± 1.676	292.2 ± 31.8
Y1	—	—	17.60 ± 3.32	704.6 ± 16.9
Y2	60.6	0.132	14.15 ± 0.92	1032.2 ± 39.7
Y3	66.4	0.116	12.00 ± 5.80	1081.6 ± 93.2
Y4	74.7	0.106	18.60 ± 1.98	1183.3 ± 25.8
Y5	50.4	0.147	12.30 ± 0.57	958.0 ± 5.9
Y6	53.9	0.140	12.60 ± 2.83	995.9 ± 59.5
Y7	73.4	0.124	12.45 ± 2.05	1174.1 ± 95.0
Y8	121.12	0.061	22.35 ± 0.21	1249.5 ± 13.6

The tensile modulus of the composites is reported against l/d in Figures 3 and 4. The experimental data are compared with the theoretical values, which were calculated with the following equations:

$$E_c(\text{theoretical}) = \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \tag{1}$$

$$E_{11} = \frac{1 + 2(l/d)BV_f}{1 - BV_f}E_m \tag{2}$$

$$E_{22} = \frac{1 + 2CV_f}{1 - CV_f}E_m \tag{3}$$

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/d)} \tag{4}$$

$$C = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \tag{5}$$

where E_{11} and E_{22} represent the longitudinal and transverse moduli, respectively, for a unidirectional

discontinuous fiber composite lamina; E_f , E_m , and E_c represent Young’s modulus for the fibers, matrix, and composite; and V_f represents the fiber volume fraction. The tensile moduli were 12.24 and 10.50 GPa for treated and untreated sisal fibers, respectively. The transverse moduli, calculated from eqs. (3) and (5), were 45.3 MPa for the composites based on mater Bi-Z and 1013.2 MPa for the composites based on mater Bi-Y.

Equations (2)–(5) were derived from the modified Halpin–Tsai equations with the following assumptions:¹⁷

1. The fiber cross section is circular.
2. The fibers are arranged in a square array.
3. The fibers are uniformly distributed throughout the matrix.
4. The matrix is free of voids.

Figures 3 and 4 show that the tensile modulus for both composites increased with the increase in l/d , according to the reported equations. However, the experi-

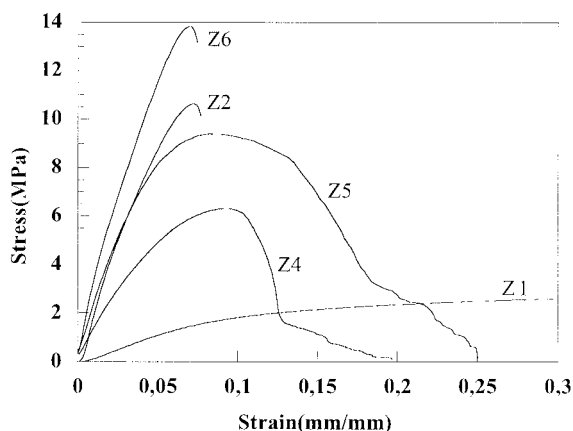


Figure 1 Stress–strain curves for composites based on mater Bi-Z.

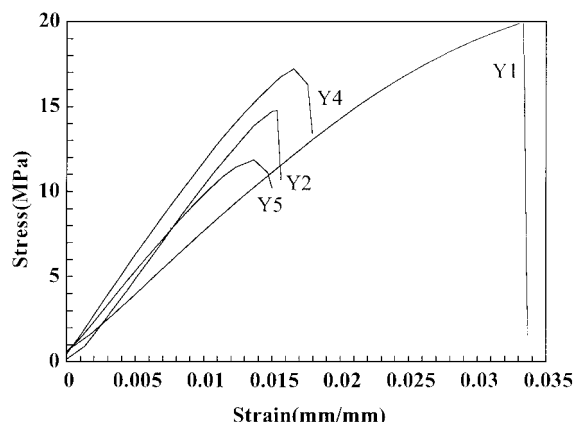


Figure 2 Stress–strain curves for composites based on mater Bi-Y.

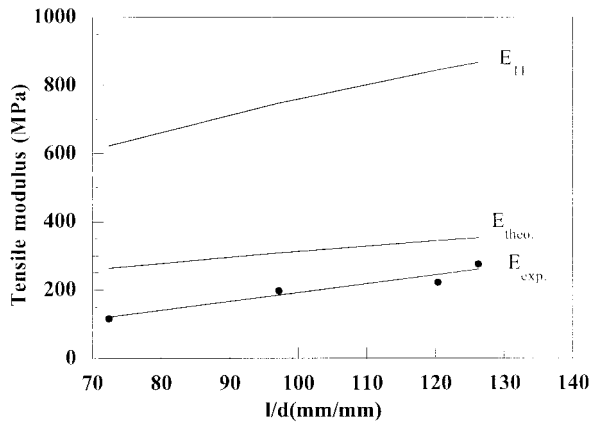


Figure 3 Effect of l/d on the tensile modulus of composites based on mater Bi-Z and sisal fibers.

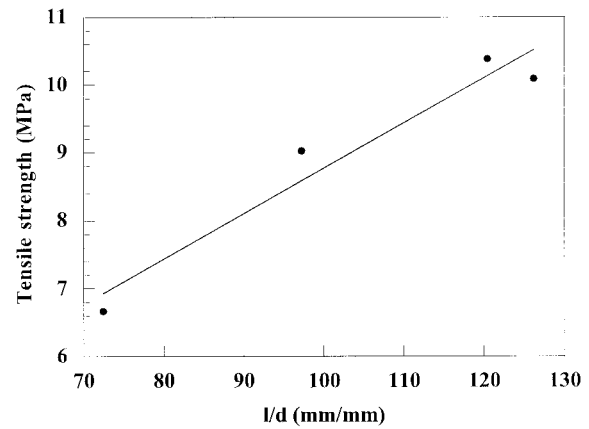


Figure 5 Effect of l/d on the tensile strength of composites based on mater Bi-Z and sisal fibers.

mental data are lower than those expected from eq. (1), and these differences are greater at low l/d values.

As shown in Figure 5 and Table II, the tensile strength also increased with an increase in l/d , and it could be analyzed with the following equation, which is used to predict the strength of composites:

$$\sigma_c = k_s V_f \sigma_f + (1 - V_f) \sigma_m \quad (6)$$

where σ_c , σ_f , and σ_m represent the tensile strengths of the composite, fiber, and polymeric matrix, respectively. The strength efficiency factor (K_S) depended on several factors such as l/d , the fiber orientation relative to the loading direction, and the degree of adhesion between the fibers and polymeric matrix.^{18,19} The tensile strengths were 213.8 MPa and 241.5 MPa for treated and untreated sisal fibers, respectively.

Table III shows K_S values calculated from eq. (6); in general, K_S increased with an increase in l/d and with the fiber treatment (sample Z6). However, the values of K_S were small, and this could be attributed to the small sizes of the fibers, which were probably lower than l_c . The effect of the fiber treatment was analyzed

by a comparison of samples Z2 and Z6. Sample Z6 had a higher tensile strength (13.03 MPa) than sample Z2 (10.39 MPa). This behavior was attributed not only to the increase in l/d (from 120.4 for Z2 to 136.7 for Z6) but also to the chemical modification of the fiber surface, which improved the adhesion between the fibers and polymeric matrix.

The tensile strength of the composites based on mater Bi-Y was lower than that of the polymeric matrix (see Table II) in almost all the systems. Also, in this case the strength was a growing function of l/d . In particular, samples Y4 and Y8 (with treated fibers), having the highest l/d values, showed higher tensile strengths than the polymeric matrix (sample Y1).

Creep properties

Generally, the creep of composite materials is affected by many factors, such as the fiber volume fraction, the temperature, the applied stress, and the adhesion between the fibers and matrix. Usually, the addition of fibers improves the creep resistance of polymeric matrices, and this improvement depends strongly on the fiber content and their dimensions, orientation, and distribution. It was reported that the use of jute fibers improved the creep resistance of polypropylene, but this improvement was strongly dependent on the fiber content and the adhesion between the fibers and matrix; an increase in the fiber volume fraction and the use of maleic anhydride-grafted polypropylene as a

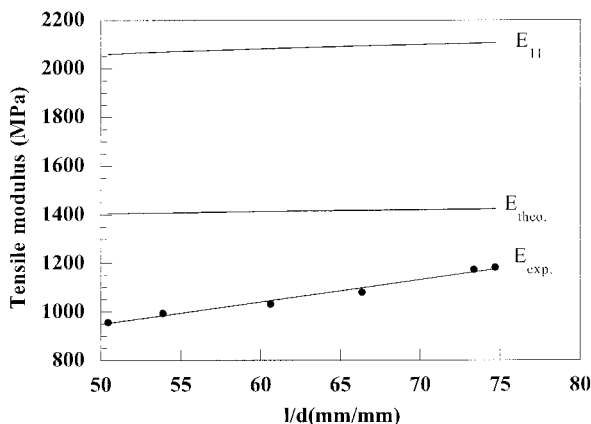


Figure 4 Effect of l/d on the tensile modulus of composites based on mater Bi-Y and sisal fibers.

TABLE III
Effect of Fiber Aspect Ratio on Strength Efficiency Factor

Sample	l/d (mm/mm)	K_s
Z2	72.4	0.078
Z3	97.2	0.132
Z4	120.4	0.164
Z5	126.2	0.157
Z6	136.7	0.277

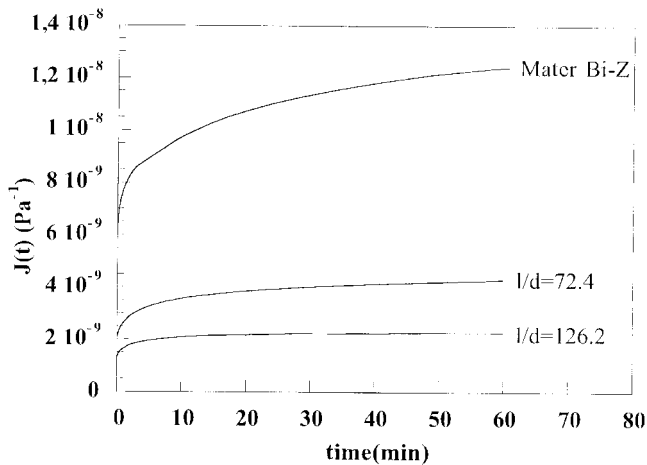


Figure 6 Creep behavior of composites based on mater Bi-Z.

coupling agent improved the creep resistance of polypropylene.²⁰

In Figures 6 and 7, the creep behavior of the biodegradable matrices is compared to the behavior of composites containing sisal fibers with different l/d values. The presence of fibers improved the creep resistance of the biodegradable polymers, and this improvement seemed to be a function of l/d .

The creep curves of all the samples recall the typical behavior of polymers above their glass-transition temperature. For these materials, the application of mechanical stress leads to a creep curve characterized by different stages: an initial elastic deformation related to the tensile modulus of the material, which is followed by a fast reorganization of the amorphous chains because of their high molecular mobility. This first creep stage is generally followed by a stabilization of the structure, which is characterized by a plateau in the creep curve. In semicrystalline polymers, the first stage can be followed by another slower deformation mechanism that is related to structural rearrange-

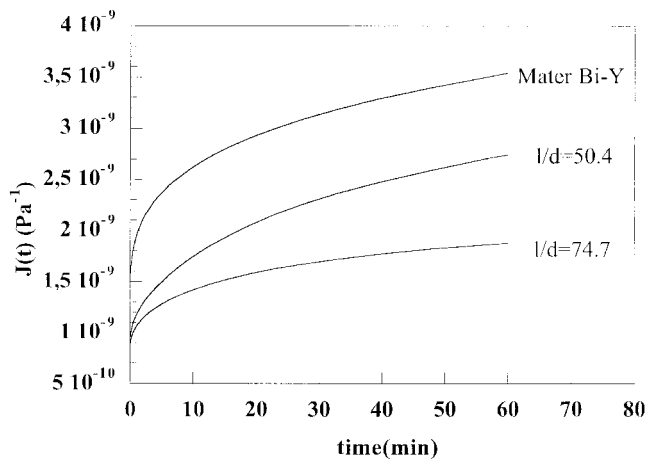


Figure 7 Creep behavior of composites based on mater Bi-Y.

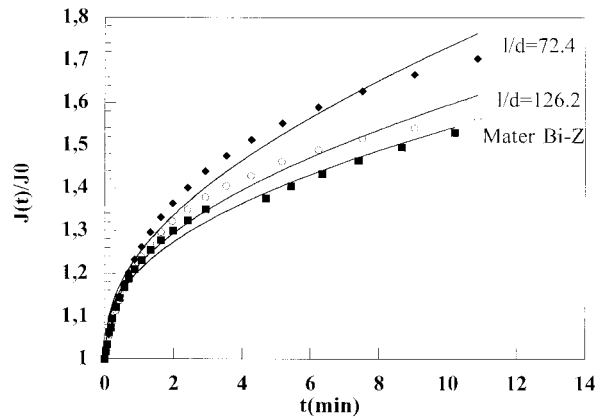


Figure 8 Theoretical and experimental creep curves of composites based on mater Bi-Z: (■) Z1, (○) Z3, and (◆) Z4.

ments of the crystalline structure. The analyzed materials did not show any plateau in the creep curves, except for sample Z3 (see Fig. 6).

As discussed previously, the explanation for the different creep behaviors of the analyzed composites is not only related to the creep behaviors of the different matrices. They are also a function of (1) the adhesion between the fibers and matrix, (2) l/d , and (3) the processing conditions, which can influence the extraction of lignin from the natural fibers and/or promote some chemical or physical modification of the components during the mixing process. The latter effects can be the results of the higher processing temperature, SR, or time of mixing employed to prepare some of the composite samples.

The creep compliance was analyzed with the following expression (Figs. 8 and 9), which is equivalent to a series of Maxwell models and was proposed by William and Watt:²¹

$$J(t)/J_0 = \exp(t/t^*)^\beta \tag{7}$$

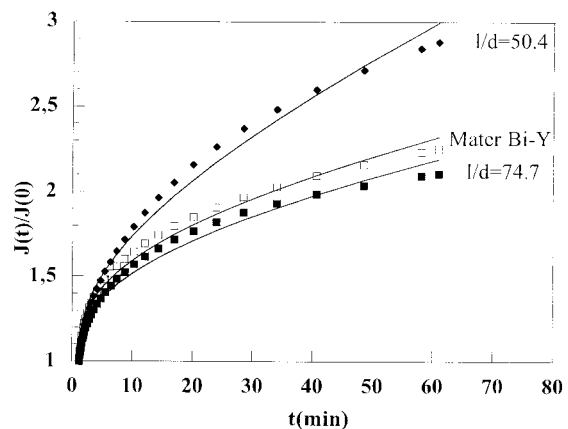


Figure 9 Theoretical and experimental creep curves of composites based on mater Bi-Y: (□) Y1, (■) Y4, and (◆) Y5.

TABLE IV
Effect of Fiber Aspect Ratio on William–Watt Parameters

Sample	l/d	t^*	β
Z1	—	104.45	0.35900
Z4	72.4	45.53	0.39613
Z3	126.2	78.81	0.36919
Y1	—	104.16	0.30787
Y5	50.4	46.12	0.35745
Y4	74.7	124.70	0.32897

where J_0 and t^* represent the initial creep compliance and the relaxation time, respectively, and β is related to the distribution of relaxation times.

The aforementioned theoretical model well describes the creep behavior of the composites based on mater Bi-Y (Fig. 9). For those composites based on mater Bi-Z, the fitting is good only in the initial part of the curves, particularly up to 10 min (Fig. 8). This is related to the differences in the chemical compositions of the two polymeric matrices. Mater Bi-Z is a blend of polycaprolactone, a semicrystalline polymer, and starch, whereas mater Bi-Y is mainly based on plasticized starch and cellulose. The initial creep of the composites based on the former polymers is, therefore, related to the creep of the amorphous part of the polymeric matrix; the creep depends on the crystalline part. Because the characteristic times of these two phenomena are very different, the model is not able to predict the creep behavior for the entire range investigated.

Table IV shows that β is only slightly affected by the addition of the fibers and l/d , but t^* is greatly affected. Contrary to what we expected, the composites Z4, Z3, and Y5 had lower characteristic t^* values than the polymer matrices (Z1 and Y1). However, an increase in l/d was followed by an increase in t^* . These results suggest that there is not a simple relationship between l/d and the creep of a composite. The effect of the processing conditions on both the polymeric matrices and the fibers should also be taken into account. In some cases, the higher processing temperatures could result in polymer degradation and lignin extraction from the fibers, which could induce two opposite effects on the creep behavior of the composites: it could plasticize the polymeric matrix, thereby reducing the relaxation time of the matrix (cf. samples Z1/Z4 and Y1/Y5), and it could lead to different surface properties of the fibers, which are responsible for fiber/matrix adhesion. The increase in l/d (samples Z4/Z3 and Y5/Y4) did not alone justify the increase in t^* , especially from sample Y4. For this reason, we think that the higher temperature (180°C) and longer mixing time (6 min) employed during the preparation of this composite modified the creep properties of the polymeric matrix.

CONCLUSIONS

The effects of the processing conditions on the mechanical and viscoelastic properties of composites based on sisal fibers and biodegradable polymers (mater Bi-Z and mater Bi-Y) were studied. Both the tensile and creep behavior depended strongly on the nature of the polymeric matrix and on the processing conditions, such as the temperature, SR, and time of mixing.

Composites based on mater Bi-Z (PCL/starch blends) were reinforced with sisal fibers; this was confirmed by the increase in both the elastic modulus and tensile strength. Composites prepared with mater Bi-Y (plasticized starch and cellulose) had higher elastic moduli and lower tensile strengths (except for sample Y8). The increase in the elastic moduli led to an increase in the creep resistance because the elastic contribution (J_0) to the creep compliance was lower. Finally, the increase in l/d , obtained under different processing conditions, led to materials with higher elastic moduli and creep resistance.

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