

Effects of the Moisture and Fiber Content on the Mechanical Properties of Biodegradable Polymer–Sisal Fiber Biocomposites

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ABSTRACT: The matrix of the composites that were used in this work was a commercial blend based on starch and cellulose derivatives. The biodegradable polymer was reinforced by short-sisal fibers with a range in fiber content of 5–15 wt %. The effects of humidity on the diffusion coefficients, equilibrium moisture content, and mechanical properties were studied. Equations obtained from microscopic mass balances for diffusion in solids were used to predict the absorbed humidity in both components (the sisal fibers and

biodegradable polymer) and in the composites as a function of time. Different model predictions of the composite diffusion coefficients as a function of the filler concentration were also examined, and they were found to be in agreement with the experimental results. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 4007–4016, 2004

Key words: biodegradable; blends; composites; mechanical properties

INTRODUCTION

All synthetic polymers absorb moisture when they are in a humid atmosphere or immersed in water. The sorption of water by nonpolar polymers containing a filler depends mainly on the nature of the filler.¹

Agrowastes and agroforest materials, for example, wood fibers, sisal, and bagasse, are slowly growing in a market of reinforced plastics and filled polymers presently dominated by glass fibers and other mineral reinforcements. The use of natural fibers is interesting because of their renewable nature, low cost, low density, and amenability to chemical modification.^{2,3}

Polymeric matrices filled with vegetable reinforcements offer a high specific stiffness and strength, flexibility during processing with no harm to the equipment, a low density, and a low cost-per-volume basis.⁴

Many matrices absorb moisture reversibly by Fickian diffusion. Impurities may be present causing non-Fickian processes to occur, which may lead to reversible effects. The situation becomes more complex with the aggregate of a second phase, the vegetal reinforcement. Under these circumstances; the presences of the filler modifies the response of the resin to a humid environment, especially when the two components independently have significantly different responses.

Absorbed moisture not only affects the dimensional stability but also the mechanical properties of the com-

posite because the water can act as a plasticizer. Consequently, the study of the diffusion of moisture in synthetic polymer–vegetable fiber composites is actually of practical and academic interest.

The matrix of the composites that was used in this study was a commercial blend based on starch and cellulose derivatives. The effects of water and other plasticizers on starch have been studied previously,^{5,6} and these studies concluded that the material was very sensitive to water absorption. However, no results were found in the literature about the effect of the humidity on the biodegradable polymer and its composites with natural fiber.

The aim of this study was to examine the moisture diffusion process in a composite material obtained from a cellulose derivative–starch blend matrix and sisal short fibers. The effect of the moisture on the mechanical properties was also studied, and it could be useful to select this material instead of a nonbiodegradable thermoplastic.

THEORETICAL APPROACH

Solid materials absorb moisture when they are immersed in water or when they are placed in a humid atmosphere until the process reaches the equilibrium state.

If one assumes that the moisture absorption process in a solid material is controlled by diffusion and if

- The composite is homogeneous material with an effective diffusion coefficient (D_{eff}).

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- The diffusion occurs into a planar sheet of material so thin that all the diffusing substances enter through the plane faces and a negligible amount enters through the edges.
- The sheet of material is exposed to a constant surface concentration [constant percentage relative humidity (RH%)].
- The sheet of material initially has a uniform concentration (e.g., uniform moisture content).

Then, the total amount substance entered into the sheet at time t (M_t) can be expressed as⁷

$$\frac{M_t - M_0}{M_\infty - M_0} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{D_{\text{eff}} t}{h^2}\right)\right]}{(2j+1)^2} \quad (1)$$

where M_0 is the weight of dry material, D_{eff} is the diffusion coefficient in the normal direction to the surface, h is the thickness of the sheet, and M_∞ is the total amount of diffusing substance entered into the sheet after exposition at constant moisture content at infinite time.

Equation (1) may be approximated by the expression⁷

$$\frac{M_t - M_0}{M_\infty - M_0} = 1 - \exp\left[-7.3 \left(\frac{D_{\text{eff}} t}{h^2}\right)^{0.75}\right] \quad (2)$$

Experimental evidence indicates that the maximum moisture content is insensitive to the temperature but depends on the moisture content of the environment. For a material immersed in a liquid

$$M_\infty = \text{Constant (liquid)} \quad (3)$$

For a material exposed to humid air, M_∞ depends on the RH%, according to the relationship⁷

$$M_\infty = a(\text{RH}\%)^b \quad (4)$$

where a and b are fitting parameters.

The time required for a material to attain at least 99.9% of its maximum possible moisture content (t_m) is

$$t_m = \frac{0.67h^2}{D_{\text{eff}}} \quad (5)$$

The time required to reach the maximum moisture content is insensitive to the moisture content of the environment but depends on the temperature by means of D_{eff} .

If one considers the fiber as a long cylinder in which the surface concentration is maintained constant and diffusion occurs only in the radial direction, the diffu-

TABLE I
Equilibrium Moisture Content Average of at Least Four Samples Conditioned at 30, 60, and 90 RH%

	30 RH%	60 RH%	90 RH%
Biodegradable matrix	1.24 ± 0.04	3.12 ± 0.24	15.05 ± 0.31
5 wt % sisal fiber composite	1.33 ± 0.06	3.18 ± 0.19	14.01 ± 0.18
10 wt % sisal fiber composite	1.33 ± 0.065	3.17 ± 0.22	13.60 ± 0.22
15 wt % sisal fiber composite	1.33 ± 0.07	3.37 ± 0.18	13.95 ± 0.24
Sisal fibers	0.648 ± 0.05	1.064 ± 0.07	10.61 ± 0.17

sion controlled uptake in the specimen is represented by the following equation:⁸

$$\frac{M_t - M_0}{M_\infty - M_0} = \frac{4}{\sqrt{\pi}} \left(\frac{D_f t}{r_f^2}\right)^{1/2} - \frac{D_f t}{r_f^2} - \frac{1}{3\sqrt{\pi}} \left(\frac{D_f t}{r_f^2}\right)^{3/2} + \dots \quad (6)$$

where r_f is the cylinder radius or half of the fiber diameter obtained by optical microscopy.

To describe the effective thermal or electrical conductivity of a composite material consisting of a continuous polymeric matrix and a reinforcing solid; two types of analysis have been used, and these analyses can be extended to any diffusion process.

First, the process of diffusion in an ideal void-free composite primarily depends on⁹

1. The diffusivity of the continuous matrix (D_m) and the diffusivity of the reinforcement (D_f).
2. The volume fraction of the matrix ($1 - V_f$) and the filler V_f .
3. In the case of fibrous filler, the spatial distribution and orientation of the fibers in the matrix.

Second, the effective diffusivity of the composite (D_c) also depends on the dimensions of the fibers and the degree of anisotropy of the relevant properties of the fibers and the matrix.

Limits on the effects of the various parameters on the diffusion coefficients of composites may be obtained by consideration of the two simple cases for the distribution of fibers in a composite: series and parallel distributions of fibers in the matrix.

These arrangements allow one to obtain the following expressions:

1. The fibers and matrix are arranged in series with respect to the flux of mass:

$$D_c = \frac{D_m D_f}{V_f D_m + (1 - V_f) D_f} \quad (7)$$

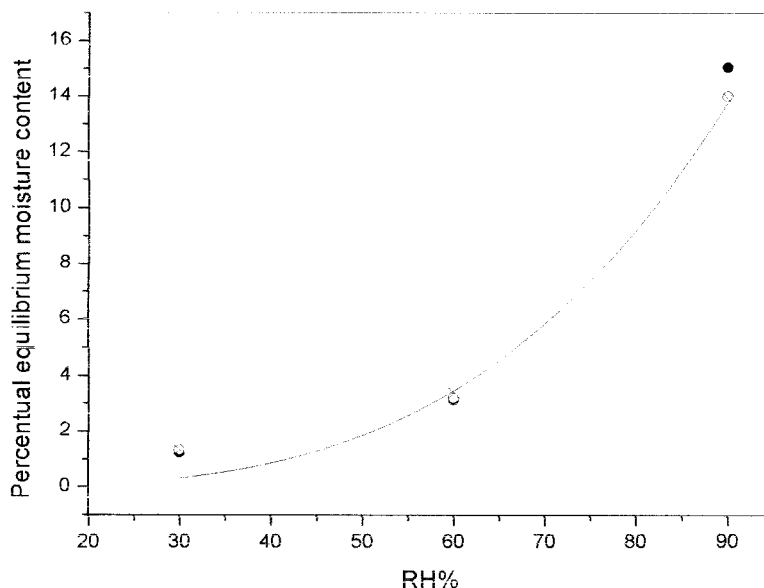


Figure 1 Nonlinear fitting for the equation $M_{\infty} = a(RH\%)^b$ for the (●) matrix and (○) 5, (▲) 10, and (+) 15 wt % sisal fiber composites.

- The flux is parallel to the two sections of material in the unit cell volume:

$$D_c = V_f D_f + (1 - V_f) D_m \tag{8}$$

Bruggeman’s model derived the expression for the conductivity of the dispersions of spherical or cylindrical particles, and it is applied for the diffusion coefficient:¹⁰

$$V_f \frac{(D_f - D_c)}{(D_f + D_c)} + (1 - V_f) \frac{(D_m - D_c)}{(D_m + D_c)} = 0 \tag{9}$$

EXPERIMENTAL

Materials

MaterBi-Y was a commercial blend based on cellulose derivatives, starch, and additives (Novamont, Novara, Italy). It was used as a biodegradable matrix. The elastic modulus of this material, measured by ASTM 638, was 2.1–2.5 GPa, the maximum stress was 640 MPa, and the glass-transition temperature was 105°C, as reported in the technical data. The glass-transition temperature was tested with a DMA 7-e (PerkinElmer, Connecticut).

Brascorda Brazil (Paraiba, Brazil) supplied the sisal fibers. The fibers were used as received without further treatment. The average length and fiber diameter of the sisal fibers were determined by optical microscopy over 100 fibers. The length was 7.2 ± 0.6 mm, and the diameter was 0.3 ± 0.05 mm. The density of the fibers was determined by pycnometry in water, and it was 1370 kg/m^3 .

The mold had a rectangular cavity $200 \times 100 \times 3$ mm in size with a gate located in the center of the length side. The cellulose derivative–starch blend matrix and the sisal fibers were incorporated into the injection-molding machine (Sandretto 60 tn) (Milan, Italy) without previous mixing. This procedure was chosen to preserve, as much as possible, the length and the diameter of the fibers. In fact, the conventional compounding technique (extrusion and injection) can ensure a good dispersion of fibers, but it also results in a considerable reduction in the fiber length and diameter.¹¹

Methods

Water sorption

Humid environments were prepared in hermetic boxes maintained at 20°C with aqueous solutions of sulfuric acid (17, 40, and 51 wt %) to ensure 90, 60, and 30 RH%, respectively.¹²

Short sisal fiber samples (about 1.5 g) were dried until a constant weight was reached before they were exposed to wet environments for short intervals of time in which the weights were recorded.

Composite and neat matrix specimens were kept in the humid environments to monitor the weight gain resulting from moisture sorption. The specimens dimensions were $60 \times 20 \times 3$ mm. All of the samples were dried until a constant weight was reached before they were exposed to the humid environments.

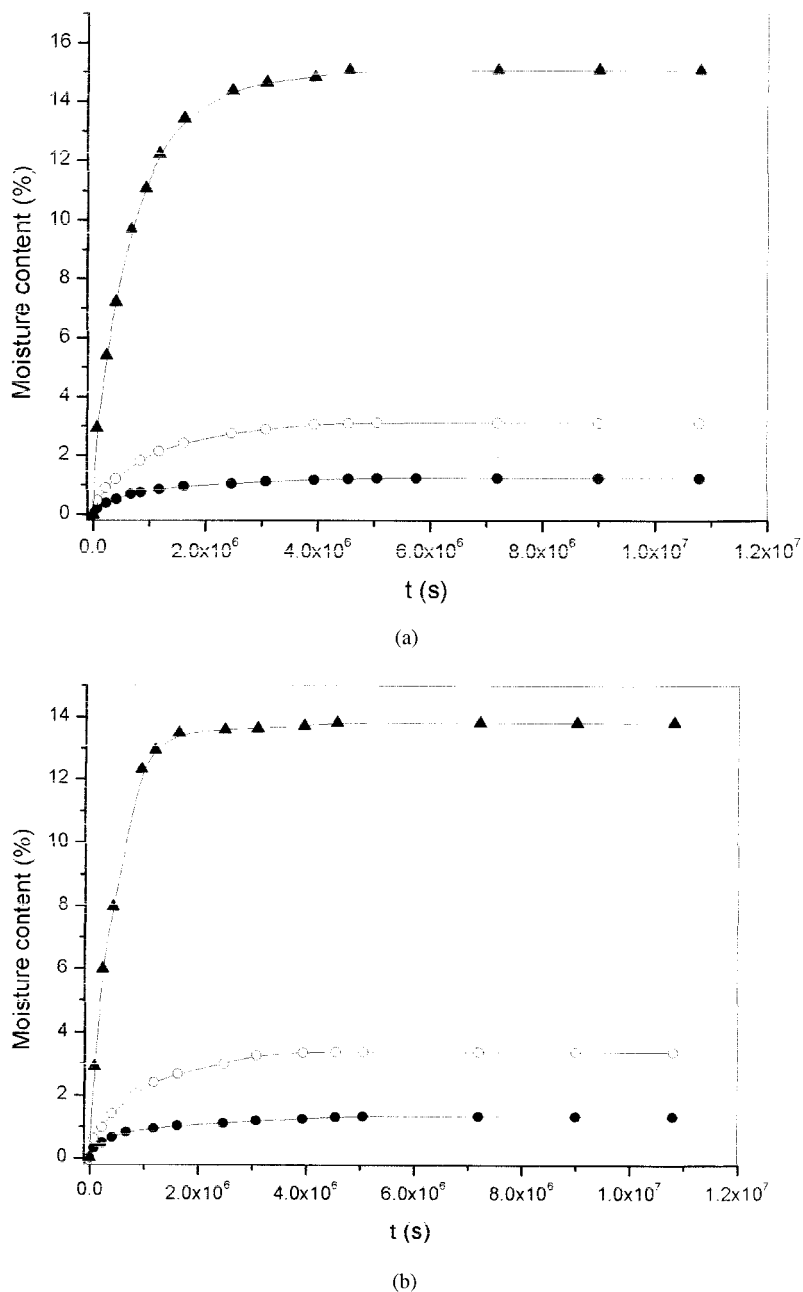


Figure 2 Moisture content as a function of time at different RH% values: (●) 30, (○) 60, and (▲) 90 RH%. The line indicates the union of the experimental points: (a) matrix and (b) 15 wt % sisal fiber composite.

TABLE II
Effective Diffusion Coefficients Calculated for Used Materials

	D_{eff} (mm ² /s)		
	30 RH%	60 RH%	90 RH%
Biodegradable matrix	$8 \times 10^{-7} \pm 2.3 \times 10^{-8}$	$8.3 \times 10^{-7} \pm 2.33 \times 10^{-8}$	$1.23 \times 10^{-6} \pm 3.34 \times 10^{-8}$
5 wt % sisal fiber composite	$9.55 \times 10^{-7} \pm 4.2 \times 10^{-8}$	$1 \times 10^{-6} \pm 2.75 \times 10^{-8}$	$1.38 \times 10^{-6} \pm 4.7 \times 10^{-8}$
10 wt % sisal fiber composite	$9.07 \times 10^{-7} \pm 3.1 \times 10^{-8}$	$9.25 \times 10^{-7} \pm 3.1 \times 10^{-8}$	$1.59 \times 10^{-6} \pm 7.2 \times 10^{-8}$
15 wt % sisal fiber composite	$9.42 \times 10^{-7} \pm 3.6 \times 10^{-7}$	$9.65 \times 10^{-7} \pm 2.6 \times 10^{-8}$	$1.66 \times 10^{-6} \pm 7.5 \times 10^{-8}$
Sisal fibers	$3.92 \times 10^{-6} \pm 3.2 \times 10^{-7}$	$6.97 \times 10^{-6} \pm 5.5 \times 10^{-9}$	$7.33 \times 10^{-6} \pm 5.05 \times 10^{-9}$

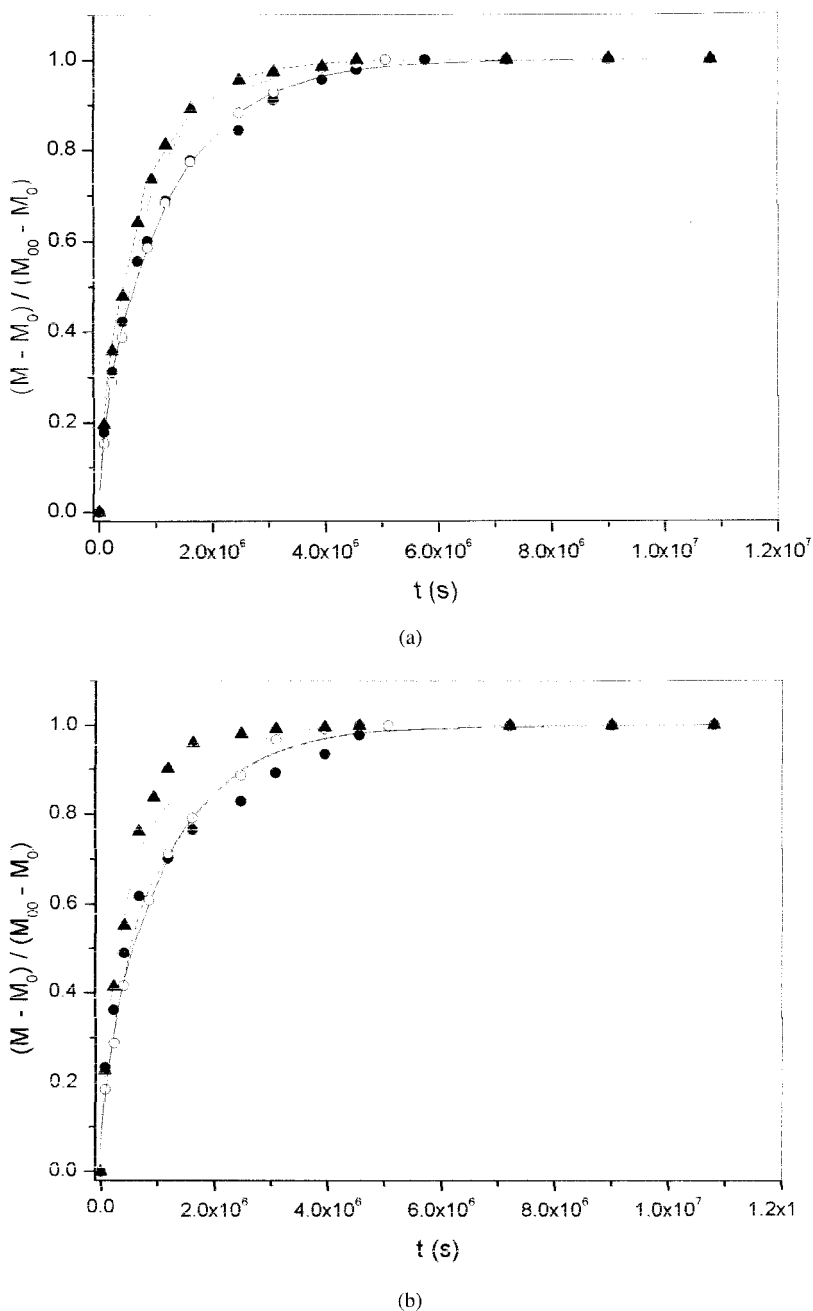


Figure 3 Comparison of experimental data and the curve obtained with D_{eff} for different RH% values [(---) 30, (—) 60, and (···) 90 RH%] for (a) the matrix and (b) 15 wt % sisal fiber composite.

Mechanical testing

Three-point bending tests were performed on matrix and composites in accordance with ASTM D 790-93 procedure A on an Instron testing machine (UK). At least four tests for each sample were run.

RESULTS AND DISCUSSION

Table I summarizes the final (equilibrium) moisture content reached by the neat sisal fiber, the matrix, and the composites in 30, 60, and 90 RH% environments.

The equilibrium moisture content of the sisal fibers was lower than the matrix value. This result was related to the composition of the fiber (cellulose, hemicellulose, and lignin) and the biodegradable matrix (starch, cellulose derivatives, and additives). Starch is one compound that easily absorbs water. When the fiber content increased, the decrease in starch and the increase in fiber content should have reduced the equilibrium moisture, but the results showed that there was a slight increase in the relative moisture content, possibly because of the effect of a poor interphase

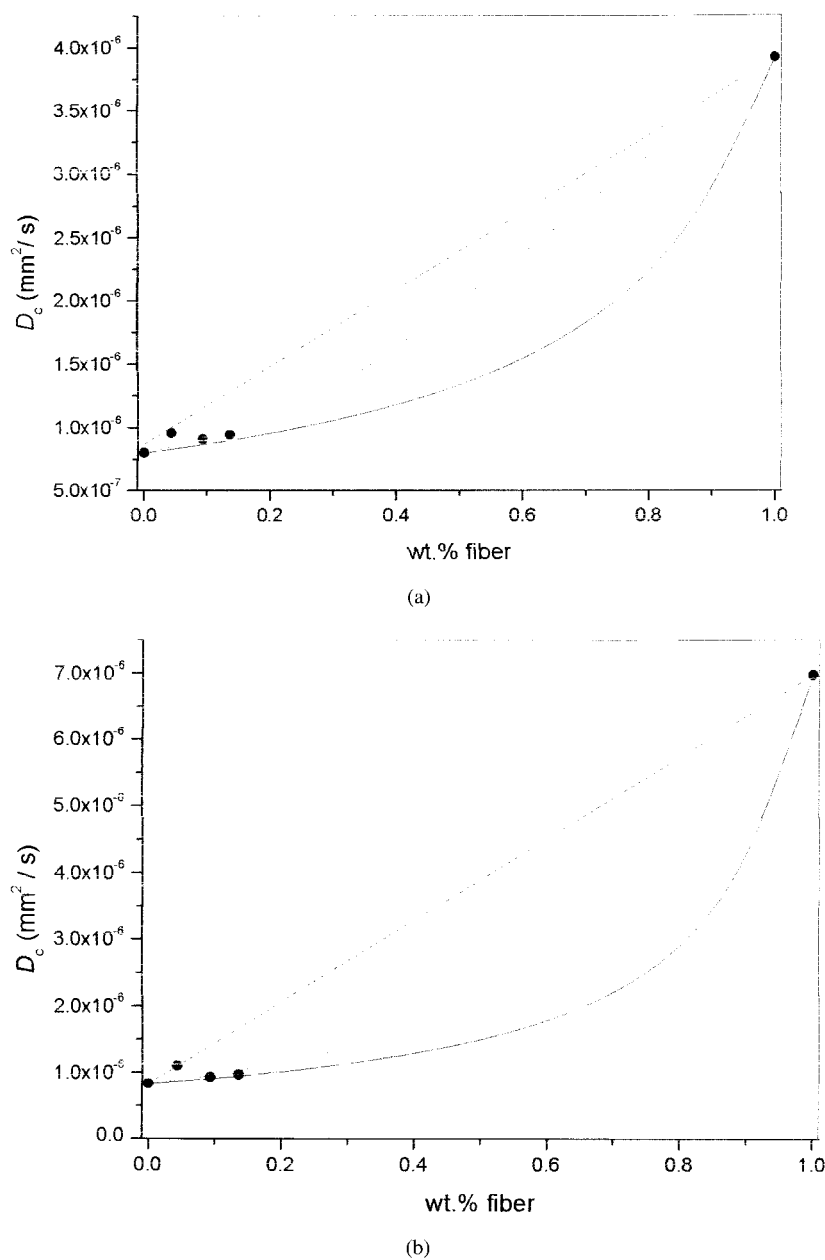


Figure 4 Comparison between composite D_{eff} values with curves predicted by different models [(---) series, (—) parallel, and (· · ·) Bruggeman models] for (a) 30, (b) 60, and (c) 90 RH%.

when the fiber content increased. The equilibrium moisture content changes more when the RH% increases (i.e., when the driving forces increase) than when the fiber content increases.

Equation 4 was used to calculate parameters a and b . Figure 1 show the fittings. The average values obtained were similar for all of the materials:

$$M_{\infty} = 20.8(\text{RH}\%)^{3.65} \quad (10)$$

As shown in Figure 2(a,b), the moisture content of the matrix and the 15 wt % sisal fiber compos-

ite was plotted as a function of time for different RH% values to illustrate the behavior described previously.

D_{eff} values were calculated with eq. (1) for the matrix and composites and with eq. (6) for the fibers taken as cylinders. The results are shown in Table II. A comparison between the theoretical predictions and the experimental data is shown on Figure 3(a,b) for the matrix and 15 wt % sisal fiber composites, respectively. The model prediction was in agreement with the experimental data. There did not seem to be differences between the materials.

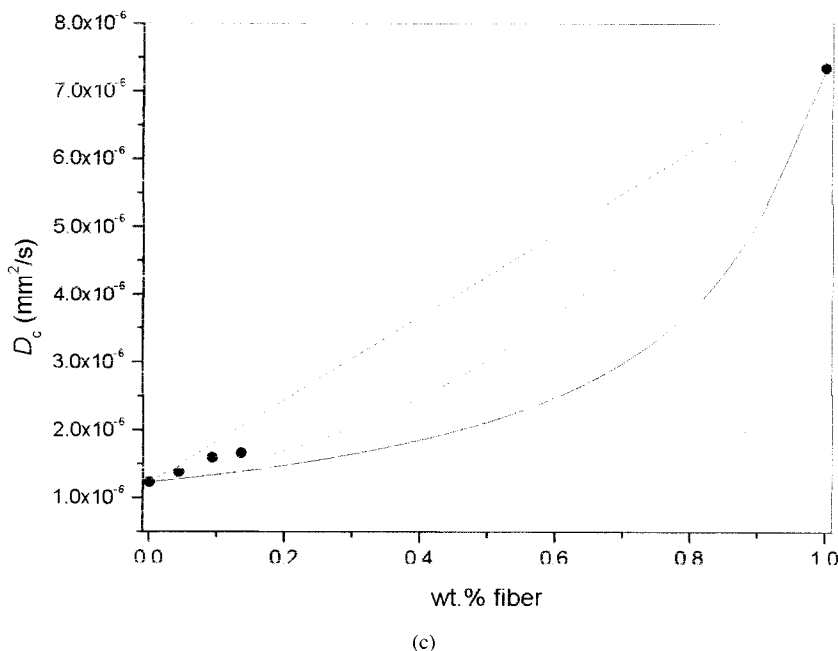


Figure 4 (Continued from previous page)

Theoretical models were used to predict the composite diffusion coefficients as a function of the fiber concentration. The results are shown in Figure 4 for 90 RH% for the series, parallel, and Bruggeman models. The diffusion coefficient values behaved more like the series model than the parallel one. Bruggeman is a combination of both models and presented the best fitting because the fibers were randomly orientated, some were in arranged in series and some were arranged in parallel.

Figure 5 shows the results obtained in the three-

point bending tests of dry samples. The modulus increased as fiber content increased, as we expected. Both models fit the experimental values because the errors were higher than the model prediction values.

Figure 6(a,b) shows the changes in flexural modulus for the matrix and 15 wt % sisal fiber composites after immersion. As illustrated in this figure, the modulus loss was important for all RH% values used for both the matrix and the composites. For the matrix, the loss was lower than for the 15 wt % sisal fiber composites. For both the matrix and the composites, the decrease

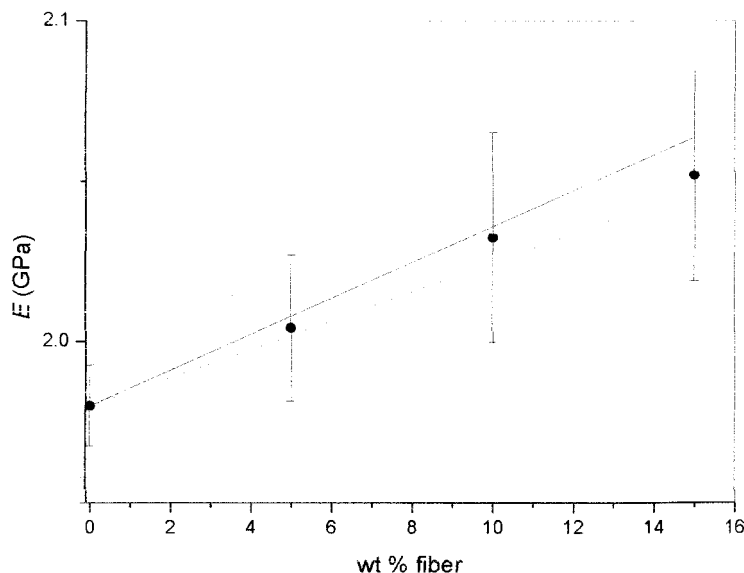


Figure 5 Flexural modulus of dry materials for different contents of fiber: (---) series and (—) parallel models.

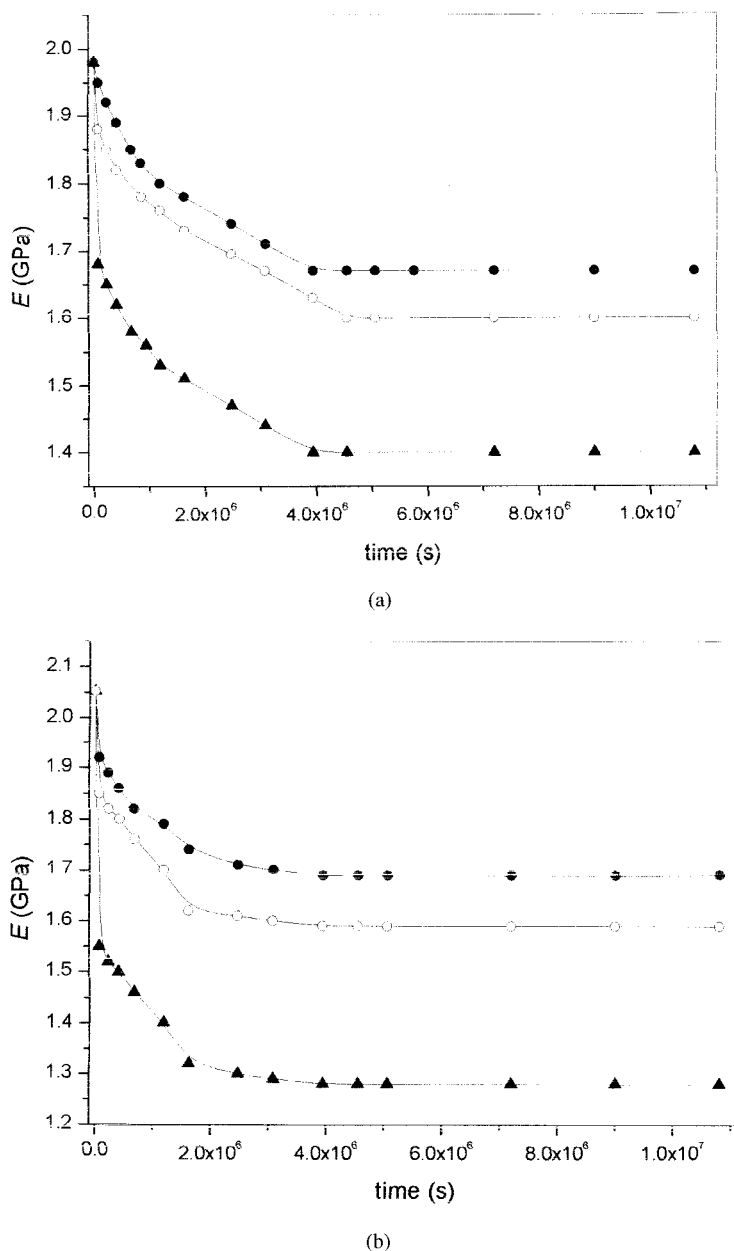


Figure 6 Changes in the modulus of the wet samples for (a) the biodegradable matrix and (b) 15 wt % sisal fiber composite.

in flexural modulus was more abrupt at higher RH% values.

Table III shows the modulus loss for all of the materials used at different RH% values. Humidity affected the composites more than matrix, but the differences were not so significant. This major effect was probably caused by the interphase.

One useful result of the study was the value of the modulus as a function of the water absorption when the material was located in a humid atmosphere. Figure 7(a,b) shows the change in the modulus of the matrix and the 15 wt % sisal fiber composite as a function of the moisture content of the sample. The behavior of the moisture absorption process showed

TABLE III
Modulus Loss After Humidity for Different Materials

Material	Modulus loss					
	30 RH%		60 RH%		90 RH%	
	E_{∞}^a (GPa)	Loss (%)	E_{∞} (GPa)	Loss (%)	E_{∞} (GPa)	Loss (%)
Biodegradable matrix	1.67	15.66	1.60	19.19	1.40	29.29
5 wt % sisal fiber composite	1.68	16.22	1.60	20.12	1.34	33.14
10 wt % sisal fiber composite	1.69	17.12	1.60	21.08	1.32	35.18
15 wt % sisal fiber composite	1.69	17.64	1.59	22.51	1.28	37.62

^a E_{∞} is the equilibrium modulus of the equilibrium moisture value (M_{∞}).

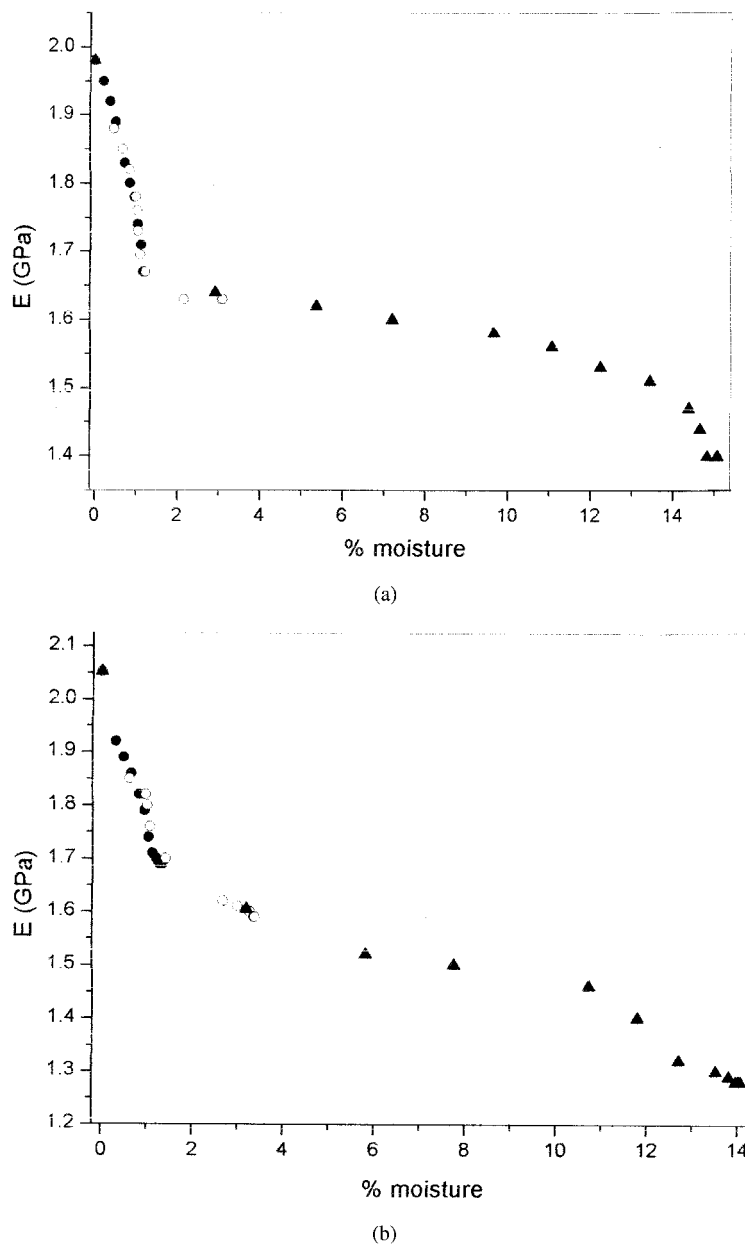


Figure 7 Change in the modulus of the wet samples for different RH% values: (●) 30, (○) 60, and (▲) 90 RH%.

that there were two zones in the process. The first zone may have been related to the absorption of water through the starch, and the second process may have been related to the absorption of cellulose acetate and cellulose fibers. The sisal fibers acted as a reinforcement; as a consequence, the decrease in the modulus was less abrupt.

CONCLUSIONS

The moisture sorption of cellulose derivative-starch blends, sisal fibers, and their composites were studied at different RH% values.

Despite the fact that the sisal fibers absorbed less moisture than the matrix, the equilibrium moisture content depended more on the RH% than the fiber content in the studied range. The interphase may have influenced the equilibrium content because when the fiber content increased, the interphase or voids in the composites also increased.

The diffusion coefficients were similar for the different fiber contents. In this case, the fiber presented higher diffusion coefficients values than the matrix and composites. The values showed slight increases in the diffusion coefficient with the fiber content only for 90 RH%.

From theoretical models together with the diffusion coefficients of each component, the D_c values were estimated. The obtained values were useful for representing the behavior of the different materials at 30, 60, and 90 RH%.

Different models were used to derive the D_c values from the diffusion coefficients of the fibers and the matrix.

The mechanical properties determined for the wet samples were poor. In all cases, the mechanical properties worsened as the humidity of the environment increased. When the fiber content increased, the loss of flexural modulus slightly increased, but the effect of RH% changed more than the fiber content. By means of the superposition of the different samples obtained at different RH% values, it was possible to obtain a relation between the modulus and the moisture content.

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