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# Moisture diffusion in polyester–woodflour composites

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## Abstract

The understanding of water–polymer interactions in polymeric composite materials is critical to the prediction of their behavior in applications where they are exposed to water or humid environment. Moisture diffusion in unsaturated polyester–woodflour composites exposed to environments kept at room temperature and different relative humidities was investigated. Equations obtained from microscopic mass balances for vapor diffusion in solids were used to determine the effective diffusion coefficients of the different woodflours, neat resin and composites. The effect of the size and shape of the composite specimens used in the experimental work on the final moisture content was also evaluated. Different models were used to predict the composite effective diffusion coefficients as a function of filler concentrations.

*Keywords*: Woodflour composites; Water diffusion; Moisture sorption

## 1. Introduction

Agrowastes and agroforest materials, e.g. sawdust, wood fibers, sisal, bagasse, etc. are slowly penetrating the reinforced plastics market, presently dominated by glass fibers and other mineral reinforcements. This kind of fillers has very good mechanical properties and low density, and can be loaded into polymeric resin matrices to make useful structural composite materials.

For many applications of filled polymers, knowledge of properties such as permeability, thermal and electrical conductivities, diffusion coefficients, thermal expansion, and density is important. Unfortunately, in comparison with the effects of fillers on mechanical behavior, much less attention has been paid to such composite properties.

All synthetic polymers absorb moisture in a humid atmosphere or when they are immersed in water. The sorption of water by nonpolar polymers containing a filler depends mainly on the nature of the filler [1]. Thus, for hydrophilic fillers such as sawdust and woodflour, an increment in water sorption may be expected.

Moisture diffuses into polymers to different degrees depending upon a number of molecular and microstructural aspects [2]:

1. polarity of the molecular structure, presence of chemical groups capable of forming hydrogen bonds with water;
2. degree of crosslinking;
3. presence of residual ‘monomers’ and/or other water attracting species, e.g. glass surfaces;
4. crystallinity of the polymer (well-defined crystallites are inaccessible to water).

Many matrix resins absorb moisture reversibly by Fickian diffusion, but resin chemical structure and microstructure are complex, both in crosslinking density and polarity. Adventitious impurities may be present. These factors cause non-Fickian processes to occur, which may or may not lead to reversible effects. The situation becomes more complex with the aggregate of a second phase: the vegetal reinforcement. Under these circumstances, the presence of the filler modify the response of the resin to humid environments, especially when the two components independently have significantly different responses.

Although completely rigorous and proven solutions for the problem of the diffusion of vapors or gases through polymers have not been developed, it can be readily seen that the diffusion process in a two-component system depends upon numerous factors, such as type, shape and orientation of the filler particles, characteristics of the matrix and interfacial properties.

It is well known that the presence of water reduces the glass transition temperature ($T_g$) of the polymers and hence the maximum useful temperature of the composite. Residual

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stresses may also be enhanced if moisture diffusion leads to a non-linear thermal expansion coefficient/temperature profile. Absorbed moisture not only affect the dimensional stability but also the mechanical properties of the composite. Consequently, the study of the diffusion of moisture in synthetic polymer–vegetable filler composites is actually of practical and academic interest.

The aim of this work is to study the characteristics of the moisture diffusion process in a composite material obtained from an unsaturated polyester resin and woodflour. This type of fillers are usually chemically modified in order to change its water affinity and to enhance the dispersion and adhesion with the matrix. Some results obtained for modified woodflour and derived composites are also presented for completeness. Equations obtained from microscopic mass balances for diffusion in solids were used to predict absorbed humidity in both components (woodflours and neat resin) and in the composites as a function of time. Effective diffusion coefficients were used, which include any non-Fickian effect that may be present in the system (e.g. capillary transfer of moisture and water diffusion through the microscopic and submicroscopic structure of wood [3]). Different model predictions of the composite diffusion coefficients as a function of filler concentration are also presented and their agreement with experimental results is discussed.

## 2. 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 an equilibrium state. However, in some cases, the omnipresent latent heat effects may complicate the determination of the diffusivity. Nevertheless, over the range of temperature and moisture concentration that prevails in typical applications of composites, the thermal diffusivity is about $10^6$ times greater than the moisture diffusion coefficient. Thus, the thermal diffusion takes place $10^6$ times faster than the moisture diffusion. As a result, the temperature will reach the equilibrium long before the moisture concentration does. This observation allows to solve the mass balance separately from the balance of energy [4].

Assuming that the moisture absorption process in a solid material is controlled by diffusion, and considering that:

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

the total amount of diffusing substance entered into the sheet at time $t$ ($M_t$) can be obtained from [5] the equation:

$$\frac{M_t}{M_\infty} = 1 - \sum_{0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[ \frac{-D\pi^2}{4l^2} (2n+1)^2 t \right] \tag{1}$$

where $D$ is the diffusion coefficient, $2l$ is the thickness of the sheet and $M_\infty$ is the total amount of diffusing substance entered into the sheet after an infinite time.

If we deal instead with long cylinders in which the surface concentration is maintained constant, and the diffusion occurs only in the radial direction, the early stages of diffusion controlled uptake in the specimen are represented by [5] the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left( \frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\sqrt{\pi}} \left( \frac{Dt}{a^2} \right)^{3/2} + \cdots \tag{2}$$

where $a$ is the cylinder radius.

However, to predict the total amount of diffusing substance entering or leaving a sphere of radius $a$, with constant concentration on the surface, the following equation may be used:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp\left[ \frac{-D\pi^2 n^2 t}{a^2} \right]. \tag{3}$$

Unfortunately, little attention has been given to the study of the diffusivity of polymer composite materials, although the study of thermal and electrical conductivities in filled materials has a specially long history. Conveniently, the laws of transport phenomena for thermal and electrical conductivities, magnetic permeability, diffusivity and dielectric constants are often similar in form, so that, with appropriate changes in nomenclature and allowance for intrinsic differences in detail, a general solution can be used as a basis for characterizing several types of transport behavior [6]. Thus, some equations developed to predict thermal conductivity in filled materials (including the appropriate changes in nomenclature) will be presented and used to estimate the diffusivity of the composites.

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 employed. The first, and usually the simplest approach, rests on the assumption that a composite material may be considered as a network of resistances. The following analysis is applied universally to all related conduction phenomena and the symbol $D$ may represent thermal conductivity, electrical conductivity, diffusion coefficient, dielectric constant, or permeability [7].

The process of diffusion in an ideal, void-free composite will primarily depend on:

1. the diffusivity of the continuous matrix, $D_m$ and that of the reinforcement, $D_f$;
2. the volume concentration of the matrix $(1 - V_f)$ and the filler $V_f$; and

3. in the case of fibrous filler the spatial distribution and orientation of the fibers in the matrix.

In the last case, the effective conductivity $D_c$ of the composite will also depend on the dimensions of the fibers and the degree of anisotropy of the relevant properties of the fibers and matrix materials.

Limits on the effect of the various parameters on $D$ may be obtained by considering the two simpler cases for the distribution of continuous fibers in a composite: series and parallel distribution of the fibers in the matrix. These arrangements allow to obtain the following expressions:

# fibers and matrix arranged in series with respect to the flux of mass

$$D_c = \frac{D_m D_f}{V_f D_m + (1 - V_f) D_f} \tag{4}$$

# flux is parallel to the two sections of material in the unit cell volume

$$D_c = V_f D_f + (1 - V_f) D_m. \tag{5}$$

Different approaches must be followed to solve the problem of diffusion in composites formed by a continuous matrix, loaded with discontinuous filler particles. In this work, small particles of wood (maximum average diameter = 57 μm) instead of continuos or long fibers were used as fillers in a polymeric matrix, thus the predictions obtained from equations derived for particulate systems will be analyzed in the following paragraphs. This is the case of the Kerner equation [6], which assumes that the thermal conductivity could be considered as a weighed linear superposition of the component conductivities. Then, for spheres suspended in a matrix, the following equation is obtained:

$$D_c = \frac{\sum_{i=m,f} D_i V_i 3D_f/(D_i + 2D_f)}{\sum_{i=m,f} V_i 3D_f/(D_i + 2D_f)}. \tag{6}$$

Bruggeman [7] derived the following for the conductivity of dispersions of spherical or cylindrical particles:

$$V_f \frac{(D_f - D_c)}{(D_f + D_c)} + (1 - V_f) \frac{(D_m - D_c)}{(D_m + D_c)} = 0. \tag{7}$$

The thermal conductivities of porous media (voids filled with liquids or gases or solid ‘obstacles’) are also correlated by Rusell’s equation [8]. In the nomenclature employed in diffusion process the expression become:

$$D_c = D_m \left[ \frac{\beta V_f^{2/3} + 1 - V_f^{2/3}}{\beta (V_f^{2/3} - V_f) + 1 + V_f^{2/3} + V_f} \right] \tag{8}$$

where $\beta$ is the ratio of the diffusivity of the obstacles to that the continuos phase ($D_f/D_m$). Eq. (8) is applicable when the particle size is reasonably uniform.

## 3. Experimental

### 3.1. Materials

The matrix was a solid unsaturated polyester resin (RQ 426, Perlinac S. A., Argentine), based on bisphenol A-fumarate. The pellets were solubilized in and then cross-linked with styrene in a 60:40 proportion (resin:styrene) using benzoyl peroxide (Lucidol 0.75, Akzo Chemical S. A) as initiator, 1.5% wt. with respect to the total reaction mixture.

The chosen filler was woodflour (average particle size less than 57 μm; aspect ratio varying approximately from 1 to 5) from *Eucaliptus Saligna* (Entre Rios, Argentina). In order to achieve different levels of filler–polymer interaction, part of the woodflour was pretreated by soaking in a 10% wt. aqueous solution of NaOH for 1.5 h at room temperature. After that, the fibers were esterified by reflux in a 4.08 N xylene solution of maleic anhydride (MAN) during 24 h. The filler obtained in this way is less polar, and hence, less hygroscopic than the starting one.

Molded plates of composite material were obtained compounding the filler (untreated, NaOH treated or esterified) with the polyester resin in selected proportions in an intensive mixer. The mixture (a high-viscosity, paste-like material) was cured in a metal mold (145 mm of diameter and about 3 mm of thickness) at 80°C and 3.8 MPa of pressure during 1.5 h, and finally, postcured at 150°C during 2 h. Control samples of neat resin (initially liquid samples) were also prepared by pouring the polymer between two glass slides and curing the sample with the same temperature history as the composites.

Composite and neat resin specimens of approximately $3 \times 26 \times 70\ \text{mm}^3$ (sheets) or $2 \times 2 \times 4\ \text{mm}^3$ (small short bars) were cut from the molded plates for testing.

The detailed description of the chemical characterization of the filler and composite preparation can be found in a previous publication [9].

### 3.2. Procedure

Humid environments at 20°C were prepared in hermetic containers using aqueous solutions of sulfuric acid (18 and 35 wt.%) to ensure 90 and 60 relative humidity (RH).

Woodflour samples of about 1 g were exposed to moisture during different time intervals, and the weight changes were recorded at regular intervals of time.

Composite and neat resin specimens were kept in the humid environments to monitor the weight gain resulting from moisture sorption. The samples remained in these conditions up to 170 days to ensure that the time was enough to reach the equilibrium moisture content.

All the samples were dried until constant weight determined with a sensitive balance (±0.001 g), previously to be exposed to the humid environment.

Table 1
Percentual equilibrium moisture content (EMC, %), average of at least 3 tests samples conditioned at 60 and 90 RH

| Material | Woodflour (weight %) | 60 RH | | 90 RH | |
|---|---|---|---|---|---|
| | | Sheets | Small short bars | Sheets | Small short bars |
| Matrix | 0 | 0.34 ± 0.04 | — | 0.55 ± 0.02 | — |
| Composite | 20 | 1.04 ± 0.05 | 2.82 ± 0.27 | 2.20 ± 0.15 | 3.75 ± 0.26 |
| | 40 | 1.99 ± 0.24 | 3.53 ± 0.70 | — | 5.52 ± 0.10 |
| Woodflour | 100 | 8.70 ± 0.30 | | 18.22 ± 0.40 | |

## 4. Results and discussion

### 4.1. Composite material

Table 1 summarizes the final (equilibrium) moisture content (EMC) reached by the neat woodflour and by the composites made from untreated woodflour (sheets and small short bars) in 60 and 90 RH environments as a function of the wt.% of filler. As expected, the moisture saturation levels of these materials increase as the filler concentration increases (owing to the polar-hygroscopic nature of the woodflour) and as the relative humidity of the ambient increases (increment of the driving force). In Fig. 1 the moisture content of the composites (sheets) was plotted as a function of the time for specimens with different percentage of filler, in order to illustrate the behavior described above.

For the composites studied, specimens of two different sizes were tested. In the case of large samples (3 mm × 26 mm × 70 mm), the area perpendicular to the thickness direction is much larger than the areas of the borders (edges), thus, these specimens can be considered as plane sheets. Instead, the small short bars (2 mm × 2 mm × 4 mm) have all the sides of comparable and small dimensions, the center of the specimen is close to the borders in all directions and the moisture that enters through the "edges" cannot be neglected. Table 1 shows that small bars reach a higher equilibrium humidity content than larger samples. Fig. 2 shows the water uptake vs. time for the 40% untreated woodflour composites, with specimens of different sizes. It can be noticed the smaller dispersion of the experimental results obtained from sheets vs. those obtained from the small volume bars. This is a consequence of the absolute weighing errors associated with the technique, which affect relatively more the moisture content values of the smaller sample.

A simple rule of mixtures applied to the equilibrium moisture uptake of a 40% untreated woodflour composite would predict an EMC of 3.68% (at 60 RH, $\mathrm{EMC}_{\mathrm{woodflour}} = 8.70$, $\mathrm{EMC}_{\mathrm{matrix}} = 0.34\%$) [9]. This last value is quite close to the measured value, 3.53% corresponding to small samples, but is far larger than the 1.99% measured in larger specimens. This unexpected behavior can be explained considering the different absorption features that may occur in the specimen near the edges.

Particles close to the edges have less restrictions to swell during water absorption that particles in the middle of the piece. Since, water absorption in wood is accompanied by swelling, particles far from the edges with larger mechanical constraints from the surrounding media may never reach the same equilibrium water content of a free particle. Of course, this would be more noticeable in sheet specimens, as for the small bars the center of the piece is always near the edges.

In other words, the larger area/volume ratio of the small bars would be the reason why they reach a larger EMC and one closer to that predicted by a rule of mixtures.

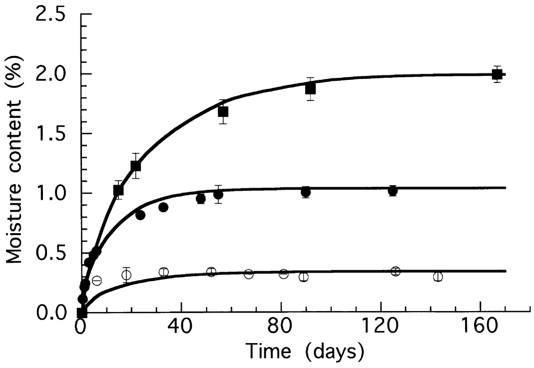

Fig. 1. Moisture content as function of time for composites made from different concentrations of untreated woodflour at 60 RH. Experimental determinations were made from sheets and the curves were obtained from fitting the data to Eq. (1). Here ○: 0%wt. (neat resin); ●: 20% wt.; ■: 40% wt.

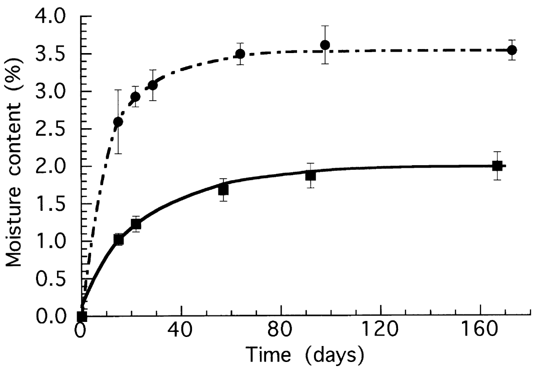

Fig. 2. Comparison of the experimental moisture content at 60 RH for the material loaded with 40% by weight of untreated woodflour. Experimental points corresponds to two different specimens: ■, sheets; ●, small short bars. Fitting curve for sheet specimen was obtained using Eq. (1).

Table 2
Diffusion coefficients of neat resin and composites filled with woodflour (determined from experimental value of sheets). Woodflour particles were taken as long cylinders or spheres of diameter = 57 μm. Diffusion coefficients were obtained at 60 RH

| Material | Woodflour (weight %) | Diffusion coefficient (cm$^2$/s) |
|---|---|---|
| Matrix | 0 | $1.51 \times 10^{-8}$ |
| Composite | 20 | $8.27 \times 10^{-9}$ |
| | 40 | $5.47 \times 10^{-9}$ |
| Woodflour | 100 (cylinder) | $2.73 \times 10^{-11}$ |
| | 100 (sphere) | $1.51 \times 10^{-11}$ |

However, for most of the practical applications of these materials (housewares, decorative panels, automobile panels), the required geometry is that of panels; large areas with a relatively small thickness, where the edge effects are negligible. For that reason, the diffusion of water in sheet specimens was investigated (the corresponding EMC being considered, as well as the one dimensional moisture diffusion).

Table 2 summarizes the values calculated for the effective diffusion coefficients of the different materials as a function of the concentration, calculated from the measurements made at 60 RH for sheets. Eq. (1) was utilized in order to do that, because the dimensions of the samples are large enough to ensure that the moisture entering through the edges is negligible. The calculated diffusion coefficient of the neat resin was found to be in agreement with the values reported in bibliography for similar polymers. For example, Whitaker and coworkers [10] found diffusion coefficients of $1.3 \times 10^{-8}$ and $0.64 \times 10^{-8}$ cm$^2$/s for two different commercial unsaturated polyester resins (crosslinked with styrene).

All the experimental data obtained from sheets were fitted with Eq. (1), taking the average diffusion coefficient as the only fitting parameter. Fig. 1 also show that this model represent quite well the experimental moisture uptake of composites filled with untreated woodflour data up to long times.

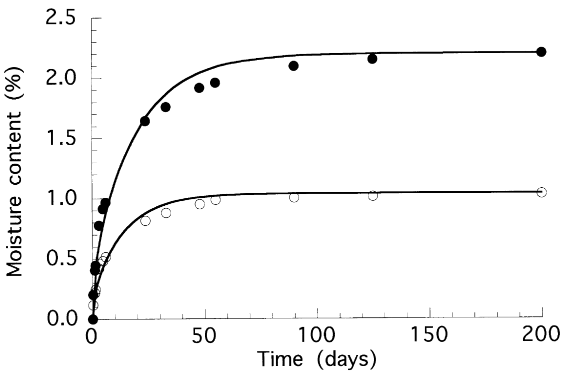

Fig. 3. Comparison between theoretical predictions and experimental moisture content of composites made from 20% of untreated woodflour at 60 and 90 RH. The effective *D* was taken as the value calculated from the experimental data at 60 RH. Here ●: 90 RH; ○: 60 RH.

Fig. 3 is a comparison of experimental data and theoretical predictions for the material loaded with 20% by weight of woodflour under different RH environments. Both curves were calculated from the diffusion coefficient obtained from fitting the 60 RH data. It can be seen, that the calculated behaviors (at 60 and 90 RH) using a single value for the diffusion coefficient were very satisfactory.

It is important to remark that the calculated diffusion coefficients were strongly dependent of the equilibrium moisture content (EMC), that is of the $M_\infty$ in the Eqs. (1)–(3). Thus, it is very important that the samples reach equilibrium with the environment, in order to use the experimental data to predict diffusion coefficients or rate of water uptake. This point has not been carefully considered in many publications [11,12] and pseudo equilibrium conditions have been chosen for comparisons or calculations, i.e. $M_\infty$ selected as the humidity content reached at the time of ending the test, which is selected arbitrarily as a fixed number of hours or days.

## 4.2. Woodflour

An attempt to obtain an estimation of the diffusion coefficients of the wood particles was made. In order to do that, two simple geometric forms were selected to represent the woodflour particles: long cylinders and spheres. It is obvious that none of these simple shapes are able to describe the real appearance of a particle, but they represent extreme cases.

Then, diffusion coefficients of the woodflour were estimated using Eqs. (2) and (3) and the values obtained are presented in Table 2. The effective diffusion coefficients were determined from the fitting of the experimental ratios $M_t/M_\infty$ taken at 60 RH. Arbitrarily, the particle diameter was taken as 57 μm (sieve aperture). Since the diffusion coefficient of water in wood is known to be concentration dependent (e.g. increases with moisture content [13]) the values calculated are the average diffusion coefficients. This procedure has been used previously by several authors [14–16] in order to average concentration dependent coefficients over the whole range of concentration. The woodflour samples reach EMC in a much shorter time (approximately three days) than the neat resin and composites (approx. 170 days). This must not lead to the wrong conclusion that water diffusion is faster in woodflour. The shorter time to reach equilibrium is a result of the much larger exposed area, approximately 2.0 m$^2$/g (BET area [17]) in woodflour and $5.9 \times 10^{-4}$ m$^2$/g (average) in the sheet specimens of resin and composites.

Fig. 4 shows the comparison between theoretical predictions for cylinders and spheres and experimental data recorded at 60 RH for untreated woodflour. Both approaches are effective in describing the experimental behavior, but, as the curve used to describe the behavior of the cylinders was derived for short times only, it cannot represent the behavior of the wood particles at long times.

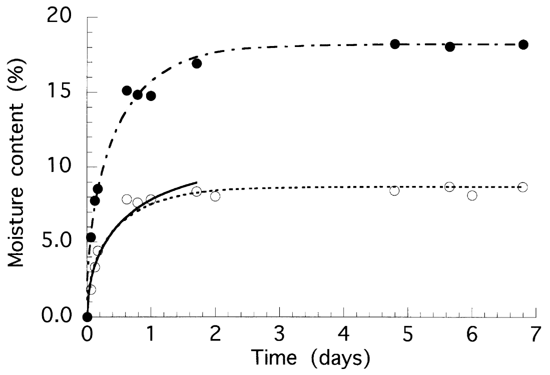

Fig. 4. Comparison between experimental data recorded at 60 and 90 RH for untreated woodflour and theoretical calculations for spheres and cylinders. Experimental results: ● 90 RH; ○ 60 RH; Predictions: – – – Sphere 90 RH; – – – Sphere 60 RH; —Cylinder 60 RH.

Actually, the filler diffusion coefficient should be an intermediate value. Moreover, the adopted value of 57 μm only represents the maximum particle average diameter and smaller particles are present. The situation is even more complex, as the filler shape is irregular, the size of the particles is variable and the untreated woodflour could form agglomerates in the composite (owing to the high polarity of the wood), while an esterified woodflour is better dispersed. Besides, the capillaries of the wood structure are filled with air or water vapor in woodflour samples, while they may be at least partially filled with resin, when forming the polyester composites. Thus, in fact, the values listed before are only indicatives mainly of the order of magnitude that could be expected for the diffusion coefficient of this kind of reinforcing filler.

Fig. 4 also shows the moisture uptake for untreated woodflour measured at 60 and 90 RH together with the theoretical prediction for spheres, selected for simplicity of the calculations. The effective woodflour diffusion coefficient was obtained from fitting the 60 RH data and it was then utilized to predict the water uptake curve at 90 RH environment. It is clearly seen that the estimated *D* used in Eq. (3) successfully model the water diffusion into the woodflour. In other words, although the coefficients are known to be dependent of the moisture content, the average diffusion coefficients determined from the $M_t/M_\infty$ recorded at 60 RH, predict satisfactorily the measurements at 90 RH.

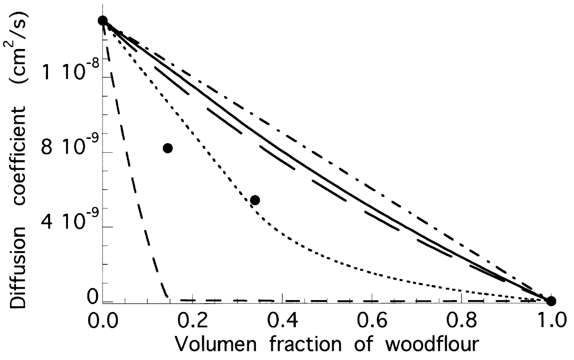

Fig. 5. Comparison between composite effective diffusion coefficients with curves predicted by Eqs. (4)–(8). The effective $D_f$ was taken as the value calculated assuming that the filler was a perfect sphere. – – – Eq. (4); – · – · – Eq. (5); – – Eq. (6); - - - - Eq. (7); — Eq. (8).

From the results obtained, it is evident that the diffusion coefficients decrease with woodflour concentration ($1.5 \times 10^{-8}$ cm$^2$/s for the neat resin and approximately $1.5 \times 10^{-11}$ cm$^2$/s for woodflour, and intermediate values for the composites). An explanation of this behavior may be necessary because the high hygroscopicity of wood falsely leads one to expect also high diffusion coefficients. However, being woodflour an hygroscopic material, the polar groups existent in its chemical structure represent a potential energy “sink” that can attract and bind water molecules. Consequently, the hydrogen bonding become a limiting factor in the diffusion of water molecules into the wood particles. Models developed for the cases of diffusion accompanied by chemical reactions yield similar results. Reaction results in the immobilization of the diffusing species and contribute to delay their transport.

The above justification was discussed previously by several authors in order to describe the behavior of the water molecules diffusing in polar systems. For example, Park and coworkers [18] stated that the diffusion retardation of small molecules depends on the density of the H-bonding moieties in the polymer matrix. They also showed that the H-bonding between diffusant and polymer matrix retards the diffusion of the probes and increases the activation energy of diffusion. Tamai and coworkers [19] established that the mobility of the water molecules is significantly lowered around polymer chains for both translational and rotational motions. This is partly because of the hydrogen bonds between water and polymers around the hydrophilic groups and partly because of the structuralization of water around hydrophobic groups. Willet [15] studied the water sorption kinetics of starch filled polyolefins blended with copolymers of several acrylates. The measured *D* values were low and ranged between $3.4 \times 10^{-10}$ and $4.7 \times 10^{-10}$ cm$^2$/s (for 0.11 and 0.44 of starch weight fraction, respectively). Han et al. [20] studied the water sorption and diffusion behaviors of several films of photosensitive polyimide (another polar polymer, capable of forming H-bonds with water) and found that the diffusion coefficients ranged between $1.4 \times 10^{-10}$ and $4.21 \times 10^{-9}$ cm$^2$/s.

### *4.3. Prediction of composite diffusion coefficients*

The utility of different theoretical models derived for the prediction of the diffusivity of the composites as function of the filler concentration was analyzed. It is important to recognize that none of the selected expressions include fitting parameters, therefore, only the diffusivity of the constituent phases and the filler volume fraction are necessary to estimate the behavior of the composite. The

Table 3
EMC at 90 RH and diffusion coefficients of composites filled with esterified woodflour

| Woodflour (weight %) | EMC (90 RH) | Diffusion coefficient (cm$^2$/s) |
|---|---|---|
| 20 | 2.37 ± 0.22 | $4.90 \times 10^{-9}$ |
| 40 | 4.19 ± 0.15 | $2.86 \times 10^{-9}$ |
| 55 | 5.23 ± 0.23 | $1.18 \times 10^{-9}$ |

effective $D_f$ was arbitrarily fixed as the value calculated assuming that the filler was a perfect sphere.

The measured diffusion coefficients for the untreated woodflour series are compared with the prediction of Eqs. (4)–(8) in Fig. 5. It is clear that the experimental data lie between the two extremes (series and parallel arrangements) as it was expected. It can also be noticed that (except for the lower limit equation, which predicts incorrect results) the only expression that can represent the steep decrease of the diffusivity owing to the presence of the filler is Bruggeman's expression (Eq. (7)).

As the value of $D_f$ used in these calculations was only an estimated value, a calculation using a coefficient 10 times larger was also used to predict the composite behavior. In the range of concentrations studied, this change do not modify the observed trend, the major differences being noticed at 34% filler volume, where the original predictions give a $D_c = 4.9 \times 10^{-9}$ cm$^2$/s and the calculations with a larger $D_f$ predicts $D_c = 5.25 \times 10^{-9}$ cm$^2$/s (experimental value, $D_c = 5.47 \times 10^{-9}$ cm$^2$/s). Both $D_f$ values lead to the prediction of the steep drop in $D_c$ with filler volumetric fraction and thus, it is concluded that Bruggerman's expression best represents the observed behavior.

### 4.4. Treated woodflours

Samples of treated woodflour and the derived composites were also used to study the water sorption behavior. The EMC showed variations according to the treatment used. The water uptake for 20% composites was higher if the woodflour was treated with alkali and lower if it was esterified (3.12 and 2.37% respectively at 90 RH).

Table 3 shows the EMC and the calculated diffusion coefficients of composites made with different concentrations of MAN treated woodflour. EMC increases with increasing filler content while the diffusion coefficients showed diminishing values. Thus, these results confirm that the trends observed for water sorption properties as a function of the filler concentration are general for this type of composites.

## 5. Conclusions

Moisture absorption of composites and woodflour untreated and treated chemically in different ways were accurately represented through the use of microscopic equations of diffusion in solid materials derived for simple geometric shapes (plane sheet, cylinder, sphere). From this theoretical models the diffusivity of the composites and constitutive phases could be estimated. The obtained values were useful to represent the behavior of the different materials at 60 and 90 RH.

EMC of the composites studied was found to be dependent on the size and shape of the samples tested. This is an important feature to consider when a practical application of these materials is being considered.

The diffusion coefficient of the filler was approximately three orders of magnitude smaller than the diffusivity of the matrix. This behavior can be attributed to the formation of hydrogen bonds between polar groups of woodflour and water molecules, which delays the diffusion of the last species into the wood particles.

Expressions derived initially to predict the thermal conductivity of composite systems were used in this work to derive the diffusivity of the composites from the diffusion coefficients of filler and resin. Experimental measurements were reasonably fitted with the Bruggeman equation, which does not require fitting parameters, consequently, it is an attractive alternative to estimate the diffusivity of particulate filled materials.

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