Moisture Diffusion into Palm/Polypropylene Composites in Sodium Chloride Solutions

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ABSTRACT: A previous study showed that it was feasible to use wood fibers obtained from palm-tree branches to reinforce polypropylene. It was the objective of this study to investigate the moisture-sorption characteristics of palm-fiber/polypropylene composites and the effect of using a compatibilizer on that important material property. The results of the investigation showed that the amount of moisture absorbed at saturation by polypropylene during immersion in distilled water and various salt solutions increased significantly with the introduction of palm fiber into the polymer. On the other hand, the use of maleated (maleic anhydride modified) polypropylene (Epolene E-43) as the compatibilizer did not have a significant effect on the amount of moisture intake of palm/polypropylene composites at saturation. However, there was a significant change in the moisture-diffusion rate with the incorporation of the Epolene E-43 compatibilizer into the composites: the compatibilizer resulted in a significant increase in the diffusion rate. The moisture diffusivity was not affected by the solution type for the palm/polypropylene composite specimens without any compatibilizer, but some increase in the mass diffusivity was observed as the purity of the solution increased (as the salt concentration decreased) when the Epolene E-43 compatibilizer was used in the palm/polypropylene composites. J Appl Polym Sci 106: 2575–2579, 2007

Key words: biofibers; compatibilization; composites; diffusion

INTRODUCTION

Composite materials based on fibers of natural polymers, such as wood cellulose fibers, and thermoplastics have attracted attention because of their remarkable environmental and economical advantages. The advantages of using cellulosic fibers as reinforcements in thermoplastics include low densities, low cost, a nonabrasive nature, the possibility of high filling levels, low energy consumption, high specific properties, biodegradability, and worldwide availability. Moreover, wood plastics are resistant to insects, rotting, and slippage, are attractive and paintable, are stiffer than plastics, and used as wood.[1–5]

Polypropylene (PP)/wood-fiber composites have attracted special attention because of the superior properties of PP in comparison with other thermoplastics, including heat resistance, moisture resistance, low density, excellent mechanical and electrical properties, and easy processibility by all processing methods (molding, extrusion, film, and fiber manufacturing).[6–10]

However, the inherent polar and hydrophilic nature of cellulosic fibers and the nonpolar characteristics of polyolefins create difficulties in compounding and result in inefficient composites. Fortunately, it has been shown that the use of compatibilizing and coupling agents for treating fibers before, or as an addition to, the compounding step enhances the compatibility and adhesion between the fibers and the matrix and the fiber dispersion in the matrix, improving the mechanical properties.[11–17]

Maleated (maleic anhydride modified) PP has been particularly successful as a coupling agent in cellulose/PP composites, improving the mechanical properties as a result of enhanced interfacial adhesion.[1,3,18,19]

Palm trees are abundantly available in the kingdom, and PP is locally produced by SABIC (Jubail, Saudi Arabia). In a recent study,[20,21] proponents investigated the feasibility of using wood fibers obtained from waste palm-tree branches to reinforce PP. They investigated the influence of the processing parameters (fiber loading, degree of mixing, mixing temperature, and use of compatibilizers) on the characteristics of PP/cellulose-fiber composites. It was shown that it was feasible to produce composites with up to 40% fiber that had strength comparable to that of the pure polymer with simple processing equipment and with minimum pretreatment of the fibers. In this project, we investigated the water-sorption characteristics of

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palm-fiber/PP matrix composites and the effect of using a compatibilizer on that important material property.

Water sorption is a serious problem that is expected to take place in cellulose/palm-fiber composites. The diffusion of liquid in polymer composites can be visualized as a series of jumps in which Brownian motion of chain segments of the polymer produces transient voids in the vicinity of the liquid penetrant, enabling it to move within the polymer. The temperature dependence of diffusivity is described by the Arrhenius law, and the activation energy is related to the amount of energy required for the process of diffusion.[22]

The assessment of material behavior in a real service environment involves the exposure of the material to a simulated environment for a certain period and the evaluation of the exposed specimen for changes in the properties. Water- and fluid-immersion tests have been widely used to evaluate changes in the properties of polymeric materials.[23,24] Water-immersion tests are performed by the immersion of specimens in distilled water, and fluid-immersion tests are performed by the immersion of specimens in a fluid to which the material may be exposed during industrial use (usually a sodium chloride solution).

The emphasis was placed on determining the moisture-absorption behavior of palm-fiber/PP matrix composites under complete immersion in distilled water and in NaCl solutions. The moisture intake of the composites was measured as a function of the specimen type, concentration of the sodium chloride solution, and exposure time.

MATHEMATICAL FORMULATION

When diffusion is restricted to one dimension, such as when a thin film of thickness l is absorbing a fluid according to Fick's law,[25] and diffusion into the edges of the film can be ignored, the amount of the diffusant taken up by the sheet at time t (M_t) can be determined as follows:[26]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^{\frac{1}{2}}} + 2\sum_{n=0}^{\infty}(-1)^n \text{ierfc}\frac{nl}{2(Dt)^{\frac{1}{2}}}\right) \quad (1)$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient (D); M_∞ is the equilibrium sorption attained theoretically after infinite time. The value of D can be deduced from the observation of the initial gradient of a graph of M_t/M_∞ as a function of $(t/l^2)^{1/2}$. This observation is made easier by the fact that, for a constant value of D, the graph for a sorption experiment is a straight line, within the normal limits of experimental error, for M_t/M_∞ as high as about 50%. That is, at short times, when M_t/M_∞ is less than 0.5, eq. (1) can be approximated as follows:[26]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}} \quad (2)$$

EXPERIMENTAL

Materials

The materials used in this investigation included date palm fibers, a PP matrix (obtained from SABIC), and a coupling agent, maleated PP (Epolene E-43; Eastman Chemicals Co.).

The palm branches were initially shredded into small pieces with a mechanical shredder. The shredded fibers were sieved to remove fines and nonfibrous materials present in the branches.

The compounding of the wood fibers, resin, and compatibilizer was performed with a model S-650/G126 single-screw extruder (Brabender Instruments, South Kackensack, NJ). The components were physically mixed in a bowl and then transferred to the extruder. The compatibilizer was Epolene E-43. It has been shown to produce well-compatibilized composites.[20] The compatibilizer was in a powder form and was dispersed well within the mixture before extrusion. The temperature of the extruder was 200°C, and the temperature of the dye was 220°C. The composite thus obtained from the extruder was granulated into small pellets and transferred into a compression molder (model Auto C press, Carver Inc., Wabash, IN). A sheet was pressed at 260°C for 6 min at 10 ton/dm^2. The film was then cooled to room temperature by being placed in air.

Diffusion tests

Relatively thin composite sheets (e.g., $30 \times 30 \times 1\ mm^3$; see Fig. 1) for the moisture-diffusion tests were molded from the prepared pellets with a Carver press (Wabash, IN). Three pieces of each particular material [PP, untreated palm-fiber-reinforced PP (30 wt % fiber), and compatibilized palm/PP composite (30 wt % fiber and 4 wt % compatibilizer)] were immersed in a solution for several months at room temperature. At various intervals, the test specimens were removed from the solution and weighed with an analytical balance with good precision after the removal of surface wetness with clean tissue. The amount of liquid absorbed was recorded as a function of time.

To investigate the influence of sodium chloride on the absorption, five test solutions were used in the investigation: (1) distilled water, (2) a 100 ppm sodium chloride solution, (3) a 1000 ppm sodium chlo-

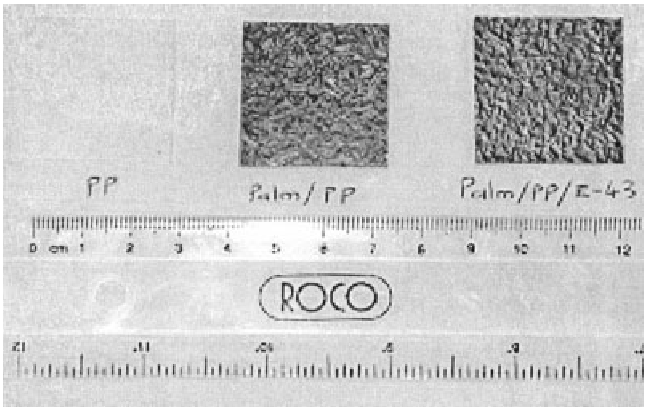

Figure 1 Sample photograph of the specimens used in the water-diffusion study.

ride solution, (4) a 0.5*M* sodium chloride solution, and (5) a 1.0*M* sodium chloride solution.

RESULTS AND DISCUSSION

Moisture-diffusion experiments were continued over 3 months, and the diffusion in the palm-fiber/PP composite specimens reached equilibrium in about 70 days. Figures 2–6 present plots of the diffusant intake versus the immersion time in each of the five test solutions (distilled water and NaCl solutions with 100 ppm, 1000 ppm, 0.5*M*, and 1.0*M* concentrations) for the three specimen types (PP, untreated, palm-fiber-reinforced PP, and compatibilized palm/PP composite).

The amount of moisture absorbed at saturation by PP increased significantly during immersion in any of the solutions tested with the introduction of palm fibers into the polymer. It took about 6×10^6 s for all the composite specimens to get saturated with moisture. The amount of moisture intake by PP without any fiber content was negligible, and the experimental data were not significant enough to quantify the diffusion.

No significant improvement was observed in the amount of moisture intake of the palm/PP composite at saturation with the use of Epolene E-43 as the compatibilizer during immersion in distilled water (Fig. 2) and a 100 ppm salt solution (Fig. 3). Even though there seems to be some effect of the compatibilizer in reducing the moisture intake at saturation in the solutions with higher salt contents in Figures 4–6, it is not very significant, and when the data of the other two specimens for each case, not included in the figures, are also considered, it is seen that this is a result of scatter in the experimental data.

The results do not show a consistent trend for the effect of the solution type on the amount of moisture absorbed by the palm/PP composite specimens. Even though the results for the uncompatibilized palm/PP

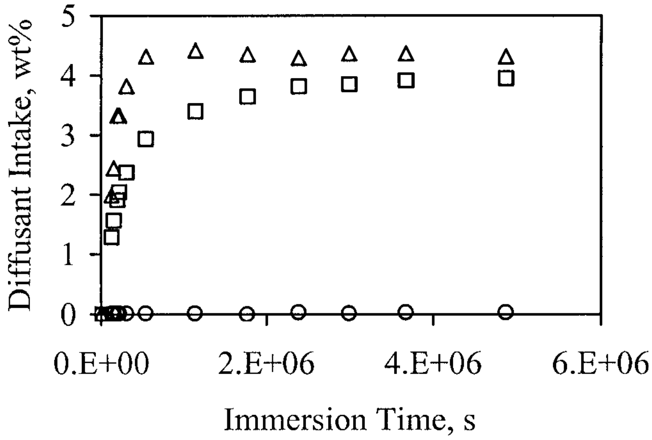

Figure 2 Diffusant intake versus the immersion time in distilled water for (○) PP, (□) untreated palm-fiber-reinforced PP, and (△) compatibilized palm/PP composite specimens.

specimens show a slight trend of a higher amount of moisture absorption in distilled water (Fig. 2) and low-salt-content solutions (Figs. 3 and 4 for 100 and 1000 ppm concentrations, respectively) than higher salt content solutions (Figs. 5 and 6 for 0.5 and 1.0*M* salt solutions, respectively), the difference is less than 10%. In the case of the compatibilized palm/PP specimens, on the other hand, the amount of moisture absorbed in a 1000 ppm solution (Fig. 4) is as low as that in the solutions with higher salt concentrations of 0.5 (Fig. 5) and 1.0*M* (Fig. 6), whereas the specimens absorb higher amounts of moisture in distilled water (Fig. 2) and 100 ppm salt solutions (Fig. 3).

The diffusivities of moisture in palm-fiber-reinforced PP specimens (with and without a compatibilizer) in five different test solutions were determined with Eq. (2). In this method of diffusivity determina-

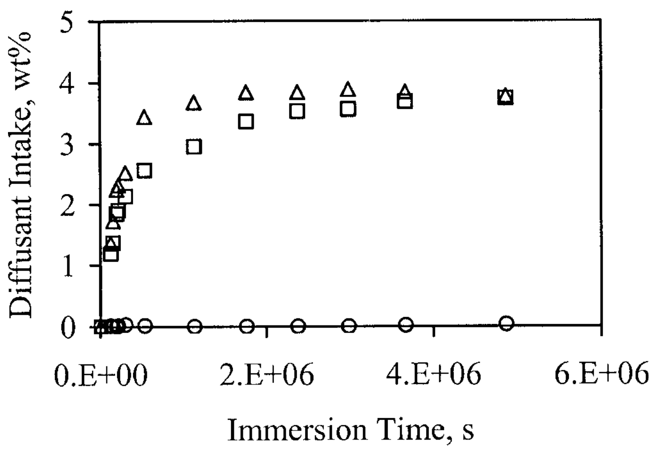

Figure 3 Diffusant intake versus the immersion time in 100 ppm NaCl solutions for (○) PP, (□) untreated palm-fiber-reinforced PP, and (△) compatibilized palm/PP composite specimens.

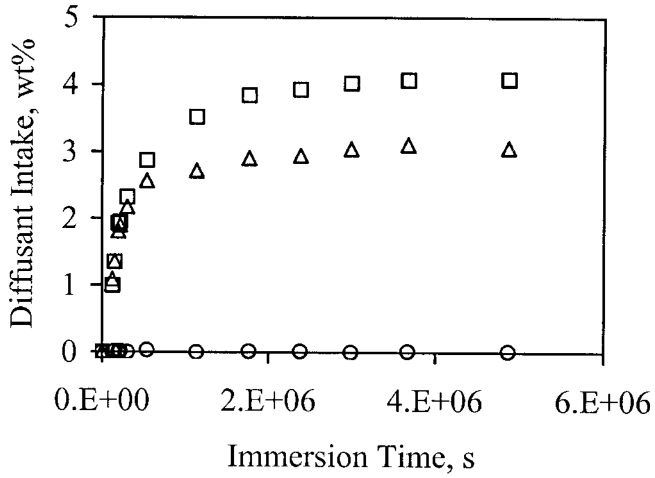

Figure 4 Diffusant intake versus the immersion time in 1000 ppm NaCl solutions for (○) PP, (□) untreated palm-fiber-reinforced PP, and (△) compatibilized palm/PP composite specimens.

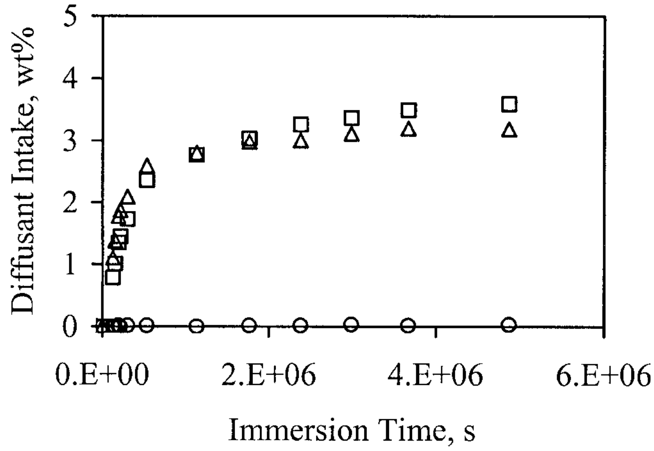

Figure 6 Diffusant intake versus the immersion time in 1.0*M* NaCl solutions for (○) PP, (□) untreated palm-fiber-reinforced PP, and (△) compatibilized palm/PP composite specimens.

tion, M_t/M_∞ is plotted against $4(t/\pi l^2)^{1/2}$, and the diffusivity is determined from the initial slope of the plot (the slope is $D^{1/2}$). The determined diffusivity values are presented in Figure 7 as the diffusivity versus the specimen type in each test solution.

There was a significant change in the moisture diffusivity values with the incorporation of the compatibilizer Epolene E-43 into the composites. However, instead of lowering the moisture-diffusion rate, the compatibilizer resulted in a significant increase in the mass diffusivity. The increase in the moisture diffusivity due to the use of Epolene E-43 in the palm/PP composite was over 100% in the case of solutions with lower NaCl concentrations (distilled water, 100 ppm NaCl solution, and 1000 ppm NaCl solution) and about 50–100% in the case of solutions with higher NaCl concentrations (0.5 and 1.0*M* NaCl solutions). The diffusivity values ranged from 6.7×10^{-9} to 1.0×10^{-8} cm^2/s for the palm/PP composite with no compatibilizer and from 1.3×10^{-8} to 2.2×10^{-8} cm^2/s for the palm/PP composite with the compatibilizer E-43.

This increase in the moisture diffusivity in the palm/PP composites with the use of Epolene E-43 might be a result of an increase in the hydrophilic nature of the fiber–matrix interphase due to the presence of the compatibilizer. However, although the diffusion rate is increased, the amount of moisture intake into the palm/PP composite at saturation is not much affected by the compatibilizer in any of the test solutions, as previously discussed. These two facts may seem to contradict each other, but they do not. During immersion in test solutions, moisture would be

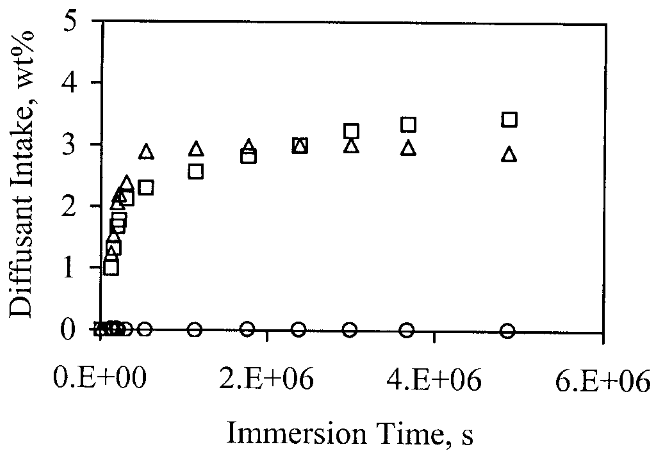

Figure 5 Diffusant intake versus the immersion time in 0.5*M* NaCl solutions for (○) PP, (□) untreated palm-fiber-reinforced PP, and (△) compatibilized palm/PP composite specimens.

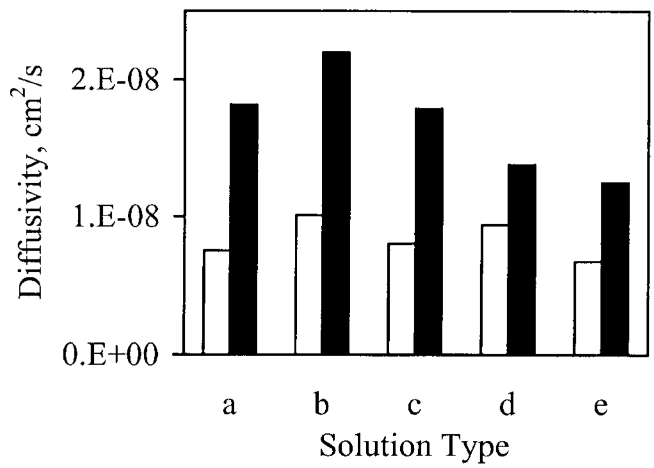

Figure 7 Mass diffusivity versus the specimen type [(□) palm/PP and (■) palm/PP/E-43] in different test solutions: (a) distilled water, (b) 100 ppm NaCl solution, (c) 1000 ppm NaCl solution, (d) 0.5 M NaCl solution, and (e) 1.0 M NaCl solution.

absorbed mainly by the fibers, which occupy 30% of the palm/PP composite, and the rate of moisture diffusion would not affect the maximum moisture amount that could be absorbed at the time at which the fibers become saturated with moisture.

The results of this investigation definitely disprove the enhancement of moisture resistance in cellulosic-fiber-reinforced thermoplastics by the use of a compatibilizer that improves the interfacial bonding between the wood fibers and the polymer matrix.

The results in Figure 7 also indicate that the effect of the solution type on the moisture diffusivity is not significant in the case of palm/PP composite specimens without any compatibilizer. However, even though it is not so significant in light of the scatter in such diffusion data, the mass diffusivity seems to increase as the purity of the solution increases (as the salt concentration decreases) when the compatibilizer Epolene E-43 is used in the palm/PP composite.

CONCLUSIONS

The followings can be concluded from the findings of this study.

The amount of moisture absorbed at saturation by PP during immersion in distilled water and 100 ppm, 1000 ppm, 0.5*M*, and 1.0*M* NaCl solutions increased significantly with the introduction of palm fiber into the polymer.

No significant improvement was observed in the amount of moisture intake by the palm/PP composite at saturation with the use of Epolene E-43 as the compatibilizer.

The moisture-diffusion rate, on the other hand, was affected significantly by the incorporation of Epolene E-43 into the composites: the compatibilizer resulted in a significant increase in the mass diffusivity.

The effect of the solution type on the moisture diffusivity was insignificant in the case of palm/PP composite specimens without any compatibilizer. However, some increase in the mass diffusivity was observed as the purity of the solution increased (as the salt concentration decreased) when Epolene E-43 was used in the palm/PP composite.

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