Measurement of Moisture Diffusivity through Layered-Silicate Nanocomposites

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Layered-silicate nanoparticles, when distributed within the matrix of a fiber-reinforced polymer (FRP), can retard the diffusion of environmental moisture and other chemicals to the fiber–matrix interface where their presence can result in delamination and fiber weakening. Thus, the use of nanoparticles helps to preserve the integrity of FRPs and to prolong the service life of composites when these are used in outdoor applications such as bridges and utility poles. In the present work, diffusion coefficients of water, brine, and alkali were determined at several different temperatures by soaking clay/vinyl ester nanocomposites in the different liquids and measuring the increase in weight with increasing time of immersion. It was found that the measured diffusivities decreased with increasing clay content. However, the reduction in water diffusion coefficient was found to be less severe when steady permeation experiments were carried out. This result is theoretically explained based on the hydrophilic nature of the clay surface that tends to immobilize some of the moisture. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 3249–3256, 2005
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Introduction

Glass-fiber–reinforced polymer (GFRP) composites incorporating thermosetting polymer matrices are now being used in the construction and repair of bridges and other civil structures.[1] However, widespread use of GFRPs in construction, where a service life in excess of 50 years is desired, has been hindered by the lack of long-term durability and performance data on which to base design calculations. A particular difficulty has been that atmospheric moisture can diffuse to the fiber–matrix interface and cause both delamination and fiber weakening.[2] One way to reduce moisture ingress is to reduce the "effective" moisture diffusion coefficient, and this can be achieved by dispersing clay platelets in the matrix polymer, forming a nanocomposite; the diffusing molecules have to travel around the flakelike barriers, and the additional path length, by itself, is predicted to substantially decrease the diffusivity (see, for example, Cussler et al.[3] and Yano et al.[4]). Note that the most common variety of clay for nanocomposite synthesis is montmorillonite.[5,6] It is a swelling clay consisting

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of layers formed by a condensation of two silicon–oxygen tetrahedral sheets and one aluminum or magnesium–oxygen–hydroxyl octahedral sheet; the layer thickness is 0.96 nm and the lateral dimensions are of the order of a few hundred nanometers each. These layers generally exist stacked together, and they have to be separated or exfoliated to be effective mass-transfer barriers. However, the clay is inherently hydrophilic, and a surface treatment is needed to make it organophilic for ease of dispersion in a polymer even when mechanical shear is used.

In our previous work,[5] we studied moisture diffusion through vinyl ester samples containing up to 5 wt % of organically treated montmorillonite; sorption experiments were done on rectangular cross-sectional strips within which the clay platelets were partially exfoliated. It was found that water diffusivity decreased to half its value in the neat resin when the clay content was only 1 wt %. The present research is a continuation of the prior work, and here we have examined moisture diffusion through the nanocomposite using both sorption and permeation methods; there is a difference in the results, and this is partially explained on a theoretical basis. We also present data on the diffusion of brine and alkali through both the neat polymer and through the nanocomposite, and these data provide a clue to other reasons why the diffusivity obtained from sorption experiments differs from the corresponding value obtained from permeation experiments.

We note that the addition of passive mass-transfer barriers in a polymer can only retard the rate of diffusion and not eliminate diffusion altogether. However, the timescale of diffusion through a structure such as a bridge deck is so long that, unless atmospheric humidity is always high, the natural reversal in concentration gradient, resulting from a change in seasons or the cessation in waterlogging, should prevent moisture from reaching very far into the composite material. When the nanofiller is clay, as in the present case, it is hydrophilic in nature, and this has an additional beneficial effect. Any moisture that does diffuse into the GFRP tends to become sequestered on the clay surface and does not reach the surface of the reinforcing fibers. Indeed, we have found[7] that the presence of montmorillonite in the GFRP increased its durability, and this is demonstrated by the scanning electron micrographs shown in Figure 1. Figure 1a shows the fracture surface of a freshly prepared GFRP sample without clay; the fibers are circular in cross section, and there is good bonding between the fibers and the matrix. Figure 1b shows that after 2 months of being soaked in distilled water, the GFRP is severely damaged to the extent that the fiber cross section has become noncircular. Note that, as expected, the fibers that were closer to the sample surface were damaged to a greater degree than those that were situated away from the surface. Finally, Figure 1c shows that, with the addition of 5 wt % clay, the damage that is visible in Figure 1b can be avoided. Thus, adding clay appears to help in making polymer nanocomposites more durable, although these simple experiments cannot be expected to help quantify the increase in service life.

Materials Used and Sample Preparation

The polymer used in this work was DerakaneTM 411-350 Momentum epoxy vinyl ester resin obtained from the Dow Chemical Co. (Midland, MI), and it contained 45 wt % dissolved styrene; this is a slightly different chemical form of the polymer that we used in previous investigations.[5] It was cured at room temperature, as recommended by the manufacturer. One wt % of methyl ethyl ketone peroxide (9% active oxygen) was used as the initiator, whereas 0.03 wt % of 6% cobalt naphthenate was used as a catalyst. Both of these chemicals were purchased from Sigma Aldrich Co. (St. Louis, MO). To formulate the nanocomposites, Cloisite 10A®, a montmorillonite treated with benzyl (hydrogenated tallow alkyl) dimethyl quaternary ammonium chloride, was used as received from Southern Clay Products (Gonzales, TX); the organic content of this treated clay is approximately 39 wt %. Sodium hydroxide used in this study was obtained from Aldrich Chemical (Milwaukee, WI), whereas sodium chloride was obtained from Fisher Scientific (Pittsburgh, PA).

Transparent samples of neat vinyl ester were prepared by pouring the mixture of resin, initiator, and catalyst into a Teflon® mold. Typical dimensions of the samples used for transient diffusion experiments were 50 × 12.5 mm, with the thickness ranging from 0.2 to 0.7 mm. The polymer was allowed to cure at room temperature for 24 h, and it was subsequently postcured in an oven for 3 h at 95°C; differential scanning calorimetry showed that these conditions led to complete curing and resulted in a glass-transition temperature (T_g) of 117°C. In the case of vinyl ester resin–clay nanocomposites, the organically treated clay was added to the liquid resin and manually stirred. The mixture was then degassed in a vacuum oven to remove air bubbles. The catalyst and initiator were then added, and the resin was poured into the molds and subjected to the same cure cycle as the neat resin. Similar procedures were used to make samples for the steady permeation experiments, although now all the samples were square in shape (60 × 60 mm), but the region for mass transfer was circular, with a diameter of 50.7 mm. Additional details are available in Rana's thesis.[7]

Material Characterization

As reported previously,[5] X-ray diffraction scans on the nanocomposite samples were indicative of either exfoliation or breakdown of the ordered structure of clay. Low-magnification transmission electron micrographs of the same samples showed that the clay was reasonably uniformly distributed, and the clay platelets were randomly oriented. High-magnification micrographs, however, revealed the presence of aggregates made up of two to ten platelets; the distance between adjacent platelets in these aggregates ranged from 4.4 to 5 nm, whereas the platelet length ranged from 80 to 180 nm. Thus, the clay is only partially exfoliated, and this has consequences for the resulting barrier properties.

Diffusion Tests and Data Analysis

To determine the improvement in barrier properties of a nanocomposite compared to the neat polymer, one may carry out water absorption tests. Here one immerses a sample in water and measures the amount of water absorbed in a fixed amount of time; barrier properties are considered to have been improved if the amount of moisture absorbed decreases with added nanofiller.[8,9] However, more quantitative information can be obtained by computing the diffusiv-

Figure 1. **(a) SEM of as-prepared GFRP sample; (b) SEM of GFRP sample after immersion in distilled water at room temperature for 2 months; (c) SEM of GFRP sample containing 5 wt % Cloisite 10A® after immersion in distilled water at room temperature for 2 months.**

ity from either sorption experiments or permeation experiments. In the present work, transient diffusion tests were conducted by immersing the various samples in distilled water or alkali of pH 13 or 0.1 M salt solution at a constant temperature ranging from 4 to 62°C. Beakers containing these solutions were closed at the top with aluminum foil to prevent evaporation. A refrigerator was used to conduct experiments at temperatures below room temperature, whereas an oven was used at temperatures above room temperature. The samples were periodically removed, blotted dry with lint-free tissue, weighed, and reimmersed in the beaker. Readings were initially taken as frequently as every 30 min, and the experiment was continued until there was no weight gain recorded over a period of 10 days. The balance used had an accuracy of 1 μg, and at least three replicate runs were carried out for a given set of conditions. To compute the diffusion coefficient from data on mass gain as a function of time, one may use Fickian theory. For unfilled samples, the process of one-dimensional, unsteady diffusion is governed by[10,11]

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

in which c is the concentration of the diffusing species, t is time, x is the position in the diffusing direction, and D is the diffusion coefficient or diffusivity. Upon solving Eq. 1 with constant boundary conditions, we obtain moisture uptake (that is, increase in sample mass) M_t to be

$$\frac{M_t}{M_\infty} = \left[1 - \sum_0^\infty \frac{8}{(2n+1)^2\pi^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right]\right] \tag{2}$$

where M_∞ is the equilibrium increase in sample mass and $2l$ is the sample thickness. At the initial stages of diffusion, the solution for Fick's law at small times reduces to

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi(2l)^2}\right)^{1/2} \tag{3}$$

so that the diffusion coefficient can be computed from the initial slope of M_t/M_∞ vs. $t^{1/2}/2l$ using short-time water-uptake data.[11]

Another method of determining the moisture diffusion coefficient is by steady permeation experiments. Red sealing wax was used to attach a polymer film to the mouth of an aluminum dish containing 4 g of anhydrous $CaCl_2$ desiccant; the diameter of the polymer film that was exposed to moisture was 50.7 mm. The sealed assembly was weighed and put inside a chamber that was maintained at a constant relative humidity (RH) of 77% at a temperature of 25°C. As moisture diffused into the dish, the mass of the assembly progressively increased, and the rate of increase of mass ultimately became constant. This was determined by periodic weighing of the assembly using an electronic balance. To attain a steady state in a short amount of time, the polymer films were initially saturated with water vapor at the relative humidity level of the chamber. Knowing the steady mass flux, the diffusion coefficient can be calculated as the ratio of the flux to the concentration gradient. Given that the absolute humidity inside the assembly can be taken to be negligible, the concentration gradient is simply the ratio of the moisture content in the polymer in equilibrium with 77% RH at 25°C to the thickness of the film.

When diffusion takes place through a polymer film containing dispersed platelets, the diffusing molecules have to go around these barriers. The morphology that is likely to be most effective in reducing diffusivity is one where the flakelike barriers are positioned parallel to the film surface and perpendicular to the direction of mass transport. This idealized geometry is shown in Figure 2; although this is only rarely achieved (but see Figure 5 of Yano et al.[4]), it is useful from the perspective of theoretically calculating the maximum improvement in barrier properties.[4] As seen from Figure 2, the path length for steady diffusion increases, say by a factor of λ, as compared to the unfilled case. In addition, the area for mass transfer decreases by a factor $(1 - \theta)$. Thus, in a steady permeation experiment, the measured diffusion coefficient D_s should equal $(1 - \theta)D/\lambda$, if D is the diffusion coefficient for mass transfer through the neat polymer. Note that both λ and θ should increase with increasing concentration. Note also that the measured diffusivity should not be influenced by any moisture that becomes bound to the (hydrophilic) surface of the filler particles. In other words, if an increase in the diffusion path is the main mechanism by which the clay platelets reduce diffusivity, then the percentage reduction in the diffusion coefficient of moisture on adding a certain amount of clay to polymer should be identical to the percentage reduction in the diffusion coefficient of any other molecule, say oxygen, under similar conditions. Furthermore, this percentage reduction should not depend on the temperature at which the measurements are made. This expectation is not fulfilled in (transient) sorption experiments (see, for example, published data in Tortora et al.[12]).

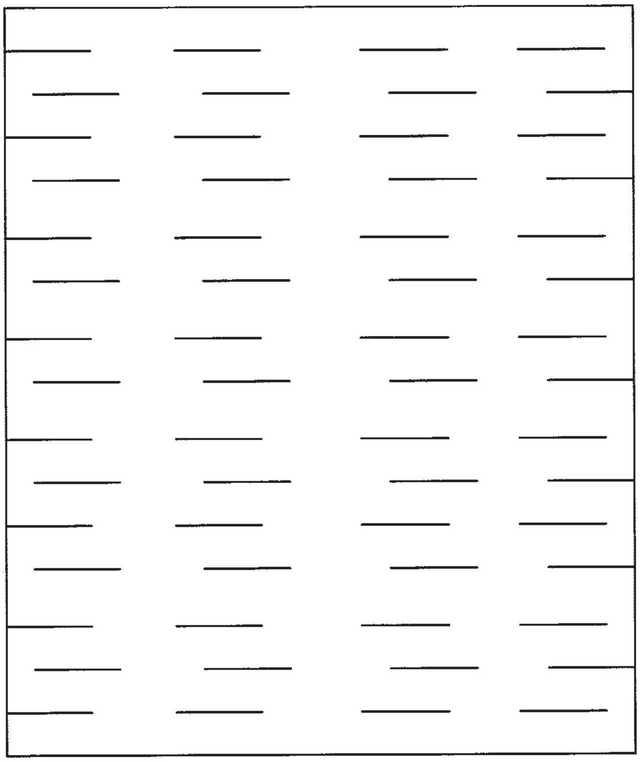

Figure 2. Morphology of a model layered-silicate nanocomposite.

Upon considering transient diffusion, one finds that the mass balance is altered by the presence of clay, and one has

$$(1-\phi)\frac{\partial c}{\partial t} = -(1-\theta)\frac{\partial n_x}{\partial x} \tag{4}$$

where ϕ is the volume fraction of clay in the polymer. If we now let the flux n_x equal $-(D/\lambda)(\partial c/\partial x)$, Eq. 4 becomes

$$\frac{\partial c}{\partial t} = \frac{D(1-\theta)}{(1-\phi)\lambda}\frac{\partial^2 c}{\partial x^2} \tag{5}$$

and the effective transient diffusivity D_t is given by

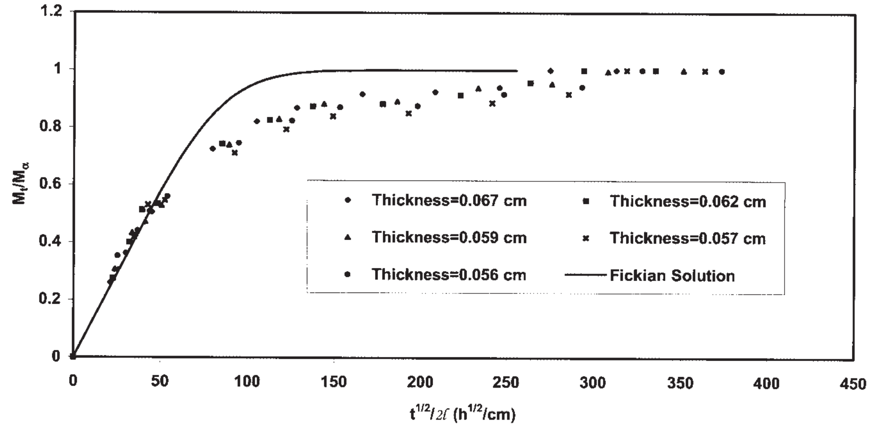

Figure 3. Water sorption curve of postcured neat resin at 25°C.

$$D_t = \frac{D(1-\theta)}{(1-\phi)\lambda} \tag{6}$$

Finally, then

$$D_s/D_t = 1 - \phi \tag{7}$$

Because $\phi < 1$ it is obvious from Eq. 7 that D_t would be greater than D_s and both D_t and D_s would be less than D, clearly demonstrating that (1) both the effective steady-state and transient diffusivities would decrease as a result of the introduction of the nanoparticles and (2) the effective transient diffusivity would reduce less than the steady-state diffusivity. For these conclusions to be quantitatively valid, however, the nanocomposite morphology must be the one described in Figure 2, and the filler particles must not interact with the diffusing molecules.

Results and Discussion

Water sorption through neat resin

Figure 3 shows the fractional increase in mass of vinyl ester samples plotted vs. $t^{1/2}/2l$ upon immersing neat resin coupons in distilled water at 25°C. As expected, based on Eq. 3, water uptake increases linearly at short times, but it levels off at longer times as equilibrium is attained; the equilibrium moisture content is about 0.66 wt %, and it takes a little over 11 days for equilibrium to be reached. Figure 3 demonstrates that data from different runs superpose, but moisture diffusion does not faithfully follow the predictions of Eq. 2 (solid line). In other words, the process of moisture diffusion through the neat resin is slightly non-Fickian because there is a mismatch between theory and data at intermediate times. This finding, which differs from our previous results,[5] could be explained by the minor change that was made in the chemical composition of the resin by the manufacturer. Although better agreement can be obtained between data and theoretical predictions if the theory is modified to, say, make the diffusivity depend on moisture content, we have chosen not to do this here because the conclusions we seek to draw are not influenced by whether the Fickian theory holds exactly.

The moisture diffusion coefficient computed from the initial slope of the solid line in Figure 3 is 0.74×10^{-6} mm^2/s, and this is somewhat lower than the value measured by Shah et al.[5] because of the slightly higher value of the equilibrium moisture content in the present case. When experiments were done at 4°C, results were qualitatively similar to those displayed in Figure 3. In quantitative terms, although the diffusion coefficient was significantly lower at 0.14×10^{-6} mm^2/s, the equilibrium moisture content was only slightly lower at 0.6 wt %. Consequently, it took twice as long to reach equilibrium at 4°C compared to the time taken at 25°C. At a temperature of 42.5°C, sorption experiments did not seem to reach equilibrium even after 20 days, and instead there was a reduction in sample mass beyond this time. It seemed that the vinyl ester was hydrolyzing, and this speculation was confirmed when the temperature of the experiment was raised to 62°C. Now the samples degraded visibly after only 4 days of immersion, and the experiments were discontinued. Clearly, in the case of this particular resin, an increase in temperature cannot be used to shorten the timescale of the diffusion experiments. We hasten to add, though, that the vinyl ester used for bridge applications is different from the one used here, and it cures at a high temperature. The resin used here was chosen for convenience because it can be cured at room temperature.

Influence of clay on moisture sorption

The water-sorption behavior of nanocomposite samples containing different amounts of montmorillonite was qualitatively similar to that of neat resin samples at each temperature examined. All the samples showed a linear initial uptake, and the calculated diffusion coefficients are listed as a function of clay content in Table 1 at both 4 and 25°C; at a given level of added clay, the percentage change in diffusion coefficient is found to depend on temperature. Although there is some scatter in the results, it is seen that, at each temperature, the trend is for the diffusion coefficient to decrease as the clay content in the resin increases. At room temperature, the addition of only 1 wt % clay appears to reduce the diffusivity by 46%, whereas at the 5 wt % clay level, the reduction in diffusivity is almost 91%. The incorporation of an additional amount of clay in the vinyl ester may reduce the moisture diffusion coefficient further, but this may also lead to deterioration in other properties. Thus, there is likely to be an optimum in the amount of added clay; this was

Table 1. Measured Values of Moisture Diffusivity and Equilibrium Moisture Content of Vinyl Ester Resin Samples

System	Diffusion Coefficient × 10^6 (mm^2/s) 4°C	Diffusion Coefficient × 10^6 (mm^2/s) 25°C	Equilibrium Moisture Content (wt %) 4°C	Equilibrium Moisture Content (wt %) 25°C
Neat resin	0.14	0.74	0.60	0.66
1 wt % Cloisite 10A®	0.11	0.40	0.85	1.13
2 wt % Cloisite 10A®	0.11	0.28	0.90	1.34
5 wt % Cloisite 10A®	0.07	0.06	0.97	2.08

not determined as part of this study. It should be noted that the extent of diffusivity reduction achieved using these transient experiments seems to be quite large, but similar results have been obtained by us and by others, as well.[5,12]

As opposed to the decrease in diffusivity with clay addition, the equilibrium moisture content of the nanocomposite sample was found to increase, albeit in a nonlinear fashion, with an increase in the amount of clay; these results are also listed in Table 1. Note that the standard deviation for all the diffusivity data is of the order of 0.02×10^{-6} mm^2/s, whereas for the equilibrium moisture content it is 0.01 wt %. As noted in the past,[5] the reason for the higher equilibrium water content with increasing amounts of clay is the tendency of the treated clay to attract moisture. Even though the surface treatment that is given to the clay tends to make it organophilic, it still retains its hydrophilic character; when the treated clay was exposed to 75% relative humidity at 25°C, for a period of 720 h, it increased in weight by almost 19% as opposed to a 60% increase in weight for nonsurface-treated clay.[5] For the nanocomposite samples, it was also found that, at both 4 and 25°C, the time to reach equilibrium in these experiments was approximately 2 months. Thus, despite the generally higher diffusivity values at the higher temperature, the timescales for diffusion are essentially similar because of the correspondingly larger equilibrium moisture contents at the higher temperature (see Table 1).

Results of sorption experiments conducted at 42.5 and 62°C using nanocomposite samples were essentially similar to the results on neat resin samples. At 42.5°C, a slow increase in sample mass was followed by a decrease in sample mass after about 25 days of immersion, and this did not seem to be influenced by the percentage of clay in the sample. A visual inspection of the samples revealed the presence of tiny craters on the surface. At 62°C, all the samples began to dissolve/degrade after 4 days of water immersion. However, the samples containing clay appeared to maintain their physical integrity much better, and this effect was very pronounced at the highest clay loading, that is, 5 wt % in our case. Even so, some kind of chemical or physical modification of this polymer is necessary to prevent polymer degradation if contact with hot water is likely to occur.

In summary, then, adding clay to vinyl ester progressively reduces moisture diffusivity as measured in transient sorption experiments. However, the surface-treated clay retains its hydrophilic character and, as a result, the equilibrium moisture content of the nanocomposites increases with amount of added clay. Both these facts mean that the time to reach concentration equilibrium can stretch into several months and, if unimpeded, water diffusion can go on for a very long time, even in thin samples.

Sorption of brine and caustic soda into nanocomposites

Experiments, similar to those conducted using distilled water, were also carried out using 0.1 M NaCl solution and a NaOH solution of pH 13. The diffusion coefficients were calculated as before, and results for diffusivity and percentage equilibrium weight gain for the salt solution are displayed in Table 2 at temperatures of 4 and 28°C. When one compares the results presented in Table 2 with those given in Table 1, one notices that (1) clay is much less effective in reducing the diffusivity of brine than distilled water, and (2) brine adsorbs to a much lesser extent on the clay particles. Indeed, at 4°C, the equilibrium brine content of the nanocomposite samples is, for all practical purposes, independent of the amount of added clay. In other words, there is no interaction between the filler particles and the diffusing molecules at 4°C.

If we accept the hypothesis that the mechanism by which nanoparticles reduce the diffusion coefficient is the additional path length encountered by the diffusing species, then, given that the nanocomposite structure is not changed by the choice of the diffusing molecule, the same percentage change in diffusivity ought to be observed regardless of the chemical nature and size of the diffusing molecule or the temperature of measurement. These requirements are obviously not met by the data in Tables 1 and 2. We also note that others too have observed that, for the same amount of clay in a sample, the sorption method yields a larger reduction in the diffusion coefficient when the diffusing molecule adsorbs on the clay than when it does not.[12] An explanation is clearly in order.

From the various structural models available in the literature,[3,4] we know that the predicted diffusion coefficient should depend sensitively on the physical structure, or equivalently the filler agglomeration level, of the nanocomposite; in particular, there should be a substantial difference in the diffusion coefficient when the clay is exfoliated compared to when it is intercalated. Unfortunately, this difference cannot be picked up in sorption experiments when the diffusing molecule, such as distilled water, adsorbs significantly onto the clay surface, and the amount of adsorbed moisture is comparable to or more than the amount of moisture that can be dissolved in the polymer. When moisture enters the nanocomposite, it is attracted to the clay surface, and water molecules preferentially go to the surface of the clay platelets that they encounter first before diffusing further into the polymer. It is only when the surface of these filler particles is completely saturated with moisture that additional water molecules seek out the next set of clay

Table 2. Measured Values of Brine (0.1 M NaCl) Diffusivity and Equilibrium Weight Gain Values of Vinyl Ester Resin Samples

System	Diffusion Coefficient × 10^6 (mm^2/s) 4°C	Diffusion Coefficient × 10^6 (mm^2/s) 28°C	Equilibrium Moisture Content (wt %) 4°C	Equilibrium Moisture Content (wt %) 28°C
Neat resin	0.12	0.66	0.58	0.68
1 wt % Cloisite 10A®	0.12	0.43	0.66	0.88
2 wt % Cloisite 10A®	0.08	0.37	0.59	0.95
5 wt % Cloisite 10A®	0.08	0.26	0.61	1.09

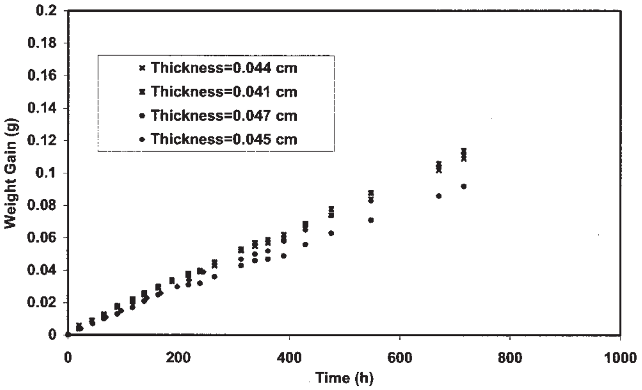

Figure 4. Water permeation curve of postcured neat resin at 25°C.

platelets and so on. In this situation, it is clear that as long as water molecules are not excluded from approaching the surface of each clay platelet present in the nanocomposite, the rate of water uptake will not depend on the level of exfoliation (or dispersion) provided that the clay is uniformly distributed in the polymer matrix. As a consequence, when the diffusing molecule is strongly attracted to the clay surface, the results of a sorption experiment will indicate the maximum possible reduction in diffusivity, and this corresponds to complete filler exfoliation. However, the observed reduction in diffusion coefficient will become progressively less as the level of interaction between the diffusing species and the filler particles is reduced to zero. This is what is observed in Tables 1 and 2. We note that untreated clay generally contains sodium or calcium ions between the different clay layers, and these ions are exchanged with organic cations during surface treatment. We speculate that not all the sodium ions are replaced with organic ions in this process, and the interaction between the sodium ions in the clay and the sodium ions in the brine is responsible for the reduced moisture absorption when nanocomposite samples are immersed in the brine. Thus, the results for brine diffusion at 4°C are more representative of the nanocomposite structure than water diffusion results at room temperature, and these indicate that the clay contained in the nanocomposite samples used in the present research was not fully exfoliated.

Brine diffusion experiments were carried out at higher temperatures as well, but, as in the case of distilled water, the samples began to degrade in about 6 to 8 days, and the experiments were terminated. The same phenomenon was observed with the NaOH solution but at room temperature; at a temperature of 42.5°C, it took only 24 h for samples to degrade. Alkali diffusion data could be obtained at 4°C and these were almost identical to the NaCl data at the same temperature.[7]

Water permeation through nanocomposites

Periodic weight-gain data for the aluminum dish assembly used for permeation experiments are shown in Figure 4 for neat resin films. It is seen that, in each of the four cases, a steady state is attained after nearly 200 h. When corresponding runs were carried out with nanocomposite films, results were similar, but the time to achieve steady state increased with increasing clay amount, reaching 600 h for samples containing 5 wt % clay. As mentioned earlier, the diffusion coefficient D_s can be calculated from the measured steady-state mass flux as

$$D_s = \frac{\text{Mass transfer rate}}{\text{Sample area}} \frac{\text{Sample thickness}}{\text{Concentration}} \tag{8}$$

where, in the calculation of the concentration gradient, the moisture concentration in the polymer film in equilibrium with 77% relative humidity at 25°C is used in place of the concentration difference because one side of the film (the inner surface) is maintained at zero moisture content; this equilibrium concentration was found to be 11.96 mg/cm^3 for neat vinyl ester.

The calculated diffusivities are listed in Table 3, and whereas the diffusion coefficient value for diffusion of water through vinyl ester is comparable to that measured using sorption experiments, such is not the case for the nanocomposites. Although, as expected, the numbers in Table 3 decrease as the montmorillonite content in the vinyl ester is increased, showing the beneficial effect of clay addition, the percentage decrease is much smaller than what would be anticipated based on Eq. 7 and the diffusion coefficient results seen earlier in Table 1. Indeed, Table 3 shows that the percentage reduction in diffusion coefficient on adding clay is closer to the percentage reduction in the diffusion coefficient of brine at 4°C. In this regard, we note that the moisture content in the nanocomposite films in equilibrium with 77% RH at 25°C was slightly higher than 11.96 mg/cm^3, and it increased with increasing clay content.[7] Had we used these values in the computation of the steady concentration gradient in Eq. 4, the percentage reduction in the diffusion coefficient values would have approached the 4°C brine values. We also note that results of permeation experiments available in the literature show relatively modest fractional reductions in the diffusion coefficient on incorporating layered silicates within polymers.[12-16] We believe that this is explained, in part, by the fact that the clay is not properly dispersed, and there are short circuits available to the diffusing molecules.

All of the above suggests that barrier properties of nanocomposites should be measured using steady-state permeation experiments because this is clearly a more severe test of improvement in barrier properties; transient sorption experiments are evidently not very sensitive to the extent of clay exfoliation when the diffusing molecules can interact strongly with the clay. In other words, the use of sorption results may lead to erroneous conclusions concerning the improvement of barrier properties upon clay addition. In closing, we also note that in our most recent work, and using the same system in conjunction with commercial water–vapor permeation equipment (Mocon, Inc., Minneapolis, MN), we have found that[17] measured diffusivities are independent of the imposed relative humidity

Table 3. Measurements of Water Vapor Permeation at 25°C through Vinyl Ester Resin Films

System	Diffusion Coefficient × 10^6 (mm^2/s)
Neat resin	0.75
1 wt % Cloisite 10A®	0.70
2 wt % Cloisite 10A®	0.67
5 wt % Cloisite 10A®	0.64

gradient and, to within experimental error, the temperature of measurement does not influence the relative decrease in diffusivity obtained on adding clay. Clearly, expectations associated with a tortuous path being the cause of diffusivity reduction are met in this situation, and the immobilization of moisture on the clay surface does not influence the steady permeation results.

Conclusions

The results of this research demonstrate that montmorillonite can reduce moisture transport through polymers such as vinyl ester. The measured reduction in moisture diffusivity on clay addition, though, appears to be larger in sorption experiments than that in permeation experiments, and this seems to be related to the fact that results of sorption experiments are not very sensitive to the extent of filler exfoliation when the diffusing molecule is strongly adsorbed on the filler surface. Permeation experiments are thus preferable to sorption experiments, and these might even be used to estimate the effectiveness of a given processing technique to exfoliate clay platelets.

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