Models of Moisture Diffusion Through Vinyl Ester/Clay Nanocomposites

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Three different theories dealing with mass transport through polymer-clay nanocomposites are discussed. The first one is a Langmuir type model; the second one is a Drozdov type model and the third one is a mesoscopic model. The Langmuir and Drozdov type models address adsorption of the solvent on the clay particles, while the mesoscopic model relates the viscoelastic properties of the polymer chains to the diffusion process. Experimental results of water moisture through vinyl ester nanocomposites made with two different clay particles are modeled and discussed. © 2007 American Institute of Chemical Engineers *AIChE J,* 54: 364–371, 2008
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Introduction

Hybrid organic–inorganic nanocomposites, have shown impressive improvement on mechanical,[1,2] thermal, flame resistance,[3] as well as gas barrier properties.[4] Those improvements are due to the dispersion of the inorganic nanofillers in the organic matrix. Polymer-clay nanocomposites have been widely investigated[5–7] and they have shown substantially improved barrier properties.[8,9]

Most of the published work deals with experimental observations and more work on the theoretical side is required. Under some conditions, the diffusion process through polymer-clay nanocomposites becomes non-Fickian. Theories involving extended tortuous paths,[10,11] silicate clay orientation and delamination,[11] adsorption on the clay particle surface and interactions among clay particles,[12,13] polymer, and solvent penetrant have been presented.[14,15]

Here we compare the water transport predictions of three different theories for the diffusion through vinyl ester-clay nanocomposites.

Mathematical Models

We discuss three theories that have been developed to model the anomalous water moisture diffusion through vinyl ester membranes: a Langmuir type model, Drozdov's model and a mesoscopic model.

Langmuir type model

The Langmuir type diffusion model assumes that when the penetrant diffuses into the polymer matrix, there is also equilibrium between sorption and desorption of solvent molecules on the nano-filler surface. Carter and Kibler[16] assumed the penetrant to be divided into two phases, a mobile phase and a bounded phase. Molecules of the mobile phase diffuse through the polymer. They may bond at certain sites. At the same time, bound molecules can be released from the bonded sites and become mobile.

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Equilibrium is reached when the rates per unit volume become equal. That is to say,

$$\gamma n_\infty = \beta N_\infty \tag{1}$$

where γ is the probability per unit time at certain unspecified sites that mobile molecules become bound; β is the probability per unit time at certain unspecific sites that bound molecules become mobile; n is the number of mobile molecules per unit volume and N is the number of bound molecules per unit volume. The starting equations are:

$$\frac{\partial n}{\partial t} = D_\gamma \frac{\partial^2 n}{\partial x^2} - \frac{\partial N}{\partial t} \tag{2}$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \tag{3}$$

where D_γ is the constant diffusion coefficient for the mobile molecules.

When γ, β are small compared to the parameters that determine the rate of saturation for a one dimensional sample of thickness l, the moisture uptake is given by,

$$\begin{aligned} M_t = M_\infty \Bigg\{ & \frac{\beta}{\beta+\gamma} e^{-\gamma t} \left[1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2n+1)^2} e^{-K(2i+1)^2 t} \right] \\ & + \frac{\beta}{\beta+\gamma} \left(e^{-\beta t} - e^{-\gamma t} \right) + \left(1 - e^{-\beta t} \right) \Bigg\} \quad 2\gamma, 2\beta \ll K \end{aligned} \tag{4}$$

and $K = \pi^2 D_\gamma / l^2$.

The following approximation holds for small exposure time ($Kt < 0.7$),

$$M_t \approx \frac{4}{\pi^{3/2}} \left(\frac{\beta}{\beta+\gamma} M_\infty \right) \sqrt{Kt} \tag{5}$$

For larger times ($t \gg 1/K$)

$$M_t \approx M_\infty \left(1 - \frac{\gamma}{\beta+\gamma}\, e^{-\beta t} \right) \tag{6}$$

Drozdov type model

Drozdov et al.[13] also assumed adsorption of penetrating solvent on the nano-fillers. However in this model the penetrant molecules cannot leave the sites where they bounded. Here we start from the Drozdov et al. equations, but we use different dimensionless variables to solve those equations.

The starting equations include mass-conservation:

$$\frac{\partial c}{\partial t} = \frac{\partial J}{\partial x} - \frac{\partial N}{\partial t} \tag{7}$$

and a first order adsorption equation

$$\frac{\partial N}{\partial t} = kc(N_1 - N) \tag{8}$$

where c is the penetrant concentration at time t at position x; N is the concentration of penetrant molecules immobilized on the nano-filler surfaces; k is the rate of adsorption; N_1 is the total number of sites where penetrant molecules can be bounded, and J is the mass flux and can be expressed by Fick's law:

$$J = D_{\mathrm{D}} \frac{\partial c}{\partial x} \tag{9}$$

where D_{D} is the diffusion coefficient.

We introduce the following dimensionless variables:

$$\begin{aligned} & x^* = \frac{x}{l}, \quad c^* = \frac{c}{n_0}, \quad c_1 = \frac{N}{n_0} \\ & t^* = \frac{tD_{\mathrm{D}}}{l^2}, \quad De = \frac{1/kn_0}{l^2/D_{\mathrm{D}}}, \quad C = \frac{N_1}{n_0} \end{aligned} \tag{10}$$

where n_0 is the equilibrium penetrant concentration on the polymer surface. In the subsequent text, we will omit the superscript (*).

Drozdov et al. used a variable K with dimensions of m^2/s. Here, we use a dimensionless variable De instead. This is a characteristic adsorption time over a diffusion time, or the rate of diffusion over the rate of adsorption. This variable allows for the determination of the importance of the diffusion and adsorption. Equations 7 and 8 can now be written as:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - \frac{1}{De} c(C - c_1) \tag{11}$$

$$\frac{\partial c_1}{\partial t} = \frac{1}{De} c(C - c_1) \tag{12}$$

the boundary and initial conditions are:

$$\begin{aligned} c(0,x) &= 0, \quad c_1(0,x) = 0 \\ c(t,0) &= 1, \quad c_1(t,0) = C \\ c(t,1) &= 1, \quad c_1(t,1) = C \end{aligned} \tag{13}$$

The relative mass gain can be expressed as:

$$\Phi(t) = \frac{1}{1+C} \int_0^1 [c(t,x) + c_1(t,x)]dx \tag{14}$$

Mesoscopic model

Liu and De Kee[14] derived a set of governing equations for diffusion through polymer nanocomposite membranes. The governing equations for a one dimensional diffusion process through polymer nanocomposite membranes are given by:

$$\rho \frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{15}$$

$$J = -\rho D \left(\frac{\partial c}{\partial x} + \mathrm{E}_{11} \frac{\partial m_{11}}{\partial x} + \Lambda_{11} \frac{\partial A_{11}}{\partial x} \right) \tag{16}$$

$$\begin{aligned} \frac{\partial m_{11}}{\partial t} = & \frac{F}{\rho(1-c)} \frac{\partial m_{11}}{\partial x} - m_{11} \frac{\partial}{\partial x} \left(\frac{J}{\rho(1-c)} \right) \\ & - \lambda^{\mathbf{m}} G_0 (1-c) \left[\left(\left(1 - c(2 - c_{\mathrm{eq}}) \right) \frac{m_{11}}{k_{\mathrm{B}} T/K} \right) - 1 \right] \end{aligned} \tag{17}$$

$$\frac{\partial A_{11}}{\partial t} = \frac{\partial}{\partial x} \left(\frac{J}{\rho(1-c)} A_{11} \right) - \lambda^{\mathbf{A}}_{1111} c \Gamma_1 \tag{18}$$

Equation 15 is the mass conservation. Equation 16 is associated with momentum transfer and is an extension of Fick's first law. It includes a convective flux due to the relaxation of the viscoelastic polymer (characterized by a conformation tensor **m**) as well as a convective flux due to the relaxation of the complex interfaces between the nano-particles (characterized by an area tensor **A**) and the polymer matrix. Equation 17 describes the time evolution of the polymer chain structural changes and is associated with polymer elasticity. Equation 18 defines the interface evolution of the nano-fillers. The quantities m_{11} and A_{11} are the (1,1) components of conformation (**m**) and area (**A**) tensors respectively. Parameters E_{11} and Λ_{11} represent the importance of the polymer and the complex interface relaxation respectively. They are the (1,1) components of tensors **E** and Λ, $\lambda^{\mathbf{m}}$ and $\lambda^{\mathrm{A}}_{1111}$ are two non-negative parameters, G_0 is the modulus of elasticity of the polymer, k_B is the Boltzman constant, K is a characteristic elastic constant, and T is the temperature. The interaction between the nano particles and the penetrant is characterized by an interaction parameter Γ_1. The dimensionless forms of Equations 13–16 yield four dimensionless parameters: Π, $De_{\mathbf{m}}$, Θ, and $De_{\mathbf{A}}$. They are given by:

$$\Pi = \frac{k_\mathrm{B} T E_{11}}{K c_\mathrm{eq}} \tag{19}$$

$$\Theta = \frac{\Lambda_{11}}{\lambda c_\mathrm{eq}} \tag{20}$$

$$De_{\mathbf{m}} = \left(\frac{k_\mathrm{B} T}{G_0 \lambda^{\mathbf{m}} K}\right) \Big/ \left(\frac{l^2}{D}\right) \tag{21}$$

$$De_{\mathbf{A}} = \left(\frac{1}{\lambda \lambda^{\mathbf{A}}_{1111} c_\mathrm{eq}^2 \Gamma_1}\right) \Big/ \left(\frac{l^2}{D}\right) \tag{22}$$

Π relates the polymer elasticity to the mixing properties of the polymer and the solvent. $De_{\mathbf{m}}$ is a Deborah number related to polymer relaxation. Θ is a quantity that relates the complex interface to the mixing properties and De_A is a Deborah number that associates the interface relaxation to the diffusion. Detailed derivations and some applications of the governing equations have been presented in a previous paper.[14] The following boundary and initial conditions are applied (the superscript * has been omitted).

$$\begin{aligned}
&c = 0 \quad \text{at} \quad x > 0\,, \quad \theta = 0\\
&c = 1 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = 1\,, \quad \theta \geq 0\\
&m_{11} = 1 \quad \text{at}\, x > 0, \quad \theta = 0\\
&m_{11} = \frac{1}{\left(1 - c_\mathrm{eq}\right)^2} \quad \text{at} \quad x = 0 \quad \text{and} \quad x = 1\,, \quad \theta \geq 0\\
&\mathrm{A}_{11} = 1 \quad \text{at}\, x > 0, \quad \theta = 0\\
&\mathrm{A}_{11} = 1 - c_\mathrm{eq} \quad \text{at} \quad x = 0 \quad \text{and} \quad x = 1, \quad \theta \geq 0
\end{aligned} \tag{23}$$

The following dimensionless variables are used:

$$\begin{aligned}
&c^* = \frac{c}{c_\mathrm{eq}}, \quad \theta^* = \frac{t}{l^2/D}, \quad x^* = \frac{x}{l}, \quad m_{11}^* = \frac{m_{11}}{k_\mathrm{B} T/K}\\
&J^* = \frac{J}{\rho D c_\mathrm{eq}/l}, \quad \mathrm{A}_{11}^* = A_{11}\,\lambda
\end{aligned} \tag{24}$$

We consider Π, Θ, De_m, and De_A to be constant.

Comparison of the three models

All three approaches originate from Fick's classical laws.

$$J = -\rho D_\mathrm{F} \frac{\partial c}{\partial x} \tag{25}$$

$$\rho \frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{26}$$

where D_F is the Fickian diffusion coefficient. The Langmuir and Drozdov's type models assume penetrant adsorption on the nano-filler surfaces. The Drozdov type model can be recovered from the Langmuir type model by assuming only adsorption of penetrant molecules on the nano-filler. Equations 3 and 8 are the different adsorption expressions. The Langmuir type model allows for an approximated analytical solution. Drozdov et al., provided a numerical solution for one specific problem. We modified Drozdov's model and introduced a dimensionless time De, which relates adsorption and diffusion. This parameter can easily identify whether the permeation process is Fickian or not. The other parameter (C) represents the percentage of penetrant bonding on the filler surface over the total penetrant. With higher filler concentration, more penetrant would be adsorbed on the filler surface, and C would increase.

Unlike the Langmuir and Drozdov type models, the mesoscopic theory does not assume adsorption during the diffusion process. It is associated with polymer chain and polymer-nano-filler interface relaxations.

Drozdov et al. addressed decreasing chain mobility due to the presence of nano-fillers, but their approach does not address the effect of polymer viscoelasticity on the diffusion process. The mesoscopic approach does so by including a conformation tensor **m**. Indeeed the dimensionless time De_m is related to polymer relaxation. The characteristic time $(k_\mathrm{B}T)/(G_0\lambda^{\mathbf{m}}K)$ is associated with polymer structural change and (l^2/D) is a characteristic diffusion time. The mesoscopic approach also includes an area tensor **A** that describes the complex interface between the polymer matrix and the nano-filler. The dimensionless time $De_{\mathbf{A}}$ is related to the complex interface relaxation.

We recommend the mesoscopic approach for situations where strong interactions of the nano-filler with the polymer matrix (as verified by dynamic mechanic analysis (DMA) for example) are present. When strong solvent adsorption on the nano-filler occurs, along with weak interactions between the filler and polymer matrix, we recommend using the Langmuir and Drozdov type models. The Drozdov type model identifies with a strong and irreversible adsorption situation. The mesoscopic theory is more sensitive to the dispersing of the nano-fillers (through parameter λ, associated with one-half of the spacing between layers), while the Langmuir and Drozdov type models do not strongly identify with the morphology of the nanocomposites.

Experimental

We consider experimental data on water transport through vinyl ester nanocomposites made with two different surface treated montmorillonite clays, one labeled as VMC (vinyl monomer clay), and the other CLO (Cloisite 10A®). Here

Figure 1. TEM image of a 5.0 wt % CLO (3.05 wt % MMT) nanocomposite sample at 200,000× magnification.

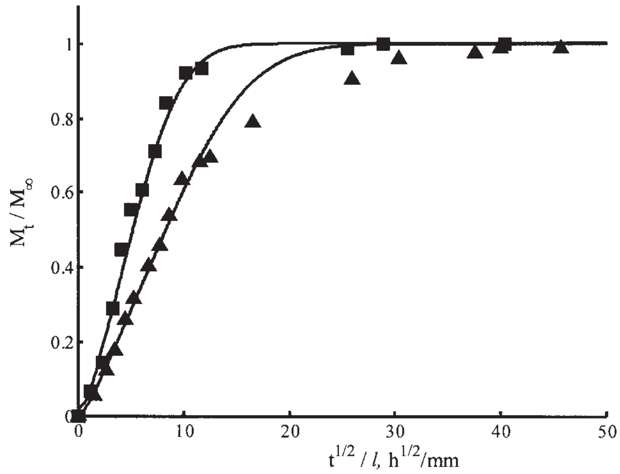

Figure 3. Normalized mass uptake (M_t/M_∞) vs. $(\sqrt{t}/l)$ for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) VMC.

(—) prediction of Fick's laws.

we give a brief description of the experiment. More details can be found elsewhere.[12,17]

The VMC was prepared by treating Cloisite Na® with vinyl benzyl trimethyl ammonium chloride as follows. Thirty grams of Cloisite Na® (Southern Clay Products, Gonzales, TX) was dispersed in 800 ml of distilled water with constant stirring for five hours. Separately, 6.35 g of vinyl benzyl trimethyl ammonium chloride (Sigma Aldrich) was dissolved in 80 ml of water. After 5 h, the vinyl benzyl trimethyl ammonium chloride solution was added drop by drop to the clay dispersion. The mixture was stirred for another three hours, and the organo-MMT was filtered using a vacuum filter and dried in an oven at 100°C. It was later ground in a ball mill. The organic content of VMC was 22% by weight.

The CLO, Cloisite 10A®(Southern Clay Products., Gonzales, TX), a montmorillonite treated with benzyl (hydrogenated tallow alkyl) dimethyl quaternary ammonium chloride, was used as received. The organic content of Cloisite 10A® is ≈ 39% as determined by loss of weight on ignition.

The polymer used was DERAKANE™ 411-350 epoxy vinyl ester resin (Dow Chemical), containing 45 wt %

Figure 2. TEM image of a 5.0 wt % VMC (3.9 wt % MMT) nanocomposite sample at 150,000× magnification.

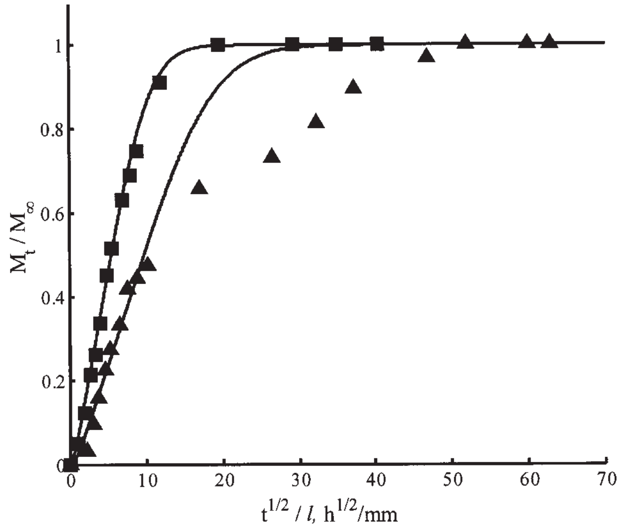

Figure 4. Normalized mass uptake (M_t/M_∞) vs. $(\sqrt{t}/l)$ for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) CLO.

(—) prediction of Fick's laws.

Table 1. Model Parameters for Langmuir Type Transport of Water Through Vinyl Ester-Clay Nanocomposites

		With VMC (%)				With Cloisite 10A (%)			
Sample	Pure Polymer	0.5	1	2.5	5	0.5	1	2.5	5
l (mm)	0.4995	0.1970	0.1834	0.1676	0.1845	0.2537	0.2116	0.2201	0.1884
C_{eq}	0.00137	0.0054	0.0073	0.0087	0.0088	0.0055	0.0077	0.0086	0.0137
Fickian									
$D_F \times 10^7$ (mm^2/s)	7.030	5.533	4.072	2.398	2.187	4.878	4.153	2.944	1.575
Langmuir type model									
$D_\gamma \times 10^7$ mm^2/s	–	72.423	36.456	14.601	9.277	78.744	32.461	11.101	6.145
γ	–	1.243	0.621	0.272	0.095	0.668	0.356	0.044	0.029
β	–	0.475	0.312	0.192	0.089	0.221	0.198	0.047	0.029

dissolved styrene. The resin was mixed with 0.5 wt % of 6% cobalt naphthenate catalyst (Sigma Aldrich) at room temperature. Additionally, 0.05% of 99% N, N dimethyl aniline (Lancaster Synthesis, Pelham, NH) was used as an accelerator, while 1.5% of methyl ethyl ketone peroxide with 9% active oxygen (Sigma Aldrich) was the initiator.

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, initiator and accelerator were then added, and the resin was poured into Teflon molds and was allowed to cure at room temperature for 24 h, with subsequently postcure in an oven for 3 h at 90°C. The dimensions of the molds are 50 × 12.5 mm and the thickness of the film ranges from 0.2–0.6 mm. The nanocomposite structure was probed with the help of X-ray diffraction, transmission electron microscopy and differential scanning calorimetry. Shah et al.,[17] showed the structure characterizations of the nanocomposites (XRD and TEM), the thermal property (DSC) as well as mechanical property tests (tensile strength). Figures 1 is a characteristic TEM picture of a 5.0 wt % CLO nanocomposite sample. It shows all possible platelet morphologies, namely exfoliated, intercalated and stacked structures within the sample. This suggests that the monomer wets the clay surface easily. Figure 2, is a TEM picture of a 5.0 wt % VMC nanocomposite sample, which reveals that the clay is in the form of large tactoids and stacks. That is: the clay exists as tactoids, and the clay platelets are, at best, intercalated.

Diffusion tests were performed by immersing the rectangular cross section samples, having a dry mass ranging from 120 to 400 mg, in distilled water at room temperature (25°C). The samples were stored in a controlled humidity chamber, and it is estimated that they contained 0.05 ± 0.005 wt % water when diffusion experiments were started. The samples were periodically removed, blotted with a dry lint-free tissue, weighed and reimmersed in the water. A typical experiment lasted ten days, and on the first day, readings were taken as frequently as every 15 min. The balance used had an accuracy of 1 μg, and 3–5 replicate runs were carried out for a given set of conditions. We will use the diffusion results to demonstrate the comparison of the three different models.

Results and Discussion

The Fickian diffusion coefficient D_F can be calculated using Eq. 27[12]:

$$D_F = \frac{\pi}{16}\left(\frac{M_t/M_\infty}{\sqrt{t}/l}\right)^2 \qquad (27)$$

where $(M_t/M_\infty)/(\sqrt{t}/l)$ is the slope of M_t/M_∞ vs. $\sqrt{t}/l$, for $M_t/M_\infty < 0.5$.

Figure 3 compares Fickian model predictions for water diffusion through vinyl ester polymer with 0.5 and 5 wt % VMC. Clearly, the diffusion through vinyl ester with 5 wt % VMC is non-Fickian, while the transport through the lower clay concentration nanocomposite film is more Fickian-like. Figure 4 supports a similar conclusion for CLO nanocomposites. Table 1 lists the average Fickian diffusion coefficient D_F for all cases. Although this parameter looses meaning, especially for high clay concentration nanocomposites, it shows a decreasing trend with increasing clay concentration.

Limiting forms (Eqs. 5 and 6) were used to compute the Langmuir type model predictions shown in Figure 5 for water transport through vinyl ester polymer with 0.5 and 5 wt % VMC particles. Figure 6 illustrates the situation for the CLO case. Both figures portray a satisfying simulation for the non-Fickian diffusion process. Table 1 lists the calculated D_γ, γ and β values. The diffusion coefficient D_γ decreases

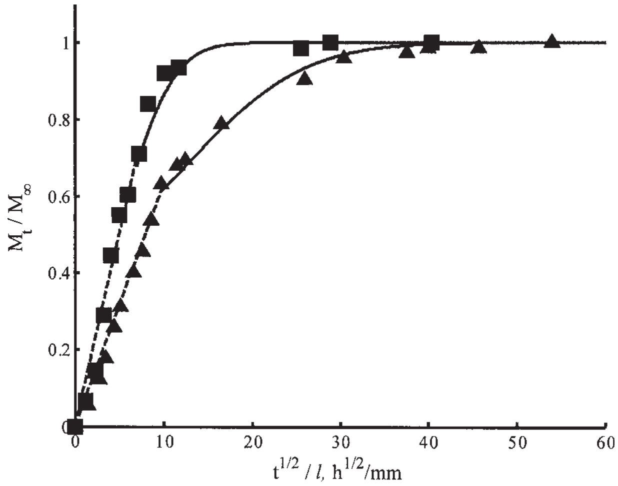

Figure 5. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) VMC.

(---) prediction of Langmuir type model (Eq. 5); (—) prediction of Langmuir type model (Eq. 6).

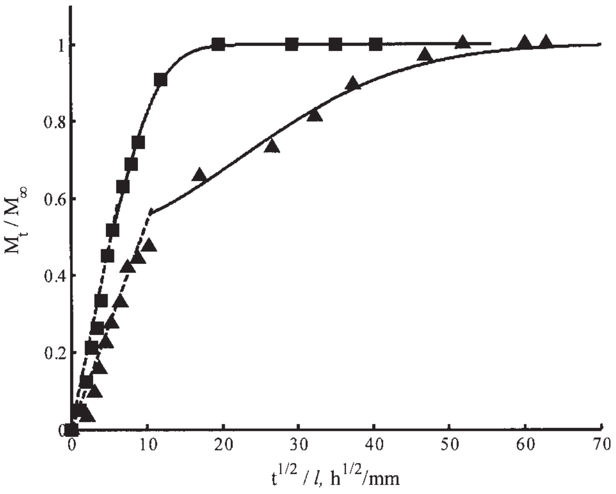

Figure 6. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) CLO.

(---) prediction of Langmuir type model (Eq. 5); (—) prediction of Langmuir type model (Eq. 6).

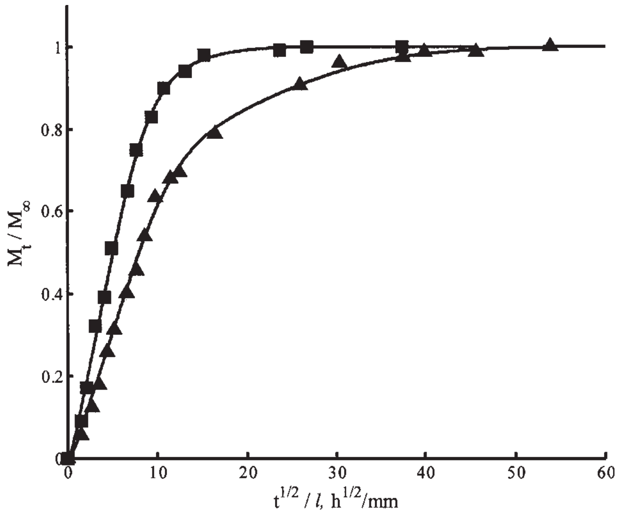

Figure 8. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) VMC.

(—) prediction of a Drozdov type model (Eqs. 11–14).

with increasing clay concentration for both the VCM and CLO cases, and the values are substantially larger than the calculated Fickian diffusion coefficients. The probability parameters γ and β decrease with increasing clay concentration, consistent with reduced solvent sorption/desoprtion on a particular clay site.

We show that for the modified Drozdov type model introduced here, that for very small or very large *De*, the diffusion process is Fickian like. However, for $De \sim 1$, the diffusion process is non-Fickian, as shown in Figure 7. The magnified part of the curve shows the small difference in diffusion curves for very large and very small *De*. Thus, *De* is an indication of whether the diffusion process is Fickian or not.

Equations 11, 12, and 14 with boundary and initial conditions (Eq. 13) are solved numerically by the finite difference method as described in Drozdov et al.[13] Figures 8 and 9 show quantitative agreement between the Drozdov type model predictions for water transport through vinyl ester with 0.5 and 5 wt % VMC and CLO particles. The model parameters are listed in Table 2. The diffusion coefficient D_D decreases with increasing clay concentration. The maximum bounded water concentration on the clay particles *C* increases with increasing clay concentration. The dimensionless time *De* approaches one with increasing clay concentration, indicating that the adsorption rate is comparable to the diffusion rate.

Comparing the results obtained from the Langmuir and Drozdov's type models, we observe that although they share the same assumption that adsorption occurs on the clay sur-

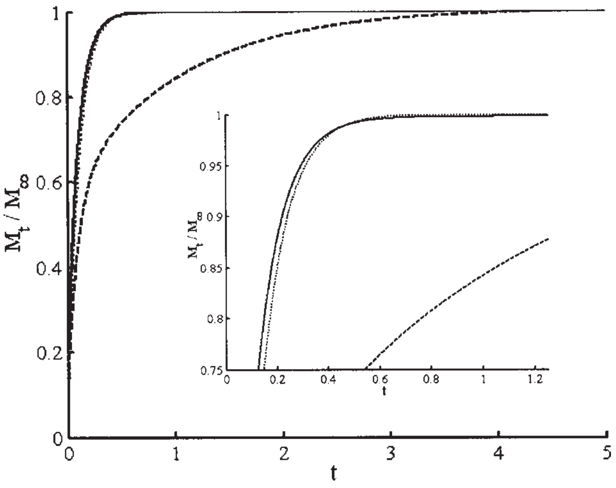

Figure 7. Effect of dimensionless time De on normalized mass uptake (M_t/M_∞) vs. dimensionless time *t* with *C* = 0.55.

(—) $De = 1000$; (---) $De = 1$, (…) $De = 0.001$.

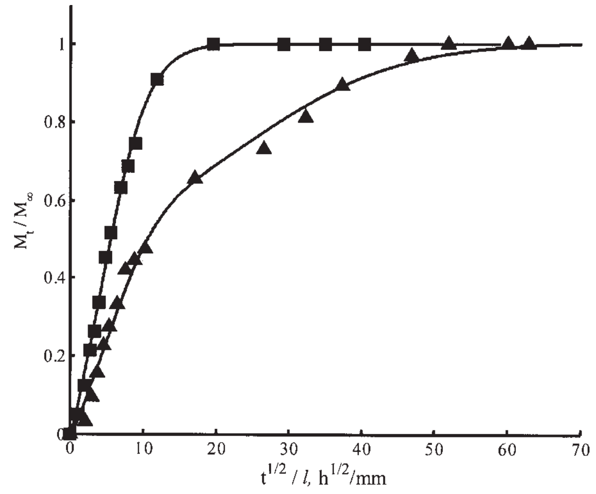

Figure 9. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) CLO.

(—) prediction of a Drozdov type model (Eqs. 11–14).

Table 2. Model Parameters for Drozdov Type Transport of Water through Vinyl Ester-Clay Nanocomposites

		With VMC (%)				With Cloisite 10A (%)			
Sample	Pure Polymer	0.5	1	2.5	5	0.5	1	2.5	5
l (mm)	0.4995	0.1970	0.1834	0.1676	0.1845	0.2537	0.2116	0.2201	0.1884
C_{eq}	0.00137	0.0054	0.0073	0.0087	0.0088	0.0055	0.0077	0.0086	0.0137
Fickian									
$D_{\mathrm{F}} \times 10^7$ (mm^2/s)	7.030	5.533	4.072	2.398	2.187	4.878	4.153	2.944	1.575
Drozdov type model									
$D_{\mathrm{D}} \times 10^7$ (mm^2/s)	–	6.667	5.556	4.167	4.694	5.556	6.111	4.750	3.889
C	–	0.09	0.15	0.26	0.3	0.09	0.21	0.34	0.69
De	–	0.34	0.38	0.40	0.83	0.20	0.87	1.30	1.33

face, the results are quite different. The diffusion coefficients obtained via the Langmuir model are much higher than D_{F}, especially for the low clay concentration nanocomposites, where the two numbers should be close. This shows that the model results (D_γ) are not reliable to portray this system, although the parameters provide a good fit the experimental data. The results derived from the Drozdov type model are more reasonable, with a diffusion coefficient D_{D} close to D_{F}. In addition, the parameters used in the Drozdov type model have a more straight forward physical meaning than the ones in the Langmuir model. The variable C increases with high clay concentration, as previously mentioned. This increase also relates to the higher mass uptake of water in the nanocomposites. For the VMC and CLO systems with the same clay loading, the CLO nanocomposites have exfoliated and VMC nanocomposites have intercalated clay structures.[17] This caused the difference between the values of C for the two cases. The dimensionless time De clearly demonstrates the importance of adsorption on the diffusion process.

We also use the finite difference method to discretize the partial differential Eqs. 15–18. The boundary conditions (Eq. 23) are incorporated into the spatial discretization and the initial conditions (Eq. 23) are used to start the solution. Here, a dimensionless length of 20 sections was considered and the central difference formulation was applied. All calculations were run on a 1.8 GHz PC computer using MATLAB software. The model parameters were obtained by trial and error. Quantitative agreement between model predictions and experimental data are shown in Figures 10 and 11. Table 3 lists the obtained parameter values. The model predictions reveal that the polymer structural change (characterized by Π and $De_{\mathbf{m}}$) has a more pronounced effect on the mass uptake than the change of the complex interface, characterized by Θ and $De_{\mathbf{A}}$. The magnitude of Π increases with increasing clay concentration; that is: the effect of polymer structural change plays a dominant role in the diffusion process, causing the deviation from Fickian diffusion. The polymer relaxation dimensionless time $De_{\mathbf{m}}$ approaches 1 with increasing clay concentration, indicating that the polymer relaxation time is comparable to the diffusion time. The evolution of the complex interface is less important in this system, and the complex interface relaxation dominates the diffusion time. We investigated $De_{\mathbf{A}}$ values ranging from 10 to 10^3. $De_{\mathbf{A}} = 10^3$ for all cases indicated that the complex interface relaxation dominates the diffusion time. Table 3 shows an almost constant diffusion coefficient D, especially for the vinyl ester

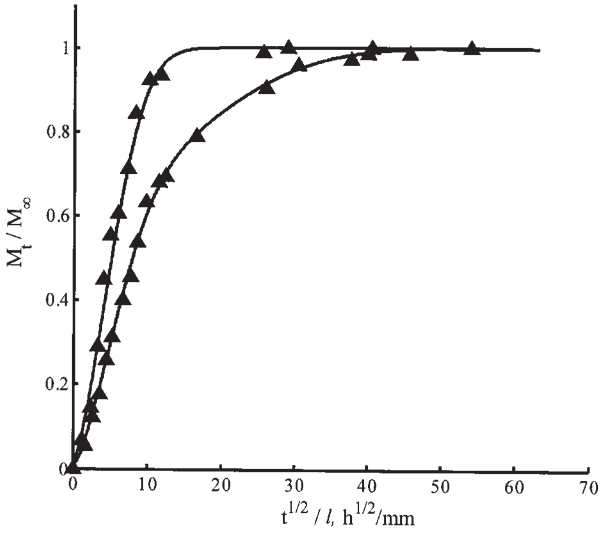

Figure 10. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) VMC.

(—) prediction of the mesoscopic model (Eqs. 15–18).

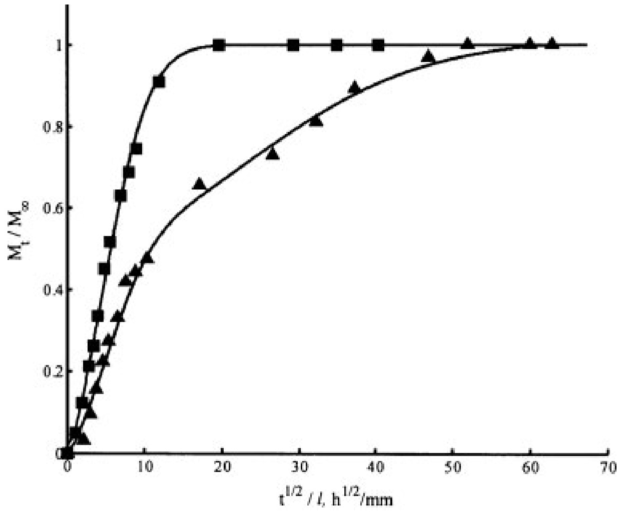

Figure 11. Normalized mass uptake (M_t/M_∞) vs. ($\sqrt{t}/l$) for water/vinyl ester nanocomposites with 0.5 (■) and 5 wt % (▲) CLO.

(—) prediction of the mesoscopic model (Eqs. 15–18).

Table 3. Model Parameters for Mesoscopic Model Transport of Water Through Vinyl Ester-Clay Nanocomposites

		With VMC (%)				With Cloisite 10A (%)			
Sample	Pure Polymer	0.5	1	2.5	5	0.5	1	2.5	5
l (mm)	0.4995	0.1970	0.1834	0.1676	0.1845	0.2537	0.2116	0.2201	0.1884
Ceq	0.00137	0.0054	0.0073	0.0087	0.0088	0.0055	0.0077	0.0086	0.0137
Fickian									
$D_F \times 10^7$ (mm^2/s)	7.030	5.533	4.072	2.398	2.187	4.878	4.153	2.944	1.575
Mesoscopic model									
$D \times 10^7$ (mm^2/s)	–	6.944	6.944	6.944	6.944	6.111	6.389	5.833	6.667
Π	–	−0.1	−13.5	−16.5	−21	−12.1	−16	−21	−21
De_m	–	0.01	0.3	0.55	0.81	0.11	0.9	1.6	1.3
Θ		25	22	20	18	0.5	1.1	3.1	3.5
De_A		1000	1000	1000	1000	1000	1000	1000	1000

with VMC particles, indicating that the dispersion of the clay particles mainly affects the viscoelastic properties of the polymer.

Both the Drozdov type model and the mesoscopic model can successfully describe non-Fickian diffusion, but they consider the problem from a different point of view. The Drozdov type model considers the interaction of the solute and the nano-filler, while the mesoscopic model focuses on the interaction between the polymer matrix and the nano-filler. The two interactions may be important in the case of a system such as discussed here, and future work will focuss on incorporating these two approaches.

Conclusions

We compared the performance of three models describing water mass transport through vinyl ester nano-composite membranes. The Langmuir and Drozdov type models describe solvent adsorption on the nanoclay particles. A mesoscopic model relates the viscoelastic properties of the polymer chains to the diffusion. The magnitude of a dimensionless time in the Drozdov type model indicates whether the diffusion is Fickian or not.

The Langmuir type model predicted the highest values for the diffusion coefficients. All three models predicted a decreasing trend with increasing clay concentration.

The mesoscopic model predicted substantial polymer relaxation behavior with almost constant diffusion coefficients, suggesting that the presence of the clay particles mainly affect the viscoelastic properties of the polymer, confirming the importance of polymer relaxation in the case of non-Fickian processes.

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