

## Water uptake of polymer/clay nanocomposites: Model development

B. Kouini<sup>1,\*</sup>, N. Ouslimani<sup>2</sup>

<sup>(1)</sup> Laboratory of coatings, Materials and Environment, M'Hamed Bougara University –  
Boumerdes 35000, Algeria

<sup>(2)</sup> M'Hamed Bougara University –Boumerdes 35000, Algeria

\*Corresponding author: E-mail: kouinib@univ-boumerdes.com ;Tel/Fax: +213 024 91 15 05

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### ABSTRACT/RESUME

**Abstract:** Numerous models have been proposed for modeling water diffusion behavior in polymers and polymer composites. The most common approach is to apply Fick's law to simple single-free-phase diffusion, due to its simplicity and mathematical tractability [1]. However, it has been demonstrated that diffusion of water in some glassy polymers is anomalous (non-Fickian). Two main approaches are proposed to model the anomalous diffusion. One is the Langmuir-type model for diffusion (LMD), assuming that absorbed water molecules consist of mobile and bound phases [2,3]; the other is the diffusion with time-varying diffusivity model (DTVd), where a constant coefficient of diffusion is replaced by a decreasing function of time (by analogy with a relaxation modulus for a viscoelastic solid) [4,5]. Several models have been proposed to predict the behavior of composites based on the analogy between thermal conductivity and diffusivity [6,7]. The most extensively cited model in polymer/clay nanocomposites is the Nielsen model, which predicts that relative permeability is only a function of the aspect ratio at a given loading of clay, for all percents [8].

### I. Introduction

Recently, polymer/clay nanocomposites (PCNs) have attracted great interest since they frequently exhibit unexpected hybrid properties synergistically derived from both components. One of unique properties was its low water absorption and excellent barrier properties due to long delaminated clay layers in polymeric matrix [1]. The water absorption mechanism of PCNs is influenced by two factors [2]. The first is that the clay is hydrophilic and hence absorbs more water than most of the thermoplastic used as matrix, leading to an increase in the equilibrium water absorption with the clay content. The another factor is that clay layers dispersed in the nanometer scale in a matrix can increase the free path of water molecules to pass through the nanocomposites network compared with the pure matrix which leads to lower water absorption.

### II. Fick's law

Moisture absorption is generally considered to be independent of moisture concentration. The diffusion of

moisture into cured epoxy resin is generally considered to obey Fick's law [3]:

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

Where  $M_\infty$  is the maximum water uptake in the sample mass,  $D$  is diffusivity and  $2l$  is the sample thickness. The solution for Fick's law short times then reduces to the previous equation for the initial stage of diffusion:

### III. Anomalous (non-Fickian) models

#### III.1. Langmuir model of diffusion (LMD)

Water is considered to occur in two categories: one free for diffusion, and the other trapped, not free to move in polymers. At a given time and place in a polymer, there are  $c(t)$  mobile  $H_2O$  molecules per unit volume, which can diffuse with a diffusivity  $D$  and become linked or trapped in the polymer with a probability  $\gamma$ . At a certain time and place there are  $C(t)$  trapped molecules per unit volume, which become

mobile with a probability  $\alpha$ . According to the Langmuir theory of adsorption [4,5], the concentrations of mobile and trapped molecules at equilibrium,  $c_\infty$  and  $C_\infty$  respectively, satisfy the relation:

$$\gamma C_\infty = \alpha C_\infty \quad (2)$$

Diffusion of water molecules through the matrix is described by the mass conservation law:

$$\frac{\partial c}{\partial t} = \frac{\partial J}{\partial x} - \frac{\partial C}{\partial t} \quad (3)$$

Where  $J(t,x)$  is the mass flux, which conforms to simple diffusion theory (Eq. (1)), and the diffusivity remains independent of water concentration, as in Fick's model. Thus, for the one-dimensional case, concentrations at position  $x$  and time  $t$  satisfies the coupled pair of equations:

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} + \frac{\partial C}{\partial t} \quad (4)$$

$$\frac{\partial C}{\partial t} = \gamma c - \alpha C \quad (5)$$

Boundary conditions of the above equation are:

$$C(x, 0) = c(x, 0) = 0 \text{ at } -l \leq x \leq l \quad (6)$$

$$c(\pm l, t) = c_l(t), \quad t \geq 0 \quad (7)$$

An approximate moisture uptake  $M_t$  can be obtained [9]:

$$\frac{M_t}{M_\infty} = 1 - \frac{\gamma}{\gamma + \alpha} e^{-\alpha t} - \frac{8}{\pi^2} \frac{\alpha}{\alpha + \gamma} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left\{-\left[\frac{\pi(2n+1)}{2l}\right]^2 Dt\right\} \quad (8)$$

### III.2. Diffusion with time-varying diffusivity (DTVD)

For an unstressed isotropic viscoelastic polymer, time varying effective diffusivity can be expressed in the form of a Prony series [6]:

$$D(T, t) = D_0(T) + \sum_{r=1}^n D_r(T)(1 - e^{-t/\tau_r}) \quad (9)$$

Where  $D_0$  and  $D_r$  are the unknown temperature-dependent Prony coefficients,  $\tau_r$  is the corresponding time, and  $n$  is the number of terms in the Prony series. As  $D(T, t)$  is assumed to be uniform through the thickness of specimen, the governing equation for one-dimensional diffusion is still effective:

$$\frac{\partial c}{\partial t} = D(t) \frac{\partial^2 c}{\partial x^2} \quad (10)$$

The concentration boundary conditions are

$$c(\pm l, t) = c_l(t) \quad (11)$$

Defining a change in variable:

$$dU = D(t)dt \quad (12)$$

Giving

$$U(t) = \int_0^t D(t')dt' \quad (13)$$

With this change of variable, Eq. (11) reduces to

$$\frac{\partial c}{\partial U} = \frac{\partial^2 c}{\partial x^2} \quad (14)$$

The modified boundary conditions in terms of variable  $U$  take the form:

$$c(\pm l, U) = c_l(U) \quad (15)$$

Upon solving Eq. (16), moisture uptake  $M_t$  can be obtained [9]:

$$\frac{M_t}{M_\infty} = \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-(2n+1)^2 \pi^2 U}{4l^2}\right] \right] \quad (16)$$

Substituting Eq. (10) into (14):

$$U(t) = \int_0^t \left[ D_0(T) + \sum_{r=1}^n D_r(T)(1 - e^{-t'/\tau_r}) \right] dt' \quad (17)$$

$$U(t) = D_0(T)t + \sum_{r=1}^n D_r \left[ t + \tau_r (e^{-t/\tau_r} - 1) \right] \quad (18)$$

Substituting Eq. (19) into (17) gives (20):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \times \exp\left\{-\frac{(2n+1)^2 \pi^2}{4l^2} \left[ D_0 t + \sum_{r=1}^m D_r [t + \tau_r (e^{-t/\tau_r} - 1)] \right] \right\} \quad (19)$$

### IV. Models for composites

In studying the kinetics of diffusion, small molecule diffusion in polymers is often considered analogous to thermal conduction Shen and Springer [8] proposed a theory of moisture diffusion in unidirectional composites, based on the analogy between thermal conductivity and diffusivity.

$$D_{11} = D_m(1 - v_f) + D_f v_f \quad (20)$$

$$D_{22} = (1 - 2\sqrt{v_f/\pi} D_m + \frac{D_m}{B_D} \left[ \pi - \frac{4}{\sqrt{1 + (B_D^2 v_f/\pi)}} \right] \times \tan^{-1} \frac{\sqrt{1 - (B_D^2 v_f/\pi)}}{\sqrt{1 + (B_D^2 v_f/\pi)}}) \quad (21)$$

where  $D_{11}$  and  $D_{22}$  are diffusivities parallel and normal to the fibers (longitudinal and transverse directions),  $D_m$  and  $D_f$  are the diffusivities of matrix and fiber,  $v_f$  is the volume fraction of the fibers, and  $B_D$  is defined as following equation:

$$B_D = 2 \left( \frac{D_m}{D_f} - 1 \right) \quad (22)$$

As the diffusivity of fibers such as carbon or glass is small compared to the diffusivity of the matrix ( $D_m \gg D_f$ ), and Eqs. (21) and (22) reduce to ( $v_f < 0.785$ )

$$D_{11} = D_m(1 - v_f) \quad (23)$$

$$D_{22} = (1 - 2\sqrt{v_f/\pi}) D_m \quad (24)$$

case, exfoliated and ordered nanocomposites, was first considered. Organoclay platelets are assumed to do not absorb water molecules Shirrell and Halpin[12] derived the composite diffusivity based on the analogy between diffusivity and shear stiffness. The longitudinal diffusivity ( $D_{11}$ ) is the same as Eq.(24), but the transverse diffusivity ( $D_{22}$ ) is obtained by the following equation:

$$D_{22} = D_m \frac{1 + \zeta \eta v_f}{1 - \eta v_f} \quad (25)$$

$$\eta = \frac{D_f/D_m - 1}{D_f/D_m + \zeta} \quad (26)$$

Where  $f$  is the aspect ratio

## V. Barrier model

Nielsen proposed a simple, two-dimensional model that assumes perfect registry of the fillers parallel to the surface of the film [10]. The model predicts that relative permeability is a function of the aspect ratio alone at given clay loading for all percents.

A fairly simple equation was derived by Nielsen for a two-dimensional case, as follows:

$$P_f/P_u = v_p + (L/2W)v_f \quad (27)$$

where  $P_f$  is the permeability of the composites,  $P_u$  is the permeability of the polymer,  $v_p$  is the volume fraction of the polymer,  $v_f$  is the volume fraction of the fillers,  $L$  is the average length of the filler face, and  $W$  is the average thickness of the filler.

The  $L/W$  ratio of clay is critical in contributing to the barrier in the model. Experimental data show that this model predicts the permeability behavior of nanocomposites reasonably well at very low loadings of clay (less than 1 wt%); at higher clay loadings, the data deviate substantially from the model [13].

## VI. Model development for nanocomposites

As organoclay is used as reinforcement in polymers, the clay platelets may play an important role in changing the diffusion path of diffusing molecules in an anisotropic fashion, by hindering them from straight diffusion. To study the effect of morphology of nanocomposites on diffusivity, the simplest.

## VII. Conclusion

Models for the diffusion of water into polymers and composites have been reviewed and models for the diffusion of water into nanocomposites have been developed.

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