Composite Structures 108 (2014) 111–118

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

A concentration-dependent diffusion coefficient model for water sorption in composite ☆

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ARTICLE INFO

Article history:
Available online 18 September 2013

Keywords:
Molecular diffusion
Concentration-dependent diffusivity
Activation energy
Polyphthalamides

ABSTRACT

The phenomenon of diffusion coefficients depending on concentration has been observed and studied experimentally for many years. This is particularly the case for the inter-diffusion in metals [1] but has also been observed on various polymeric systems [2]. This study presents a concentration-dependent diffusion coefficient model for water sorption in a polymer matrix composite. It has been developed by studying the water uptake of a polyphthalamide short glass fiber reinforced material. According to experimental data, we postulate that the diffusion coefficient follows a modified Arrhenius equation with a concentration dependence of the pre-exponential factor but also of the activation energy. This choice is related to the evolution of the glass transition temperature during sorption, which has a profound influence on transport properties. The coupled partial differential equation of the model is solved for some applied examples by using an easy-to-implement finite difference scheme.

1. Introduction

For several decades, polymeric materials have been increasingly used in many industrial fields and amongst others, water distribution equipment is an example [3]. Indeed, ease of implementation, low production costs and adapted mechanical properties are assets that now allow polymers to replace traditional metallic materials such as copper alloys. For domestic "hot"[1] water supply and structural component under water pressure, some of high-performance polyamides such as reinforced polyphthalamides (PPA) have proved to be efficient [4]. The sustainability of hydraulic equipment is nevertheless a crucial issue for the industry. Most materials evolve by interaction with their hydro-thermal[2] environment [5] and to expand polymeric material use, designers need predictive models of age-dependent properties [6–9]. The present paper is an initial response to this objective since it proposes a model based on physical processes able to give the water concentration over time and anywhere in the material. All results reported in this paper relate to a polyphthalamide matrix reinforced with short glass fibers. The reasoning of this paper rests on the fact that the diffusion coefficient, which will be described in the following paragraph, depends not only on the temperature but also on the concentration of water itself.

1.1. The diffusivity, fundamentals on transport phenomena

In 1855, based on the experiments of Graham [10], A. Fick was the first to propose a conceptualization of molecular diffusion process by studying salt movement in liquids [11,12]. He drew considerable inspiration from the analytic theory of heat conduction published by J. Fourier thirty-three years earlier [13]. Diffusion is the phenomenon governing the transport of material just as conduction is the mechanism of heat transfer. In the case of molecular diffusion, molecules are transported from a higher concentration region to one of lower concentration; it is a spontaneous phenomenon. For a transient state diffusion (t denoting time), to know the rate at which concentration C is changing at any given point in space, we have to use the well known Fick's second law (1)[3]; which can be written as (2) for a one dimensional problem, x denotes the space variable. D is the *diffusion coefficient* or *diffusivity*[4] in dimensions of [length^2 time^{-1}].

$$-\frac{\partial}{\partial t}\int_{\Omega} C d\Omega = \int_{\Omega} \underline{\nabla}\cdot\underline{J} d\Omega \quad \Rightarrow \quad \frac{\partial C}{\partial t} = -\underline{\nabla}\cdot\underline{J} = \underline{\nabla}\cdot(D\underline{\nabla}C) \tag{1}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \quad \text{or} \quad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad \textit{if } D \textit{ is constant} \tag{2}$$

☆ Application to a polyphthalamide short glass fiber reinforced composite.

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[1] We consider here that hot is less than 70 °C.

[2] The term "hydro-thermal" implies a simultaneous exposure to relative humidity or water immersion and to elevated temperatures.

[3] $\underline{\nabla}$ denotes here the divergence operator and $\underline{J}$ the *diffusive flux vector field*, a molecular transport mechanism which tends to homogenize the intensive quantity even in the absence of macroscopic motion of the medium.

[4] Which can be compared to the *thermal diffusivity*, i.e. the *thermal conductivity* divided by density and *specific heat capacity* at constant pressure.

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http://dx.doi.org/10.1016/j.compstruct.2013.09.007

An early criticism of Fick's work was related to its assumption of a constant diffusivity Eq. (2) and numerous situations are known where this assumption is not valid. If the temperature-variance of diffusion coefficients was soon considered, especially by S. Arrhenius and J.H. van't Hoff, it took a few years for a concentration dependency to be considered. For metal alloys, C. Matano was one of the first to prove that, "the diffusion rate of A atoms into a B atom crystal lattice is a function of the amount of A atoms already in the B lattice" [1]. From the 1960s, similar observations were made for the water sorption in polymers and composites [14–16,2]. In the first section of this paper, we focus on the experimental water sorption kinetics for a short glass fibers reinforced PPA matrix. The water uptake for various thermal conditions have been recorded between 40 °C and 70 °C, coupled with immersion or relative humidities comprised between 40% RH and 100% RH. We then show the sorption kinetics depend on a temperature and water concentration.

1.2. A molecular based model to account for the diffusivity concentration dependency

As we have just pointed out, the effects of water and temperature can be followed by sorption measurements. Experimentally, the water uptake can be plotted versus time[5] and different types of absorption mechanisms might be seen [17]. The simplest one is described by a Fickian law and generally applies to glassy or rubbery polymers outside the glass transition temperature (Tg) zone. Since the Tg plays a key role in the diffusion kinetics [18,19], some authors observe a "concentration dependency" of the transport properties in its vicinity [20]. It is now widely accepted that this non-Fickian behavior results from the coupling between the diffusion, the viscoelastic relaxation of the polymer and chain motions [21]. Over the last few decades, models that have been developed to describe diffusion in polymers have fallen into two main categories:

i *Free volume models* that consider the molecules diffuse through free voids [14]. As the temperature or the concentration is changed, the free volume and the occupied volume will both evolve leading to the sought dependency.

ii *Molecular models* that analyze the polymer chain motions due to the penetrant by considering molecular forces. A penetrant molecule may exist in a hole of sufficient size and can "jump" into a neighboring hole once it acquires a sufficient energy. It is a thermally activated process and is linked to the apparent *activation energy* of diffusion entering into an Arrhenius law.

We adopt below this second approach for which one of the pioneers was Meares [22]. Having experimentally highlighted the concentration dependency in the first section of this paper, we then postulate that the diffusion coefficient follows a modified Arrhenius equation with a concentration dependence of the pre-exponential factor but also of the activation energy Section 3.2. In the last section, we use a finite difference scheme for solving the diffusion transient equation obtained and we show some applied examples.

2. PPA sorption kinetics

Polyphthalamides are thermoplastic synthetic polymers already used in the automotive industry where their chemical resistance and temperature stability are sought; one example could be the turbine water pump or water valves [23]. The semi-aromatic nature of PPA gives them higher mechanical properties than their aliphatic polyamides counterparts, especially at high temperatures associated with humid conditions. Indeed, the presence of aromatic rings has many advantages such as an increase in the glass transition temperature but also results in better resistance to hydrolysis, and better dimensional stability. Both amorphous and crystalline grades are available and they could be reinforced by glass fibers, as is the case in this study.

To obtain such materials, it is necessary to replace a certain amount of the adipic acid of PA66 by a terephthalic acid (TPA) or isophthalic acid (IPA).[6] The PPA considered in this study is a block copolymer PA6T-PA6I for which all the adipic entering the composition of PA66 has been replaced by terephthalic and isophthalic acids. To further increase its dimensional stability, this copolymer is then reinforced by short glass fibers (50% in mass).

2.1. Water sorption experimental observations

The water uptake in the material can be characterized by two physical quantities: the *diffusion coefficient* related to the kinetics of absorption and the *saturated concentration* related to the maximum amount of water that the material can absorb. These two parameters can be identified on thin plates with the sorption curves which connect the exposure time to the hydro-thermal environment. The samples which have been used in this study were one millimeter thick injection molded plates ($100 \times 100\ \text{mm}^2$).[7]

Before ageing, all samples were dried over silica gel in an oven at 40 °C and stayed at this temperature until stabilization of the mass. In this way the reference dry level for measuring the water uptake could be identified. Mass gains as a result of water uptake, were then recorded by removing the sample from its ageing environment and by weighing it periodically on a precision balance.[8] During the sorption test, the evolution of the water concentration C in the composite can be followed as a function of time t by evaluating the ratio between the mass uptake $\Delta M = M(t) - M_0$ and the initial reference mass of the specimen M_0. It is then possible to know the sorption kinetics and if an equilibrium occurs, determine the saturated concentration value C_∞.

Regarding the composite hydro-thermal environment, ageing mechanisms can occur at various levels: water and temperature affect the constituents properties but can also affect fiber/matrix interface. The latter is by far the most feared because it quickly leads to the loss of the composite material "nature". Water penetration can cause swelling and plastification of the matrix and the main effect is to lower the glass transition temperature by several degrees.

Sorption kinetics are presented in Fig. 3 with an analytical estimation of the diffusivity which will be described in Section 2.2. Except for Fig. 1, experimental data points reported in this paper correspond to the average of three samples with a corrected standard deviation of less than 3% for the largest variability. Below 70 °C and whatever moisture conditions studied, no significant mass loss of the material was observed. It was also seen that in those hydro-thermal conditions the diffusion effects seems to be reversible: at the top of Fig. 1, sorption data points are displayed for three samples under isothermal 70 °C and 70% relative humidity conditions; the samples were subjected to a first sorption

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[5] Preferably the square root of time.

[6] ASTM-D5336-03, Standard Specification for Polyphthalamide (PPA) Injection Molding Materials.

[7] This sample size allow a mono-dimensional diffusion through the thickness to be considered, thus eliminating the difficulties associated with the injection induced anisotropy [4,24]. However, it was possible to extrapolate the results to larger thicknesses, as long as the diffusion was kept mono-dimensional [4].

[8] Mettler AT250 with 0.01 mg readability to 50 grams and 0.1 mg readability to 200 g capacity.