Monitoring and simulations of hydrolysis in epoxy matrix composites during hygrothermal aging

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ABSTRACT

In this paper, we studied the water transport in thermoset matrices. We used Fourier Transform Infrared analysis (FTIR) during sorption/desorption experiments to investigate the interaction between sorbed water and the epoxy network. Our results demonstrated that the polymer matrix undergoes hydrolysis. We found that the chemical species involved in the reaction process was the residual anhydride groups. These results support the physical basis of the three-dimensional (3D) diffusion/reaction model. We finally showed that this model is able to reproduce multi-cycle sorption/desorption experiment, as well as water uptake in hybrid metal/epoxy samples. We simulated the 3D distributions of the diffusing water and the reacted water.

1. Introduction

The use of fiber-reinforced polymers in aircraft fuselage allows aircraft manufacturers to develop lightweight and multifunctional composite structures with high mechanical performance along with resistance to chemical and physical degradation. Metal reinforcements [1] or conductive nano fillers [2] need to be added to the Carbon Fiber Reinforced Composites (CFRP) to enhance their electrical and thermal properties. One way to do this is co-bonding a expanded foil to the external side of the composite using an epoxy-based adhesive. Under service conditions, these hybrid structures can be exposed to humidity and temperature cycles. A durability assessment of these materials is necessary to end up with optimized structure designs and maintenance strategies. The phenomenological overview of the problem presented by Lubineau et al. [3], highlighted the various couplings involved in the aging process. Water uptake leads to degradation of mechanical properties [4,5] as well as swelling [6–8] and can additionally lead to chemical degradation [9] or microstructural changes [10]. Then, multiple aging mechanisms can combine to result in damage of the matrix and the interfaces.

A crucial starting point in understanding the aging of hybrid composites is to perform modeling and simulation of the moisture sorption process in the epoxy network, that are both accurate and robust to long-term extrapolation. This requires an in-depth physical understanding to validate the modeling approach. Epoxy resins can exhibit complex sorption behaviors that cannot be captured by the Fickian model [11]. Sorption experiments conducted on several epoxy systems often reveal anomalies in the mass uptake of neat polymer specimens [10,12–15]. Explaining such behaviors requires distinguishing between the different forms of water that can be found in the wet polymer. Part of the sorbed water exists as molecular water and is either free in the network and the microvoids [10,16] or involved in physical interactions with polymer chains or other water molecules [16,17]. The other part of the water is involved in hydrolysis reactions [9,15]. Hence, the overall amount of sorbed water cannot be considered as a unique aging indicator because these various species have different effects on the polymer. It is therefore necessary to examine the sorption mechanisms and establish relationships between the types of water and the subsequent evolution of the material's properties and swelling. For this purpose, the spectroscopy techniques can be used to investigate the nature of the water sorption mechanisms. Nuclear Magnetic Resonance (NMR) can track physical interactions [16,17] while Fourier Transform Infrared (FTIR) techniques are suitable to investigate chemical effects [9,18,19]. In [20], the authors quantified the changes in concentrations of the reaction products from their IR peaks area. In addition, Leger et al. [10] showed that Scanning Electron Microscopy (SEM) reveals morphological changes.

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We proposed and identified in [21] a general modeling framework for prediction of the spatial distribution of species concentrations. This model was based on a competitive diffusion/reaction scheme and relied on a heterogeneous description of the material in which local model parameters depend on both the local amounts of diffusive and reacted water. Yet, it is clear that the retained approach is a generic scheme that accounts for different possible underlying mechanisms. As a result, it is necessary to refine the phenomenology in order to elucidate the mechanisms responsible for the non-classical sorption behaviors of polymer matrix composites. The objective of this paper is to validate our approach by (1) clarifying the physical basis of the model by monitoring chemical and microstructural changes (FTIR, SEM), (2) and by demonstrating the capability of the model in complex situations. In particular, we investigate water uptake under cyclic humidity conditions. Also, we note that the model's parameters are local properties such that this framework allows us to assess moisture uptake in a complex structure. We study the particular case of the water transport in an epoxy matrix with a three-dimensional (3D) metal network in this work.

In the next section, the bases of the diffusion–reaction scheme are reviewed. We next describe, in Section 3, an anhydride-cured epoxy resin and a metal reinforced polymer (expanded metal foil impregnated in an epoxy matrix). We give details of the experimental procedures in Section 4, with particular focus on gravimetric analysis and spectroscopic techniques (FTIR). We monitored the morphological and chemical changes in the polymer using electron microscopy and FTIR. We used the FTIR results to discuss the reactive mechanisms involved in the aging of the epoxy matrix. We finally illustrate numerical simulations of the fully coupled diffusion–reaction process in complex configurations.

2. A non-homogeneous diffusion–reaction scheme for moisture uptake

The experimental results reported in [21] revealed that the epoxy system studied here does not exhibit Fickian behavior. The proposed diffusion–reaction scheme describes water transport as a competition between (1) diffusion, which can involve several fundamental mechanisms (free volume, water/polymer interactions) and (2) a reactive process that can induce certain changes in the polymer (structure or microstructure). The diffusion is fully coupled with the reaction through non-constant Fickian parameters. We consider a phenomenological description of the reactive process, based on a first-order chemical reaction (Eq. (1)) between diffusing water, w (mol/m^3), and a reactive substrate, R (mol/m^3), leading to the production of a complex, Y (mol/m^3):

$$w + R \leftrightarrows Y \tag{1}$$

The governing equations of the proposed phenomenological model were detailed in [21] and are briefly reviewed below:

Conservation equations

$$\frac{\partial w}{\partial t} = -div(\underline{j}) + r_w \tag{2}$$

where $\underline{j}$ is the mass flux of diffusing water and r_w describes the formation/dissociation kinetics of the complex.

$$\frac{\partial Y}{\partial t} = r_Y \tag{3}$$

$$\frac{\partial R}{\partial t} = r_R \tag{4}$$

Constitutive equation

Diffusion law

$$\underline{j} = -D(Y)\left(\underline{\nabla}w - \frac{w}{w_s(Y)}\underline{\nabla}w_s(Y)\right) \tag{5}$$

where w_s is the maximum reachable water concentration. The diffusivity, $D(Y)$, and the solubility, $S_0 + S_1 \cdot Y$, are dependent on the progress of the reaction.

$$D(Y) = D_0 + D_1 \cdot Y \tag{6}$$

$$w_s(Y) = (S_0 + S_1 \cdot Y)a^e p_{sat} \tag{7}$$

where a^e is the water activity in the environment and p_{sat} is the saturation vapor pressure in air.

Reaction kinetics

$$r_w = -k_h(T)wR + k_r(T)Y \tag{8}$$

$$r_R = -k_h(T)wR + k_r(T)Y \tag{9}$$

$$r_Y = k_h(T)wR - k_r(T)Y \tag{10}$$

k_h and k_r are the rate constants for the forward and the reverse reactions, respectively. From a general viewpoint, the temperature effects can be taken into account [21]. Hence, the diffusivity and the solubility obey to an Arrhenius-type law, and the two rate constants are also temperature dependent.

We previously described an optimization procedure to identify the model parameters that are summarized in Table 1 [21].

We can envisage several physical interpretations to explain our experimental observations. First, the second stage in the sorption curve could be attributed to hydrolysis of reactive groups available in anhydride cross-linked epoxy systems. Those can be either (1) the residual epoxy or anhydride groups that are in excess [15,22] or (2) the ester groups [20].

Nevertheless, microstructural changes, such like microcavities or microcracks, could be another responsible mechanism [10]. We note that, despite they tremendously differ from a physics viewpoint, all these mechanisms could be generalized in an apparent diffusion/reaction scheme as in [21]. In this paper, we attempted to validate the diffusion–reaction scheme by answering some of the questions regarding the physical foundations of the model. This required a suitable characterization of the epoxy system under investigation, which is detailed in the next section.

3. Materials

3.1. The anhydride-cured epoxy system

The epoxy-based matrix was the commercially available EPO-LAM 2063 system (supplied by Axson Technologies). It consisted

Table 1
Parameters of the diffusion–reaction model: values identified using the optimization process [21].

Parameter	Unit	Optimal value
D_0	m^2 s^{-1}	4.5×10^{-12}
S_0	mol m^{-3} Pa^{-1}	0.0597
D_1	mol^{-1} m^5 s^{-1}	-1.24×10^{-14}
S_1	Pa^{-1}	1.676×10^{-4}
R_0	mol m^{-3}	4.5×10^3
k_h	mol^{-1} m^3 s^{-1}	8.535×10^{-10}
$\frac{k_r}{k_h}$	mol m^{-3}	6.5×10^3