



# A fully coupled diffusion-reaction scheme for moisture sorption–desorption in an anhydride-cured epoxy resin

Jalal El Yagoubi<sup>a,\*</sup>, Gilles Lubineau<sup>a</sup>, Frederic Roger<sup>a</sup>, Jacques Verdu<sup>b</sup>

<sup>a</sup>King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia

<sup>b</sup>Arts et Metiers ParisTech, Laboratoire PIMM, 151 Boulevard de l'Hopital, 75013 Paris, France

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## ABSTRACT

Thermoset materials frequently display non-classical moisture sorption behaviors. In this paper, we investigated this issue from an experimental point of view as well as in terms of modeling the water transport. We used the gravimetric technique to monitor water uptake by epoxy samples, with several thicknesses exposed to different levels of humidity during absorption and desorption tests. Our results revealed that the polymer displays a two-stage behavior with a residual amount of water that is desorbed progressively. We proposed a phenomenological reaction-diffusion scheme to describe this behavior. The model describes water transport as a competition between diffusion and the reaction, during which the local diffusivity and solubility depend on the local advancement of the reaction. We then implemented our model using COMSOL Multiphysics and identified it using a MATLAB-COMSOL optimization tool and the experimental data. We discussed the relation between the hydrophilicity of the product of the reaction and the diffusion behavior. We examined the reaction-induced modification of the water concentration field. It is worth noting that part of the phenomenology can be explained by the presence of hydrolyzable groups.

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## 1. Introduction

In aeronautical and aerospace engineering, most currently used composites rely on epoxy-based thermoset materials because of their excellent mechanical properties that remain relatively stable even under warm temperature conditions. Yet, during flight, these composites are commonly exposed to both thermomechanical cycling and high humidity. One consequence of these severe environmental conditions is the progressive modification over time of the epoxy's behavior. To be properly designed, these epoxy resins require full characterization under environmental conditions. We focus on water sorption behaviors in short-term aging of epoxies in this paper.

Water uptake has a detrimental effect on the mechanical properties of polymers. First, water is known to act as a plasticizer for such materials. A decrease in the glass transition temperature ( $T_g$ ) is observed [1–4], reducing the maximum operating temperature. De Neve et al. [2] reported a decrease in the glass transition temperature of 25 °C with a 3% mass uptake, as well as a drop in the glassy (3.4 GPa–2.2 GPa) and rubbery modulus (70 MPa–25 MPa)

as a function of the mass uptake. In a different epoxy system, Alessi et al. [5] showed a decrease of the fracture toughness ( $0.8 \text{ MPa m}^{0.5}$ – $0.5 \text{ MPa m}^{0.5}$ ) after immersion for one week in distilled water at 70 °C. In addition, the ingress of water leads to an increase in the volume of the polymer [1,4,6–10]. Commonly, the global hydric strain, derived from the volume increase, is linked to the mass uptake by a macroscopic coefficient of moisture expansion. Hence, water uptake modifies both the stress/strain distribution inside the structure and the local mechanical properties of the constitutive material. Moreover, in many cases (heterogeneous materials, complex structural shapes, cyclic conditions) the concentration of water is not homogeneous. Understanding of the gradient of water absorption and the consequential material modification is needed to predict micromechanical damage.

A convenient way to investigate absorption kinetics from a macroscopic point of view is to monitor the mass uptake that accounts for the overall amount of water molecules absorbed by the material using gravimetric analysis. These tests lead to a useful overall understanding of water sorption. Gravimetric curves can reveal Fickian behaviors or complex features (frequently called anomalies [11]) that suggest that there are complex underlying mechanisms.

Many experimental works have reported non-classical sorption behaviors. A typical non-classical behavior frequently encountered

\* Corresponding author. Tel.: +966 (0)565 560 239.

E-mail address: [jalal.yagoubi@kaust.edu.sa](mailto:jalal.yagoubi@kaust.edu.sa) (J. El Yagoubi).

involves two-stage with (1) an initial linear increase with respect to the square root of time (according to Fick's model) and (2) a deviation from Fick's model without stabilization of the mass uptake for the investigated time window [4,6,9,10,12–18]. A number of authors proposed several explanations for these observations, some of which are mentioned below. The first family of models is based on the assumption of non-constant parameters in the classical Fickian model. These include the diffusion parameter that governs the diffusion rate and the concentration at the boundary.

- Based on experimental measurements in [19,20] proposed a model with a concentration-dependent diffusion parameter that is reduced under high relative humidity.
- The anomalies of the sorption behaviors reported by [7,13,21] were interpreted under the framework of molecular relaxation theory. A time-dependent diffusion parameter was used to reproduce the experimental observations.
- The model proposed by Weitsman [22] is often used to describe the two-stage sorption behavior of viscoelastic materials. The retardation process due to viscoelasticity was taken in consideration in this model using time-dependent boundary conditions.

These approaches are suitable and used to fit absorption curves but fail in reproducing some of the experimental observations particularly during desorption. Therefore, another family of models considers the partition of water uptake into two species that are commonly called “bonded” and “unbonded” water molecules. There is currently no consensus on the definition of these terms:

- In the Carter and Kibler model (Langmuir-type model) [23], “bonded” water refers to the molecules that create low energy bonds with hydrophilic sites while “unbonded” water refers to water transported in free volume. In Ref. [24] the suggestion is made that a physical interpretation be offered in the light of NMR analysis performed on wet samples.
- In Ref. [17], the deviation from the Fickian model is attributed to microcavities developed during absorption. It is assumed that the “bonded” water is a combination of both the “bonded” and free water following the classical Langmuir description. Free water is the water that resides in the voids that are created.
- The incomplete cure of the epoxy is also used as a justification for non-Fickian behavior [4,9,15]. A reasonable explanation is given by [15]. It focuses on the hydrolysis of the residual epoxy groups. The “bonded” water would correspond to the part of sorbed water that has reacted with the epoxy.

It is worth noting that in common in these three models is that they are based on a diffusion-reaction scheme. Nevertheless, the models differ in some aspects that can be highlighted when a desorption test is performed.

In this paper, we propose a phenomenological reaction-diffusion scheme. Local material parameters depend on the local advancement of both the diffusion and the reaction mechanisms. This model unifies and extends the approaches mentioned to create a framework that can reproduce both sorption and desorption behaviors on samples of various thicknesses. An experimental validation of the approach is proposed and a initial insight about the identification strategy used in this model is offered.

In the remainder of this paper, we first describe the commercial epoxy resin under study as well as the sample preparation method. Then, we investigate the sorption behavior of the resin using the gravimetric technique. We present our model formulation in the fourth section. Then, we present results from numerical

simulations using COMSOL Multiphysics software and we identify the parameters using an original identification strategy in MATLAB-COMSOL. Finally, we discuss the reaction-induced modification of the diffusion behavior and the consequences on the water concentration field.

## 2. Materials and methods

A commercially available epoxy system with a high glass transition temperature (EPOLAM 2063 supplied by Axson Technologies) was the focus of our study in this research. As its viscosity at 75 °C is very low, this resin is used in the manufacturing of composites using transfer molding or infusion techniques. It is a two-component epoxy resin based on a mixture of several epoxy monomers. It is mainly a blend of cycloaliphatic epoxy resin and a diglycidyl ether of bisphenol-A (DGEBA) resin. The resin was mixed at 75 °C with an anhydride hardener, also provided by Axson Technologies, with a volume ratio of 1:1 (100:107 mass ratio) that corresponds to the stoichiometry between the anhydride and the epoxy. The mixture was stirred for 15 min at the same temperature to obtain a homogeneous blend. Then, an adequate quantity of resin was poured into a flexible thermoplastic mold with a non-stick surface. Degassing was performed inside a vacuum chamber (Struers Citovac) at 0.1 bar. The epoxy preparation was completed following the two-step curing cycle recommended by the supplier and described hereafter. First, the blend was kept at 80 °C for 6 h and then cooled to the ambient temperature. After removal from the molds, the samples were heated to 180 °C and post-curing was completed after 4 h. The neat resin sheets were then maintained inside a desiccator at room temperature.

The glass transition temperature  $T_g$  of the resin was evaluated by a dynamic mechanical analysis (DMA) instrument (Netzch DMA 242 C) in the three-point bending mode at 1 Hz and 5 °C/min. The measured value (135 °C) was significantly lower than the maximum  $T_g$  given by the supplier (190 °C). Incomplete curing of the epoxy was confirmed by DMA performed at various post-curing times. Table 1 shows that the  $T_g$  increased as the post-curing time increased. It is clear that the retained curing cycle used in this experiment did not fully cure the epoxy, and the conversion was less than 1. Below, part of the phenomenology is explained by the presence of residual epoxy and anhydride that did not react and this observation becomes important there. Finally, three specimen thicknesses were considered:  $2L = 1$  mm,  $2L = 435$   $\mu$ m and  $2L = 250$   $\mu$ m. To meet equipment specifications, 10 mm by 15 mm samples were obtained by cutting the raw plates using a diamond saw. The thickness of each specimen was adjusted by grinding the surfaces with SiC abrasive paper (# 1000) (scattering of the thickness was about 4  $\mu$ m).

## 3. Experimental results

The gravimetric analysis was conducted on a IGASorp-HT system (Hiden Isochema). This instrument is a dedicated system that monitors mass uptake and sorption kinetics including

**Table 1**  
Evolution of the glass transition temperature ( $T_g$ ) of EPOLAM 2063 as a function of the post-curing time. The standard curing cycle is 6 h at 80 °C + 4 h at 180 °C.

Post-curing cycle	$T_g$ (°C)
Standard	135
Standard + 2 h at 180 °C	160
Standard + 4 h at 180 °C	180
Standard + 6 h at 180 °C	180

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