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Hysteresis in the relation between moisture uptake and electrical conductivity in neat epoxy

Gilles Lubineau[a], Anwar Sulaimani[a], Jalal El Yagoubi[b], Matthieu Mulle[a], Jacques Verdu[c]

[a]King Abdullah University of Science and Technology (KAUST)
Physical Science and Engineering Division, COHMAS Laboratory
Thuwal 23955-6900, Saudi Arabia
[b]Univ. Bordeaux, I2M, UMR 5295, F-33400 Talence, France
[c]Arts et Metiers ParisTech
Laboratoire PIMM, 151 Boulevard de l'Hopital
75013 Paris, France

Abstract

Monitoring changes in electrical conductivity is a simple way to assess the water uptake from environmental moisture in polymers. However, the relation between water uptake and changes in conductivity is not fully understood. We monitored changes in the electrical volume conductivity of an anhydride-cured epoxy polymer during moisture sorption-desorption experiments. Gravimetric analysis showed that the polymer exhibits a two-stage sorption behavior resulting from the competition between diffusive and reactive mechanisms. As expected, the macroscopic electrical conductivity increases with the diffusion of water. However, our most surprising observation was severe hysteresis in the relation between water uptake and electrical conductivity during the sorption and desorption experiments. This indicates that change in the electrical conductivity depends on both the water uptake and the competition between the diffusive and reactive mechanisms. We studied samples with various thicknesses to determine the relative effects of the diffusive and reactive mechanisms. This is an important observation as it means that general electrical monitoring techniques should be used cautiously when it comes to measuring the moisture content of polymer or polymer-based composite samples.

Keywords: Epoxy, Moisture sorption, Hydrolysis, Electrical properties, Diffusion

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*Corresponding author: gilles.lubineau@kaust.edu.sa

1. Introduction

Epoxy resin polymers are used in a wide range of industrial products, including electronic components, electrical insulators and structural adhesive components. In aeronautical applications, in which epoxy resin polymers are preferred for stiffness and durability, these polymers are exposed to extensive moisture from the environment, which can endanger the integrity of the structures. Indeed, the absorption of environmental moisture (i.e. water uptake) leads to a decrease in the glass transition temperature [1–4] and a decline in the mechanical performance [4–6] of the polymer. Water uptake has also been found to modify some physical properties of epoxy systems, such as their thermal [7] and electrical conductivity [8]. Dielectric analysis has been conducted [9, 10] on these physical changes to investigate the interaction between the water and the surrounding polymer. Several studies have focused on the kinetics of water absorption into the bulk of neat epoxy materials [11–14]. The physical and chemical interactions were found to be numerous and varied.

In a previous paper [15], we proposed a fully coupled diffusion-reaction scheme to describe the water uptake of epoxy resins. The underlying hydrolysis mechanism was fully studied in [16]. Our previous observations suggest that the relationship between the mass water uptake and the change in conductivity is complex in epoxy systems. Here, we test the influence of water uptake on the macroscopic electrical volume conductivity of epoxy materials during sorption and desorption cycles. We observe that the total change in conductivity is not directly related to the water uptake, but rather depends on the alternation of diffusion and reaction mechanisms that take place between the polymer and the water.

2. Materials and methods

The samples were made from a commercial epoxy system (EPOLAM 2063, Axson Technologies). The resin was a blend of bisphenol-A diglycidyl ether and cycloaliphatic epoxy monomers. The resin was mixed with an anhydride hardener in a mass ratio of 100:107. We produced three thicknesses of neat epoxy samples, $250 \pm 7\mu$m, $510 \pm 5\mu$m and $934 \pm 5\mu$m. The sample mold consisted of two stainless steel plates that were internally coated with a release agent and bolted together with a spacer sheet placed between. The samples were cured for six hours inside a vacuum chamber at 80 °C and then post-cured for four hours inside a universal oven at 180 °C. Dynamic mechanical analysis determined the glass transition temperature (T_g) to be 140 °C. This T_g was lower than the maximum reachable T_g (180 °C). This observation was consistent with the Fourier transform infrared (FTIR) spectroscopy that revealed peaks corresponding to residual anhydride and epoxy groups, suggesting that the curing of the resin was incomplete [15, 16].

3. Experiment methods

First, the samples were dried at 50 °C under a primary vacuum for two days. Second, the samples were conditioned inside a climatic chamber at 50 °C and 60% relative humidity for 96 hours (sorption). Finally, the samples were next subjected to desorption under a primary vacuum inside a vacuum chamber at 50 °C for 96 hours. Every eight hours, a sample of each thickness was removed from the chamber to be superficially dried, and gravimetric analysis was performed by weighing the sample with an analytical balance to measure the mass uptake (m_w) as per Eq.(1),

$$m_w = \frac{m - m_d}{m_d}, \tag{1}$$

where m is the current weight of the epoxy specimen and m_d is its initial weight measured at the end of initial conditioning phase.

Then, the out-of-plane direct current volume conductivity was measured according to ASTM standard D257 [17] using a Keithley 6517B electrometer [18]. Four hundred volts were applied across the sample thickness and the resistance, R, was determined. Then, the electrical conductivity (σ_s) was calculated using Eq.(2),

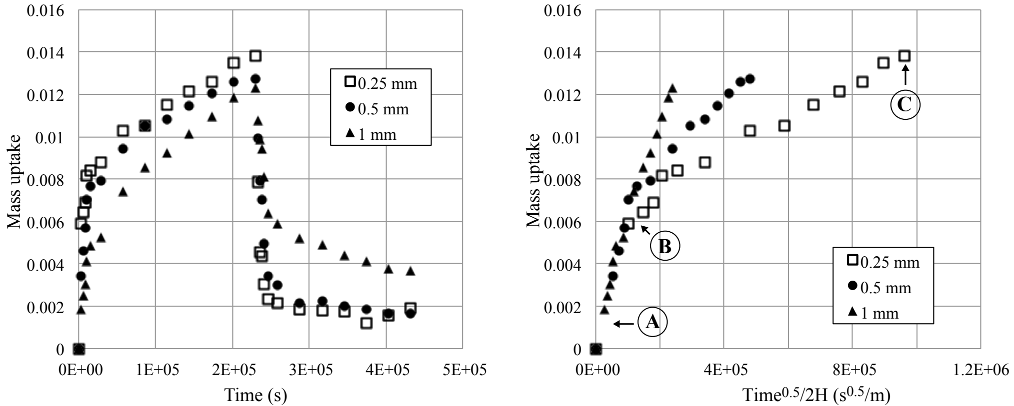
$$\sigma_s = \frac{2H}{R}, \tag{2}$$

where H is the half thickness of each plate.

4. Results and discussion

We plotted the water uptake based on mass (mass uptake) in relation to time and to the reduced time, $\sqrt{t}/2H$, in Fig. 1(a) and Fig. 1(b). During the first 10^5 $s^{1/2}.m^{-1}$ (from point A to point B), the curves of three sample thicknesses coincide and have a slope of about 6.10^{-8} m.$s^{-1/2}$. This initial behavior is interpreted here in terms of Fick's diffusion.

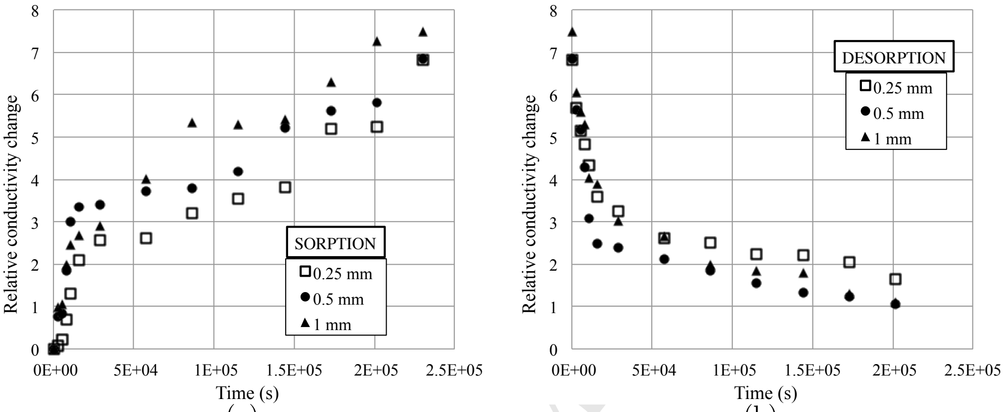
However, classic Fickian equilibrium mass uptake is not observed. Rather, the coupled diffusion-reaction model introduced in [15] describes very well the hydrolysis that contributes significantly to the mass uptake after 10^5 $s^{1/2}.m^{-1}$ (point B). As the water uptake of the epoxy resin increases, hydrolysis of the polymer network caused by the diffusing water leads to a change in the effective diffusion parameter and in the solubility of water in the network. So, after point B, the material reacts slowly with the water, causing a supplementary mass increase. The curves shown in Fig. 1(b) diverge after point B because the reaction to the water diffusion is a volume-scalable mechanism, in contrast to the Fickian diffusion that depends on the thickness of the sample (i.e. a thickness-scalable mechanism). The reaction begins as soon as the water penetrates the sample, but the corresponding mass uptake becomes significant only after point B. In the thinnest sample (0.25 mm), diffusion and reaction are well-separated; the physical equilibrium is reached just after point B and the remaining mass gain is due to hydrolysis.



(a) (b)

Figure 1: Mass uptake in relation (a) to time and (b) to the reduced time $\sqrt{t}/2H$.

The changes in the electrical conductivity of the samples are plotted in Fig. 2 and Fig. 3. These results show that water uptake causes a complex increase in conductivity that cannot be explained by the water uptake alone. Fig. 3 also reveals strong differences between the thin and thick samples. In the thicker samples (1 mm), a biunivocal relationship can be observed between the conductivity and the water uptake; in the thinner samples (0.25-0.5 mm), a hysteresis is observed that is stronger when the sample is thinner.



(a) (b)

Figure 2: The change in electrical conductivity during (a) sorption and (b) desorption. The initial conductivity, σ_s, is $3.7 \pm 0.4 \cdot 10^{-15} S/m$, $3.9 \pm 0.5 \cdot 10^{-15} S/m$, $3.4 \pm 0.4 \cdot 10^{-15} S/m$ for the 0.25 mm, 0.5 mm and 1 mm films, respectively. The quantity on the y-axis is the relative change in conductivity defined as $(\sigma_s(t) - \sigma_s(t = 0))/\sigma_s(t = 0)$.

To better understand this hysteresis in the thin samples, we must identify the responsible dipolar groups or ions. The time scales for diffusion and hydrolysis are very different for the 0.25 mm sample, so the two processes can be considered uncoupled as a first approximation (the ratios of the diffusion characteristic time to the reaction characteristic time are given in Table 1 for different sample thicknesses).

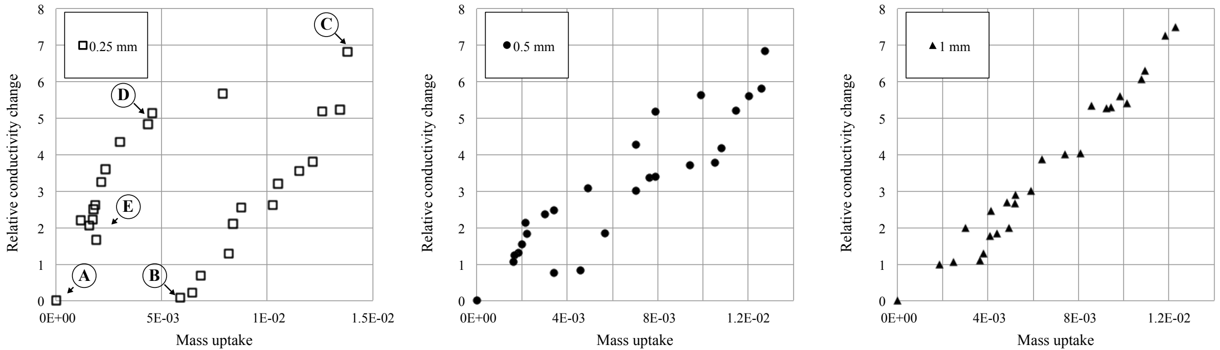
For these thin samples, the increase in conductivity is negligible until the water uptake reaches 0.5% (point A to point B, Fig. 3(a)). This is when the water uptake is mostly linked to the diffusion of the water. However, this diffusing water has a very limited effect on the conductivity. Point B corresponds to the beginning of the hydrolysis, which triggers a completely different response. Hydrolysis creates highly polar species that cause

Thickness	Diffusion τ_D (10^4s)	Ratio κ/τ_D
250±7	1.25	24.2
510 ±5	5.2	5.8
934±5	17.4	1.7

Table 1: Comparison of the diffusion characteristic time ($\tau_D = \dfrac{H^2}{D}$) with the reaction characteristic time (κ) [15].

the conductivity to increase. Since the sample was partially uncured, some residual epoxy and anhydride groups will still remain. We have shown previously [16] that both functional groups (epoxy and anhydride) are affected by hydrolysis. The epoxide groups form 1,2 diols, whereas the anhydride groups form carboxylic acids. Hydrolysis, mostly found in the anhydride clusters, results in highly polar and hydrophilic functional groups that promote the formation of hydronium (H_3O^+) ions [19]. From point B to point C, the conductivity increases monotonically with the water uptake as more hydronium ions are created and the mobility of these ions also increases. From point C to point D, the change in water uptake is mainly related to the desorption of excess diffusing molecular water. The conductivity is almost unchanged as most of the ions remain in the sample. From point D to point E, the reverse reaction starts to have a significant effect on the electrical conductivity. Ionized species are extracted from the sample and the material begins to recover its initial properties (point A). This suggests that that the hydrolysis is fully reversible. Thus, the relationship between the water uptake and the conductivity exhibits a strong hysteresis during the cycle illustrated by points A through E. It very clearly shows that the macroscopic electrical properties are not reliable indicators of the total water uptake.

Since the ratio of sorbed water to hydrolysis products (hydronium ions) tends to increase with increasing sample thickness for the time interval under study, it is expected that the amplitude of the hysteresis decreases with increasing sample thickness, as shown in Fig. 3.



(a) (b) (c)

Figure 3: Relationship between changes in electrical conductivity and mass uptake. The initial conductivity, σ_s, is $3.7 \pm 0.4 \cdot 10^{-15} S/m$, $3.9 \pm 0.5 \cdot 10^{-15} S/m$, $3.4 \pm 0.4 \cdot 10^{-15} S/m$ for the 0.25 mm, 0.5 mm and 1 mm films, respectively. The quantity on the y-axis is the relative change in conductivity defined as $(\sigma_s(t) - \sigma_s(t = 0))/\sigma_s(t = 0)$.

5. Conclusion

We observed a two-stage sorption behavior in a partially cured epoxy system with residual anhydride functional groups. We described this behavior based on a fully coupled diffusion-reaction scheme. The water uptake caused a significant increase in the electrical conductivity, but it is clear that the relation between the water uptake and the change in electrical conductivity is not biunivocal. Our results suggest that the physically sorbed water has a negligible effect on electrical conductivity, but that hydrolysis leads to a very significant increase. This was explained by the formation of hydronium ions when water is exposed to the highly polar groups created by the hydrolysis. This is an important observation as it means that electrical monitoring techniques should be used cautiously when it comes to measuring the moisture content of polymer or polymer-based composite samples.

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