Resistive Response of Carbon-Black-Epoxy Nanocomposites Upon Exposure to Moisture

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ABSTRACT

Water ingress in composite structures is an extremely costly problem, and its detection before related damage begins to appear is of utmost importance. Nanocomposites, based on epoxy matrices and Carbon Black fillers (CB), are promising humidity sensors that can be integrated in composite structures during production. Nevertheless, the effects of water uptake on the electrical properties of CB-epoxy films have scarcely been reported. Therefore, this paper sheds light on the resistive response ($\Delta R/R_0$) of CB-epoxy film sensors (1.5, 2.5, 3.5 and 4.5 wt%CB) hand-coated and screen-printed on glass substrates, and then conditioned in a moist environment (~ 97 %RH). Films (1.5 wt%CB) based on a filler loading close to the Electrical Percolation Threshold (0.5-1.5 wt%CB) have shown an important increase of their resistance, most likely due to a drop of the tunneling currents. By drawing a parallel between previous work of Fauche et al. (2023) and this study, a Parallel Exponential Kinetics (PEK) model is used and describes very well the kinetics of the resistive responses (water uptake and release regimes), except for the two 2.5wt%CB sensors. In moist conditions, an equilibrium $(\Delta R/R_0)_\infty$ of 53.4% for the hand-coated film and 38.4% for the screen-printed film was estimated for the 1.5wt%CB sensors, and thereby revealing a stronger sensitivity to moisture than films produced by Luo et al. (2007) and Llobet et al. (2014) with a maximum $\Delta R/R_0$ of 2.5%. This suggests that CB-epoxy film sensors ($\leq$1.5 wt%CB) have a great potential to detect high relative humidity in composite structures.

INTRODUCTION

Water ingress in composite structures can lead to a reduction of the mechanical properties of fiber-reinforced polymer composites [1], a gain of weight in sandwich composites [2], both finally associated with a loss of their structural coherence [3]. More generally, the ingress of water in the structural components of aerospace, civil, and industrial structures is potentially dangerous and an extremely costly problem (e.g. in-flight failure). Thus, detecting humidity inside these structures before damage begins to appear is of utmost importance and can be tackled by sensors.

A specific class of sensors, chemiresistors, exhibits a change of its electrical resistance upon contact with chemical species (e.g. water) and has been extensively investigated. In previous works [4,5], a chemiresistor highly sensitive to water was produced from a hygroscopic thermoplastic matrix (polyvinyl alcohol) filled with conductive fillers. However, the applicability of such a sensor is limited because it cannot withstand temperatures above 200°C (pyrolysis), hence thermoset epoxy is a promising matrix for producing temperature-resistant sensors that can be embedded in composites. Nevertheless, epoxy is an excellent electrical insulator and requires thus the additional dispersion of conductive fillers such as Carbon Black (CB). In CB-epoxy sensors, a common phenomenon called electrical percolation is observed, which is when the fillers randomly distributed in the epoxy matrix form a conductive path. Around a critical filler loading, called the Electrical Percolation Threshold (EPT), a sharp drop of the resistivity of the epoxy by many orders of magnitude is observed [6].

In a previous study by Fauche et al. (2023) [7], the immersion of CB-epoxy bulk sensors (cylinders) in ultrapure water revealed a non-linear increase of the resistance as the function of the water uptake, most likely due to the rise of the tunneling distances between CB fillers induced by matrix swelling. In contrast, the electrical behavior of CB-epoxy film sensors exposed to moisture has scarcely been reported [8,9]. Thus, the study presented in this paper aims to shed light on this unexplored area, and the resistive response of CB-epoxy films exposed to anhydrous and moist environments is documented. All moisturized films revealed a higher resistance increase than the ones found in the existing literature.

MATERIALS AND METHODS

Raw materials

To produce sensitive nanocomposites, a two-component epoxy system (SiPreg SR8500/KTA313 Sicomin, McTechnics – Belgium) and conductive carbon black fillers (Ketjenblack® EC-300J, Akzo Nobel Chemicals B.V – The Netherlands) were used. The DGEBA epoxy resin and polyamine-based hardener were mixed according to the weight ratio 100:21, respectively. The Carbon Black (CB) involved in this study is a furnace black grade, with an apparent bulk density of 125-145 kg/m^3, a pore volume of 310-345 ml/100g (DBP) and a relatively high surface area of about 800 m^2/g (BET).

Sensor manufacturing

About 4.3 g of epoxy resin was weighed and added to a 10 mL glass vial, and then a given amount of CB fillers was added to reach a specific filler loading (wt%CB) in the cured sensor. The mixture was manually stirred for 2 min using a spatula, and then a sonotrode ultrasonicator (Sonifier® SFX150 Branson) was used to break down CB agglomerates into smaller clusters. By the end of the sonication step, about 0.9 g of hardener was weighed, manually stirred into the dispersion for 2 min and then degassed under vacuum at 30°C for 15 min. Subsequently, the uncured dispersion was coated on UV/ozone-treated glass substrates according to two casting techniques. First, a screen-printing technique involving a polyester screen mesh was used. Second, a manual film applicator was used to produce "hand-coated films". The freshly-casted coatings were cured at 70°C for 1 h and then post-cured at 130°C for 40 min. Note that screen-printed films were slightly thinner (50-60 µm thick) than the manually-casted ones (80-90 µm thick). Finally, silver epoxy glue was applied on the two extremities of the sensors to create the necessary electrical contacts (electrodes). Stripped copper cables were then connected to the silver-coated areas before encapsulating the whole with a thick layer of insulating epoxy to prevent any detrimental interactions of moisture with the electrodes.

Electrical-humidity test

Prior to the measurement of the initial sheet resistance (R_0) in anhydrous conditions, sensors were dried in oven at 60°C for 24 h and then cooled down to room temperature in a desiccator. A two-step procedure was then adopted to measure the relative resistance change $\Delta R/R_0 = [R-R_0]/R_0$ of sensors exposed to moisture at 22 ± 2°C as shown in Figure 1. First, sensors were conditioned in an anhydrous airtight chamber (desiccant inside), and in a next step R_0 was measured with a Keithley 2700 multimeter. Second, using saturated salt solutions (potassium sulfate), the relative humidity (%RH) of the chamber was modified (~97 %RH) and the sheet resistance (R) of moisturized sensors was measured over time. In addition, once saturation was apparently reached, the airtight lid of the chamber was removed to dry the films in open air (40-50 %RH) while the resistance was being logged. Further drying was also performed in a convection oven set at 60°C for about 3 days, and then the resistance was measured again in the same anhydrous airtight chamber. Besides, specimens exhibiting resistances beyond 120 MΩ could not be conditioned in the chamber because of the limit range of the Keithley 2700. Nevertheless, the resistance of such specimens was exclusively measured in anhydrous conditions with another electrometer (Keithley 617).

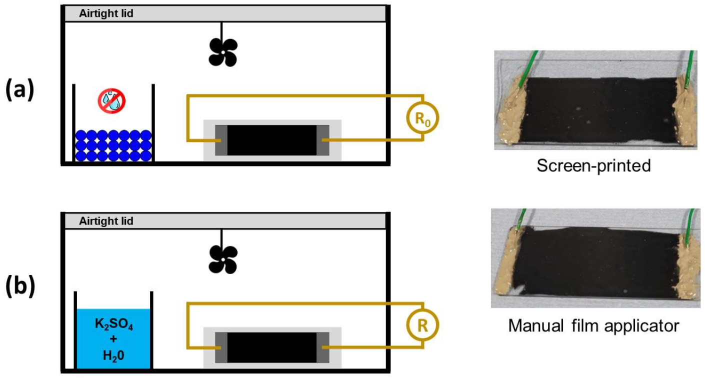

Figure 1. Schematics of the in-house humidity chamber (a,b). Coatings (shown on the right) were characterized in anhydrous (a) and moist (b) conditions.

RESULTS AND DISCUSSION

Electrical Percolation Threshold (EPT)

The EPT of CB-epoxy sensors was investigated as it is well-known that particle-filled polymer materials based on a filler loading around the EPT are very sensitive to external stimuli (e.g. temperature, strain, pressure) [10–12]. In particular, our previous work, Fauche et al. (2023) showed that two CB-epoxy bulk sensors (1.3 and 2.0 wt%CB) based on a filler loading very close to the EPT (1.7 ± 0.1 wt%CB) exhibited a stronger resistance-water uptake response than the specimen beyond the EPT (3.0 wt%CB). Nevertheless, the EPT of coatings is likely to be different than the one associated to bulk sensors because the thinner the sensing material is the higher the probability that the first ohmic path is created and thereby reducing the EPT. Therefore, the sheet resistance of coatings based on different filler loadings (0.5, 1.0, 1.5, 2.5, 3.5 and 4.5 wt%CB) was measured in anhydrous conditions and then compared (Figure 2). Similar to the percolation curve (burgundy curve) drawn from knowledge of the bulk resistivity, we also observed an abrupt drop of the sheet resistance by many orders of magnitude around a filler loading between 0.5 and 1.5 wt%CB. This suggests that the EPT associated to film sensors belongs in this filler loading range, i.e. the EPT has shifted towards smaller filler loadings with respect to the bulk sensors (1.7 ± 0.1 wt%CB).

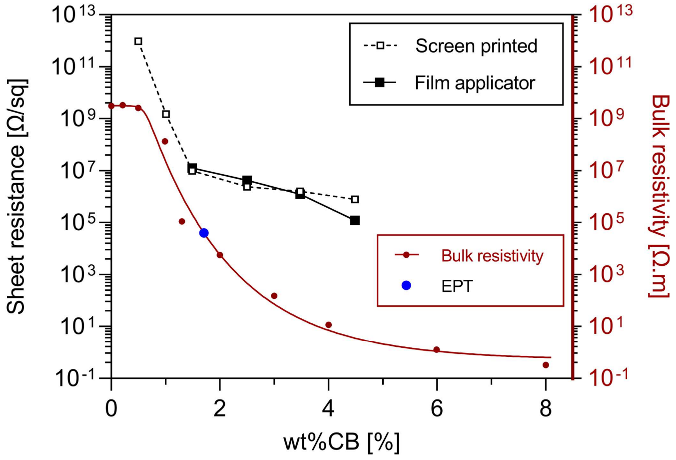

Figure 2. Comparison of the sheet resistance of CB-epoxy coatings versus the bulk resistivity of CB-epoxy cylinders measured during a previous study (Fauche et al. (2023)).

Resistive response

Epoxy materials are well-known to be subject to plasticization and long-term relaxation phenomena, both induced by water uptake. Thus, the water uptake kinetics can be modelled by a double exponential decay model called "Parallel Exponential Kinetics" (PEK) as shown in Eq. (1):

$$M_t = M_\infty \left[\varphi \left(1 - exp\left(-\frac{t}{\tau_1} \right) \right) + (1 - \varphi) \left(1 - exp\left(-\frac{t}{\tau_2} \right) \right) \right] \tag{1}$$

where M_t is the water uptake, M_∞ the equilibrium water uptake, φ the quasi-equilibrium coefficient (≤ 1), t the time of exposure, τ_1 and τ_2 two time constants, characteristic of each process. This two-step kinetic process has been widely reported to describe water sorption kinetics of a wide range of materials such as Nafion films [13], and CNTs-epoxy nanocomposites [14]. Moreover, this model was also successfully used in the work of Fauche et al. (2023) to describe the water diffusion in CB-epoxy bulk sensors immersed in water [7]. Besides, several authors have reported comparable kinetics regarding the resistive response of composites upon water uptake [14,15], which is given by the PEK model shown in Eq. (2):

$$\frac{\Delta R}{R_0} = \left(\frac{\Delta R}{R_0}\right)_\infty \left[\varphi\left(1 - exp\left(-\frac{t}{\tau_1}\right)\right) + (1-\varphi)\left(1 - exp\left(-\frac{t}{\tau_2}\right)\right)\right] \tag{2}$$

where $(\Delta R/R_0)_\infty$ is the equilibrium relative resistance change. Similarly, the resistive response kinetics of CB-epoxy coatings upon drying (release) are given by Eq. (3):

$$\frac{\Delta R}{R_0} = A - \left[A - \left(\frac{\Delta R}{R_0}\right)_{r,\infty}\right] \cdot \left[\varphi'\left(1 - exp\left(-\frac{t}{{\tau_1}'}\right)\right) + (1-\varphi')\left(1 - exp\left(-\frac{t}{{\tau_2}'}\right)\right)\right] \tag{3}$$

where A is the relative resistance change observed by the end of the water uptake regime and $(\Delta R/R_0)_{r,\infty}$ is the equilibrium relative resistance change upon water release.

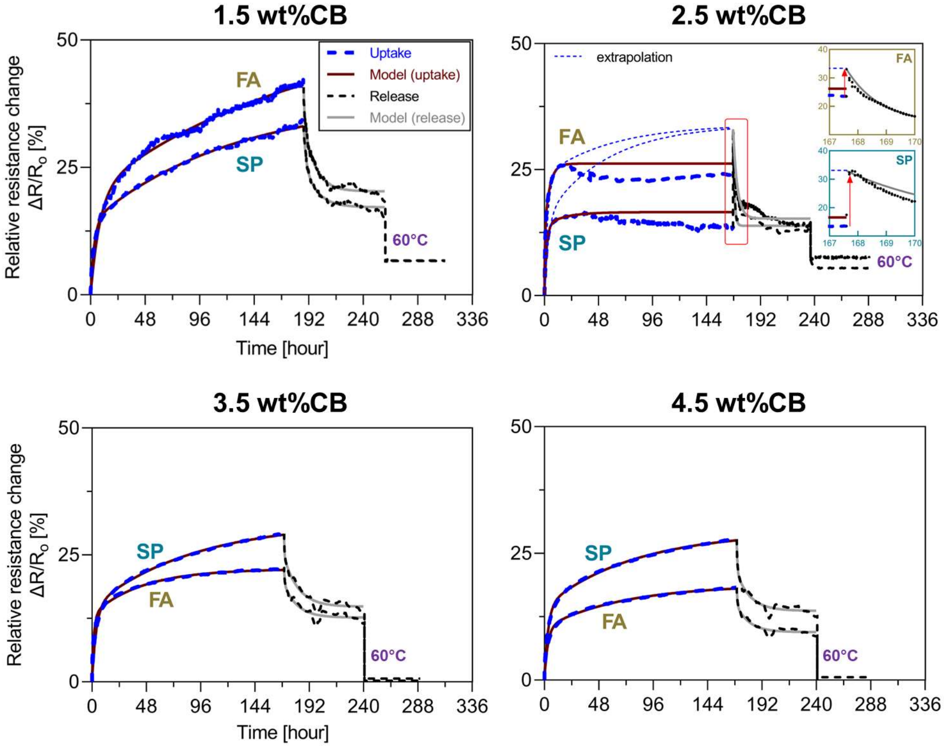

Figure 3. Resistive response of CB-epoxy film sensors exposed to moisture (water uptake), and then dried (water release) according to a two-step procedure: in open air and then in oven at 60°C. The PEK model was used to fit both water uptake and release regimes, except for the two 2.5 wt%CB coatings that exhibited a peculiar behavior (see insets). SP and FA represent the coatings produced by screen-printing and film applicator, respectively.

A good agreement between the experimental data and the models described by Eq. (2) and Eq. (3) was systematically obtained for the resistive response (water uptake and release regimes) as shown in Figure 3 for 1.5, 3.5 and 4.5wt%CB films. However, the two 2.5wt%CB films exhibited a peculiar behavior, i.e. we observed a continuous decrease of the resistance beyond 24 h of exposure despite being in a closed moist chamber. Therefore, a significant deviation from the PEK model was noticed. In addition, this anomaly was also observed during the first drying stage, i.e. a sudden increase of the resistance was detected as soon as the lid of the chamber was removed before decreasing again. Nevertheless, if the first part of the resistive response (<24 h) is extrapolated to the maximum value observed as soon as the lid was removed (~167 h), a credible shape is revealed. In other words, it can be assumed than an unknown issue has happened during the recording of the resistance, which can be potentially due to weak electrical contacts resulting from an excess of the hardener in the cured contacts (yellowish instead of a grey aspect). Besides, the 2.5wt%CB coatings also showed peculiar resistive kinetics upon drying because they do not follow the PEK model but rather a one-order model (single time constant), which is obtained if $\varphi' = 1$ and $\tau_2{}' \to 0$. More generally, the calculated parameters of the kinetics models associated to the water uptake and release regimes are given in TABLE I.

Furthermore, we observed a higher sensitivity of all CB-epoxy films to moisture than the ones described in two other studies since we found that the $(\Delta R/R_0)_\infty$ is from 6 up to 36 times higher than the ones reported by Luo et al. [8] and Llobet et al. [9] (~ 1.5 and ~ 2.5%, respectively). This can be explained by a longer exposure time to moisture, a higher %RH and a better procedure to disperse CB fillers in epoxy.

Moreover, the $(\Delta R/R_0)_\infty$ was observed to be maximal for the 1.5wt%CB coatings whereas it was minimal for the 4.5wt%CB films. More generally, $(\Delta R/R_0)_\infty$ dropped with a rise of the filler loading. In our previous work, bulk sensors were found to exhibit a higher sensitivity to water uptake for a filler loading (1.3-2.0 wt%CB) near the EPT (1.7 ± 0.1 wt%CB) than their percolated counterpart (3.0 wt%CB). And, since the conduction mechanism in such a sensor is mostly dominated by tunneling around the EPT, it was assumed that the water uptake mostly affects the tunneling distances between CB fillers. These observations turn out to be also consistent with the electrical behavior of moisturized film sensors (1.5 wt%CB) near the EPT (0.5-1.5 wt%CB).

Additionally, thicker coatings tend to induce a slightly better sensitivity to moisture because for the two 1.5wt%CB film sensors, the resistive response of the hand-coated film was observed to be above the one produced by screen-printing. Nevertheless, differences of shapes between these two films may also explain dissimilarities in terms of their resistive response. The production of screen-printed films allows to print shapes that are relatively symmetrical (e.g. rectangular) unlike with film applicators which lead to non-symmetrical films (see Figure 1). Such influence is however beyond the scope of this paper.

Finally, unlike the 3.5 and 4.5 wt%CB sensors, the drying of the most promising sensors (1.5 wt%CB) in oven at 60°C revealed a certain hysteresis of the response because the final resistance was not identical to R_0. This is conceivable because residual water may still exist in the matrix due to strong interactions with the matrix (hydrogen bonding), as well as swelling can lead to irreversible changes of the cross-linked network. Higher temperatures, in particular above the glass transition temperature (100-120°C) of the matrix should remove this residual water [16]. Nevertheless, recovery of the sensing material upon drying is not a requirement for the target applications.

TABLE I. PARAMETERS OF THE PEK MODEL FITTED TO THE RESISTIVE RESPONSE OF SENSORS MOISTURIZED (WATER UPTAKE), AND DRIED IN OPEN AIR (WATER RELEASE).

WATER UPTAKE REGIME		**1.5 wt%CB**	**2.5 wt%CB**	**3.5 wt%CB**	**4.5 wt%CB**
Screen -printed	$(\Delta R/R_0)_\infty$ [%]	38.4	16.6	31.5	29.3
	φ [-] x 10^{-1}	3.69	8.34	4.68	4.93
	τ_1 [hour]	3.18	1.91	3.73	3.25
	τ_2 [hour] x 10^2	1.24	0.18	0.90	0.79
Film applicator	$(\Delta R/R_0)_\infty$ [%]	53.4	26.2	22.2	18.8
	φ [-] x 10^{-1}	3.75	4.55	5.93	5.49
	τ_1 [hour]	8.14	0.47	1.68	3.02
	τ_2 [hour] x 10^2	1.85	0.04	0.44	0.69
WATER RELEASE REGIME		**1.5 wt%CB**	**2.5 wt%CB**	**3.5 wt%CB**	**4.5 wt%CB**
Screen -printed	A [%]	33.2	33.0	29.2	27.8
	$(\Delta R/R_0)_{r,\infty}$ [%]	17.2	14.4	14.8	13.7
	φ' [-] x 10^{-1}	4.58	1*	3.18	4.66
	$\tau_{1'}$ [hour]	1.95	5.05	0.35	0.59
	$\tau_{2'}$ [hour]	11.5	0*	12.6	12.1
Film applicator	A [%]	40.7	33.0	22.1	18.3
	$(\Delta R/R_0)_{r,\infty}$ [%]	20.3	13.9	12.7	9.5
	φ' [-] x 10^{-1}	3.25	1*	3.06	4.07
	$\tau_{1'}$ [hour]	0.85	1.17	0.66	0.61
	$\tau_{2'}$ [hour]	9.98	0*	11.9	11.3

* Arbitrary values set to fit a one-order kinetic model

CONCLUSIONS

CB-epoxy film sensors (0.5, 1.0, 1.5, 2.5, 3.5 and 4.5 wt%CB) were manufactured, casted on glass substrates by two techniques (screen-printing and film applicator), and then characterized in anhydrous conditions to identify the Electrical Percolation Threshold (EPT). An abrupt drop of the sheet resistance by multiple orders of magnitude was observed for a filler loading range from 0.5 to 1.5 wt%CB, which is related to the EPT. In other words, the EPT associated to film sensors has shifted towards smaller filler loadings with respect to their bulk counterparts (EPT = 1.7 ± 0.1 wt%CB).

Moreover, we observed a higher sensitivity to humidity (~ 97 %RH) for the two 1.5wt%CB films sensors than the other films (2.5-4.5 wt%CB) because of their closest vicinity to the EPT. This is consistent with the previous work of Fauche et al. (2023), in which bulk sensors (1.3 and 2.0 wt%CB) near the EPT exhibited a higher resistance increase upon water uptake than in the percolated sensor (3.0 wt%CB).

Furthermore, by drawing a parallel between previous work of Fauche et al. and this study, a Parallel Exponential Kinetics (PEK) model was used and described very well the kinetics of the resistive response during both water uptake and release regimes, except for the 2.5wt%CB films which showed a peculiar behavior. In moist conditions, an equilibrium $(\Delta R/R_0)_\infty$ of 53.4 % for the hand-coated film and 38.4% for the screen-printed film was estimated for the 1.5wt%CB sensors, and thereby revealing a stronger sensitivity to moisture than films produced by Luo et al. (2007) and Llobet et al. (2014) with a maximum $\Delta R/R_0$ of 2.5%. As a result, CB-epoxy film sensors (≤1.5 wt%CB) have a great potential to detect high relative humidity in composites although the resistive response needs to be further tuned with e.g. CB fillers of higher hydrophilicity.

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