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# Water transport in epoxy/MWCNT composites

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ABSTRACT

Moisture and water uptake of epoxy/multi-wall carbon nanotube (MWCNT) composites was studied in a wide range of atmosphere relative humidity and temperatures. Addition of up to 1 wt.% of MWCNTs into the neat epoxy resulted to the twofold decrease of the diffusivity, while the levels of moisture/water uptake remained unchanged. The positive effect on the reduction of the diffusion coefficient diminishes with the increase of temperature. Differences in the water transport properties and plasticization ability of the neat polymer and its nanocomposites are explained by the free volume considerations and the polymer–water interactions, which are verified by the results of thermomechanical analysis. Water uptake by the nanocomposites resulted to a lower decrease of the storage modulus than that of the neat epoxy.



## 1. Introduction

Epoxy resins are widely used as matrices for structural composite materials and adhesives in aerospace, automobile and civil industries due to their good thermal and mechanical properties and chemical resistance combined with satisfactory processing characteristics. In most applications, such materials have the potential of being exposed to a humid environment and elevated temperature immersion and susceptible to water uptake. High tendency of epoxy matrices to moisture absorption from the environment is one of the reliability concerns for composites. The absorbed moisture has deleterious effect on the physical and mechanical properties of epoxies and can, therefore, greatly compromise the performance of the epoxy-based component. By acting as an efficient plasticizer and increasing the polymer chain mobility, absorbed moisture diminishes the glass transition temperature ($T_g$), reduces the modulus and mechanical strength as well as induces swelling of the polymer [1–11]. The transport of water in epoxy systems and long-term performance of epoxy-based composites under environmental conditions are of great practical importance and are still under investigation.

Incorporation of nano-structured carbon fillers, in particular multi-wall carbon nanotubes (MWCNTs), into epoxy matrices may improve their effective properties and introduce "sensing functionality" by increasing the electrical conductive properties of the material. The combination of a nanotube-modified matrix together with conventional fibre-reinforcements provides a new generation of multifunctional materials with health monitoring capabilities [12–14]. The wider application of nanocomposites requires greater understanding of material performance and the ability to resist environmental effects during long-term use. The development of a comprehensive understanding of the mechanisms of ageing and environmental exposure related deterioration for purposes of prediction of service life and durability is of great importance to the further use of such systems.

The nano-sized inclusions may influence the properties of environmentally-conditioned nanocomposites in two

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ways: they reduce the rate and/or the level of water uptake due to the barrier properties of the filler and improve the overall mechanical properties of the plasticized nanocomposites [15–19]. The bonding and dispersion state of the absorbed water has a strong influence on the diffusion behaviour and plasticization ability of the material. Knowledge of the bonding character of water molecules in polymers is the most important and fundamental to understand hygrothermal effects. Although numerous studies have been devoted to the investigation of water uptake and hygro- and hydrothermal effects of different epoxy resins [2–11], water diffusion modes and related mechanisms in this kind of materials are still not fully understood. Only few reports on this topic are available in the literature for epoxies reinforced with nano-structured carbon fillers [15–17].

In the present study, we investigated the moisture uptake and swelling of MWCNT-based epoxy composites in a wide range of atmosphere humidity and water uptake under various temperatures. The aim of the study was to determine the rate and the level of moisture/water uptake of the materials and to estimate the influence of MWCNTs on plasticization ability of the neat epoxy. In addition, dynamic thermal mechanical analysis (DMTA) of "as-produced" and "aged" samples was done to give an insight into structural changes of the neat epoxy and its nanocomposites caused by their hygro- and hydrothermal ageing. The effects of moisture/water uptake and hygro-/hydrothermal ageing on the mechanical properties and sensing functionality of the nanocomposites will be highlighted in the next study.

## 2. Experimental procedure

A commercially available DGEBA-based L135i/H137i epoxy system (Momentive Specialty Chemicals, Stuttgart, Germany) was used as a matrix polymer. This system is characterised by $T_g$ of about 100 °C and a very low viscosity. It is a common resin for infusion processes, e.g. resin transfer moulding (RTM). The choice of the epoxy system for this study was influenced by its wide use in conventional fibre-reinforced composites, such as wind power plants, and thus the potential for employing the nano-modified electrically conductive matrix with multifunctional properties for structural health monitoring applications.

As-produced multiwall carbon nanotubes (MWCNTs) (Baytubes C150P, Bayer, Germany) were used as fillers. The nanocomposites filled with different contents of the fillers – 0.3, 0.5, and 1 wt.% – were produced via a common shear-mixing technique [14]. Required amounts of the nanotubes were manually mixed into the resin (L135i) and subsequently dispersed using a lab-scale three-roll-mill (Exakt 120E; Exakt GmbH, Norderstedt, Germany). After dispersing the fillers in the epoxy resin, the amine hardener (H137i) was added in the ratio 100:30. The obtained suspension was mixed for 10 min by stirring at 200–600 rpm under vacuum, cured for 24 h at room temperature (22 °C) and post-cured at $T$ = 80 °C for 15 h as recommended by the supplier. A detailed description on the processing of the nanocomposites is given in [20]. Both, the neat epoxy and the nanocomposites are studied in the glassy state.

Bar-shape samples of average dimensions 2.2 × 10 × 110 mm were cut from the plates and polished with sandpaper. One group of samples was maintained in the reference dry condition and called as "as-produced" samples. The remainder were placed in groups of 5 into each of several hygro- and hydrothermal conditioning environments ("aged" samples). Humid conditions with different values of atmosphere relative humidity RH = 47%, 77%, and 98% were created by using saturated salt solutions of KCNS, NaCl, and $K_2SO_4$ at $T$ = 20 °C, respectively (denoted as RH47%, RH77% and RH98%, respectively). Water uptake was studied on samples immersed in distilled water at $T$ = 20, 50, and 70 °C (denoted as W20, W50, and W70, respectively). Samples from each environment were removed periodically, weighed, and dimensionally measured. After samples reached moisture/water equilibrium, DMTA tests were conducted.

The moisture/water uptake was detected gravimetrically with an accuracy of 0.01 mg. The relative moisture/water content $w$ [%] was determined as weight gain per unit weight:

$$w = \frac{m_t - m_0}{m_0} \times 100$$

where $m_t$ is the weight of the wet sample at time $t$, and $m_0$ is the weight of the reference sample.

Actual dimensions of each sample conditioned at $T$ = 20 °C and 50 °C were measured with an accuracy of 0.001 mm. Swelling strain $\varepsilon_{sw}$ [%] was calculated as relative change of length of the sample:

$$\varepsilon_{sw} = \frac{l_t - l_0}{l_0} \times 100$$

where $l_t$ is the length of the wet sample at time $t$, and $l_0$ is the length of the reference unexposed sample. At least five replicate samples of each composition were used for each measurement in moisture and water uptake tests and swelling and the average data are shown in the graphs below.

Dynamic thermal mechanical analysis (DMTA) was carried out in order to evaluate contributions of moisture/water ingress induced phenomena in the neat epoxy and its nanocomposites. The DMTA experiments were performed on Eplexor 500 N device of Gabo Qualimeter with bar samples 2.2 × 5 × 40 mm. The measurements were carried out in tensile mode (1 N) at a frequency of 10 Hz from 20 °C to 160 °C at a heating rate of 3 K per min. Hydrothermal ageing effects were studied on samples of the neat epoxy and nanocomposite filled with 0.5 wt.% of MWCNTs immersed into water under $T$ = 50 and 70 °C. In the rest cases, the neat epoxy and nanocomposites filled with 0.3, 0.5, and 1 wt.% of MWCNTs were tested. The DMTA measurements were done for two duplicate "as-produced" and "aged" samples.

## 3. Background

As a basis for understanding and interpretation of the experimental results, some terms used within the study

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