



Water uptake of epoxy composites reinforced with carbon nanofillers

S.G. Prolongo^{a,*}, M.R. Gude^b, A. Ureña^a

^a Dpt. of Materials Science and Engineering, University Rey Juan Carlos, ESCET, C/Tulipán s/n, Móstoles 28933, Madrid, Spain

^b Foundation for Research, Development and Application of Composite Materials (FIDAMC), Avda. Rita Levi Montalcini 29, Getafe 28906, Madrid, Spain

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ABSTRACT

The water absorption behaviour of neat epoxy resin and reinforced with different contents of carbon nanotubes (CNTs) and nanofibres (CNFs) is reported. The water absorption was monitored gravimetrically and its effect on the thermal and mechanical properties was studied. The maximum water content absorbed significantly decreases with the addition of nanofillers, especially in epoxy/CNT composites. This decrease is higher than the behaviour predicted from ideal mixing law. The evolution of glass transition temperature during ageing confirms that water uptake causes several phenomena, such as plasticization and postcuring matrix processes. The effect of water absorption on mechanical properties changes during hygrothermal ageing. At the beginning, the mechanical strength decreases but then it is recovered. This is justified by the presence of different mechanisms of water absorption and interaction with the epoxy matrix.

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1. Introduction

Carbon nanotubes (CNTs) and nanofibres (CNFs) have attracted much attention from researchers worldwide because of their unique combination of excellent properties. Their addition to polymeric matrix is being widely investigated due to the important enhancements caused on physical, mechanical and electrical properties. These materials could be applied to the whole gamut of technologies ranging from microelectronics to aerospace [1–3].

The matrix system investigated in this work is an epoxy resin commonly used for fibre reinforced composites for aircraft applications. One of the main drawbacks of neat epoxy resins is the high tendency to water uptake in humid environments [3]. Numerous researches have been carried out in order to explain this phenomenon [4–9]. However, there is no universal model to support all sorption phenomena and water diffusion modes due to the complexity of molecular interactions between matrix and water. Some authors proposed the existence of two types of absorbed water molecules: free and bound water [5,6]. Water molecules first occupy free volume of the matrix and some of them become bonded to specific chain segment of polar groups of epoxy resins through hydrogen or covalent bonds. However, Apicella and Nicolais [7] proposed three different modes for the water absorption of epoxy systems: bulk dissolution of water in the epoxy network, moisture sorption onto surface of holes that define the excess free volume and water uptake through bonding with hydrophilic groups of resin. The best approaches to study the water absorption of epoxy

resins are those based on Fick's law [8–10] and Langmuir two-phase model [9].

In spite of the wide bibliography published on characterisation of epoxy nanocomposites with carbon nanofillers, no work has been found about the hygrothermal ageing of these materials. This is probably due to the complexity of phenomena and heterogeneous morphology of nanocomposites. However, it is well known that the water absorption would cause numerous unwanted effects, such as swelling, plasticization and in certain cases degradation [3–5,12–14]. These may significant affect to the main properties of these composites. The main applications of these materials, such as matrix of composites and adhesives in aerospace, automobile and civil industries, are associated to their enhanced mechanical properties and high electrical conductivity regard to neat epoxy resin. Both could be significantly affected by water absorption in humid environments.

This study explores the water uptake of epoxy composites reinforced with carbon nanofillers, analysing the effect of water ingress on the behaviour of these materials. Two different nanoreinforcements, CNT and CNF, have been used in order to determine the influence of nanofillers nature and their morphology. The effect of nanofiller content and their dispersion degree have been also analysed.

2. Experimental

2.1. Materials

The nanocomposites were manufactured from diglycidyl ether of bisphenol A (DGEBA, 178 g/epoxy equivalent) and

* Corresponding author. Tel.: +34 914888292; fax: +34 914888150.

E-mail address: silvia.gonzalez@urjc.es (S.G. Prolongo).

4,4'-methylenedianiline (DDM, 49.6 g/amine hydrogen). Both were purchased from Sigma–Aldrich. CNTs and CNFs were used as nanoreinforcements. The used multi-walled carbon nanotubes were produced through Catalytic Carbon Vapour Deposition (>99% C) and functionalized with amino-groups (<0.5% w/w) by Nanocyl (NC3152). The average length of CNTs is less than 1 μm and they have an average diameter of 10 nm. CNFs, provided by Antolin (GANF1), were also employed, whose diameters vary between 20 and 100 nm, and its average length is close to 35 μm .

2.2. Fabrication of nanocomposites and hygrothermal ageing

The procedure applied for manufacturing of nanocomposites was published in previous works [15,16]. A weighed amount of nanofiller, CNTs or CNFs, was first dispersed in chloroform. Epoxy monomer was added to the solution, whose suspension was mixed by high shear mixing (150 rpm) for 30 min at 45 °C and then sonicated for 45 min using a 50–60 Hz sonicator. Next, the solvent was removed by continuous stirring at 90 °C during 24 h. Finally, a stoichiometric amount of DDM was added into the mixture and next the curing reaction occurred. The applied curing treatment consisted on a heating at 150 °C during 3 h and then a postcuring process of 180 °C for 1 h. In order to enhance the chemical reaction between the amino groups of carbon nanotubes and oxirane rings of epoxy monomer, a thermal pre-curing treatment [17] (130 °C, 1 h) was applied to the DGEBA/CNT mixtures after the solvent evaporation and before the DDM addition. This treatment ensures the chemical reaction between epoxy matrix and amine-functionalized CNTs before the addition of hardener. Different contents of nanoreinforcements, CNTs and CNFs, were studied ranging from 0.10 wt% to 1.0 wt% regard to epoxy mass. Taking into account the previous rheological studies and measurements of nanofiller dispersion degree, different loads of CNTs (0.10 and 0.25 wt%) and CNFs (0.25 and 1.0 wt%) were added into epoxy matrix [16].

Prior to ageing, the weight of each sample was determined. Samples with different geometry were aged in an environmental chamber (Dycometal CCK 125) at 55 °C and 95% of relative humidity, following the standard UNE-EN-ISO 4611. During the period of ageing study, gravimetric measurements were performed on balance (Mettler Toledo AX205) with a measurement precision of 10^{-5} g. At selected times, different samples were removed from the chamber, dried superficially and cooling to ambient temperature prior to their characterisation.

2.3. Characterisation

Differential scanning calorimetry (DSC) measurements were carried out in a Mettler Toledo mod. 821 apparatus, calibrated with indium and zinc. Two scans were carried out at a heating rate of 10 °C/min from 20 to 300 °C. Glass transition temperature (T_g) was taken at the middle point of the heat capacity change. Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever bending mode using a DMTA Q800 V7.1 from TA Instruments. All the experiments were done at 1 Hz frequency, by bending deformation, scanning from 20 to 250 °C using a heating rate of 2 °C/min. The maximum of $\tan \delta$ vs. temperature plots was used to identify the α -relaxation associated to the glass transition. Two scans have been performed for each sample, whose dimensions were $35 \times 12 \times 1.5 \text{ mm}^3$. The mechanical characterisation of composites was carried out by tensile test (MTS Alliance RF/100), following the ASTM D638 standard (Type IV probes) at 5 mm/min. Six probes were tested by test. The fracture surfaces were covered with Au (Pd) and observed by Scanning Electron Microscopy (SEM, Hitachi S-3400N) and Field Emission Gun Scanning (FEG–SEM) Electron Microscopy (Nova NanoSEM FEI 230) in order to analyse the fracture mechanisms involved.

3. Results

The results of the gravimetric studies for water uptake are presented in Fig. 1. The added contents of nanofillers were different as a function of its nature: CNTs (0.1 and 0.25 wt%) and CNFs (0.25 and 1.0 wt%). In previous works [15–17], we determined the maximum content of CNTs and CNFs, which could be added to epoxy resin and obtaining good dispersion. These loads were 1.0% for CNFs and 0.25% for CNTs. Composites reinforced with these percentages or higher ones presented large agglomerations (>1 μm) while resins with lower contents showed a good distribution of nanofillers into epoxy matrix. The behaviour of sorption curves has been already observed by other authors for neat epoxy resin [4–7] and composites of epoxy matrix reinforced with long carbon fibres [12,18]. The first stage conforms to Fickian diffusion, as it is confirmed by the linear relation between the absorbed water percentages versus ageing time while the water absorption becomes controlled by relaxation at long ageing times. The diffusion coefficients (D) were calculated using Fick's law and applying some simplifications [10,11] for low ageing time when the water percentage absorbed does not reach 60%. Table 1 collects the obtained values together with the maximum water content absorbed at equilibrium. The addition of nanofillers induces a significant decrease of diffusion coefficient (20–30%). This decrease is higher than the expected one. The decrease of water uptake rate is higher for composites reinforced with CNT. This could be associated with the barrier properties of nanofillers on epoxy matrix [19], which form tortuous paths, hindering the water progress and decreasing the

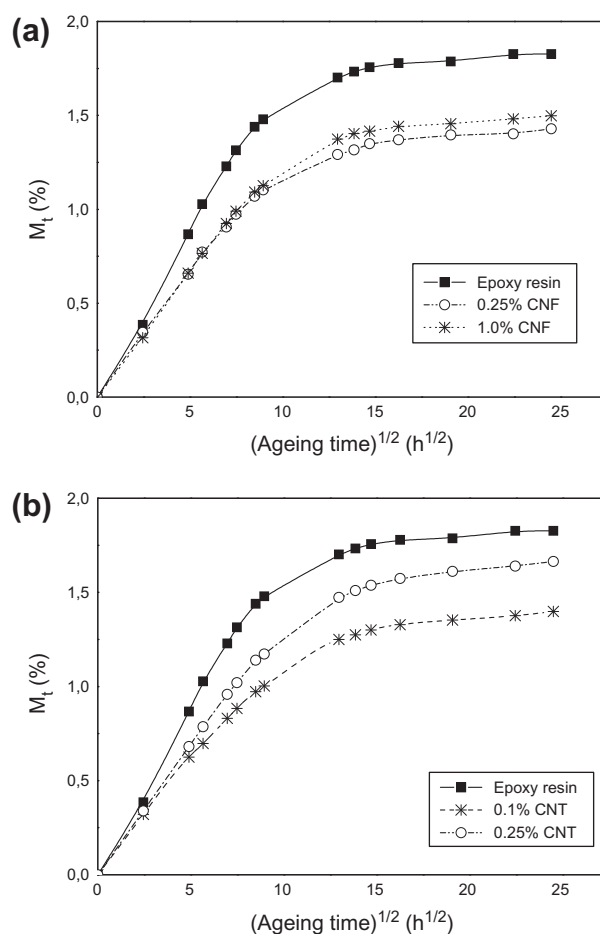


Fig. 1. Water uptake of epoxy resin and nanocomposites reinforced with CNFs (a) and CNTs (b).

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