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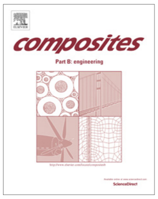

Nano-enhanced composite materials under thermal shock and environmental degradation: A durability study

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ABSTRACT

Carbon nanotubes (CNTs) were incorporated at 0.5 wt% in epoxy resin using sonication at two different levels of amplitude (50% and 100% of 400 W nominal sonication power). The CNTs modified epoxy systems were used to manufacture carbon fibre reinforced laminates (CFRPs). All specimens were subjected to thermal shock and hygrothermal exposure. The presence of CNTs did not alter the water absorption profiles for the epoxy resin, but it resulted in a spectacular 40% reduction in the water uptake at equilibrium for the CFRPs. The interlaminar shear strength of the CFRPs was not significantly affected by the thermal shock cycles; however it was reduced by 50–60% after hygrothermal exposure. The addition of CNTs led to slightly lower interlaminar shear strength values in the as-manufactured state. However their presence did not accelerate the deterioration of the strength after the environmental exposure. Although the addition of CNTs did not significantly influence the thermomechanical properties of the resin, they were beneficial in the case of the CFRPs since (i) they enhanced the storage modulus and glass transition temperature and (ii) limited the deterioration of these properties after thermal shock and hygrothermal exposure. The amplitude level during sonication which determined the dispersion state and length of the CNTs had a clear effect on the durability of the studied systems.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention as nanoscale reinforcement in epoxy resins. This is attributed to their remarkable electronic, thermal, optical, mechanical, spectroscopic and chemical properties, which relate to the tubular geometry created by the rolling of the grapheme sheet [1]. The incorporation of CNTs in epoxy matrices would be expected provide significant reinforcement as (i) the large interfacial area of the nanoscaled reinforcement is directly proportional to load transfer ability and (ii) nanotubes exhibit significantly enhanced strength compared to their micro scaled counterparts, e.g. carbon fibres. However, the level of enhancement is generally dependent on the degree of dispersion, impregnation, and interfacial adhesion of the CNTs in the polymer matrix [2–4]. Recent studies focus on the introduction of CNTs into micro-scale fibre reinforced composites to create hybrid multiscale composites. This concept provides the potential to combine benefits of the nanoscale reinforcement, such as sensing abilities and toughness, with the functionality of well-established fibre composites [5–13].

One of the limiting factors for the widespread use of epoxy based composites is related to the environmental durability of these materials. The inherent hydrophilicity of epoxy resins limits their usage in humid environments. Their degradation behaviour is highly dependent on temperature, moisture absorption levels, moisture reactions as well as the cure chemistry and kinetics of the resin system [14–16]. Moisture absorption in epoxy based composites may lead to weakening of the fibre–matrix interface [17,18], plasticization, swelling, and in some cases softening of the matrix [19]. At the same time, CNTs are well known to exhibit extremely hydrophobic behaviour. As a result, the addition of CNTs in epoxies may affect water absorption kinetics in adverse ways. On one hand, the presence of additional interfaces may favour the moisture penetration because of capillary effects. On the other hand, the introduction of the CNTs may both lead to the creation of a tortuous path and the occupation of the free volume in the epoxy network, resulting thus in the hindrance of the moisture uptake.

Although the environmental response of epoxy resins and their fibre reinforced composites has received a lot of focus, there is limited information on the environmental degradation of CNTs-reinforced composites. Some studies focus on the effect of moisture on the interlaminar interface by contact electrical resistivity measurements [20,21]. The multifunctionality of CNTs-reinforced

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composites has been assessed in terms of the interdependency of fatigue and electrical properties [22]. In the case of more complex systems, the induced changes in the electrochemical behaviour due to the interacting conductive phases have been reported [23,24]. Analytical approach on the pull-out force and the interfacial stress transfer have been proposed [25,26]. However, few reports discuss on how CNTs alter the water absorption kinetics and their influence on the durability of nanocomposites [27–32] and hybrid multiscale composites [5,32,33]. Published results are somewhat controversial; different studies on the addition of CNTs report: (a) improved resistance in water absorption [27,28,31,32], (b) limited changes only in water transport but not in equilibrium properties [30] and (c) increase in the moisture content and diffusion coefficient in the case of hybrid systems [5,33]. It is therefore obvious that the environmental effects on CNTs modified epoxies and hybrid carbon fibre reinforced plastics (CFRPs) is still an open issue, which is critical for their reliability when employed for structural components in hostile environments.

In a recent study, the significant effect of sonication duration and amplitude on the macroscopic mechanical and toughness response of CNTs modified epoxies and CFRPs was demonstrated [3]. Best results were obtained for intermediate levels of sonication duration and amplitude, which allow for appropriate dispersion without damaging the CNTs structure. As has been demonstrated, there is an optimal level for the competitive mechanisms of de-agglomeration and dispersion [34]. The objective of the current study is twofold, i.e. (a) to evaluate the performance of CNTs-modified epoxy resins and their hybrid composites after hygrothermal exposure and thermal shock conditions and (b) to compare two sonication conditions (intermediate and rigorous) in terms of their effect on the durability of the aforementioned systems. For this purpose, CNT modified epoxy resins and their CFRP counterparts were manufactured using the sonication method at two different sonication amplitudes (50% and 100% of 400 W nominal sonication power) and durations (2 and 4 h, respectively) [3]. For comparison purposes, unmodified resins and CFRPs were also prepared. All specimens were subjected to hygrothermal loadings and thermal shock cycles. The moisture uptake results were approximated by the second Fick's law. The effect of moisture uptake and thermal shock on the thermomechanical response of the unmodified and CNT modified epoxy resins and CFRPs was assessed using the Dynamic Mechanical Analysis method (DMA). The interlaminar shear strength (ILSS) of the CFRPs was also defined before and after hygrothermal exposure and thermal shock.

2. Experimental

2.1. Materials

The Graphistrength Multi Wall CNTs supplied by ARKEMA, France were used in this study. The tube diameter ranged from 10 to 15 nm and the tube length ranged from 500 nm to 1 μm. The production method of the nanoparticles was Catalyzed Chemical Vapor Deposition (CVD). A two part low viscosity epoxy resin, i.e. Araldite LY 564 and Aradur 2954, supplied by Huntsman Advanced Materials, Switzerland at a mix ratio of 100:35 by weight was used as matrix. For the 16 plies quasi isotropic laminates CFRPs, the G0947 1040 unidirectional carbon fabric by Hexcel (France) was employed as reinforcement.

2.2. Specimen preparation

The UP400S ultrasonic mixer (Hielscher) was used to disperse the CNTs into the epoxy resin. The CNTs and the resin were weighed according to the w/w provided by the manufacturer and mixed together in a beaker. A high intensity ultrasonic probe was employed for the mixing process. The temperature of the mixture was kept low by submerging the container in an ice bath [35]. In order to thoroughly investigate the effect of sonication conditions, two sonication protocols were followed. In the specimen series (designated as A) the sonication was performed at amplitude of 50%, for 2 h. In the second series (designated as B) the amplitude was set at 100% and the sonication process lasted for 4 h. The amplitude percentage corresponds to a maximum sonotrode power of 400 W at 24 kHz frequency. Once the sonication was complete, the hardener was added to the modified resin and mixed using a mechanical agitator for about 10 min. The mixture was degassed in vacuum for 10 min in order to remove entrapped air due to mixing [36]. The mixture was transferred to open silicon rubber molds and cured for 2 h at 60 °C, as recommended by the manufacturer. CNT modified epoxy as well as unmodified epoxy resin was employed as matrix for the manufacturing of 16 plies quasi isotropic laminates CFRPs, $[0/45/\text{-}45/90]_{s2}$. The CFRPs were manufactured with the hand layup method and pressed in a heated hydraulic press under the pressure of 100 bars at 60 °C for 2 h. All specimens were post-cured at 120 °C for 4 h. Hereafter, CNT modified epoxies and CFRPs will be denoted as doped materials, while the unmodified specimens as neat materials.

The test specimens were cut in appropriate dimensions for the DMA, ILSS and the water absorption tests as shown in Table 1. After cutting, the specimens were polished and sanded to remove defects induced by the cutting process.

2.3. Testing and evaluation procedure

A water bath with temperature control was used for the hygrothermal exposure of the test specimens. Before placing the specimens into the water bath, they were dried in an oven at 50 °C up to a stable weight. The water absorption of the specimens was performed by immersing the specimens into hot distilled water (80 °C). At specific time intervals the specimens were removed from the water and placed in an oven for 5 min at 30 °C. The specimens were then wiped with an absorbent paper and their mass was recorded using an electronic balance with an accuracy of ±0.1 mg. The total exposure duration was 696 h for the neat and doped epoxies and 716 h for the neat and doped CFRPs. The relative weight gain of the specimens W/W_0 (%) was determined according to Eq. (1):

$$\frac{W}{W_0} = \frac{m_i - m_0}{m_0} * 100\% \tag{1}$$

where

m_i: is the weight of the specimen at specific time intervals
m_0: is the initial weight of the dry sample

Five specimens for each material configuration were exposed and the average value of water uptake was calculated and plotted as a function of the square root of time. The experimental results were fitted using the Fick's second law [37] shown in Eq. (2):

Table 1
Dimensions of the tested specimens.

Method	Length (mm)	Width (mm)	Thickness (mm)
DMA/water absorption	60	10	4–5
Short beam test for apparent interlaminar shear strength determination – ILSS	24	12	2.4