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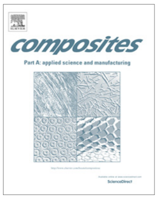

Reinforcing brittle and ductile epoxy matrices using carbon nanotubes masterbatch

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ABSTRACT

In this study, the mechanical and thermal properties of epoxy composites using two different forms of carbon nanotubes (powder and masterbatch) were investigated. Composites were prepared by loading the surface-modified CNT powder and/or CNT masterbatch into either ductile or brittle epoxy matrices. The results show that 3 wt.% CNT masterbatch enhances Young's modulus by 20%, tensile strength by 30%, flexural strength by 15%, and 21.1 °C increment in the glass transition temperature (by 34%) of ductile epoxy matrix. From scanning electron microscopy images, it was observed that the CNT masterbatch was uniformly distributed indicating the pre-dispersed CNTs in the masterbatch allow an easier path for preparation of CNT-epoxy composites with reduced agglomeration of CNTs. These results demonstrate a good CNT dispersion and ductility of epoxy matrix play a key role to achieve high performance CNT-epoxy composites.

1. Introduction

Fibre Reinforced Polymer (FRP) composites have been widely used for strengthening and rehabilitation of different elements in civil infrastructures such as steel [1], concrete [2] and masonry structures [3]. FRP composites are externally bonded to a host structure using an adhesive through which the loads are transferred from the host structure to the FRP. Thermosetting polymers such as epoxy composites are extensively used as such bonding adhesives. The popularity of epoxy composites is due to their extraordinary properties of adhesion to wide variety of adherend materials, low shrinkage ratio and resistance to abrasion. However, its relatively low tensile strength and Young's modulus, when compared with steel materials, are responsible for most failure modes occurring in FRP-steel strengthening systems [4]. Different nanofillers such as nanoclay [5], nanosilica [6], graphene sheets [7] and carbon nanotubes (CNTs) [8] have been used to enhance the mechanical properties of epoxy composites. CNTs superior mechanical properties such as high strength, high aspect ratio and elongation at failure make them ideal reinforcing fillers for epoxy matrices.

It is clear from the literature that homogeneous incorporation of CNTs into polymers can enhance the mechanical, thermal and electrical properties of the composites [9]. CNT properties such as the CNT type (single-walled CNTs (SWCNTs), double-walled CNTs or multi-walled CNTs (MWCNTs)) [10], CNT geometry (i.e. length, diameter) [11–14], CNT surface modification (covalent surface modification [15,16], non-covalent surface modification [17,18]) are parameters that can be manipulated to achieve great enhancement in composite properties. In addition, properties of CNT reinforced epoxy composites have been investigated including tensile [10,11,15], flexural [19–21], compressive [22–24], shear [25], thermo-mechanical [26–28], impact [29–31], hardness [32,33], viscosity [8,32], creep [34,35], fatigue [12,36], and high strain effect [37].

Well dispersed pristine CNTs in epoxy generally increase the Young's modulus and the fracture strength of epoxy composites, but reduce the fracture strain, the latter becoming more pronounced when the CNT percentage increases [11]. Kathi et al. [16] achieved improvements of some 17% in flexural modulus and 10% in flexural strength with a slight reduction in fracture strain by incorporation of 0.05 wt.% CNTs. They ascribe the improvement to high level of CNT dispersion and grafting of epoxy resin to CNT by an esterification reaction which led to a strong interface. Mahfuz et al. [22] examined the effect of CNT incorporation on the compressive properties and reported increases of about 166% and 126% in compressive modulus and strength, respectively. Such improvements in both modulus and strength can be attributed to the transference of load from matrix to CNTs, under

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compressive load all the CNT layers contribute and are under compression while under tensile load only the outer layer of CNTs are stressed and are under tension [24]. Moreover, it has been found that incorporating CNTs into epoxy can improve the thermo-mechanical properties of epoxy by limiting the mobility of epoxy chains and increasing the cross linking density. This behaviour can be attributed to interactions between the CNTs and the epoxy, due to the enormous surface area of CNTs [38] and acceleration of curing rate of the composites due to the high thermal conductivity of CNTs [28]. Furthermore, the introduction of CNTs increased the viscosity of epoxy which can lead to more voids during the fabrication process. Since the epoxy resin in presence of CNT exhibits high resistance to shear forces, the entered air have less chance to be excluded from the epoxy resin, which in turn prevents higher improvement in mechanical properties of CNT-epoxy composites [29,39]. Zhang et al. [34] reported a significant reduction in the CNT-epoxy creep response due to limiting the load-induced re-orientation of epoxy chains. They used 0.1 wt.% to 0.25 wt.% of SWCNTs with BYK 9076 dispersion surfactant to fabricate the CNT-epoxy composites. In other work, Zhang et al. [36] used MWCNTs to investigate the CNT-epoxy behaviour under fatigue deformation. They achieved an over 20-fold reduction in the fatigue crack propagation rate by optimising the CNT geometry and the level of its dispersion in epoxy. Using fractography analysis and fracture mechanics modelling, they demonstrated that pull out of nanotube fibres that bridge the crack interface in epoxy matrix causes the crack suppression [36].

Recent studies have investigated the effect of different parameters such as solvent type, surfactant and functionalization on the dispersion quality of CNT powders. Despite of the fact that these efforts could improve the dispersion degree of CNTs into the epoxy resin to some extent, the efficient exploitation of the potential benefit from CNT powders as structural reinforcement was not entirely satisfactory. Hence using pre-dispersed CNT masterbatch for fabrication of CNT-epoxy composite would be an interesting choice as it includes elimination of dispersion difficulties. In addition, using CNT masterbatch proposes a dust free with minimum inhalation exposure to CNTs in comparison with the fluffy CNT powders. Hence these advantages provide the sufficient motivation in order to assess the potential application of CNT masterbatch for reinforcing epoxy resin in this study.

Whilst the effect of CNT powders on the mechanical properties of CNT-epoxy composite has been frequently reported, there have been no studies on the effect of CNT masterbatch on the reinforcing epoxy matrices to date. Moreover, the exact way in which the CNT masterbatch improve the mechanical and thermo-mechanical properties in comparison with other forms of CNT is still not known.

In order to capture these research aims, two epoxies with diglicidyl ether of Bisphenol A (DGEBA) epoxy resin (Part A) with different hardener (Part B) were examined. In order to reinforce the epoxy matrices, two forms of CNTs i.e. CNT powder form and masterbatch were used.

Araldite 2011 and MBrace Saturant were chosen as ductile and brittle epoxy matrices respectively, in this study. In the present work CNT-epoxy composites were produced through the incorporation of CNT powder and a CNT masterbatch which was commercially-sourced into the epoxy resin. The morphology, tensile, flexural and thermo-mechanical properties of CNT-reinforced epoxy composites were investigated for a wide application of FRPs appropriate for civil infrastructure. Another motivation of this work is to attempt to improve the mechanical properties of the thermosetting epoxy matrices using only a very low CNT concentration. These findings will help to develop methods to create the fully dispersed CNT-epoxy composites which are applicable to promoting the application of FRPs in the strengthening and retrofitting of civil infrastructure.

2. Experimental

2.1. Materials

Two types of epoxy resins, with either ductile or brittle behaviour, were used in this study. Ductile epoxy was Araldite 2011 and brittle epoxy was MBrace Saturant. Among the different types of ductile and brittle epoxies available, Araldite 2011 and MBrace Saturant were chosen, since they are mostly common commercial resin epoxies which are widely used in reinforcing civil infrastructures. Araldite 2011 is DGEBA with average molecular weight <700, supplied by Huntsman Company, Australia, the hardener being an amine, HV953 US. This epoxy was chosen due to its high elongation at breakage which makes it ideal for loading of CNTs. Brittle epoxy i.e. MBrace Saturant is DGEBA with an amines based hardener Isophoronediamine (IPD) supplied by BASF Company, Australia. This epoxy was chosen due to its higher strength, less viscosity and less elongation at breakage compared to those of Araldite 2011 for comparison between performance of brittle and ductile epoxy in terms of CNT loading.

DGEBA is a bi-functional reactant with two epoxide groups at two ends [40–43]. The HV953 US hardener is a polyamide-based system [40]. Polyamine hardeners are made up of an organic molecule containing two or more amine groups [44]. While hardener for MBrace Saturant resin is isophoronediamine [41,42]. This curing agent is amines based molecule containing maximum two amine groups [41].

DGEBA and HV953 US curing agent are able to generate 3D cross-linked epoxy polymers through covalent bonds, which could be created between C and N atoms. Similar polymerisation reaction has been reported for cross-linked DGEBA resin with isophoronediamine [41,42]. Since the polyamide-based curing agent has more primary amine groups, they can develop a higher crosslink density composite compare with the isophoronediamine. Hence a higher crosslink density relative to the HV953 US hardener could provide a higher ductility in cross-linked DGEBA resin.

In addition, although Part A in both composites mostly consisted of DGEBA resin, they contain some unknown components which are commercially imported into the epoxy resin. Hence, these additives may affect the ductility.

MWCNTs were supplied by Nanocyl Company in two forms, i.e. powder and masterbatch. CNT powder with commercial name of NC7000 is produced via catalytic carbon vapour deposition with average diameter of 9.5 nm and average length of 1.5 μm. CNT masterbatch was EpoCyl NC R128-02 Bisphenol-A masterbatch with NC7000 CNTs.

The dispersing agent for CNT powder was BYK 9077, a high molecular weight copolymer with pigment affinic groups, which was supplied by Nuplex Resins, Australia. The solvent for dispersion of CNT powder was absolute ethanol with 99% purity from Grale Scientific, Australia.

2.2. Preparation of CNT-epoxy composites

As shown in Fig. 1, two protocols were proposed to fabricate CNT-epoxy composites with 3 wt.% CNT loading, i.e. protocol (a) for CNT masterbatch and protocol (b) for CNT powder.

Specimen were prepared by mixing Part A and Part B with weight ratio 100:80 for Araldite 2011 and 76:24 for MBrace Saturant epoxy resins based on suppliers' advice. In the protocol (a), CNT masterbatch and resin (46.11 g for Araldite 2011 or 64 g for MBrace Saturant) were stirred for 10 min using high shear mixing homogenizer at 3500 rpm, followed by 60 min sonication treatment at fixed output power of 25 W. To prevent the temperature rising, the solution was placed in a water–ice bath during the