A COMPARATIVE STUDY ON EPOXY NANOCOMPOSITES REINFORCED BY CARBON NANOTUBES: EFFECT OF FABRICATION METHODS

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ABSTRACT

Carbon nanotubes (CNTs) have caused considerable interest owing to their remarkable mechanical properties and high aspect ratio, which make them promising candidate as nanofillers to reinforce epoxy matrices. However, due their high surface-to-volume ratio they have significant interparticle van der Waals interactions, and they tend to agglomerate and form a bundle, which results in reduced mechanical properties of the composites. Although various fabrication methods have been developed for dispersing CNTs, little information has been hitherto reported on their effectiveness to uniformly distribute CNTs in epoxy matrix. In addition, the influence of CNTs dispersion quality on mechanical properties of epoxy matrix is not well understood. The present work investigates the fabrication of CNT-epoxy composites through four different protocols. Protocols 1 and 2 were performed by high shear mixing and ultrasonication treatments of unmodified CNTs, respectively. In addition to these two protocols, in protocols 3 and 4, nanocomposites were prepared by high shear mixing of surface modified CNT suspensions in epoxy resin, followed by ultrasonication treatment. Scanning Electron Microscope (SEM) analysis indicated that the protocol 4 can uniformly disperse CNTs in epoxy matrix. The tensile test indicated that 10% and 6% improvements in Young's modulus and tensile strength with similar maximum elongation to the pure epoxy resin were able to be achieved. It can be concluded that the protocol 4 allows a uniform CNT dispersion in epoxy matrix and the highest degree of reinforcement in comparison with other protocols. Therefore, protocol 4 can be used to further improve the mechanical properties of epoxy matrix through CNT filler and thereby promote wide applications of CNT-epoxy composites in Civil Engineering.

Keywords: Carbon nanotubes, Epoxy, Dispersion, CFRP, Fabrication.

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1. INTRODUCTION

The impressive mechanical properties of Carbon Fiber Reinforced Polymer (CFRP) continues to motivate researchers to apply CFRP in the retrofitting and strengthening of ageing infrastructures (Zhao and Zhang 2007). They can be employed with both a metal (Wu et al. 2012a; Wu et al. 2012b) and concrete structure (Xiao and Xiao 2004). In a CFRP strengthening system, CFRP is attached to the host structure using a wet lay-up bonding by adhesive. The role of adhesive is to transfer the load from the host structure to the CFRP and thus mechanical properties of adhesive are important to efficiently transfer load. It is clear from the literature that a major failure in CFRP-metal structure is related to weak epoxy bonds (Teng et al. 2012) and the bond performance also affects the reinforcing efficiency in concrete structures (Al-Safy et al. 2012). Therefore, there is a need to reinforce epoxy resins for a wide application of CFRP in civil engineering.

CNTs have been discovered in 1991 (Iijima 1991) and are widely studied as reinforcement nanofillers in different matrices such as epoxy resins, owing to their remarkable mechanical properties and high aspect ratio (Coleman et al. 2006). Due to the high van der Waals interaction, CNTs tend to agglomerate and form bundles resulting in poor mechanical properties of nanocomposites. Various techniques for enhancing the dispersion of CNTs in media have been reported, including ultrasonication (Korayem et al. 2012; Liao et al. 2004; Siddiqui et al. 2010), calendering (Sumfleth et al. 2010), chemical functionalization (Ma et al. 2010; Shen et al. 2007), and physical surface modification via surfactants (Loos et al. 2012; Wang et al. 2004). In ultrasonication and calendaring process, shear forces are used to break down CNT bundles to individual CNTs. However, these methods do not permanently stabilize the dispersion of CNTs. In chemical functionalization, chemical groups such as –OH and –COOH groups are covalently incorporated on to CNT surface. This method is efficient in stabilizing dispersions, but results in the creation of a large number of defects on the CNT surface. In physical surface modification, CNT surface is non-covalently treated by using dispersing agents such as surfactants. This method is particularly desirable, as it assists in retaining the original mechanical properties of CNTs.

Despite various reports on dispersion of CNTs little information has been hitherto been reported on the effectiveness of these methods to uniformly distribute CNTs in the epoxy matrix, which has been widely used in retrofitting and strengthening civil structural members. This study aims to improve the current treatment practices to fulfill the immense potential of CNT-epoxy nanocomposites for various applications in the field of civil structural members. In order to achieve the high level of CNT dispersion in the epoxy resin, four different protocols based on mixing treatments of unmodified and surface modified CNTs, were employed to fabricate CNT-epoxy nanocomposites. CNT dispersion efficiency was systematically assessed via tensile testing and SEM analysis. The present work explores the extent to which fabrication method has an effect on the effective reinforcement of CNT-epoxy nanocomposites. It was also of interest to investigate the significance of how the surface modification of CNT influenced the resultant degree of dispersion and the effect on the degree of resin epoxy reinforcement for civil engineering applications.

2. EXPERIMENTAL

2.1. Materials

The pristine multi-walled CNTs (L4060) with 40-60 nm diameter and 5-15 µm length were obtained from NTP, China with a relative purity >95 wt.%. The low viscosity, commercially available Araldite 2011 epoxy resin used was modified diglycidyl ether of bisphenol-A (DGEBA) with an amine hardener (HV 953 US) supplied by Huntsman Company, Australia. The dispersing agent was BYK9076, an alkylammonium salt of a high molecular weight copolymer, which was supplied by Nuplex Resins, Australia. The solvent was absolute ethanol with 99% purity from Grale Scientific, Australia.

2.2. Preparation of CNT-epoxy nanocomposites

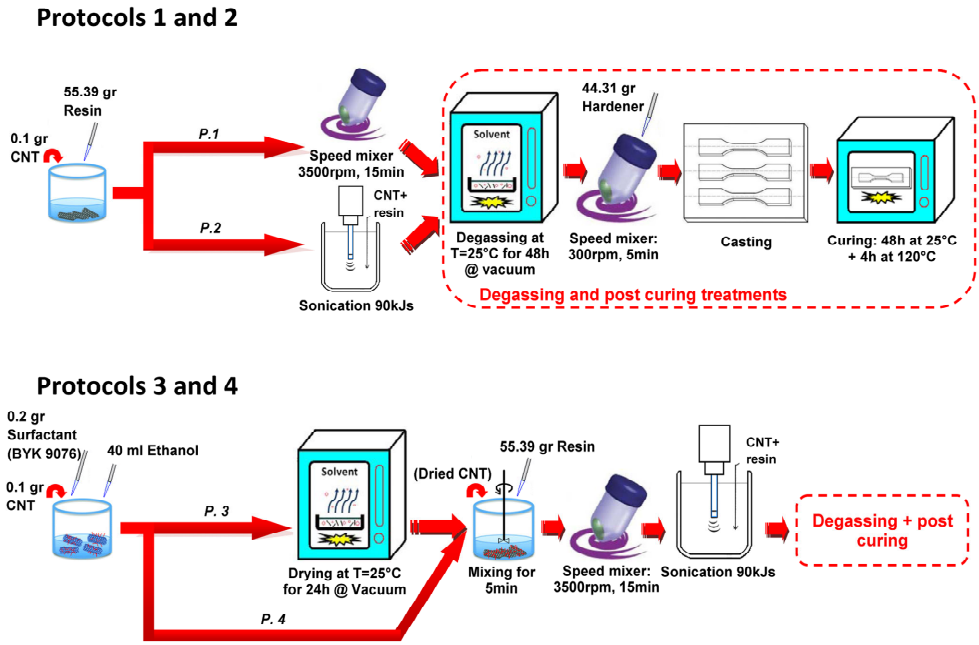

Figure 1: Schematic diagram of 4 fabrication protocols of CNT-epoxy nanocomposites. P.1: protocol 1, P.2: protocol 2, P.3: protocol 3, and P.4: protocol 4.

In order to comparatively study the effect of fabrication methodologies on the mechanical properties of CNT-epoxy nanocomposites, four different protocols have been utilized to fabricate CNT-epoxy nanocomposites as shown in Figure 1. The first two methods are based on the direct mixing of unmodified CNTs with epoxy, while the remaining two methods are based on direct mixing of surface modified CNTs. The surface of CNTs was modified by BYK 9076 copolymer when they were ultrasonically treated in the copolymer-ethanol solution to promote their dispersion in the solvent, and subsequently in the epoxy resin. The protocols are different in the procedure of mixing and dispersing CNTs in epoxy resin, but after that all protocols use the same manner for crosslinking by hardener as well as curing and post curing. In order to prepare the pure epoxy

sample, resin was put in a vacuum chamber for 48 hours to eliminate bubbles inside the resin. Then, the hardener with 100:80 weight ratio was added to degassed resin and mixture was prepared by stirring for 5 min at 300 rpm. Following this step, the blend was cast into a dog-bone shaped Teflon mold. The as-prepared pure epoxy resin samples were then mechanically polished to form smooth surfaces. The curing cycle took 48 hours at ambient temperature followed by 4 hours at 120°C.

2.3. Characterization of CNT-epoxy nanocomposites

The tensile tests were performed using a 4204 Instron machine with a 5 kN load cell following the ASTM D638-08 procedure. Samples were loaded at a crosshead speed of 5 mm/min at ambient temperature to failure. Young's modulus, tensile strength, and elongation at break of each sample were determined, based on at least three specimens per sample. Fracture surfaces of tested samples were examined using a JEOL 7001F FEG scanning electron microscope at 5 kV acceleration voltage. The samples were mounted on sample stubs and sputter-coated with around 1 nm thick Gold–Palladium coating materials.

3. RESULTS AND DISCUSSION

3.1. Tensile behavior

Tensile stress-strain curves of pure epoxy and 0.1 wt% CNT-epoxy nanocomposites prepared by 4 protocols are shown in Figure 2. Due to post curing at a higher temperature, pure epoxy exhibits a large maximum elongation of about 13%, which is desirable in CFRP reinforcing systems (Al-Safy et al. 2012). Young's modulus was determined to be 1985 MPa, which is in good agreement with the information provided by the supplier, i.e. 1904 MPa.

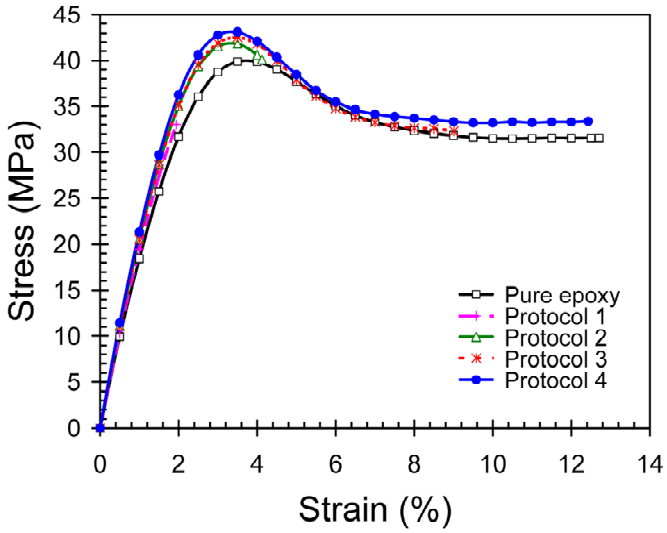

Figure 2: Tensile strain stress curve of CNT-epoxy nanocomposites prepared by 4 protocols.

Both protocols 1 and 2 significantly reduce the maximum elongation compared to the pure epoxy. Protocols 3 and 4 produce the CNT-epoxy nanocomposites with the greater tensile strength and

maximum elongation. The tensile properties derived from the stress-strain curves are tabulated in Table 1.

When compared with the pure epoxy resin, all protocols produce modest improvement on Young's modules of about 9%. The pristine CNTs via shear mixing in protocol 1 drastically reduced the strength by about 18% and the maximum elongation by about 85%. The ultrasonication in protocol 2 increases the strength by about 5.2%. This improvement indicates that the ultrasonication is essential to have a better dispersion of CNTs in epoxy matrix.

Table 1: Tensile properties of CNT-epoxy nanocomposites prepared with different protocols.

Fabrication method	*Tensile strength (MPa)*	*Maximum elongation (%)*	*Young's modulus (MPa)*
Pure epoxy	40.0	12.7	1985
Protocol 1	32.8 (-18%)*	1.9 (-85.0%)	2139 (7.7%)
Protocol 2	42.1 (5.2%)	4.7 (-63.0%)	2164 (9.0%)
Protocol 3	42.3 (5.7%)	8.7 (-31.5%)	2167 (9.1%)
Protocol 4	42.7 (6.7%)	12.7	2168 (9.2%)

* Numbers in bracket present the value difference compare to that of the pure epoxy.

Both protocols 3 and 4 lead to an enhancement of about 6% in tensile strength. However, the maximum elongation for protocol 3 was reduced by about 32%, compared to that of pure epoxy. Interestingly, protocol 4 results in a greater improvement of the maximum elongation compared to the protocols 1, 2 and 3 and was reasonably close to that of pure epoxy resin. It can be concluded that protocol 4 shows a reasonable improvement on mechanical properties of the epoxy matrix where they presented higher tensile strength and Young's modulus with similar maximum elongation to the pure epoxy resin.

3.2. Fracture surface morphology

Figure 3 shows the fracture surfaces of CNT-epoxy nanocomposites prepared by protocols 1 and 2. The CNTs remain in clusters, each of which have dimensions of about 60 μm × 60 μm when produced by protocol 1. It seems that low shear force produced by the shear mixing could not provide enough energy to disperse CNTs in epoxy matrix. It will result in stress concentration at the CNT clusters and lead to a considerable reduction in tensile strength, maximum elongation of CNT-epoxy nanocomposites, as well as a brittle failure mode in the tensile test.

For the CNT-epoxy nanocomposites prepared by protocol 2, the size of the CNT clusters is reduced to about 10 μm × 20 μm, as shown in Figure 3(b). The reduced agglomeration of CNTs in the matrix is largely due to stronger shear forces produced by bubble formation and collapse in the ultrasonication process, when compared with the shear mixer. As a result, the size of the CNT clusters was reduced and more individual CNTs were obtained. In fact, the slight improvement in tensile strength of the nanocomposites prepared by protocol 2 can be attributed to the exfoliation of individual CNTs from agglomerates. However, due to the high viscosity of epoxy matrix, the size of

the CNT clusters still remained relatively large, resulting in stress concentration, points of weakness and the reduction of the maximum elongation.

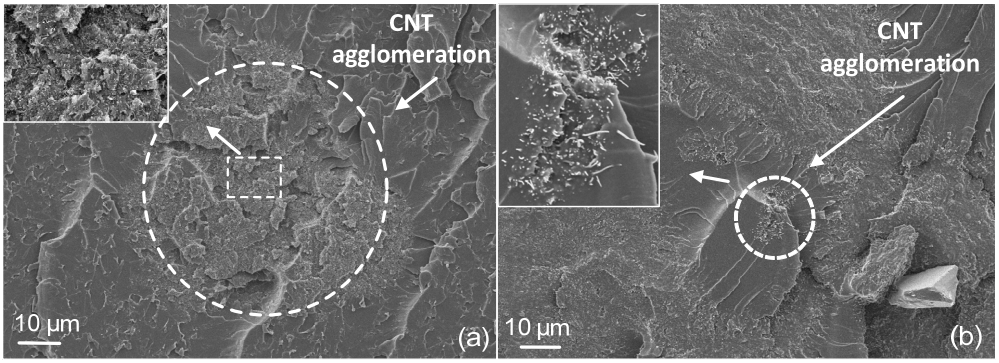

Figure 3: Fracture surface of CNT-epoxy fabricated by (a) protocol 1, and (b) protocol 2.

In protocol 3, BYK 9076 copolymer as a surfactant was adopted for dispersion of CNTs when they were ultrasonically treated in the absolute ethanol solution. The copolymer-ethanol solution was evaporated before introducing CNTs into the epoxy resin. As can be seen in Figure 4(c), both CNT clusters and individual CNTs were observed. It is proposed that surface modification of CNTs would allow an easier path for further reduced agglomeration of CNTs in the matrix and produce a higher ratio of individual CNTs. Individual CNTs are uniformly dispersed in the epoxy matrix which leads to an increase in tensile strength and Young's modulus of nanocomposites. However, re-agglomeration of CNTs formed during evaporation, as shown in Figure 4(b), resulted in stress concentration and reduced the maximum elongation of nanocomposites. To prevent CNT clusters formation, the surfactant-CNT suspension was directly mixed with epoxy resin in protocol 4.

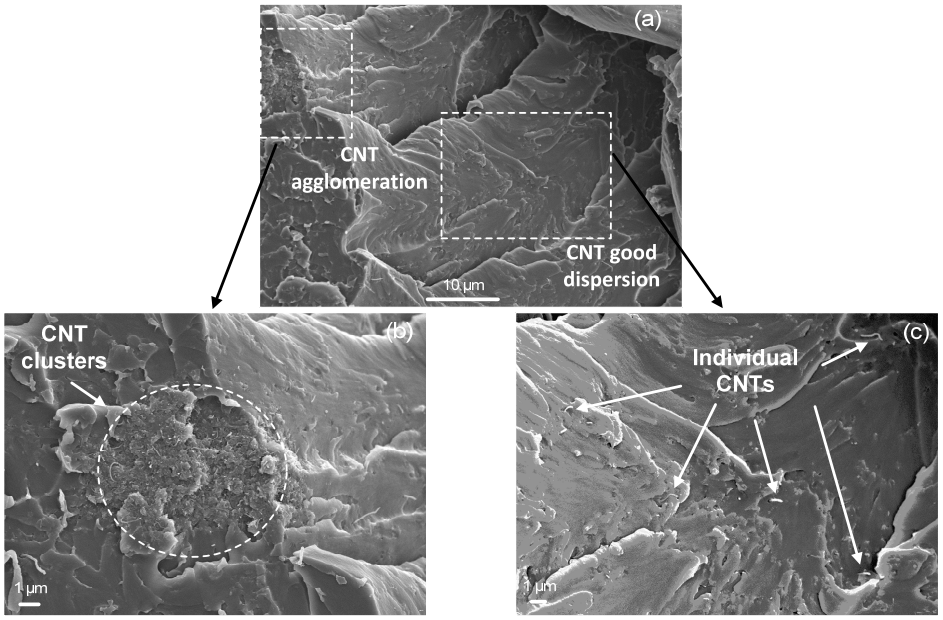

Figure 4: Fracture surface of CNT-epoxy nanocomposites prepared by protocol 3. (a) CNT agglomeration and good dispersion, (b) re-agglomeration and (c) good dispersion of CNTs.

As shown in Figure 5, the uniformly distributed CNTs can be observed at the fracture surface and no CNT agglomeration can be observed, indicating the efficiency of mixing surfactant-CNTs suspension with epoxy resin in protocol 4. This uniform dispersion of CNTs can explain the improved tensile strength and Young's modulus with a similar value of maximum elongation, when compared with pure epoxy resin.

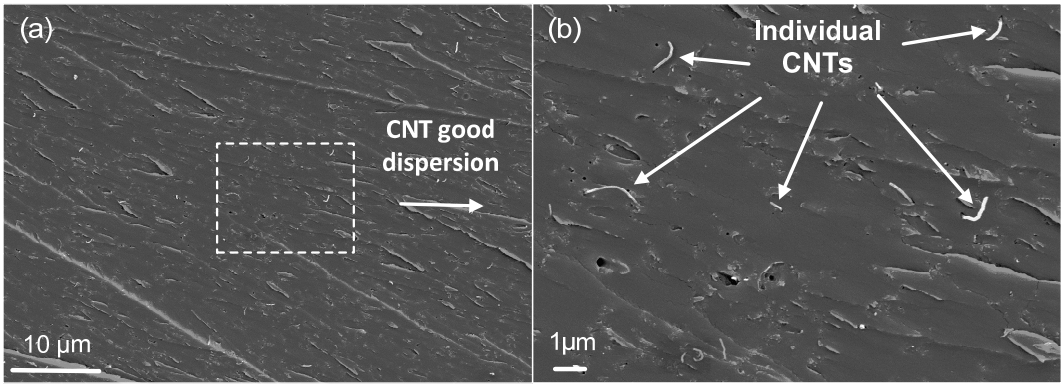

Figure 5: Fracture surface of CNT-epoxy nanocomposite prepared by protocol 4.

It is worth mentioning that protocol 4 could provide a large amount of individual CNTs in matrix and consequently improve mechanical properties of epoxy resin. However, it is still possible to further improve the tensile strength. The relatively low improvement of tensile strength can be attributed to the low interfacial interactions between the CNT and the matrix. The low interfacial interactions will allow CNT pull-out during the fracture of these nanocomposites, as can be seen in Figure 5(b). These pull-outs of the CNTs in the matrix may likely reduce the significant improvement in mechanical properties of CNT-epoxy resin nanocomposite that is sought.

4. CONCLUSIONS

In order to investigate the effect of fabrication method on mechanical properties of CNT-epoxy nanocomposites, four protocols were accomplished to prepare CNT-epoxy nanocomposites. The results demonstrated that 0.1% wt CNT-epoxy nanocomposites prepared by protocol 4 improved the tensile strength and Young's modulus by 6% and 10%, respectively, compared to the pure epoxy resin. The reduction in maximum elongation of CNT-epoxy nanocomposites prepared by protocol 3 is most likely related to CNT re-agglomeration during evaporation of solvent, and the formation of CNT clusters. The fracture surface studies suggested that the higher CNT dispersion in epoxy matrix can be achieved by protocol 4. Protocol 4 offers an effective method to improve the mechanical properties of epoxy matrix and consequently promote the application of CFRP in strengthening aging structures.

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