Effect of Functionalized MWCNTs on Mechanical Properties of Polymer Matrices†

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The effect of functionalization of multi-walled carbon nanotubes (MWCNT) on the mechanical properties of MWCNT/epoxy nanocomposites was investigated. Epoxy-based nanocomposites reinforced with MWCNTs with and without functionalization were prepared. The properties of nanocomposites were characterized using scanning emission microscopy (SEM) and tensile test. Experimental results showed that the functionalization of MWCNTs improved the dispersion of MWCNTs in epoxy matrix along with enhanced mechanical properties compared to those containing MWCNTs without functionalization. Compared to the neat epoxy, nanocomposites prepared with 1 wt % of MWCNT-COOH exhibited 39 % increase in Young's modulus and 19 % increase in tensile strength.

Keywords: Multi-walled carbon nanotube, Functionalization, Tensile strength.

INTRODUCTION

In the polymer field, epoxy resin is one of the most often used polymer matrix for advanced composite applications. The resins of this family have good stiffness and specific strength, dimensional stability, chemical resistance and also strong adhesion to the embedded reinforcement[1,2]. Over the years, many efforts have been made to modify epoxy by adding either rubber particles[3,4] or fillers[5] to improve the epoxy-based composite properties. Carbon nanotubes (CNT) are considered to be ideal for reinforcing high performance composites because of their unique mechanical, electrical and thermal properties. Different polymer/CNT nanocomposites have been synthesized by incorporating CNTs into various polymer matrices, such as polyamides, polyimides, epoxy, polyurethane and polypropylene[6]. The improvements in stiffness and strength because of the addition of CNTs in polymer matrix have been reported[7]. It is well known that CNTs have exceptionally high aspect ratio, high surface area and intrinsic van der Waals attraction among tubes resulting in their significant agglomeration which reduces the strength of nanocomposite by stress concentration effect[8]. In order to take full advantage of the extraordinary properties of CNTs, both the ability to disperse homogeneously throughout the matrix and the interfacial interaction between CNTs and polymer matrix constitute the two important factors[9]. The most effective method is chemical functionalization[10,11], which could provide functional groups on the surface of CNTs and form covalent bonding with matrix further. However, strong acid treatment would cut off CNTs' length and limit its application as high performance filler[9]. It is a crucial point to keep CNTs intact structure and generate sufficient functional groups onto CNTs.

EXPERIMENTAL

In this work, multi-walled carbon nanotubes (MWCNT) were dispersed in a mixture of sulfuric and nitric acid. Carboxylic acid-functionalized MWCNT (MWCNT-COOH) were obtained by oxidation of pristine MWCNTs. An ultrasonicator was used to process the MWCNT-epoxy nanocomposite. The effects of functionalization on the mechanical properties of MWCNTs reinforced nanocomposites were investigated. Tensile tests were conducted and the fracture surface were examined using scanning electron microscopy to reveal the efficiency of functionalized MWCNTs for strengthening and stiffening of the epoxy based nanocomposites.

Pristine multi-walled carbon nanotubes produced *via* chemical vapour deposition method were purchased from Golden Innovation Business Co. and purified to > 95 %. The MWCNTs had diameter ranging from 10nm to 30nm and the length ranging from 1-5 μm. The matrix used was part A: epoxy 6620 and part B: hardener AH150, both purchased from Glad Co. Taiwan. Distilled water was used in all procedures if necessary.

Functionalization of MWCNTs: MWCNTs were dispersed in a mixture of sulfuric acid and nitric acid with volume ratio of 3:1. The MWCNTs in solution was sonicated in an ultrasonic bath for 6 h at ambient temperature. Carboxylic acid-functionalized MWCNTS (MWCNT-COOH) were obtained by oxidation pristine MWCNTs via sonication in sulfuric-nitric acid. After sonication, the solution was diluted with large amount of distilled water. The functionalized MWCNTs were filtered through a membrane with pore size of 0.45 μm and repeatedly washed with distilled water. The concentration of acidity was measured periodically. The MWCNTs were considered to be acid free when the pH of MWCNTs in the solution is equal to the pH in the distilled water. The functionalized MWCNTs were then dried in a vacuum oven at temperature of 80 ℃ for 24 h and denotes as MWCNT-COOH.

Synthesis of MWCNT/epoxy nanocomposites: A desired amount of MWCNTs was directly added into a liquid epoxy which was preheated at 60 ℃ for 0.5 h. The solution was sonicated in an ultransonic bath for 3 h at 50 ℃ to separate the aggregation of the MWCNTs and achieve good dispersion. The solution was degassed in a vacuum oven maintained at pressure of 20 mmHg for 3 h. Then, the epoxy hardener AH150 was mixed into the MWCNT/epoxy solution and softly stirred it for 10 min. After that the solution was placed in a vacuum chamber for 0.5 h to remove the bubbles induced from the stirring. Finally, the nanocomposite suspension was poured into the dog-bone-like aluminum mould to fabricate the test specimen. The specimen is cured in a vacuum oven at temperature of 50 ℃ for 24 h. Samples without the MWCNT addition were also fabricated for comparison. Prior to the tensile test, the specimen surfaces were mechanically polished to reduce the influence of surface flaws. Specimens of neat epoxy and MWCNT/epoxy nanocomposites with two different kinds of MWCNTs, *i.e.*, pristine MWCNTs and functionalized MWCNT-COOH were prepared in the same procedures.

RESULTS AND DISCUSSION

Tensile testing: Mechanical properties of neat epoxy, MWCNT/epoxy and MWCNT-COOH/epoxy nanocomposites with different contents of MWCNTs were measured by tensile testing at a constant loading rate of 1 mm/min. Fig. 1 shows the representative stress-strain curves for neat epoxy and MWCNT-COOH/epoxy nanocomposites with various MWCNT-COOH contents ranging from 0.3-1 wt %. It can be observed that in comparison with neat epoxy, the MWCNT-COOH/epoxy nanocomposites exhibit higher Young's modulus and tensile strength but smaller strain at the break and the strain at break increases with the increase of MWCNT-COOH content. The numerical values are listed in Table-1. The Young's modulus increases from 1.15 GPa for neat epoxy to 1.61 GPa for epoxy reinforced with 1 wt % of MWCNT-COOH. At the same time, the tensile strength increases from 27.4 MPa for neat epoxy to 32.6 MPa for epoxy reinforced with 1 wt % of MWCNT-COOH. Enhancements on Young's modulus and tensile strength with the comprised strain at break are observed.

Fig. 2 depicts the stress-strain curves for MWCNT/epoxy nanocomposites with various MWCNT contents ranging from 0.3-1 wt %. It shows that both the Young's modulus and tensile strength are increasing with the increase of MWCNT feeding
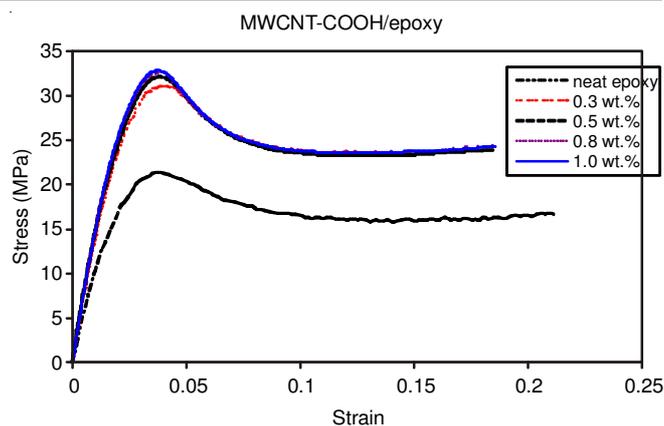

Fig. 1. Stress-strain curves for MWCNT-COOH/epoxy nanocomposites

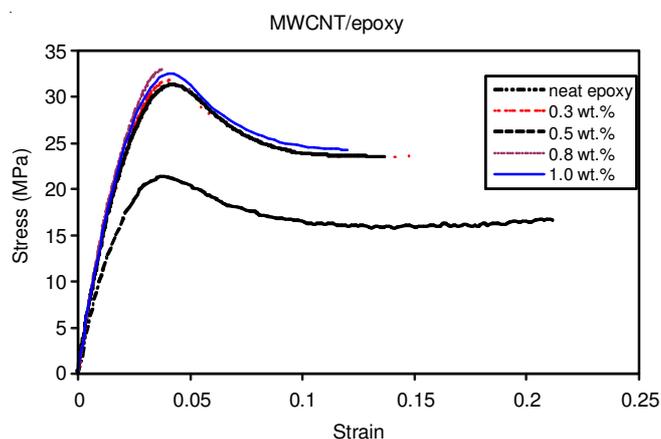| TABLE-1 MECHANICAL PROPERTIES OF MWCNT-COOH/EPOXY					
MWCNT-COOH (wt %)	0	0.3	0.5	0.8	1.0
Young's modulus (GPa)	1.15	1.50	1.54	1.56	1.61
Tensile strength (MPa)	27.4	31.5	33.1	32.3	32.6
Fracture strain	0.197	0.149	0.156	0.18	0.17
Fracture energy (J m⁻³)	4.27	3.53	3.92	4.37	4.15

Fig. 2. Stress-strain curves for MWCNT/epoxy nanocomposites

content. Table-2 lists the mechanical properties of MWCNT/epoxy nanocomposites varying with the MWCNT content. The Young's modulus and tensile strength increase from 1.15 GPa and 27.4 MPa for neat epoxy to 1.57 GPa and 33 MPa for epoxy reinforced with 1 wt % of MWCNT, respectively. At the same time, the strain at break decreases from 0.197 for neat epoxy to 0.138 for epoxy reinforced with 1 wt % of MWCNT.

TABLE-2 MECHANICAL PROPERTIES OF MWCNT/EPOXY					
MWCNT (wt %)	0	0.3	0.5	0.8	1.0
Young's modulus (GPa)	1.15	1.34	1.45	1.53	1.57
Tensile strength (MPa)	27.4	30.8	30.7	32.3	33.0
Fracture strain	0.197	0.176	0.160	0.154	0.138
Fracture energy (J m⁻³)	4.27	4.28	3.71	3.76	3.48

Functionalization not only improves the interaction and dispersion of MWCNTs in the epoxy matrix but also enhances the mechanical properties as shown in Fig. 3. It can be seen that the Young's modulus of MWCNT-COOH/epoxy is higher than that of MWCNT/epoxy. The area under the stress-strain curves in Figs. 1 and 2 can be used to calculate the strain energy density
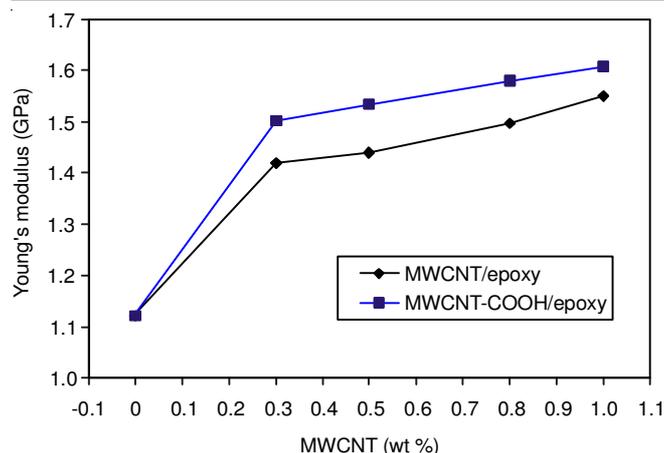
Fig. 3. Young's modulus of MWCNT/epoxy and MWCNT-COOH/epoxy

Fig. 4. SEM image of the fracture surface of MWCNT/epoxy

Fig. 5. SEM image of the fracture surface of MWCNT-COOH/epoxy

and evaluate the toughness of the materials. The area under the stress-strain curve of MWCNT-COOH/epoxy nanocomposite with 1 wt % of MWCNT-COOH is 4.15×10^6 J/m^3, while the pristine MWCNT/epoxy is 3.48×10^6 J/m^3. It shows that the strain energy during the fracture processing of the MWCNT-COOH/epoxy nanocomposites increases, resulting the increase of the toughness. An explanation of the behaviour can be attributed to the strong adhesion between the MWCNT-COOH and epoxy matrix. The onset of matrix cracking and the crack propagation will be prevented by the reinforced MWCNTs. More energy was consumed due to the destruction paths resulting in the increase of the fracture toughness.

Scanning electron microscopy (SEM) was conducted to reveal the morphology and dispersion of MWCNTs in the epoxy matrix. The fracture surface of the specimens from the tensile testing was examined. Figs. 4 and 5 illustrate the SEM images of the fracture surface of MWCNT/epoxy and MWCNT-COOH/epoxy, respectively. Most of common failures observed in MWCNTs reinforced nanocomposites are fiber fracture, fiber pullout, debonding of fiber and matrix or matrix cracking. The fracture surface shown in Fig. 4 reveals the agglomeration of MWCNTs in the epoxy matrix. This is an indication of poor dispersion resulting from a lack of interfacial interaction and weak adhesion between the MWCNTs and epoxy matrix. Incorporation of functionalized MWCNTs into the epoxy matrix increases the surface roughness making the nanocomposites more resistant to deformation. It can be observed that the functionalized MWCNTs are well dispersed in the epoxy matrix as shown in Fig. 5.

Conclusion

In this work, carboxylic acid groups were grafted onto the surface of MWCNTs by oxidation of pristine MWCNTs *via* sonication in sulfuric acid-nitric acid. The effects of functionalization of MWCNTs on the dispersion and mechanical properties of epoxy based nanocomposites were characterized through SEM and tensile testing. SEM images demonstrated that grafting carboxylic acid groups onto MWCNT surface can significantly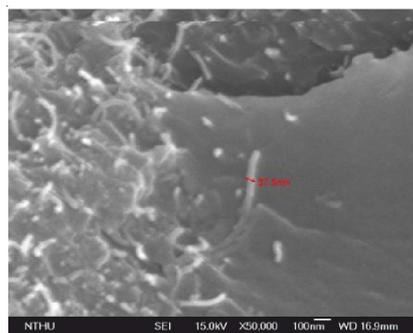 improve the dispersion of MWCNTs in epoxy matrix. The results of tensile testing showed that nanocomposites containing MWCNT-COOH exhibited better Young's modulus, tensile strength and fracture resistance than those of containing pristine MWCNTs. Above findings can be attributed to the improvements of interfacial interaction and adhesive bonding between the functionalized MWCNTs and epoxy matrix.
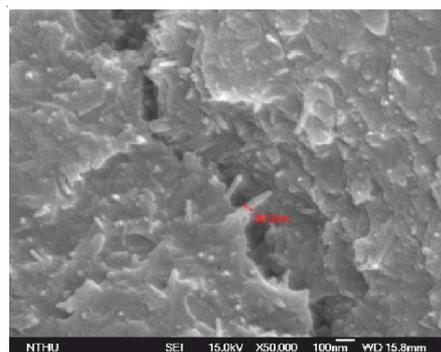
REFERENCES

1. M.R. Loos, L.A.F. Coelho, S.H. Pezzin and S.C. Amico, *Mater. Res.*, **11**, 347 (2008).
2. Y.X. Zhou, F. Pervin, L. Lewis and S. Jeelani, *Mater. Sci. Eng. A*, **452-453**, 657 (2007).
3. M. Imanaka, Y. Nakamura, A. Nishimura and T. Iida, *Compos. Sci. Technol.*, **63**, 41 (2003).
4. N. Chikhi, S. Fellahi and M. Bakar, *Eur. Polym. J.*, **38**, 251 (2002).
5. G. Xian, R. Walter and F. Haupert, *Compos. Sci. Technol.*, **66**, 3199 (2006).
6. Y.X. Zhou, P.X. Wu, Z.Y. Cheng, J. Ingram and S. Jeelani, *Express Polym. Lett.*, **2**, 40 (2008).
7. M. Theodore, M. Hosur, J. Thomas and S. Jeelani, *Mater. Sci. Eng. A*, **528**, 1192 (2011).
8. H. Meng, G.X. Sui, P.F. Fang and R. Yang, *Polymer*, **49**, 610 (2008).
9. W. Zou, Z. Du, Y. Liu, X. Yang, H. Li and C. Zhang, *Compos. Sci. Technol.*, **68**, 3259 (2008).
10. L. Liu and J.C. Grunlan, *Adv. Funct. Mater.*, **17**, 2343 (2007).
11. S.C. Her and C.Y. Lai, *Appl. Mech. Mater.*, **307**, 377 (2013).