Article

JOURNAL OF COMPOSITE MATERIALS

Journal of Composite Materials
2015, Vol. 49(16) 1961–1969

DOI: 10.1177/0021998314541306
jcm.sagepub.com
SAGE

Improvements in fatigue life of amine-functionalized multi-walled carbon nanotube-reinforced epoxy composites: Effect of functionalization degree and microwave-assisted precuring

Ehsan Moaseri, Salman Hasanabadi, Morteza Maghrebi and Majid Baniadam

Abstract

In this study, the effects of functionalization degree and precuring process were studied on the fatigue life of amine-functionalized multi-walled carbon nanotube-reinforced epoxy composites. The multi-walled carbon nanotubes were highly functionalized by ethylenediamine through a microwave-assisted method. The grafted amine moieties on the multi-walled carbon nanotubes could react with the epoxy chains of the matrix and consequently form covalent bonds between the multi-walled carbon nanotubes and the epoxy matrix. It has been found that higher functionalization degrees can lead to considerable enhancement on fatigue life of reinforced composites by increasing the dispersibility of multi-walled carbon nanotubes in the epoxy matrix and also improving the interfacial interactions between the reinforcing phase and the matrix. In the next step, the precuring process was performed by three apparatuses: oven, stirrer and microwave. While the precuring process with all three apparatuses resulted in higher mechanical properties of reinforced composites, the microwave-assisted precuring was more successful than the other two apparatuses. The reinforced composites prepared by microwave-assisted precuring experienced more than 19% improvement in the tensile strength in comparison to the non-precured composite; such improvements in the mechanical properties of reinforced composites were attributed to higher reactivity of amine moieties with the epoxy chains due to sufficient activation energy provided by microwave radiations. Observations with scanning electron microscopy indicated that highly functionalized multi-walled carbon nanotubes were uniformly distributed in the epoxy matrix; this can lead to uniform distribution of applied stress in the composites and consequently improve mechanical properties of the reinforced composites.

Keywords

Reinforced composites, functionalization degree, precuring process, mechanical properties, fractography

Introduction

Reinforced polymeric composites, with respect to their low density, high resistance, thermal stability and high-wear resistance,[1] are popular materials in the aerospace and automotive industries.[2] Epoxies are one of the most desirable polymers, which are widely used in numerous applications due to distinctive properties including appropriate mechanical, chemical and thermal resistance, low-water absorption and low shrinkage during the curing process.[3]

Addition of robust nanomaterials especially carbon structures such as carbon nanotubes (CNTs) can enhance the mechanical properties of epoxy composites.[4,5] In other words, due to high-mechanical

Chemical Engineering Department, Ferdowsi University of Mashhad, Mashhad, Iran

Corresponding author:
Majid Baniadam, Ferdowsi University of Mashhad, Mashhad, Iran, Islamic Republic of.
Email: baniadam@um.ac.ir

properties of these nanoparticles, the tolerance threshold of the epoxy composite increases, and it resists against initiation of fracture inside the composite. Among these strong nanomaterials, CNTs can be considered as an excellent choice to reinforce epoxy composites due to their exceptionally high-tensile strength and elastic modulus (approximately 150 GPa and 1 TPa, respectively).[6,7]

Polymeric nanocomposites reinforced with CNTs generally have high strength, low weight, high-thermal stability, high-electrical conductivity and chemical resistance.[8] In addition, these composites have much longer shelf life due to their high-mechanical properties.[9] Thus, they reduce the environmental problems related to residual wastes. However, fatigue phenomenon is the weakness of CNT-reinforced epoxy composites in comparison with the other strong materials such as metals.[10] Fatigue is the progressive and localized structural damage that occurs when a material is subjected to a long time cyclic loading.[11] It is the major cause of failure in the materials, which have large surface subjected to stress.

Fatigue initiates microcracks in the structure of materials and causes preterm fractures. The path of cracks in epoxy composites reinforced with CNTs is very complex. They may include one or more fatigue damage mechanisms such as matrix fracture, failure in interface or nanotube breakage.[12] Many experiments indicated that failure in interface is the predominant type of fatigue failure in CNT-reinforced composites.[13] The weak interfacial interactions between nanotubes and polymeric matrix are considered as the main reason of this failure.[14] The lack of adequate compatibility between the nanotubes and polymeric matrix leads to agglomerations of nanotubes and prevents uniform distribution of nanotubes inside the matrix. Non-uniform distribution of nanotubes causes non-uniform distribution of applied stress in the polymer matrix and consequently significant decrease in the mechanical properties of the reinforced composite.

Functionalization of CNTs is studied in the literature as an effective strategy to enhance the interfacial interactions between the CNTs and the epoxy matrix.[15,16] In such processes, various functional groups such as hydroxyl, carboxyl and amine are located on the nanotubes surface.[17] These groups increase dispersion of the CNTs in the epoxy matrix by enhancing the compatibility of CNTs with the polymeric matrix.[18,19] Among these functions, diamine groups are considered as the best choice due to their ability in formation of covalent bonds between the epoxy polymer and the CNTs. In diamine-functionalized CNTs, one of the amine functions is attached to the nanotube surface, and the other amine function remains free; these free amine moieties on the CNTs can react with epoxy chains and open the epoxide rings. These covalent bonding can noticeably enhance the strength of the nanocomposite by increasing the cross linking between the epoxy and the reinforcement phase.[16]

Recently, many researchers have endeavored to study different functionalization techniques and various amino groups to enhance the mechanical properties of the epoxy composites. Shen et al.[20] used four different amine functions to improve the tensile strength of epoxy composite. Also, Zehua et al.[21] functionalized CNTs with three types of amine functions (ethylenediamine (EDA), DDA and TETA) and used them to fabricate reinforced epoxy composite.[21] They achieved significant improvement in mechanical properties of composites. Moreover, they found that the interfacial linkage is more effective than the quality of dispersion in improving the mechanical properties.[21] However, to the best of our knowledge, the effect of functionalization degree and pre-curing process has not been studied on these interfacial interaction and consequently mechanical properties of amine-functionalized CNT-reinforced epoxy composites.

In this work, it has been endeavored to improve the fatigue life of CNT-reinforced epoxy nanocomposites based on two main scenarios. First, the effect of functionalization degree was studied on the fatigue life of nanocomposites. At the next step, the effect of precuring process of the epoxy polymer and functionalized CNTs was investigated on the interfacial interaction between the nanotubes and the matrix.

Experimental

Materials

Pristine multi-walled CNTs (MWCNTs) synthesized by chemical vapor deposition process (diameter 8–15 nm, length of 50 μm and purity >95%) were purchased from Shenzhen Nano-Tech Port Co. Both epoxy EPL-219 (bisphenol A epoxy) and associated curing agent EPH-5161 were purchased from Ghaffari Industrial Company, Iran. All the other reagents and solvents were obtained from Merck Inc.

Functionalization procedure of MWCNT

The pristine MWCNTs (0.2 g) were suspended in 100 ml of sulfuric acid/hydrochloric acid solution (3 : 1 v/v) and refluxed for 24 h to ensure sufficient purification and removal of extraneous catalytic metals. Then the purified nanotubes were washed with

deionized water until the pH value was approached 7. After drying, the purified-MWCNTs (200 mg) and $NaNO_2$ (200 mg) were mixed in 20 ml EDA and sonicated for 30 min at 50°C. Then the suspension was placed in a microwave oven equipped with a PID controller (model: TNZ4SSeries) and heated up to 90°C for 15 min. This modified device can set the output power and control the microwave radiations by switching the power on and off to keep the suspension in a constant temperature. Since there is a direct relation between microwave output power and the functionalization degree of MWCNTs,[22] three samples were prepared with 500 W (A500), 700 W (A700) and 900 W (A900) output powers. Then, all three suspensions were filtered, washed with deionized and then dried for 5 h at 60°C.

Fabrication of reinforced composites

Fifteen milligrams functionalized MWCNTs was mixed with 10 g epoxy, and the mixture was sonicated at 50°C for 4 h to get a homogeneous mixture. Afterwards, the curing agent was added, and the mixture was stirred for 10 min. Then the mixture was poured into a silicon mould and cured in an oven for 4 h under the controlled condition of 1 atm and 50°C. For precured samples, there was another step before the addition of curing agent to the mixture of MWCNTs and the epoxy. The mixture was placed in the precuring apparatus for 2 h at 70°C. According to the precuring apparatus, the samples were named 'A900-HotPlate', 'A900-Oven' and 'A900-Microwave'.

Characterizations

Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA) were used to study the type and the amount of functional groups attached to the MWCNTs. TGA data of purified and amine-functionalized MWCNTs were collected under nitrogen atmosphere on a TGA-50 Shimadzu instrument, with a heating rate of 10°C/min. The FTIR spectra were recorded by FTIR-Avatar 370 Nicolet spectrometer from 400 cm^{-1} to 4000 cm^{-1}, and the samples were placed on KBr pellets.

The tensile tests were performed using a Zwick Z250 test machine at a crosshead speed of 1 mm/min at ambient temperature. Dog-bone specimens were employed in accordance with the UNE-EN ISO 527-1 standard. The surfaces of the samples were grinded gently to reduce the influence of roughness on the mechanical properties. At least five specimens were tested for each type of composite to ensure reproducibility.

All the fatigue tests were performed at room temperature using an Instron (Fast Track 8870) material testing system. The fatigue tests were load-controlled, and the stress ratio, defined as the ratio of the minimum stress to the maximum stress, was set to be 0.1. The loading frequency was 10 Hz, and the waveform of cyclic loading was sinusoidal. The maximum applied stresses as the loading levels in the fatigue tests were selected 40%, 60% and 80% of ultimate tensile strengths to ensure that the fatigue lives of the studied specimens were in the range of 1000–100,000 cycles. Rectangular-shaped specimens (ASTM D3039) were prepared, and their edges were sanded to reduce the possibility of edge-related failures. Aluminum tabs were bonded to the ends of the specimens using a two-component epoxy adhesive to facilitate gripping. At least five specimens were tested for each type of composite to ensure reproducibility of the samples.

Fracture surfaces of the composite samples were observed using scanning electron microscope (SEM, Oxford Instruments LEO 1450VP) with an operating voltage of 30 kV. The fracture surfaces were coated with a thin gold layer before operating.

Results and discussion

Functionalization of MWCNTs

The FTIR and TGA tests were carried out to study the type and the amount of functional groups attached to MWCNTs. The FTIR spectra of purified MWCNTs, A500, A700 and A900 are depicted in Figure 1 with corresponding spectral analysis.

Unlike the pristine sample, all three functionalized samples show the characteristics of N–H stretching signals at 3300–3500 cm^{-1} and N–H bending signals at the ranges of 1640–1560 cm^{-1}, suggesting the existence of amine functions in all functionalized samples. In addition, the peak in 2850–3000 cm^{-1} and the others around 1230 cm^{-1} and 1470 cm^{-1} correspond to C–N and C–C stretching, respectively. All these peaks could justify the functionalization of MWCNTs with EDA.

Figure 2 represents the TGA results of purified MWCNTs, A500, A700 and A900 samples. Pristine MWCNTs show just one mass loss in the range of 500–700°C, corresponding to the oxidation and/or degradation of graphene layers of MWCNTs. However, in all three functionalized samples, there is another mass loss in the temperature range of 100–350°C. This mass loss can be attributed to the degradation of amino groups on the surface of the nanotubes. This decomposition behavior of amino groups is similar to the reported results of EDA-functionalized MWCNT by Chidawanyika and Nyokong.[23]

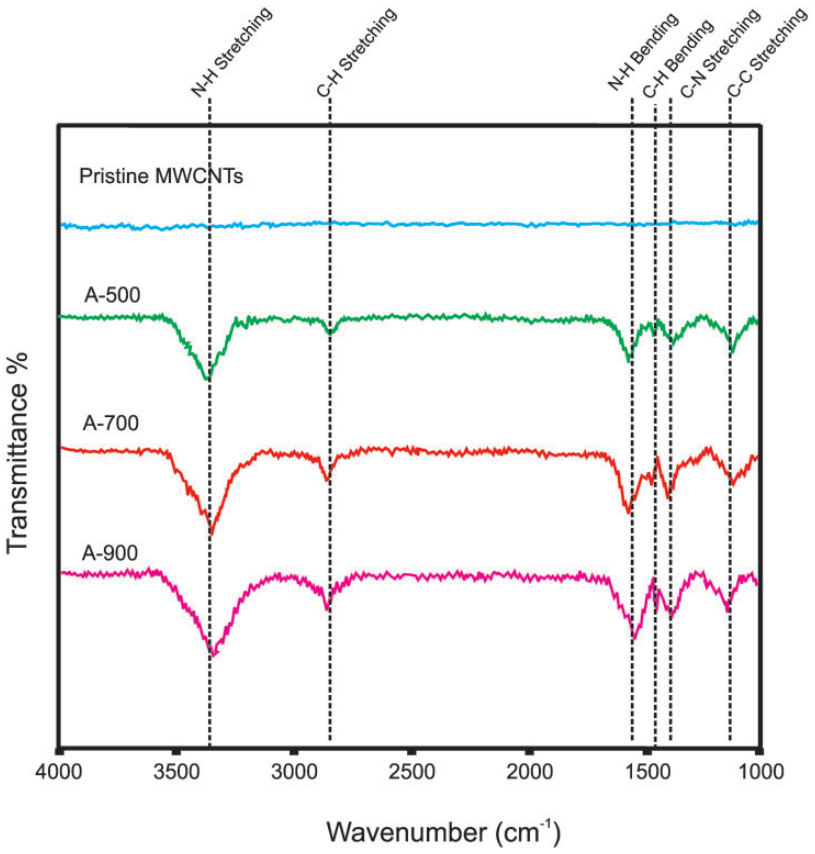

Figure 1. The FTIR spectra of pristine MWCNTs, A500, A700 and A900.

The following formula is used to calculate the functionalization degree of MWCNTs from the TGA results

$$\text{Degree of functionalization (mm/g)} = \frac{\left\{\text{Weight loss of attached function } (g) \times \frac{1000\,\text{mmol}}{\text{Molecular weight of attached function}}\right\}}{\text{MWCNTs weight loss } (g)} \quad (1)$$

The functionalization degree of all three samples is summarized in Table 1. According to the results, there is a direct relation between microwave output power and the amount of amine functions attached to the MWCNTs, as reported elsewhere.[22]

Mechanical properties of fabricated composites

Tensile testing was performed to study the effect of functionalization degree and precuring process on the overall strength of MWCNT-reinforced epoxy composites (Figure 3).

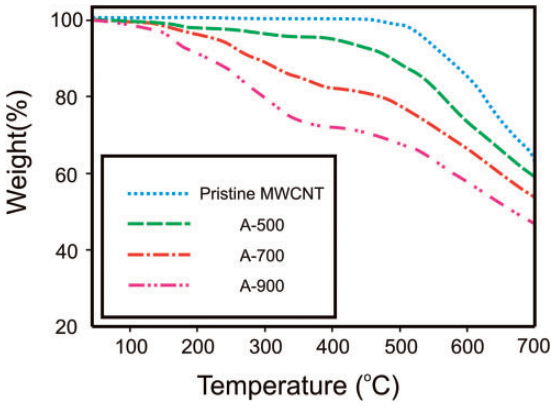

Figure 2. TGA curves of pristine MWCNTs, A500, A700 and A900 samples.

The tensile strength of epoxy composite has experienced a minor enhancement (14%) compared to the neat epoxy by incorporation of 0.2 wt% pristine MWCNTs. Interestingly, all composites reinforced with functionalized MWCNTs represent considerable improvements in their tensile strength. As it can be seen, the higher functionalization degree of MWCNTs has led to higher ultimate tensile strength of the

reinforced composites. By increasing the number of amine functions on the surface of the nanotubes, distribution of nanotubes into the epoxy matrix improved, and the probability of the formation of MWCNT agglomeration and preterm failure in composite structure were reduced. The interface of nanotubes and resin is known to be the most vulnerable region in the composite structure.[24] Therefore, the more the functions are, the more bridges between nanotubes and epoxy can be made; these bridges can significantly enhance the interfacial interactions between the reinforcement phase and the epoxy matrix. In other words, by increasing the number of grafted amine functions on the MWCNTS, the threshold of stress transfer from the epoxy matrix to the MWCNTs can be improved.

Table 1. Functionalization degree of amine-functionalized MWCNTs.

Amount of amine functions on the MWCNTs (mmol/g)	
Pristine MWCNT	0
A-500 W	1.1
A-700 W	3.6
A-900 W	6.4

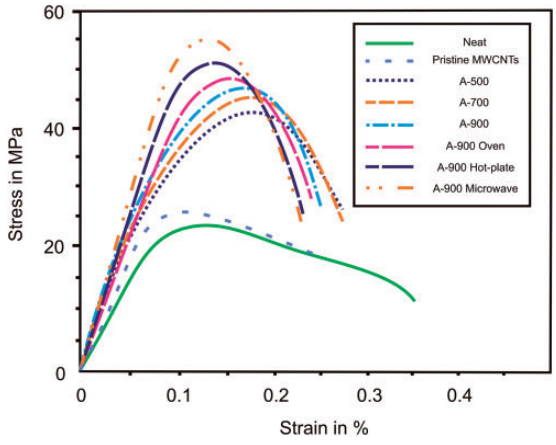

Figure 3. Stress–strain curve of MWCNT-reinforced epoxy composites.

In addition, all three precuring methods resulted in considerable improvements in the tensile strength of the composites. Evidently, the microwave-precuring process was more successful than the other two in enhancement of the mechanical properties of reinforced composites. In such precuring process, the number of covalent bonds between the nanotubes and the epoxy matrix can be enhanced, and subsequently the mechanical properties of the composites can be improved. The employed EDA function has a linear molecule structure with two free amines at the ends. During the functionalization step, these functions attached to the surface of nanotubes by one end. Theoretically, the other free amine can react with the epoxide ring of the matrix, open this ring and form covalent bond according to the following reaction (Figure 4).

The higher mechanical properties of A-900-HotPlate compared to A-900-Oven can be attributed to the fact that the mixing process of hotplate apparatus provided uniform temperature distribution inside the mixture; such suitable uniform condition can lead to higher rate in the reaction of amine moieties and the epoxide rings. Finally, it seems that microwave apparatus, which transfer heat by radiations, was more successful than the other two devices, which operate by convection heat transfer phenomenon. It is worth to note that the microwave radiations can pass through the epoxy matrix without any discernable absorption. These radiations can be absorbed only by the MWCNTs, where the energy is exactly needed for the reaction of the amine moieties and the epoxide rings of the matrix. This selective heating method may lead to higher

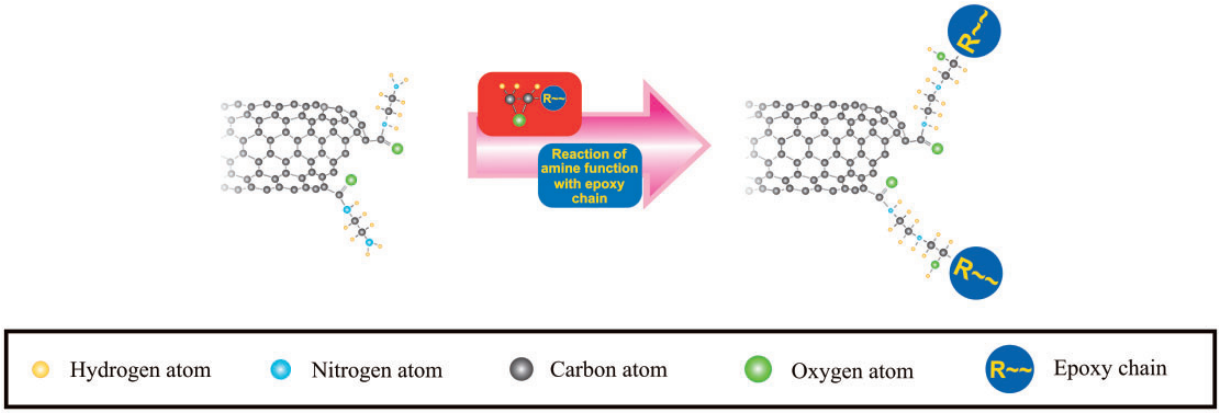

Figure 4. The reaction between the amine function of MWCNTs and the epoxide ring of the epoxy matrix.

linkages between the MWCNTs and the matrix and consequently improve the mechanical properties of reinforced composites.

Tension–tension cycling

One of the most important drawbacks of polymeric composites is their relatively low-fatigue life. To study the effect of functionalization degree of MWCNTs and the precuring process on the fatigue life of MWCNT-reinforced epoxy composites, tension–tension cycling test was performed. The results of the fatigue test are depicted in Figures 5 and 6 to investigate the effect of functionalization degree and precuring process, respectively. These data are plotted as the normalized stress ($\sigma_{max}/\sigma_{ult}$) versus the number of cycles to failure (N_f). Also, linear trends were appropriately fitted to each of them. Slope of these trend lines can indicate the durability of samples in lower stress levels that called high-cycle regimes.

As it can be seen in Figure 5, incorporation of pristine MWCNTs to the neat epoxy did not lead to any discernable improvement in the fatigue life of epoxy composite. On the other hand, the fatigue life of composites reinforced with functionalized MWCNTs experienced considerable improvement. Evidently, in all range of forces, the number of cycles for sample 'A-900' is higher than the sample 'A-700', and for

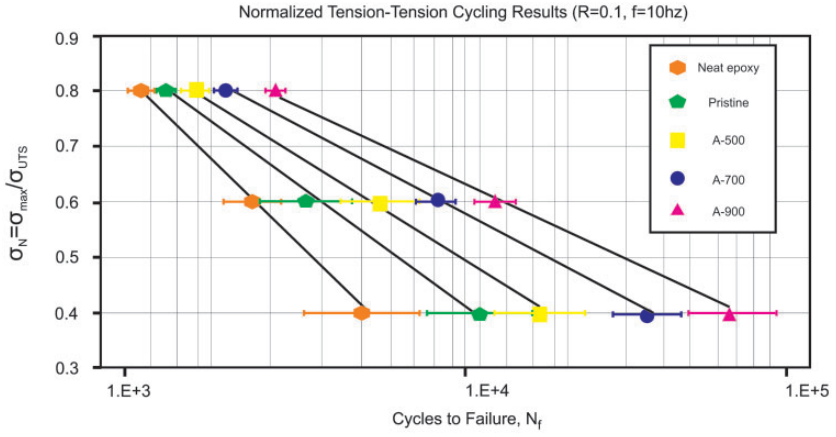

Figure 5. Normalized fatigue life of composites: neat epoxy, pristine MWCNT, A-500 MWCNT, A-700 MWCNT and A-900 MWCNT.

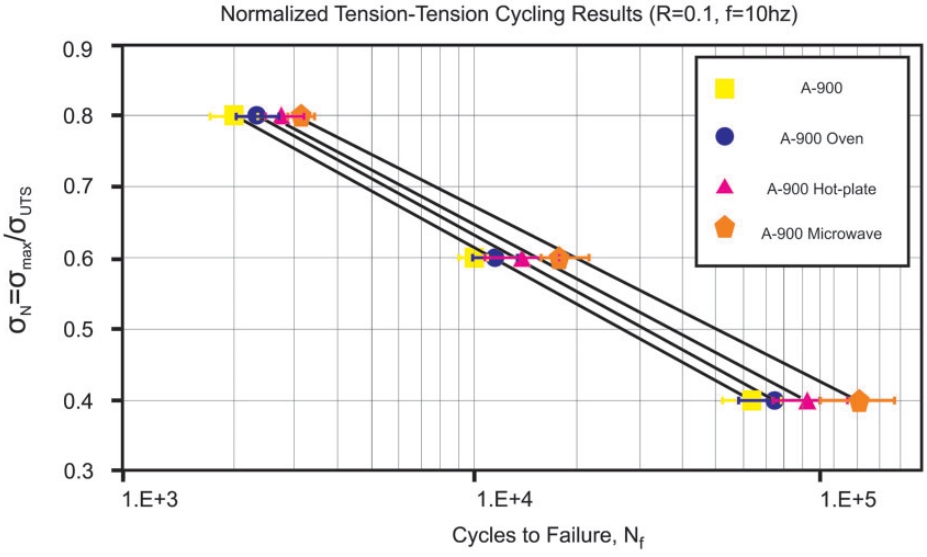

Figure 6. Normalized fatigue life of reinforced composites precured by different apparatuses.

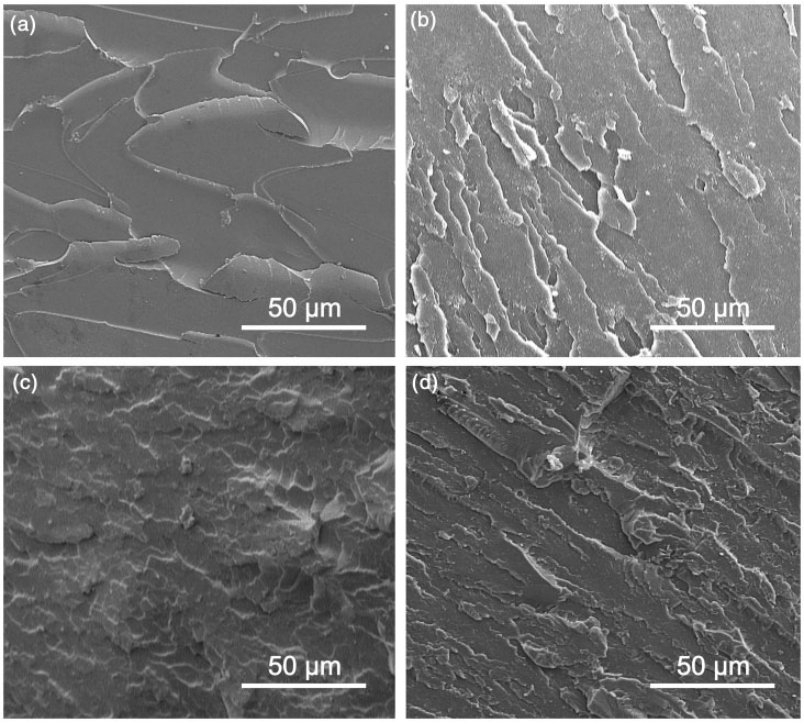

Figure 7. SEM images of the fracture surface of reinforced epoxy composite: (a) neat epoxy, (b) pristine MWCNT, (c) A-900 MWCNT and (d) A-900-Microwave MWCNT.

sample 'A-700', it is higher than the sample 'A-500'. From Figure 5, it was found that rising trend in number of cycles caused by reducing the applied force was almost linear. Hence, for different values of applied forces, the fatigue life of the composite samples could be predictable. Since the major fatigue failure mechanism in composites is pull-out of nanotubes from epoxy matrix, strengthening the interface between the nanotubes and the epoxy matrix may noticeably reduce the possibility of these failures. The results of fatigue life indicate that functionalization degree can be considered as an effective parameter on interfacial interactions between the amine-functionalized MWCNTs and the epoxy matrix. Therefore, highly functionalized MWCNTs can provide longer fatigue life of reinforced polymeric composites.

As it can be seen in Figure 6, all the three precuring processes have successfully led to improvements in fatigue life of reinforced composites. In addition, the composite procured by microwave process experienced longer fatigue life in all regimes. These improvements can be ascribed by the formation of higher bridges between the nanotubes and the epoxy matrix. Thus, more bondings caused more resistant to failure and the mechanical properties of the composites improved in this way.

Fractography of reinforced composites

SEM images of the fracture surface of the neat epoxy, pristine MWCNT, A-900 MWCNT and A-900-Microwave MWCNT-reinforced composites are shown in Figure 7, respectively. Neat epoxy (Figure 7(a)) exhibits a relatively smooth fracture surface compared to all three MWCNT-reinforced composites. In the neat epoxy, fracture phenomenon has occurred in ductile mode; on the other hand, the fractured surface of all three MWCNT-reinforced epoxy composites is coarser with sharp grooves suggesting a brittle fracture. This greater roughness may reflect the reinforcement effect of MWCNTs inside the epoxy matrix. Such grooves in the fracture surface of MWCNT-reinforced epoxy composite may stem from continuous redirections of the micro-cracks propagation during the fracture due to the presence of MWCNTs. These micro-cracks confront to nanotubes in their path and, consequently, their growth path redirect. This could be the reason of the delay in fracture of MWCNT-reinforced epoxy composite that was discussed in the previous sections.

As it can be seen in Figure 7, the fracture surface of A-900 MWCNT-reinforced composite seems to have a rougher surface compared to pristine MWCNT-reinforced composite. Similarly, the fracture surface

of A-900-Microwave MWCNT-reinforced composite represents even rougher surface than A-900 MWCNT-reinforced composite. These fracture states can be attributed to the interfacial interactions between the MWCNTs and the epoxy matrix. A-900-Microwave MWCNT, which can form strong covalent bonds with the epoxy matrix, can efficiently delay the micro-crack propagation through efficient stress transfer from the matrix to the MWCNTs; consequently, such rough fracture surface was formed due to incessant redirection of micro-crack path inside the matrix.

Conclusion

In this study, MWCNTs were functionalized by EDA with different functionalization degrees through microwave-assisted method. The effect of functionalization degree of MWCNTs was investigated on the mechanical properties of MWCNT-reinforced epoxy composites. It was found that functionalization degree plays a pivotal role in efficient reinforcement of epoxy composite. Considerable improvements have been achieved in mechanical properties of epoxy composite by reinforcing them with highly functionalized MWCNTs. In the next step, the effect of precuring process was investigated on mechanical properties of MWCNT-reinforced epoxy composites. Three different apparatuses were used for precuring process; amongst them, microwave radiations were found to be the most effective method of precuring for these composites. Based on obtained results, one can conclude that the functionalization degree of MWCNTs and the precuring process can be considered as two important parameters in ultimate mechanical properties of reinforced epoxy composites.

Acknowledgements

Mr M Karimi is acknowledged for experimental assistance.

Conflict of interest

None declared.

Funding

This work was supported by Iran Nanotechnology Initiative Council.

References

1. Paipetis A and Kostopoulos V. *Carbon nanotube enhanced aerospace composite materials: a new generation of multifunctional hybrid structural composites*. Netherlands: Springer, 2012.
2. Gorev YA and Rivkind VN. Polyester composites for shipbuilding. *Russ J Gen Chem* 2010; 80: 2098–2114.
3. Singla M and Chawla V. Mechanical properties of epoxy resin – fly ash composite. *J Miner Mater Charact Eng* 2010; 9: 199–210.
4. Gojny FH, Wichmann MHG, Köpke U, et al. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Compos Sci Technol* 2004; 64: 2363–2371.
5. Kim BC, Park SW and Lee DG. Fracture toughness of the nano-particle reinforced epoxy composite. *Compos Struct* 2008; 86: 69–77.
6. Ruoff RS, Qian D and Liu WK. Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements. *CR Phys* 2003; 4: 993–1008.
7. Wu Y, Huang M, Wang F, et al. Determination of the Young's modulus of structurally defined carbon nanotubes. *Nano Letters* 2008; 8: 4158–4161.
8. Friedrich K, Fakirov S and Zhang Z. *Polymer composites: from nano- to macro-scale*. New York: Springer, 2005.
9. Béland S. *High performance thermoplastic resins and their composites*. Elsevier Science, Norwich: Noyes Data Corporation, 1990.
10. Cotterell B. *Fracture and life*. London: World Scientific Publishing Company, 2010.
11. Kim WH and Laird C. Crack nucleation and stage I propagation in high strain fatigue – II: mechanism. *Acta Metall* 1978; 26: 789–799.
12. Yamamoto G, Shirasu K, Hashida T, et al. Nanotube fracture during the failure of carbon nanotube/alumina composites. *Carbon* 2011; 49: 3709–3716.
13. Gan Y. Effect of interface structure on mechanical properties of advanced composite materials. *Int J Mol Sci* 2009; 10: 5115–5134.
14. Park SJ and Seo MK. *Interface science and composites*. San Diego: Academic Press, 2011.
15. Tseng C-H, Wang C-C and Chen C-Y. Functionalizing carbon nanotubes by plasma modification for the preparation of covalent-integrated epoxy composites. *Chem Mater* 2006; 19: 308–315.
16. Nadler M, Werner J, Mahrholz T, et al. Effect of CNT surface functionalisation on the mechanical properties of multi-walled carbon nanotube/epoxy-composites. *Composites Part A* 2009; 40: 932–937.
17. Hamrang A and Howell BA. *Foundations of high performance polymers: properties, performance and applications*. Oakville: Apple Academic Press, 2013.
18. Wang Z, Colorad HA, Guo Z-H, et al. Effective functionalization of carbon nanotubes for bisphenol F epoxy matrix composites. *Mater Res* 2012; 15: 510–516.
19. Zhang J and Jiang D. Interconnected multi-walled carbon nanotubes reinforced polymer-matrix composites. *Compos Sci Technol* 2011; 71: 466–470.
20. Shen J, Huang W, Wu L, et al. The reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites. *Compos Sci Technol* 2007; 67: 3041–3050.

21. Zehua Q and Guojian W. A comparative study on the properties of the different amino-functionalized multiwall carbon nanotubes reinforced epoxy resin composites. *J Appl Polym Sci* 2012; 124: 403–411.
22. Moaseri E, Baniadam M, Maghrebi M, et al. A simple recoverable titration method for quantitative characterization of amine-functionalized carbon nanotubes. *Chem Phys Lett* 2013; 555: 164–167.
23. Chidawanyika W and Nyokong T. Characterization of amine-functionalized single-walled carbon nanotube-low symmetry phthalocyanine conjugates. *Carbon* 2010; 48: 2831–2838.
24. Mukhopadhyay SM and Karumuri AK. Nanotube attachment for prevention of interfacial delamination. *J Phys D Appl Phys* 2010; 43: 365301.