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Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties

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ABSTRACT

Epoxy resins are widely applied in cryogenic engineering and their cryogenic mechanical properties as important parameters have to be improved to meet the high requirements by cryogenic engineering applications. Carbon nanotubes (CNTs) are regarded as exceptional reinforcements for polymers. However, poor carbon nanotube (CNT)–polymer interfacial bonding leads to the unexpected low reinforcing efficiency. This paper presents a study on the cryogenic mechanical properties of multi-walled carbon nanotube reinforced epoxy nanocomposites, which are prepared by adding multi-walled carbon nanotubes (MWCNTs) to diglycidyl ether of bisphenol-F epoxy via the ultrasonic technique. When the temperature decreases from room temperature to liquid nitrogen temperature (77 K), a strong CNT–epoxy interfacial bonding is observed due to the thermal contraction of epoxy matrix because of the big differences in thermal expansion coefficients of epoxy and MWCNTs, resulting in a higher reinforcing efficiency. Moreover, synthetic sequence leads to selective dispersion of MWCNTs in the brittle primary phase but not in the soft second phase in the two phase epoxy matrix. Consequently, the cryogenic tensile strength, Young's modulus, failure strain and impact strength at 77 K are all enhanced by the addition of MWCNTs at appropriate contents. The results suggest that CNTs are promising reinforcements for enhancing the cryogenic mechanical properties of epoxy resins that have potential applications in cryogenic engineering areas.

1. Introduction

Epoxy resins have wide engineering applications due to their low cost, easy processability, good thermal, mechanical and electrical properties, etc. With the rapid developments in spacecraft and superconducting cable technologies, and large cryogenic engineering projects such as the International Thermonuclear Experimental Reactor (ITER), etc., epoxy resins have been increasingly employed in cryogenic engineering applications as impregnating materials, adhesives and matrices for advanced composites [1–8]. However, pure epoxy resins normally have poor crack resistance at room temperature [9–13] and could be more brittle at cryogenic temperatures [10–13], which makes them unsuitable for some cryogenic engineering applications that demand epoxy resins to have high cryogenic mechanical properties. For example, during service of epoxy resins in ITER, temperature might change from room temperature (RT) to cryogenic temperatures (like liquid nitrogen temperature 77 K etc.) or vice versa [14–16], this would induce thermal stresses within epoxy resins and thus demands epoxy resins to have high cryogenic mechanical properties to stand for internal thermal stresses. Therefore, it is of great importance to improve the cryogenic mechanical properties of epoxy resins so that they can be gainfully used in cryogenic engineering applications. Recent publications from our group have reported on epoxy toughening and strengthening of epoxy resins for enhancing cryogenic mechanical properties using flexible diamines [12], thermoplastic poly(ethersulfone) [13], silica nanoparticles [17], exfoliated montmorillonite (MMT) [18], hyperbranched polymer [19], polyurethane [20] and *n*-butyl glycidyl ether [21].

Carbon nanotubes (CNTs) are long cylinders of covalently bonded carbon atoms and have a diameter from a few angstroms to several tens of nanometers across. CNTs have exceptional mechanical properties [22–25] and thus extensive research work has been carried out on carbon nanotube (CNT) reinforced polymer composites [26–35]. However, weak interfacial bonding between CNTs and polymers leads to poor stress transfer and thus has limited the full realization of CNTs as reinforcements for polymers. Therefore, chemical functionalization of CNTs has been conducted

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to improve the CNT–polymer interfacial adhesion [32–35]. However, any attempt to create strong interfacial bonding will introduce defects into CNTs [36]. Consequently, the results for the strength and modulus are still disappointing for polymer nanocomposites. On the other hand, similar to the MMT–epoxy case [18], the interfacial bonding between CNTs and polymers can be enhanced when the temperature decreases from RT to a cryogenic temperature due to the thermal shrinkage caused by the big differences in the thermal expansion coefficients of epoxy and CNTs. It can thus be expected that carbon nanotubes are good reinforcements for polymers at a cryogenic temperature than at RT. Moreover, generally speaking, cryogenic mechanical behaviors of polymers or their composites can be significantly different from those at RT because of the effect of large thermal contraction. Therefore, it is of great fundamental and practical importance to study the cryogenic mechanical behaviors of CNT–epoxy nanocomposites that are aimed to be employed in cryogenic engineering applications.

The main purpose of this paper is to investigate the cryogenic mechanical behaviors at liquid nitrogen temperature (77 K) of carbon nanotube reinforced epoxy nanocomposites. There are two basic carbon nanotubes: single walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). MWCNTs are much cheaper than SWCNTs and so MWCNTs are chosen to reinforce epoxy resins in this study. The selected epoxy matrix is the optimized formulation of diglycidyl ether of bisphenol-F (DGEBF)/diethyl toluene diamine (DETD) system toughened by a reactive aliphatic diluent with a low viscosity [37]. The tensile and impact properties at 77 K of epoxy nanocomposites were studied and compared with those at RT. The fracture surfaces were examined using scanning electron microscopy (SEM), which is then used to illuminate the cryogenic mechanical behaviors of MWCNT–epoxy nanocomposites.

2. Experimental

2.1. Materials and sample preparation

The epoxy resin used in this work was diglycidyl ether of bisphenol-F (DGEBF, D.E.R.354, Dow Chemical Co., USA) with the epoxide weight equivalence in the range 167–174. The curing agent was diethyl toluene diamine (DETD, ETHACURE-100, Albemarle Co., USA), which is a mixture of 2,4- and 2,6-isomers. A reactive aliphatic diluent (DILUENT) with a low viscosity of 2–3 mPa s at 25 °C (Changshu Jiafa Chemistry Co, China) was used as a modifier for epoxy resin. Multi-walled carbon nanotubes (MWCNTs) produced by Showa Denko K.K. were used and the MWCNTs have a length of 10–20 μm [38]. Moreover, tens of measurements were carried out using the software SemAfore 4.0 on the SEM images of carbon nanotubes as shown in Fig. 1 to get the average diameter of carbon nanotubes and its value is estimated to be about 87 nm.

In order to get well dispersed CNTs in the epoxy matrix, the epoxy nanocomposites were prepared by the following procedures. The pristine MWCNTs (1 g) were treated using a mixture of concentrated sulfuric (98%) and nitric (70%) acids (3:1 by vol/vol). After one-hour sonication, 4 h stirring at 70 °C and exhaustive washes with deionized water, HCl was added to the acid mixture to convert the carboxylates into carboxylic acid groups on the defect sites of MWCNTs [39]. The solution was then extensively washed with deionized water until pH value reached 7. The acid-treated nanotubes were collected after vacuum filtration using a 5 μm filter funnel and drying overnight in a vacuum oven at 80 °C. The MWCNTs were dispersed in ethanol before adding DGEBF and the mixture was sonicated for 15 min using a high-power (600 W) ultrasonic machine. The mixture was then degassed at 60 °C for 5 h to eliminate the entrapped air and the remaining ethanol. Afterwards, the DETD hardener and DILUENT agent were added to the epoxy in the ratio of 31.14:20:100 by weight for DETD:DILUENT:DGEBF. The resulting solution was then evacuated for an efficiently long time (≥4 h) to avoid the formation of bubbles since the formation of voids could reduce the fracture characteristics of the samples [40]. After evacuation the mixture was transferred to an open mould. The blends were cured at 80 °C for 8 h, then 130 °C for 10 h. After curing, the blends were allowed to be cooled naturally to room temperature. Epoxy nanocomposites containing weight fractions of 0.02%, 0.05%, 0.2%, 0.5%, 1%, and 2% MWCNTs were prepared.

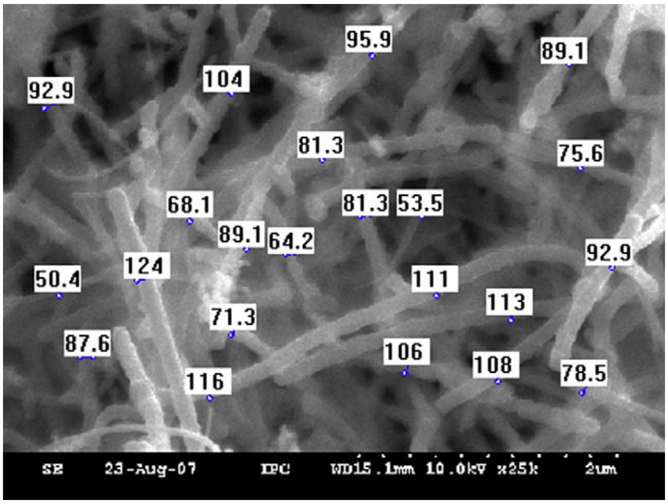


Fig. 1. Measurement of the diameters of pristine MWCNTs using the software SemAfore 4.0.

2.2. Measurement and characterization

The tensile samples were prepared according to the recommendation of ASTM D638-96. The tensile properties were measured on an RGT-20A Reger Mechanical Tester under a 10 kN load cell with a crosshead speed of 2 mm/min. The cryogenic temperature condition was achieved by dipping the samples fixed on the clamps in a liquid nitrogen filled cryostat designed in our laboratory [18,19]. The dimensions of the tensile specimens are 6 mm × 4 mm in the working section.

The Charpy impact strength of the samples was measured with a Reger Impact Tester according to the recommendation of GB/T 2571-1995. Specimens for impact testing were immersed in liquid nitrogen for over 5 min so that they could be cooled down to 77 K before being mounted onto the Impact Tester. The pendulum of the Impact Tester was released immediately against the width after the specimen was mounted onto the Impact Tester and one impact testing was completed in a couple of seconds. At least five specimens were tested for each composition.

The fracture surfaces of the specimens after impact testing were examined by scanning electron microscopy (SEM, Hitachi S-4300). Prior to examination, the fracture surfaces were cleaned using alcohol and were then coated with a thin evaporated layer of gold to improve conductivity.

3. Results and discussion

The stress–strain curves of epoxy and MWCNT/epoxy nanocomposites at both RT and 77 K are shown in Fig. 2. Clearly, the failure strain of epoxy resins at both RT and 77 K increases initially up to the maximum and then decreases with further increasing the

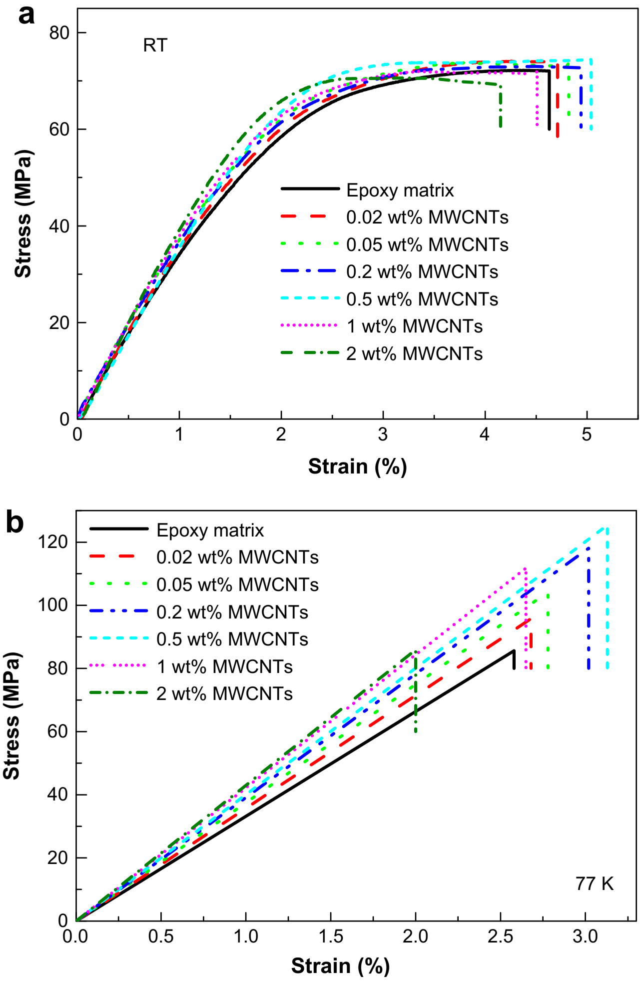
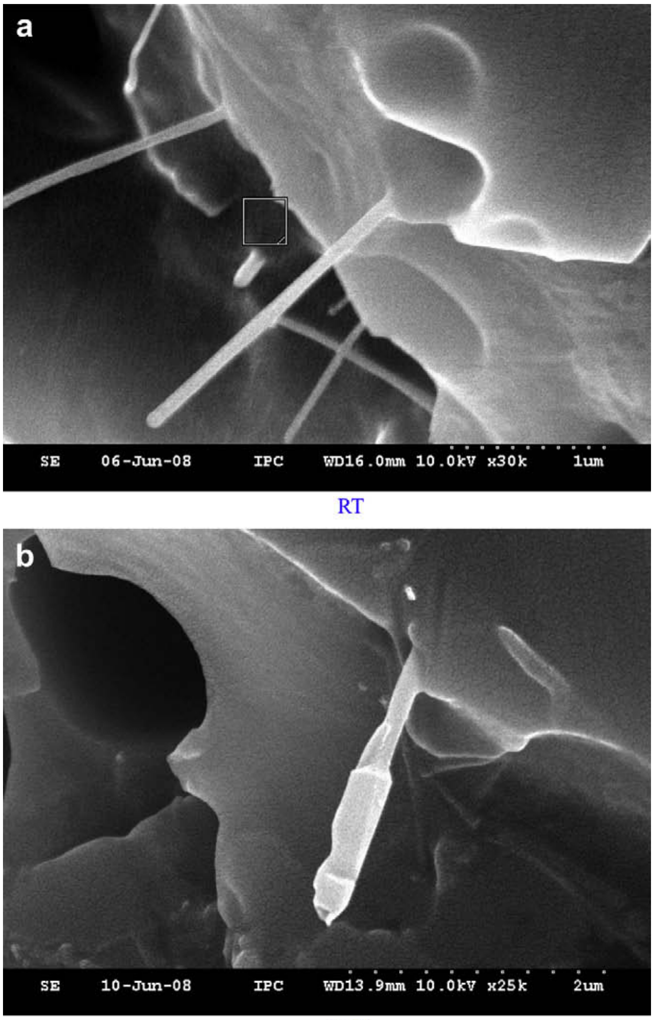


Fig. 2. Typical stress–strain cures of epoxy and MWCNT/epoxy nanocomposites at (a) RT and (b) 77 K.



RT

77 K

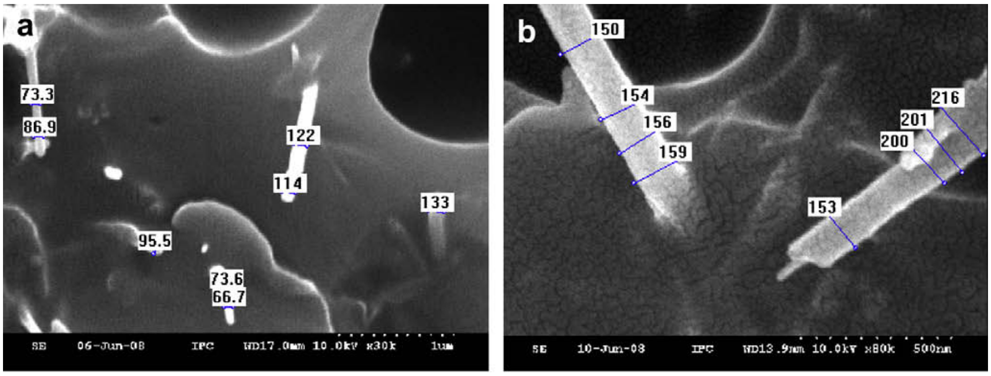
Fig. 3. SEM images showing CNTs pullout from the tensile fracture surfaces of MWCNT/epoxy nanocomposites at (a) RT and (b) 77 K.

content of MWCNTs. The MWCNT/epoxy nanocomposites exhibit relatively ductile behaviors at room temperature compared to that at 77 K and the epoxy resins show obviously brittle behaviors at cryogenic temperature for all compositions. The data for the tensile strength, Young's modulus and the failure strain of MWCNT/epoxy nanocomposites at RT and 77 K can be obtained from the tensile stress–strain curves via the commercial REGER testing Software. The results are summarized in Table 1. The error bars denote the standard deviation for the tensile properties.

It is seen from Table 1 that the tensile strength of the MWCNT/epoxy nanocomposites at RT is almost independent of the MWCNT addition. Only for the sample with the 2 wt% MWCNT content, the nanocomposite tensile strength is slightly lower than that of the epoxy matrix. This is because the mechanical strength of epoxy nanocomposites strongly depends on the CNT–epoxy interfacial bonding. When there is a poor bonding between the matrix and the CNTs, CNTs would be easily pulled out with smooth surfaces as shown in Fig. 3a. The relatively weak bonding leads to poor stress transfer from epoxy matrix to CNTs and the CNTs would have a low reinforcing efficiency, resulting in the insensitivity of the nanocomposite strength to the CNT content. At the relatively high CNT content (2 wt%), largely aggregated CNTs can be observed in the epoxy matrix to be shown later, leading to a slightly lower strength than that of the epoxy matrix. This is because the agglomeration of CNTs for the high CNT content gives rise to weak CNT–polymer interactions and high stress concentrations similar to the case of

Table 1
Tensile properties at RT and 77 K of the epoxy matrix and epoxy nanocomposites.

MWCNTs content (wt%)	Tensile strength (MPa)		Young's modulus (GPa)		Failure strain (%)	
	RT	77 K	RT	77 K	RT	77 K
0	73.39 ± 1.34	92.73 ± 1.05	2.67 ± 0.08	4.58 ± 0.02	4.62 ± 0.31	2.50 ± 0.04
0.02	73.06 ± 1.77	94.77 ± 0.45	2.72 ± 0.05	4.80 ± 0.05	4.71 ± 0.12	2.67 ± 0.03
0.05	72.20 ± 1.59	102.45 ± 2.54	2.77 ± 0.09	4.92 ± 0.08	4.82 ± 0.18	2.82 ± 0.05
0.2	73.08 ± 0.58	116.40 ± 3.37	2.83 ± 0.08	5.02 ± 0.06	4.94 ± 0.13	3.09 ± 0.07
0.5	74.40 ± 1.17	119.35 ± 2.02	3.09 ± 0.02	5.26 ± 0.07	5.04 ± 0.07	3.20 ± 0.05
1	71.58 ± 1.47	112.75 ± 1.52	3.11 ± 0.01	5.49 ± 0.08	4.51 ± 0.19	2.64 ± 0.06
2	68.83 ± 2.31	81.40 ± 3.33	3.13 ± 0.06	5.53 ± 0.04	4.15 ± 0.14	2.20 ± 0.04



RT 77 K

Fig. 4. Measurement of the fiber diameters using the software SemAfore 4.0 on the SEM images of the samples fractured at (a) RT and (b) 77 K.

clay–epoxy nanocomposites [41], resulting in the reduction of the tensile strength.

Table 1 also shows that the results for the cryogenic tensile strength at 77 K of the epoxy matrix and epoxy nanocomposites. A significant enhancement in the cryogenic strength has been observed by the addition of MWCNTs at appropriate contents. The cryogenic tensile strength reaches the maximum at the MWCNT content of 0.5 wt% followed by a decrease when the CNT content is

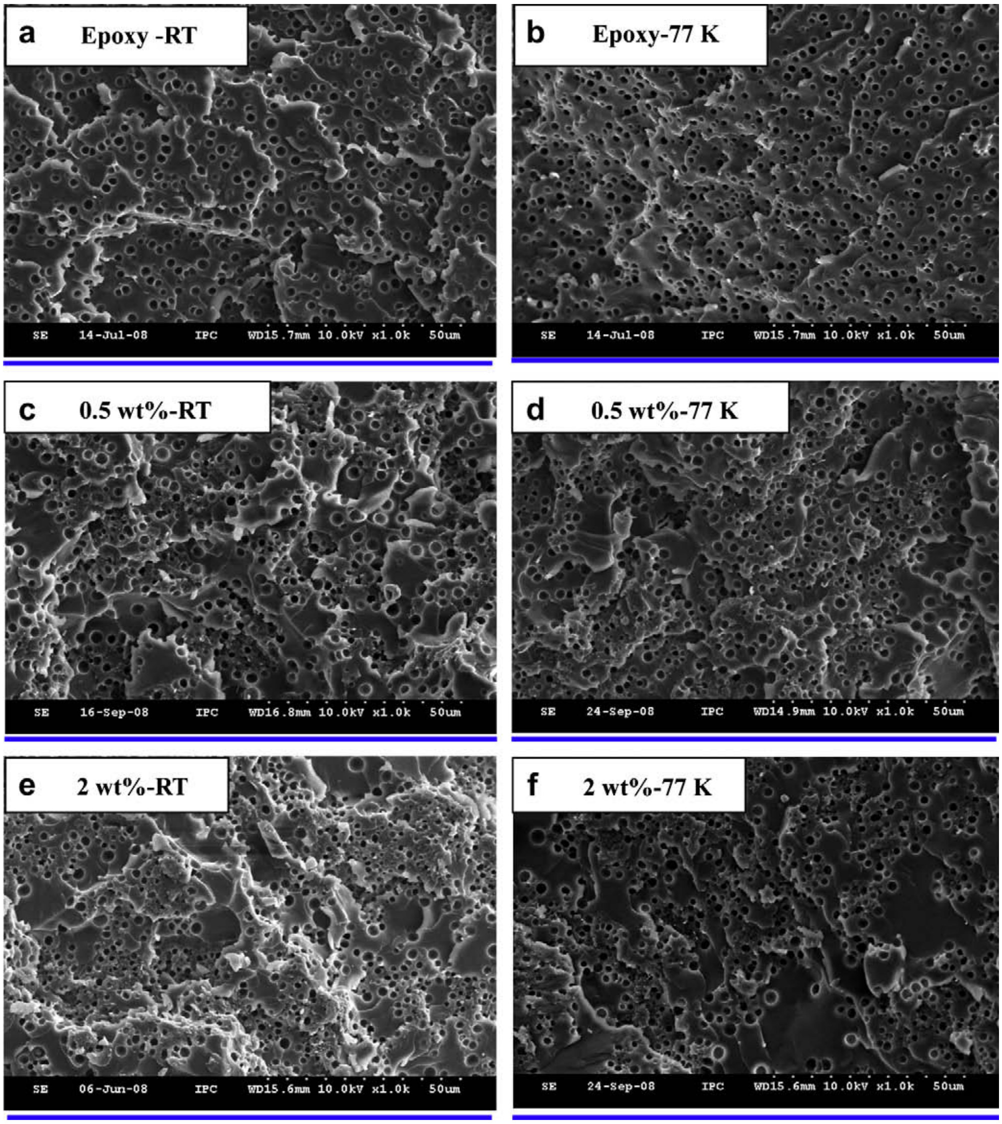
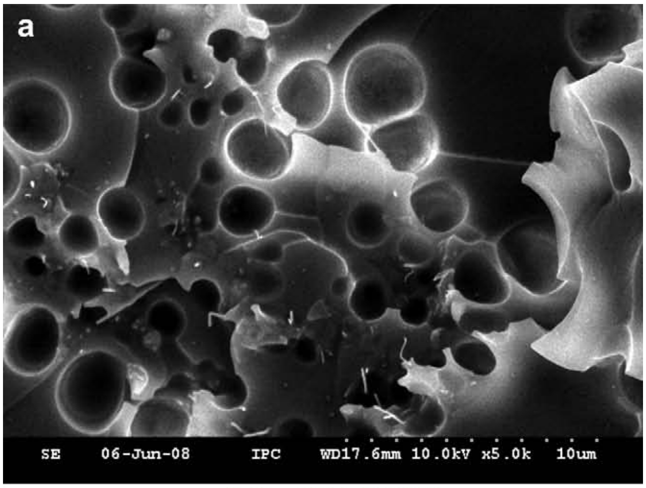


Fig. 5. SEM images of the fracture surfaces of MWCNT/epoxy nanocomposites after impact testing at RT and at 77 K: (a)–(b) the epoxy matrix, (c)–(d) the nanocomposite containing 0.5 wt% CNTs and (e)–(f) the nanocomposite containing 2 wt% CNTs.

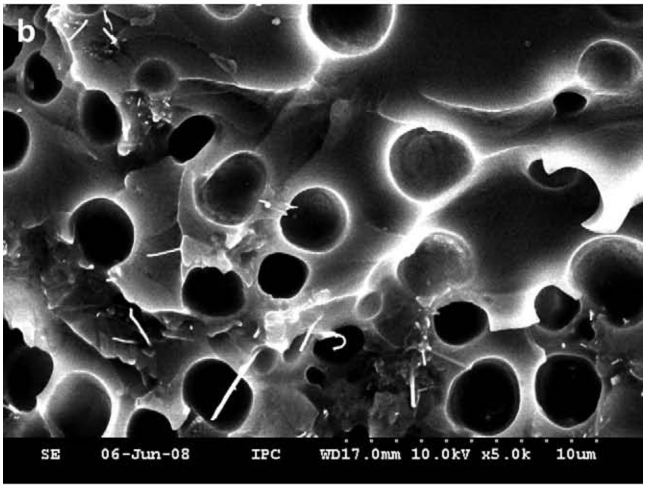
higher than 0.5 wt%. Moreover, it can be seen from Table 1 that the tensile strength at 77 K is consistently higher than that at RT with the same composition. This can be explained as follows. On the one hand, when the temperature decreases from RT to 77 K, the chemical bond and molecules of epoxy matrix will shrink and the binding forces between molecules will become strong. Thus, a larger load will be needed to break the epoxy matrix at 77 K, leading to a higher strength of the epoxy matrix at 77 K than at RT. On the other hand, the thermal contraction of the epoxy matrix due to the decrease of the temperature increased the clamping stress to the carbon nanotubes at 77 K, this would lead to a stronger CNT–epoxy interfacial bonding. As an approximation, the coefficient of thermal expansion (CTE) for the epoxy matrix was around $5.1 \times 10^{-5}\ \mathrm{K}^{-1}$ in the temperature range of liquid nitrogen temperature and RT [17]. The CTE for MWCNTs at RT was reported to be about $0.73–1.49 \times 10^{-5}\ \mathrm{K}^{-1}$ [42]. And the CTE for CNTs at a cryogenic temperature should be lower than this value because thermal expansion coefficient is closely related to thermal oscillation while intensity of thermal oscillation becomes weaker as temperature decreases, leading to a lower CTE. Indeed, as shown in Fig. 3b, the surface of MWCNTs at 77 K is attached with a large amount of epoxy matrix, which is an indication of an excellent CNT–epoxy interfacial bonding since the CNT–epoxy interfacial strength must exceed the yield strength of the epoxy matrix so that the epoxy matrix could be broken and attached on the surface of CNTs. Over 100 measurements were carried out on SEM micrographs of the fractured surfaces of the samples using the software SemAfore 4.0 as shown in Fig. 4 to get the average CNT diameters. The estimated average diameters of CNTs are respectively 93 ± 23 nm and 180 ± 61 nm for the cases of RT and 77 K, confirming that the surfaces of CNTs are quite rough and have been attached with epoxy matrix due to the strong CNT–epoxy interfacial adhesion at 77 K. Otherwise, the CNTs would be pulled out with smooth surfaces. Similarly, a strong interfacial adhesion between carbon fibers and polyamide matrix is also observed at cryogenic liquid nitrogen temperature [43]. A strong CNTs–epoxy interfacial bonding would increase the stress transfer between the epoxy matrix and the CNTs and hence enhance the CNT reinforcing efficiency. As a result, the strength of the epoxy nanocomposites has been significantly enhanced at 77 K and the cryogenic strength is much higher than those at RT. At the 2 wt% CNTs, the reduction in the strength should result from the very poor dispersion (namely aggregates) of CNTs in the epoxy matrix to be shown later.

When the temperature is decreased from RT to 77 K, internal stresses are generated in the epoxy matrix due to thermal contraction. Fracture of the matrix may be induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the epoxy resin [10,19]. In this work, the epoxy matrix has an optimal formulation and has been toughened sufficiently to stand for thermal cycling [37]. Therefore, internal stresses induced due to temperature change would not damage the epoxy matrix.

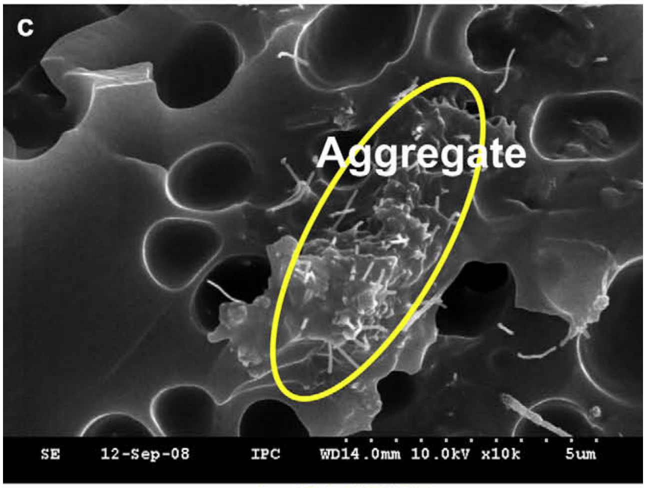
Moreover, Table 1 exhibits that Young's modulus of MWCNT/epoxy nanocomposites at both RT and 77 K increased consistently with increasing the MWCNT content. Young's modulus was increased respectively by 17.2% and 20.7% at RT and 77 K for the nanocomposites containing the 2 wt% MWCNTs compared with the epoxy matrix. Besides, Young's modulus at 77 K is higher than that at RT with the same composition. This is due to the fact that on the one hand, the molecules of the epoxy matrix become stiffer due to the restrained mobility of the molecules when the temperature decreases from RT to 77 K; on the other hand, any material would become stiffer at cryogenic temperatures and thus the CNTs would also become stiffer at 77 K than at RT. As a result, in terms of the theories for the particulate polymer composites [44] or short fiber reinforced polymer composites [45,46], it can be easily inferred that Young's modulus of the MWCNTs/epoxy nanocomposites must be higher at 77 K than at RT.



0.02 wt % MWCNTs



0.5 wt% MWCNTs



2 wt% MWCNTs

Fig. 6. SEM images of the tensile fracture surfaces of MWCNT/epoxy nanocomposites showing the dispersion of CNTs in the epoxy matrix: (a) 0.02 wt% CNTs, (b) 0.5 wt% CNTs and (c) 2 wt% CNTs.

Furthermore, it can be seen from Table 1 that the failure strain can be enhanced by the introduction of CNTs at appropriate contents into the epoxy matrix. The epoxy matrix is actually a blend

Table 2
Impact strength at RT and 77 K of the epoxy matrix and epoxy nanocomposites.

MWCNTs content (wt%)	Impact strength (kJ/m^2)	
	RT	77 K
0	37.80 ± 3.53	23.96 ± 2.34
0.02	38.74 ± 2.53	30.92 ± 2.29
0.05	39.62 ± 3.24	31.48 ± 2.66
0.2	41.39 ± 1.59	32.35 ± 4.30
0.5	49.46 ± 4.52	35.56 ± 1.92
1	42.85 ± 0.87	26.32 ± 3.74
2	39.95 ± 1.41	22.87 ± 1.58

consisting of brittle epoxy phase (DGEBF) and soft second DILUENT phase [36], showing a sea–island structure as shown in Fig. 5. The soft second DILUENT phase (island) is uniformly distributed in the brittle DGEBF phase (sea) and thus good cryogenic mechanical properties have been achieved [37]. In this work, MWCNTs are employed to further improve the cryogenic mechanical properties of brittle epoxy resin (DGEBF).

It can be seen from Fig. 6a–b that CNTs are selectively dispersed in the brittle epoxy phase (DGEBF). Of course, CNTs were also dispersed at the boundaries of the two phases. The boundaries can be regarded as part of the preliminary DGEBF phase. It is well accepted that brittle epoxy resins can be easily toughened by introduction of CNTs [26,27,40]. Therefore, the brittle epoxy phase (DGEBF) would be toughened by introduction of CNTs so that failure strain of the epoxy matrix can be enhanced by the addition of CNTs. When the CNTs content is high, the aggregated CNTs have been observed as shown in Fig. 6c. Aggregates of CNTs would give rise to weak CNT–polymer interactions and high stress concentrations similar to clay–epoxy nanocomposites [41]. As a result, both of these factors lead to the reduction of the failure stain. Similarly, this can also be used for explanation of the result for the impact strength to be presented below.

Charpy impact testing of the epoxy matrix and the MWCNT/epoxy nanocomposites was conducted at both RT and 77 K and the results are shown in Table 2. It can be seen that the introduction of MWCNTs at appropriate contents into epoxy resin can effectively enhance the impact strength (or energy) of the cured epoxy resin. When the CNT content is 0.5 wt%, the impact strength is greatly enhanced by 76.7% and 51.4% at RT and 77 K, respectively. This can be explained using the selective dispersion of CNTs in the brittle

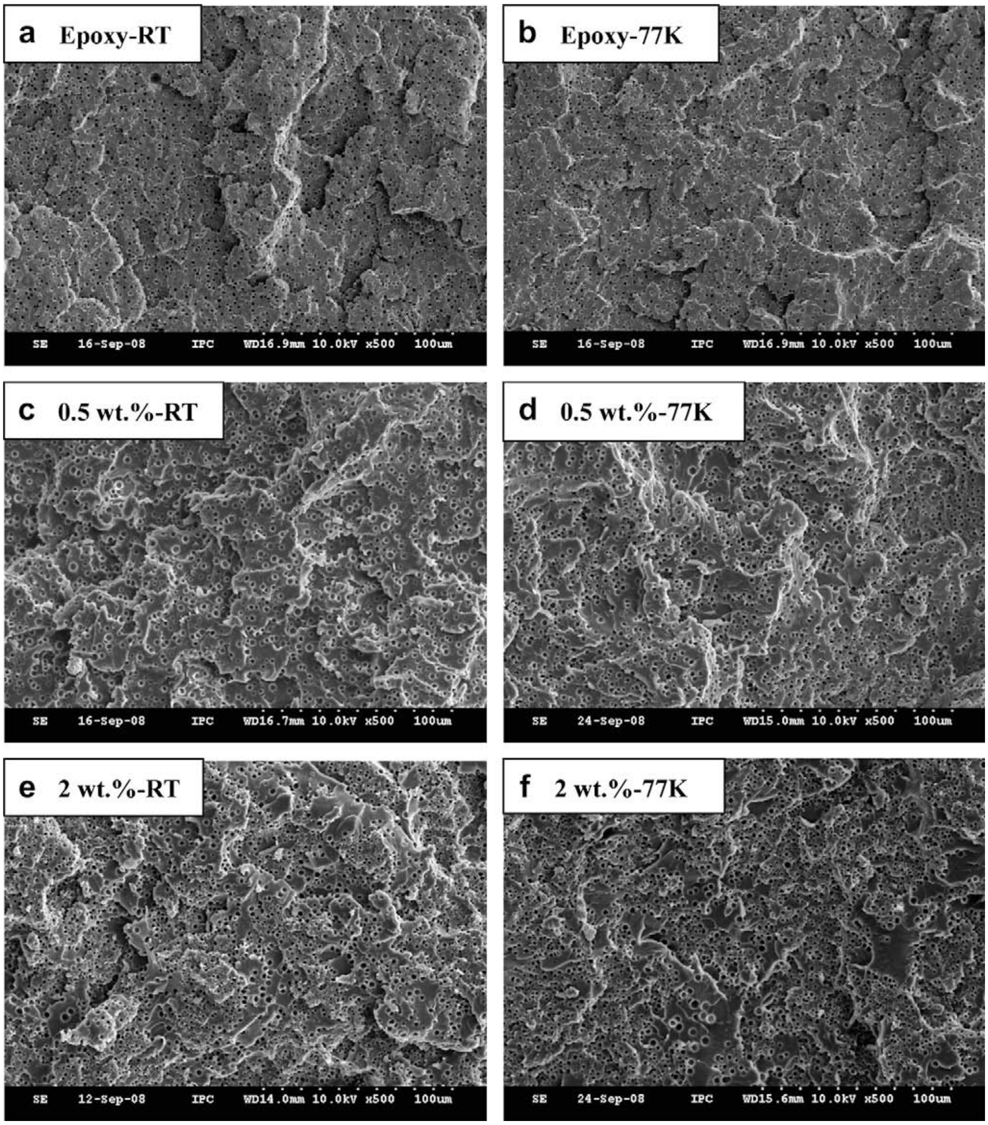


Fig. 7. SEM images with a relatively low magnification of the fracture surfaces of MWCNT/epoxy nanocomposites after impact testing at RT and at 77 K: (a)–(b) the epoxy matrix, (c)–(d) the nanocomposite containing 0.5 wt% CNTs and (e)–(f) the nanocomposite containing 2 wt% CNTs.

Table 3
Variance of the second phase size with the MWCNT content at RT and 77 K.

MWCNT content (wt%)	Second phase size (μm)	
	RT	77 K
0	1.88 ± 0.32	1.86 ± 0.29
0.02	1.90 ± 0.41	1.92 ± 038
0.05	1.95 ± 0.38	1.98 ± 0.45
0.2	2.03 ± 0.47	2.06 ± 0.39
0.5	2.05 ± 0.40	2.04 ± 0.49
1	2.06 ± 0.50	2.09 ± 0.43
2	1.98 ± 0.48	1.96 ± 0.39

DGEBF phase or at the boundaries of the two phases. This can be easily understood in terms of the synthetic sequence because MWCNTs were first mixed with DGEBF and the resulting mixture was then blended with DETD and DILUENT. Since the brittle DGEBF phase can be effectively toughened by introduction of CNTs, the impact strength (or energy) can thus be greatly enhanced by the addition of CNTs at appropriate contents when no aggregates of CNTs occur.

Table 2 also shows that the impact strength is larger at RT than at 77 K with the same composition. This is mainly because the molecular mobility of the epoxy matrix would be lowered when the temperature was down to 77 K from RT. When rapid impact loading was applied to the samples, it would be difficult to yield plastic deformation and hence relatively low impact energies were required to break the samples at 77 K.

In order to get insight into the details of the fracture surfaces, SEM images with a relatively low magnification were taken as shown in Fig. 7. It is clear that the fracture surfaces after introduction of carbon nanotubes become rougher compared to those of the pure epoxy matrix due to the resistance of CNTs to the propagation of microcracks similar to our previous study on clay–epoxy system [18]. The rougher surfaces of the nanocomposites than those of the pure epoxy matrix are indicative of the improvement in impact strength at low CNT contents. At the 0.5 wt% CNT content, the impact strength shows the highest value. At higher CNT contents, the agglomeration of CNTs occurs, this would give rise to weak CNT–polymer interactions and high stress concentrations, leading to the reduction of the impact strength. The above two competing effects result in the fact that the impact strength decreases with further increasing the CNT content.

The second phase sizes were also measured using the software SemAfore 4.0 from the SEM images of the fracture surfaces. The results are presented in Table 3. It is shown that introduction of CNTs indeed has an effect on the domain size and the addition of CNTs leads to an increase of the second phase domain size to somewhat degree possibly due to the constraint of the dispersivity of the DILUENT in the epoxy composite system by introduction of CNTs causing the increase of the viscosity of the nanocomposite system. Nevertheless, there is no direct relationship between the second phase particle size and the mechanical properties since the size changes not too much (only in micrometer scale).

4. Conclusions

In this study, the MWCNT/epoxy nanocomposites were fabricated using the ultrasonic technique and the reinforcement of the epoxy resin by MWCNTs has been examined for enhancing the cryogenic mechanical properties of epoxy resins. The reinforcing efficiency of CNTs for the cryogenic mechanical properties of epoxy resin is higher at 77 K than at RT since the CNT–epoxy interfacial bonding becomes stronger at 77 K than at RT due to thermal contraction effect. As a result, the introduction of MWCNTs at appropriate contents into the epoxy matrix has effectively enhanced the cryogenic tensile strength, Young's modulus, failure strain and impact strength. Consequently, carbon nanotubes are promising reinforcements for epoxy resins to be employed in cryogenic engineering applications.

Acknowledgements

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