Toughening of Cycloaliphatic Epoxy Resin by Multiwalled Carbon Nanotubes

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ABSTRACT: The toughness of cycloaliphatic epoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ERL-4221) has been improved by using multiwalled carbon nanotubes (MWCNTs) treated by mixed acids. The MWCNT/ERL-4221 composites were characterized by Raman spectroscopy and their mechanical properties were investigated. A significant increase in the tensile strength of the composite from 31.9 to 55.9 MPa was obtained by adding only 0.05 wt % of MWCNTs. And a loading of 0.5 wt % MWCNTs resulted in an optimum tensile strength and cracking energy, 62.0 MPa and 490 N cm, respectively. Investigation on the morphology of fracture surface of the composites by field emission scanning electron microscopy demonstrated the crack pinning-front bowing and bridging mechanisms of toughening. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1351–1357, 2008

Key words: cycloaliphatic epoxy resin; nanocomposites; multiwalled carbon nanotubes; toughness; Raman spectroscopy

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,[1] both theoretical and experimental results have suggested that CNTs have extraordinary physical and mechanical properties[2–6] due to their unique atomic structure and high aspect ratio, which make them attract wide attention in various fields,[7–9] especially as an ideal reinforcing phase in polymer matrix composites.[10–12] The studies on the CNT-reinforced polymer composites have been reported with reference to various polymer matrices, including thermoplastic and thermosetting matrices such as polyethylene,[13] polypropylene,[14] poly(methylmethacrylate),[15] polystyrene,[16] polyurethane,[17] and epoxy.[18]

Epoxy resins are the most important class of thermosetting resins, which are widely used in various application areas involving adhesives, coatings, and constructions.[19,20] Cycloaliphatic epoxy resin, characterized by epoxy ring linking to rigid cycloaliphatic ring structure and without any aromatic unsaturation, is an important embranchment of epoxy resins.

Because of its low viscosity before curing, combined with outstanding heat and chemical resistance, superior mechanical and electrical properties after curing, cycloaliphatic epoxy resin has been considered as a promising candidate for future electronic encapsulating materials.[21,22] Unfortunately, its potential applications in these more sophisticated areas have been largely hampered by its inherent brittleness and poor resistance to crack propagation arisen from its high-crosslinked structure. Numerous previous studies have reported that the toughening of the traditional epoxy resins has been achieved without loss of mechanical properties with the modification of nanofillers involving nano-SiO_2 particles, organically modified clay minerals, zeolites or aerogels, layered silicates, CNTs, and so on.[23–26] In the previous work,[27] we reported that the incorporation of nano-SiO_2 effectively improved the toughness of cycloaliphatic epoxy resin as well as the thermal stability. To our best intelligence, an examination of literatures indicated that there was no report on the modification of cycloaliphatic epoxy resin using CNTs as modifiers.

In this research, multiwalled carbon nanotubes (MWCNTs) were used to toughen the acid anhydride-cured cycloaliphatic epoxy system. Several studies have described the fact that efficient utilization of the CNTs in composites depends strongly on their homogeneous dispersion in the matrix without destroying the integrity of the CNTs.[28–31] Nevertheless, intermolecular van der Waals attraction among tubes, combined with their high surface area and
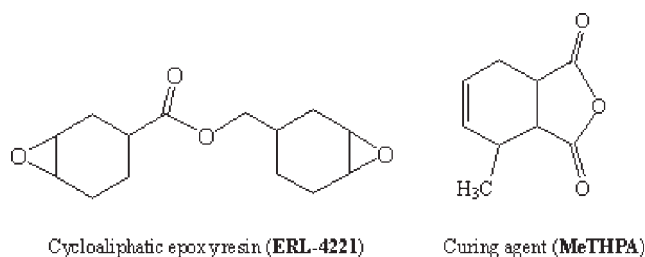
Scheme 1 Chemical structures of the epoxy and curing agent.

high aspect ratio, often leads to significant agglomeration, thus fails to transfer their potential mechanical properties to the matrix effectively. In the present studies, the mixed acid treatment of MWCNTs and an ultrasonic vibration were used to achieve the homogeneous dispersion of MWCNTs throughout the cycloaliphatic epoxy matrix. The effects of the filler content of MWCNTs on the mechanical properties of the matrix were investigated.

EXPERIMENTAL

Materials

The cycloaliphatic epoxy resin, a low viscous 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (ERL-4221), was purchased from Tianjin (China), and methyltetrahydrophthalic anhydride (MeTHPA, Puyang Huicheng Chemicals, Henan, China) was used as a curing agent. The chemical structures of the epoxy and curing agent are presented in Scheme 1. MWCNTs, 20–40 nm in diameter and 5–15 μm long, were obtained from the Shenzhen Nanotech Port, China.

Purification of MWCNTs

To remove the impurities such as carbon black and catalyst particles and to generate functional groups on the surfaces of the nanotubes, the raw MWCNTs were treated with 20% hydrofluoric acid for 3 h under magnetic stirring at room temperature and then filtered with a ultrafiltration membrane and washed with distilled water for several times. Subsequently, the residue was refluxed in 20% nitric acid for 5 h at 100°C and then filtered and washed with distilled water until the pH value of the MWCNT dispersion solution reached seven. The resulted material was dried overnight under vacuum at 60°C.

Preparation of MWCNT/cycloaliphatic epoxy composites

Both ERL-4221 and the purified MWCNTs were dispersed in THF (tetrahydrofuran). Then the compos-

ite samples, with different MWCNT loadings, were prepared by mixing the desired amount of MWCNTs with the epoxy resin by vigorous stirring at room temperature for 1 h. This was followed by sonication for another 1 h. The solvent in the system was then removed under reduced pressure. Finally, a curing agent was added to the MWCNT/epoxy composites at a stoichiometric ratio. The mixture of MWCNTs, epoxy resin, and curing agent were blended under vacuum for another 30 min at 30°C. Then, the mixture was poured into a steel mold whose surface was treated with a mold-releasing agent, and all samples were cured at 100°C for 5 h, and at 170°C for 6 h, followed by postcuring at 200°C for 2 h.

Measurements

A transmission electron microscopy (TEM) image of the purified MWCNTs was obtained with a JEM-3010 microscope. The Raman bands of MWCNTs and MWCNT/epoxy composites were examined by using a LABRAM-010 Raman microprobe system with the 632.8-nm red line of a He–Ne laser. To characterize the purified MWCNTs, the infrared spectrum was recorded on a PerkinElmer Spectrum one Fourier transform infrared spectrometer (FTIR).

Impact tests were performed by using a falling dart impact tester with a dart weight of 1 kg at room temperature. The specimens for impact testing were tinplates coated by neat epoxy or MWCNT/epoxy cured system with a coating thickness of 40–50 μm approximately. The size of tinplate was 120 × 70 × 1 mm. Methodology for calculating cracking energy was described in the previous report.[27]

Tensile strength and elongation at break were determined by WDW-10 electronic universal testing machine. Dog-bone-shaped specimens according to ASTM-D638 standard were selected in tensile tests. Tensile tests were carried out at a velocity of a 2 mm/min. For each specimen set, at least five specimens were tested, and the components and contents of all samples were described in detail in Table I. A JSM-6700 field emission scanning electron microscopy (FESEM) was used to investigate the

TABLE I
Samples of MWCNT/Epoxy Composites with Different MWCNT Contents

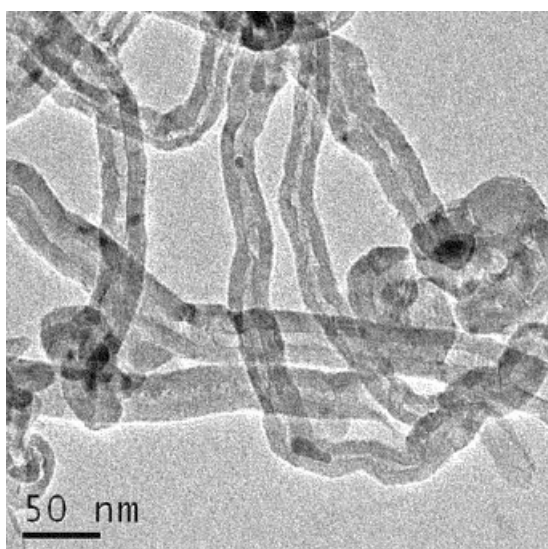| Sample number	ERL-4221 (wt %)	MeTHPA (wt %)	MWCNTs (wt %)
MWCNTs-0	100	104	0
MWCNTs-1	100	104	0.05
MWCNTs-2	100	104	0.10
MWCNTs-3	100	104	0.50
MWCNTs-4	100	104	1.00

Figure 1 TEM micrograph of purified MWCNTs.

fracture morphology of the composites after tensile test.

RESULTS AND DISCUSSION

Charaterization of purified MWCNTs

The TEM image of the purified MWCNTs showed that no structure changes took place with MWCNTs (see Fig. 1). The Raman bands of MWCNTs, as shown in Figure 2, exhibited two strong bands at 1320 cm^{-1} and 1568 cm^{-1}, confirming the multi-walled nature of the CNTs. The band at 1568 cm^{-1} (G band) corresponds to the Raman allowed optical mode E_{2g} of two-dimensional graphite, whereas the band at 1320 cm^{-1} (D band) is mainly derived from
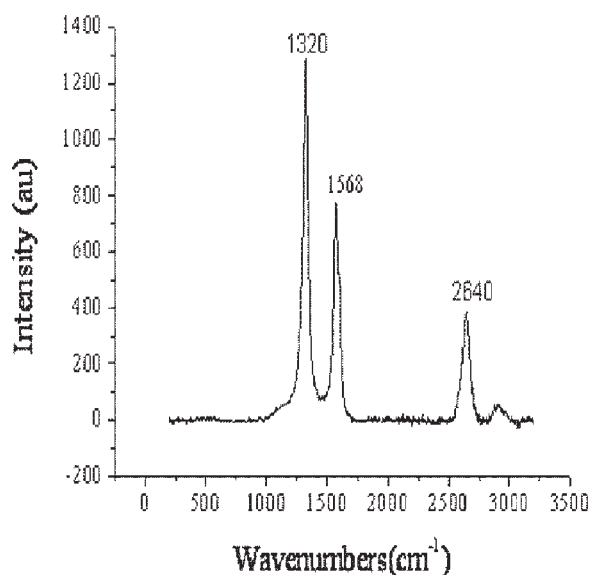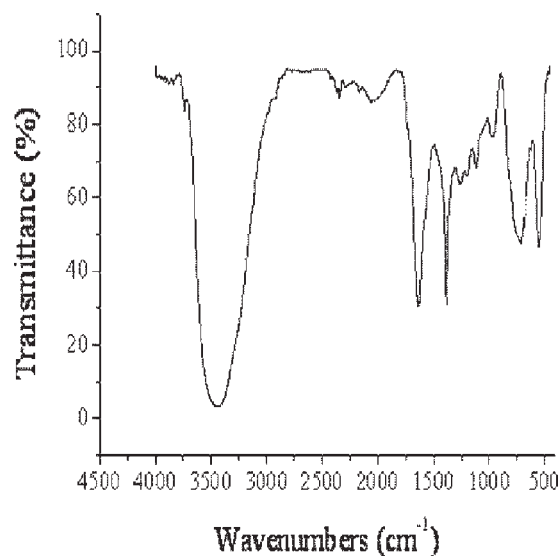

Figure 3 IR spectrum of purified MWCNTs.

disordered carbon defects of MWCNTs.[32] The relative intensity of the D band and G band (I_D/I_G) was more than one, implying that the mixed acid treatment caused surface disfigurements of MWCNTs. The FTIR spectrum of the purified MWCNTs was shown in Figure 3. It was obvious that the characteristic bands corresponding to the vibrations of —OH and —COOH groups were observed at 3454 cm^{-1} and 1640 cm^{-1}, respectively.

Raman spectra of MWCNT/epoxy composites

The high frequency parts of the Raman spectra of the MWCNT/epoxy composites with different MWCNT loadings were shown in Figure 4.
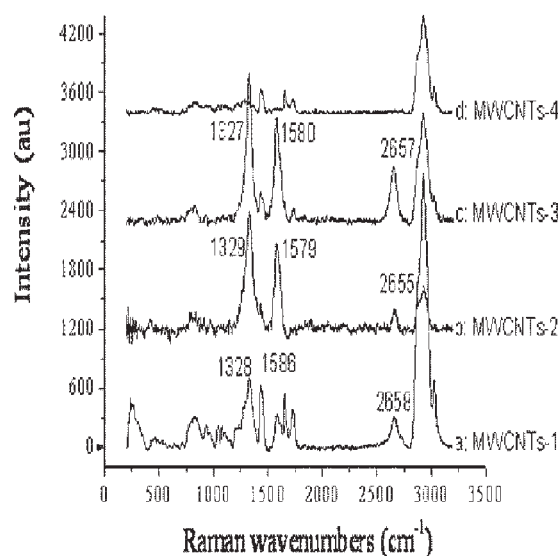

Figure 2 Raman spectrum of purified MWCNTs.

Figure 4 Raman spectra of MWCNT/epoxy composites.

Sample number	Tensile strength σ_t (MPa)	Elongation at break ε_t (%)	Cracking energy $E/N\cdot$(cm)
MWCNTs-0	31.9	2.38	196.0
MWCNTs-1	55.9	3.07	245.0
MWCNTs-2	55.0	3.57	273.6
MWCNTs-3	62.0	3.60	490.0
MWCNTs-4	58.4	3.00	372.4

As illustrated in Figure 4(a–c), the spectra exhibited similar peaks at $\sim$ 1328 and 1580 cm^{-1}, and the peak intensity was enhanced with the increase of the content of MWCNTs in the composites. In the case of the content of MWCNTs over 1.0 wt %, however, dissymmetrical G and D bands did not appear probably for the MWCNT agglomeration. From the Raman characterization of the composites, it was also observed that the G and D modes exhibited a definite upward shift. This suggested that MWCNTs were dispersed in the epoxy matrix and interacted with surrounding epoxy resin.[33]

Mechanical properties of MWCNT/epoxy composites

Results obtained from the tension tests and impact tests were tabulated in Table II as tensile strength (σ_t), elongation at break (ε_t), and cracking energy (E).

The addition of MWCNTs obviously affected the mechanical properties of the MWCNT/epoxy composites. When lower amounts of MWCNTs were added in the composites, the mechanical properties of the composites were enhanced with the increment of the addition content of MWCNTs. The MWCNT/ epoxy composite with the addition content of MWCNTs up to 0.5 wt % exhibited the best comprehensive performance. In comparison with the case of neat epoxy, its tensile strength, elongation at break, and cracking energy were improved by 94.4% (from 31.9 to 62.0 MPa), 51.3% (from 2.38 to 3.60%), and 150.0% (from 196.0 to 490.0 N), respectively. Increasing the addition content up to 1.0 wt % did not lead to a further improvement in fracture toughness.

Microstructures of MWCNT/epoxy composites

As shown in Figure 5, the fracture surfaces of the neat epoxy and the MWCNT/epoxy composites were comparatively examined by FESEM. It could be observed that the neat cycloaliphatic epoxy resin indicated a typical brittle fracture behavior by exhibiting a relatively smooth fracture surface with cracks almost parallel to the crack-propagation direction [Fig. 5(a)]. Compared to the case of the neat epoxy, the fracture surfaces of the composites presented considerably different fractography features [Fig. 5(b–e)]. The effect of the addition of MWCNTs on the toughness of the composites could also be highlighted from these micrographs of fracture surfaces. With the addition of only 0.05 wt % of MWCNTs, the fracture surface showed a mass of dendriform cracks [see Fig. 5(b)], which meant that the crack propagation in the composite of MWCNTs-1 was resisted by rigid and strong MWCNTs, and the primary crack front had to bend between tubes, then more energy was needed for a crack to propagate to produce secondary crack, thus accounting for the improved strength and toughness of the specimen of MWCNTs-1. The magnified image of Figure 5(b), as shown in Figure 5(b1), detailed that MWCNTs were homogeneously located in the epoxy matrix and pulled out slightly. This phenomenon demonstrated the existence of the strong interfacial strength between MWCNTs and the matrix resin, which attributed to an efficient transfer of the stress between the matrix and the CNTs. —COOH and —OH groups on the surface of MWCNTs could be responsible for the formation of the interfacial strength through covalent bonds to the polymeric matrix. As the loading of MWCNTs was increased, the roughness of the fracture surfaces of the composites was enhanced. Both out-of-order cracks and plastic deformation of the epoxy matrix characterized the fracture surfaces of MWCNTs-2 and MWCNTs-3 [Fig. 5(c,d)], moreover, dimple fracture appeared in their fractographies. In Figure 5(c1,d1), it was shown that many MWCNTs traveled across the crack surfaces during the fracture process, as indicated by black arrows, which indicated that MWCNTs also resisted the crack propagation by a bridging effect, thus toughening the epoxy matrix. However, when the addition content of MWCNTs increased up to 1.0 wt %, MWCNTs tended to be agglomerated, as shown in Figure 5(e1); as a result, the toughening efficiency decreased with the further increase of the MWCNT content, and the tensile strength, elongation at break, and cracking energy of MWCNTs-4 were markedly lower than those of MWCNTs-3 (Table II). Figure 5(e) exhibited steplike fracture of MWCNTs-4, which supported that the agglomeration of MWCNTs resulted in stress concentration in local areas, thus accounting for the failure of the composites. Therefore, the homogeneous dispersion of MWCNTs in the cycloaliphatic epoxy matrix was essential to strengthening and toughening the MWCNTs/ERL-4221 composites; in doing so, MWCNTs played a combining role of crack pinning-front bowing and bridging.
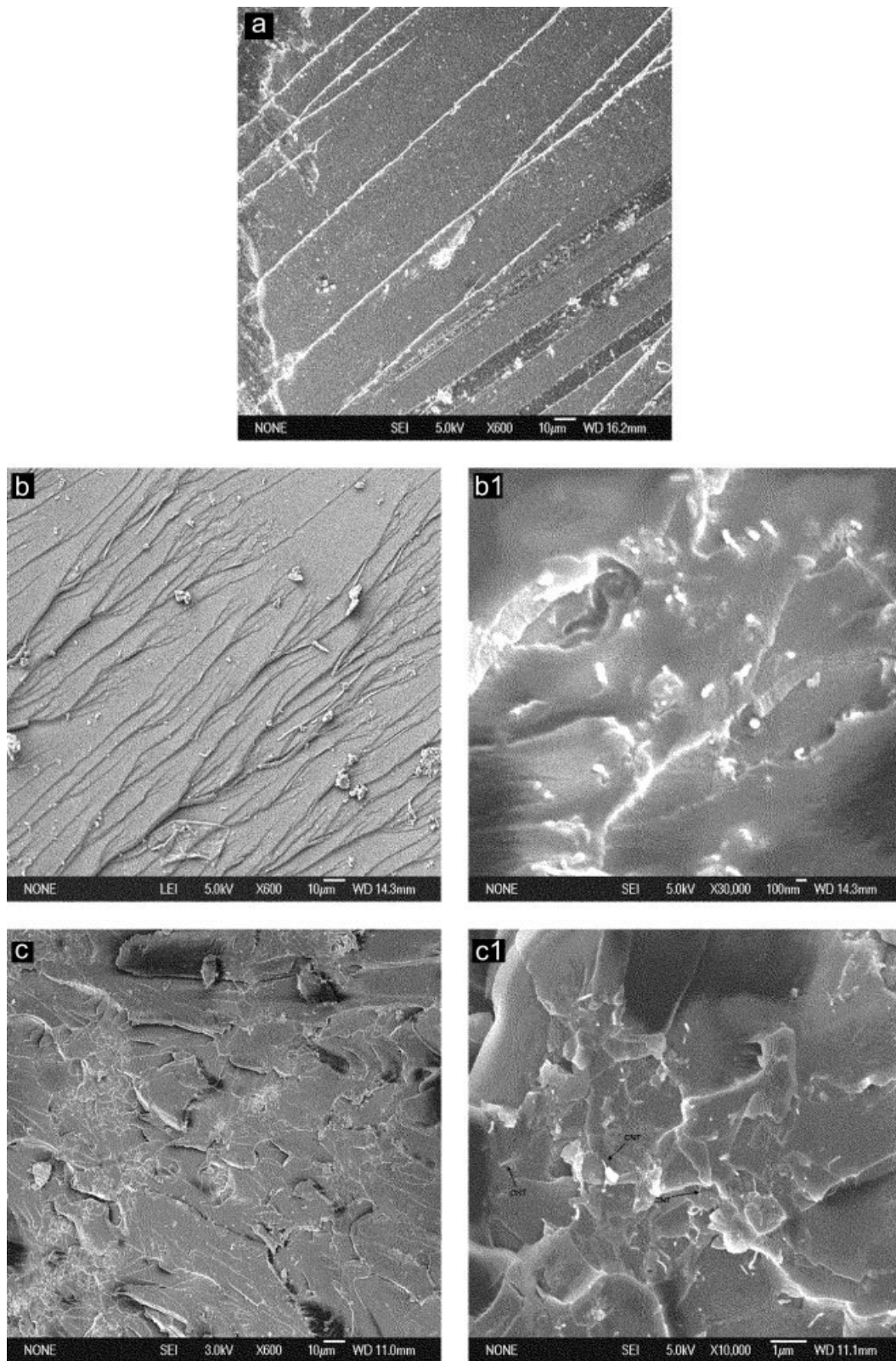
Figure 5 SEM micrographs of fracture surfaces for MWCNT/epoxy composites. (a) MWCNTs-0 (×600), (b) MWCNTs-1 (×600), (b1) MWCNTs-1 (×30,000), (c) MWCNTs-2 (×600), (c1). MWCNTs-2 (×10,000), (d) MWCNTs-3 (×600), (d1). MWCNTs-3 (×10,000), (e) MWCNTs-4 (×600), and (e1) MWCNTs-4 (×10,000).
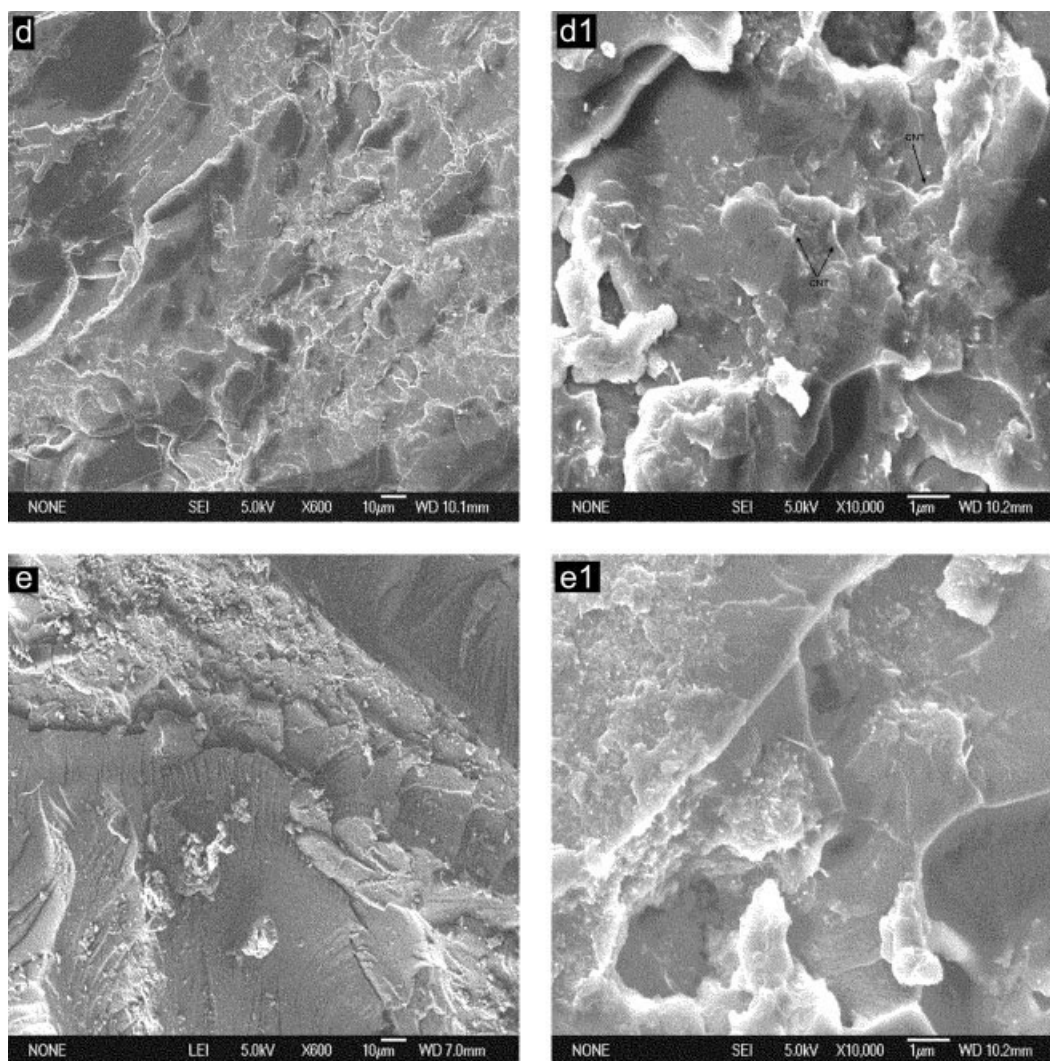
Figure 5 (*Continued from the previous page*)

CONCLUSIONS

Improvement of the toughness of cycloaliphatic ep-
oxy resin ERL-4221 by MWCNTs was studied. The
Raman spectra of the MWCNT/ERL-4221 compo-
sites indicated that MWCNTs dispersed homogene-
ously in ERL-4221 matrix and bonded strongly with
the epoxy matrix. It was discovered that the addition
of MWCNTs improved the strength and toughness
of ERL-4221 system prominently. Investigation on
the morphology of the fracture surface of the compo-
sites demonstrated the crack pinning-front bowing
and bridging mechanisms of toughening.

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