Improving the dispersion and flexural strength of multiwalled carbon nanotubes–stiff epoxy composites through β-hydroxyester surface functionalization coupled with the anionic homopolymerization of the epoxy matrix

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Abstract

Multiwalled carbon nanotubes (MWNTs) were functionalized in a two-step acid-epoxy functionalization process, in which suitable surface condition and reactivity compatible with the DGEBA epoxy resin was introduced. The use of (4-dimethylamino)-pyridine as an initiator for DGEBA homopolymerization produced covalent bonds between the functionalized MWNTs and the epoxy matrix through chain transfer reactions involving the secondary hydroxyls. This process yielded uniform MWNTs–stiff epoxy composites with significant enhancement in flexural strength without sacrificing the elastic modulus when compared to the neat resin.
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1. Introduction

The synthesis of carbon nanotube (CNT)–epoxy nanocomposites with enhanced thermal and mechanical properties requires generating uniform dispersion of the nanotubes and strong interfacial bonding for load transfer [1]. This can be accomplished by chemical modification of the surface of the CNTs. For example, when the sidewalls of CNTs were functionalized via free-radical polymerization of methyl methacrylate, an 11% increase in strength and a 21% increase in modulus were observed for an epoxy composite with 1 wt% CNTs [2]. In contrast, addition of untreated CNTs produced a sharp decrease in both properties. In another study, single-walled carbon nanotubes (SWNTs) were functionalized using a combination of open-end oxidation and sidewall fluorination [3]. Epoxy composites containing 1 wt% of these functionalized nanotubes exhibited a 30% increase

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in modulus and 18% increase in tensile strength compared to the unfilled epoxy. Similarly, the use of 0.3 wt% of fluorinated single-wall carbon nanotubes to modify an epoxy-anhydride matrix increased the storage modulus by 20% without sacrificing impact strength [4]; on the other hand, the stiffness of the cured epoxy system exerted a huge effect on the properties of the resulting composites. Drops in reinforcing properties were observed in epoxy systems with increased stiffness [5]. The interaction between the polymer chain and the functionalized carbon nanotubes as well as their relative motion dominates the final strengthening effect of these nano reinforcements.

In order to overcome the above mentioned drawbacks for the carbon nanotube–stiff epoxy systems, grafting a chemical structure to the surface of the multi-walled nanotubes (MWNTs) that is identical to that of the epoxy precursor in which the final dispersion will be prepared is an ideal choice, through which a uniform dispersions of functionalized MWNTs and a covalently bonded interface between the matrix and the reinforcement in the epoxy network could be attained [6]. Therefore, a good surface treatment of MWNTs for use in epoxy composites is to attach an epoxy monomer to a previously acid-functionalized nanotube [7]. The reaction between carboxylic and epoxy groups is catalyzed by different bases, such as tertiary amines, KOH, and triphenylphosphine [8,9]. Using KOH as a catalyst, a diepoxide monomer based on diglycidylether of bisphenol A (DGEBA) can be covalently bonded to previously COOH–functionalized MWNTs according to Eitan et al. [7]. However, they reported that no free epoxy groups of DGEBA were retained at the surface of the MWNTs (opening of both epoxy rings in these DGEBA molecules). Thus, the problem of attaining covalent bonding of DGEBA–functionalized MWNTs with the epoxy matrix remains unsolved.

The purpose of this paper is to show that the approach of Eitan et al. [7] for functionalizing MWNTs can be coupled with a suitable chemistry for the synthesis of the epoxy network. Secondly, this combined approach would achieve both uniform dispersions of MWNTs and the formation of covalent bonds on the interface. The incorporation of these MWNTs would lead to improvements for the mechanical properties of a stiff epoxy system, the brittleness of which has always been a limiting issue for the application of this class of materials.

In this work, multiwalled carbon nanotubes (MWNTs) were functionalized in a two-step process. First, carboxyl groups were introduced by a standard oxidation procedure. Subsequently, these groups were reacted with a monoepoxide (phenyl glycidyl ether, PGE), or with a diepoxide based on diglycidyl ether of bisphenol A (DGEBA), using triplenylphosphine (TPP) as catalyst, yielding β-hydroxyester groups attached to the surface of MWNTs. Thus, three different types of functionalized MWNTs were obtained: COOH–MWNTs (after the first step), and PGE–MWNTs and DGEBA–MWNTs (after the second step). The anionic homopolymerization of an epoxy monomer initiated by a tertiary amine, 4-dimethylamino pyridine (DMAP), provides the possibility of covalently bonding COOH–MWNTs, PGE–MWNTs and DGEBA–MWNTs to the epoxy matrix. The primary reactions taking place in a medium containing an epoxy monomer (DGEBA), a tertiary amine and species with COOH and OH groups are indicated in Fig. 1 [10]. The epoxy-acid reaction leads to formation of β-hydroxyester bonds. Chain transfer reactions involving a propagating alkoxide anion and the secondary hydroxyls of the β-hydroxyester groups provide a covalent coupling of PGE–MWNTs and DGEBA–MWNTs with the epoxy matrix (reactions 4 and 5 in Fig. 1).

2. Experimental section

2.1. Materials

MWNTs were obtained from a commercial source (Shenzhen Nanotech Port Co. Ltd., China). The MWNTs were produced by chemical vapour deposition (CVD) and contained ∼5% impurities, consisting primarily of amorphous carbon and transition metals, such as lanthanum and nickel. The nanotubes were 5–15 μm long and 40–60 nm in diameter (Fig. 2). Two epoxy monomers were selected for this study. The monoepoxide was phenyl glycidyl ether (PGE, Aldrich) and the diepoxide was a commercial monomer based on diglycidylether of bisphenol A (DGEBA, EPON 828, Miller–Stephenson). The initiator selected for DGEBA homopolymerization was 4-dimethylamino pyridine (DMAP, Sigma–Aldrich). Triphenylphosphine (TPP, Aldrich) was employed as a catalyst of the esterification reaction to attach PGE and DGEBA to the surface of acidified-MWNTs. The reactions are illustrated in Fig. 3. Anhydrous dimethylformamide (DMF),
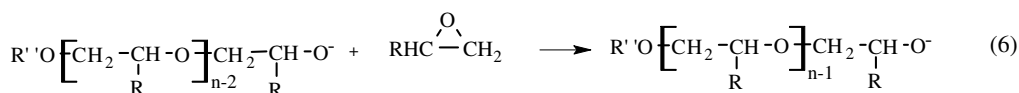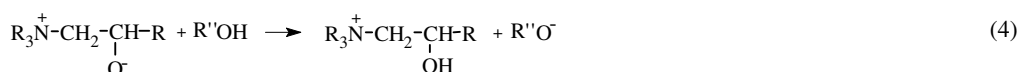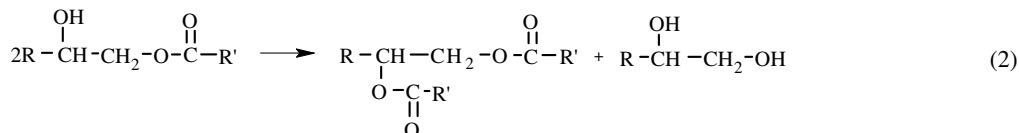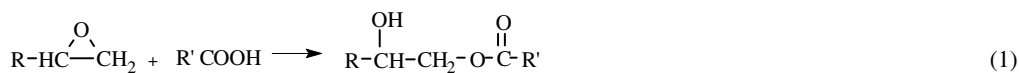
$$R\text{-HC}\overset{O}{-}CH_2 + R'COOH \longrightarrow R\text{-CH-CH}_2\text{-O-}\overset{O}{\underset{}{C}}\text{-R'} \qquad (1)$$

$$2R\text{-CH-CH}_2\text{-O-}\overset{O}{\underset{}{C}}\text{-R'} \longrightarrow R\text{-CH-CH}_2\text{-O-}\overset{O}{\underset{}{C}}\text{-R'} + R\text{-CH-CH}_2\text{-OH} \qquad (2)$$

$$R\text{-HC}\overset{O}{-}CH_2 + R_3N \longrightarrow R_3\overset{+}{N}\text{-CH}_2\text{-CH-R} \qquad (3)$$

$$R_3\overset{+}{N}\text{-CH}_2\text{-CH-R} + R''OH \longrightarrow R_3\overset{+}{N}\text{-CH}_2\text{-CH-R} + R''O^- \qquad (4)$$

$$R''O^- + R\text{-HC}\overset{O}{-}CH_2 \longrightarrow R''O\text{-CH}_2\text{-CH-O}^- \qquad (5)$$

$$R''O\left[\text{CH}_2\text{-CH-O}\right]_{n-2}\text{CH}_2\text{-CH-O}^- + RHC\overset{O}{-}CH_2 \longrightarrow R''O\left[\text{CH}_2\text{-CH-O}\right]_{n-1}\text{CH}_2\text{-CH-O}^- \qquad (6)$$

Fig. 1. Main reactions taking place during the anionic polymerization of an epoxy monomer initiated by a tertiary amine (R'COOH and R″OH represent species present in the reaction medium).
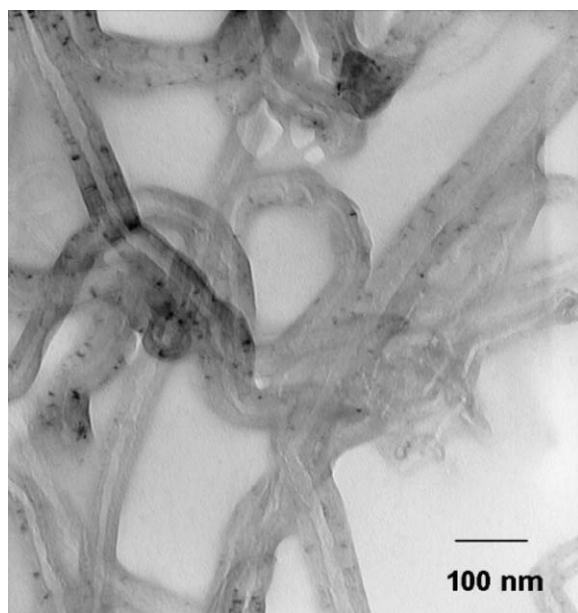

Fig. 2. TEM image of acidified MWNTs.

tetrahydrofuran (THF), and anhydrous ethanol (VWR Scientific) were used as solvents.

2.2. Preparation of COOH–MWNT

MWNTs (1 g) were dispersed in 250 ml of concentrated 3:1 H_2SO_4/70% HNO_3 following the procedure developed by Liu et al. [11]. One-hour sonication and 3-h stirring at room temperature was optimal to achieve moderate oxidation and maintain a high aspect ratio. After the acid treatment 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 MWNTs [12]. The solution was extensively washed again with deionized water until pH value reached 5–6. The acid-treated nanotubes (denoted COOH-MWNTs) were collected on a 0.45 μm PTFE membrane by vacuum filtration and dried overnight in a vacuum oven at 90 °C.

2.3. Preparation of PGE–MWNT and DGEBA–MWNT

The esterification of COOH groups with PGE or DGEBA was carried out in a DMF solution, using TPP as a catalyst (0.1 mole TPP per mole of epoxy groups). The reaction was performed by refluxing at 150 °C under nitrogen for 36 h. (The model reaction of the esterification of benzoic acid by PGE suggested that complete conversion could be attained under these conditions.) After the treatment, PGE–MWNTs and DGEBA–MWNTs were thoroughly washed with ethanol, collected with the PTFE membrane, and dried in a vacuum oven for 24 h.
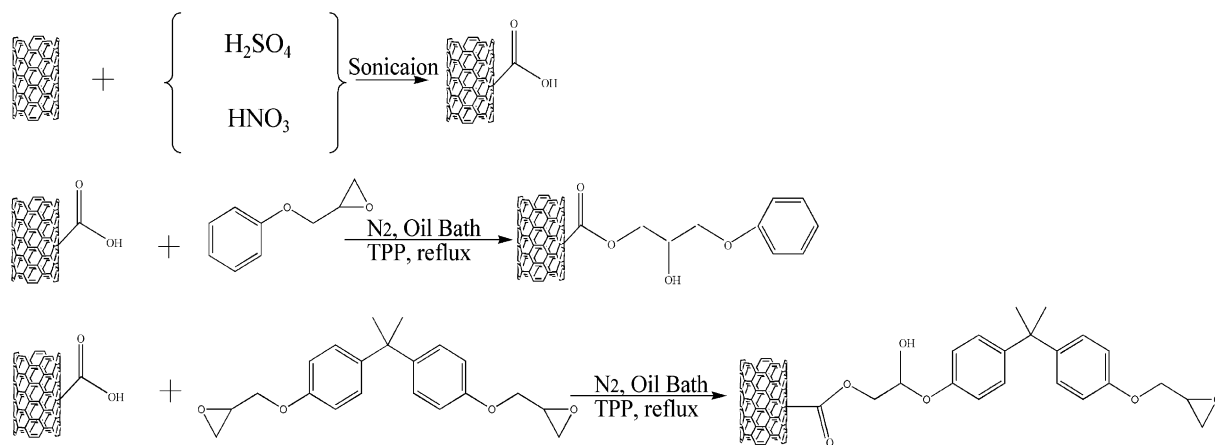
Fig. 3. Scheme of reactions used to functionalize MWNTs.

2.4. Preparation of the MWNT–Epoxy Composites

Unmodified MWNTs, COOH–MWNTs, PGE–MWNTs, and DGEBA–MWNTs were dispersed in THF using bath sonication for 5 min. DGEBA was dissolved in THF (1:1 by volume) in a dual axis high-speed mixer (Keyence HY501). Next, both mixtures were blended in the mixer and then bath-sonicated for another 5 min. Finally, THF was evaporated in a vacuum chamber at 100 °C overnight. DMAP was added to the mixture in a molar ratio of 0.08 mole DMAP per mole of epoxy groups. Further mixing (10 min) and degasification (10 min) were performed with the high-speed mixer. The final blend was cast into an aluminium mold pretreated with a release agent. The following curing cycle reported in the literature for this particular initiator was employed [13]: 3 h at 80 °C, 3 h at 120 °C, and 30 min at 160 °C. Nanocomposites contained 0.5, 1 and 3 wt% MWNTs (for modified-MWNTs, the wt% refers to that of the neat MWNT devoid of the organic part). The neat epoxy samples were also prepared following the same procedure for comparison purposes.

2.5. Characterization

Thermal gravimetry analysis (TGA 2050, TA Instruments) was employed to quantify the wt% of organic part in functionalized-MWNTs. Samples were heated to 800 °C at 10 °C/min under nitrogen. Transmission mode Fourier transform infrared spectroscopy (FTIR, Nicolet 4700) was employed to assess the presence of the organic groups in functionalized-MWNTs. Transmission electron microscopy

(TEM, Philips EM420, 120 KV), and scanning electron microscopy (SEM, Cambridge 360) were used to assess the quality of the dispersion in epoxy composites. Fracture surfaces of specimens pre-chilled by liquid nitrogen were sputter-coated with gold prior to SEM observation. Dynamic mechanical analysis (DMA 2980, TA Instruments) was carried out to determine the glass transition temperature (T_g) of the composites, defined as the onset temperature where the storage modulus exhibited a sharp decrease. Measurements were performed at a heating rate of 10 °C/min and a load frequency of 1 Hz. Flexural tests were performed on a universal testing machine using a four-point fixture according to the ASTM standard D790M, to obtain elastic modulus and flexural strength. Beam-shaped specimens were cut and polished for each type of sample for flexural and dynamic mechanical tests. Five specimens were prepared for each test. TGA (Thermogravimetric analyses) provide a measurement of the mass fraction of organic modifier that can be attached to the MWNTs (Fig. 4).

3. Results and discussion

The solubility of neat and functionalized MWNTs in water and DGEBA is shown in Fig. 5. COOH–MWNTs exhibit a good dispersibility in water but not in DGEBA. In the latter case, COOH-MWNTs agglomerate and settle to the bottom. The functionalization of MWNTs with both PGE and DGEBA led to stable and uniform dispersions in epoxy, as expected.

The observed mass loss of the unmodified MWNTs from TGA is assigned to the presence of
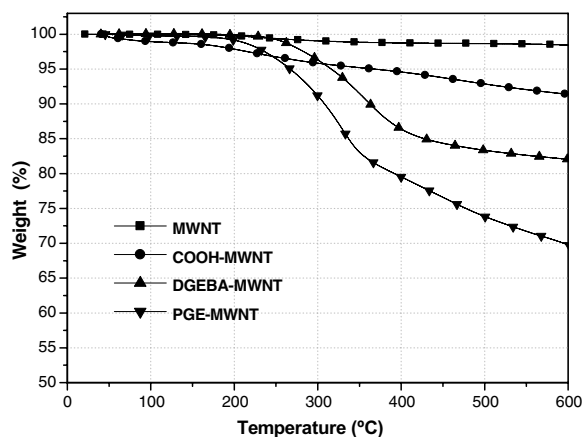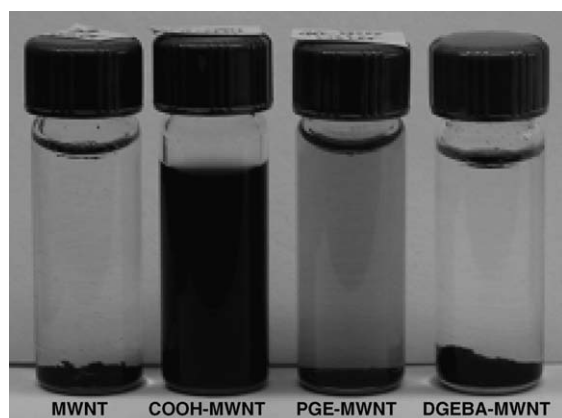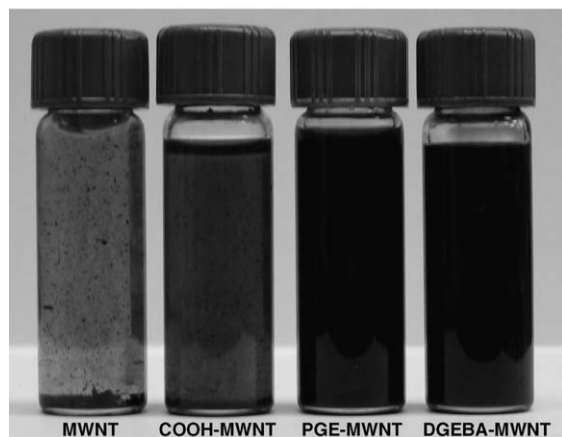
Fig. 4. TGA thermograms of neat and functionalized MWNTs.

Fig. 5. Solubility of neat and functionalized MWNTs in: (a) water and (b) DGEBA (Epon 828).

small amounts of amorphous carbon and impurities. Discounting the mass loss of carbon nanotubes, the mass fraction of organic groups eliminated at 600 °C

was close to 7 wt% for COOH–MWNTs, 16 wt% for DGEBA–MWNTs, and 28 wt% for PGE–MWNTs. These values, though approximate, indicate that: (a) the two-step surface modification process was efficient and led to a significant mass fraction of organic groups chemically bonded to MWNTs; (b) the mass fraction of PGE bonded to COOH groups was significantly larger than that of DGEBA. Additional insight is provided by comparing experimental mass fractions with those expected from a complete reaction of COOH with epoxy groups. In the case of the reaction between COOH groups and PGE, the ca. 7 g of COOH attached to 93 g of the neat MWNT can incorporate 23.3 g PGE, leading to a theoretical organic mass fraction equal to 25% at full conversion, close to the experimental value (28 wt%). This means that esterification of COOH groups by PGE was carried out to complete conversion (an amount of PGE greater than the experimental value can be explained by oligomerization of PGE by chain transfer reactions involving the β-hydroxyester group. However, the epoxy-acid reaction proceeds at a much faster rate and consequently is complete before the homopolymerization of epoxy groups) [10]. In the case of COOH groups reacting with DGEBA, the theoretical mass fraction of DGEBA attached to the surface depends on whether one or both epoxy groups participate. The results of Eitan et al. [7]. suggest that both epoxy groups participate in these reactions. Based on this assertion, 7 g of COOH groups attached to 93 g of MWNTs should incorporate 29.2 g of DGEBA. (The equivalent weight per epoxy groups of Epon 828 was 188 g/ eq.) This leads to a theoretical organic mass fraction equal to 28%, which is significantly higher than the experimental value (16%). Possibly, steric restrictions do not allow a complete reaction of DGEBA with COOH groups.

FTIR spectra also corroborate the attachment of PGE and DGEBA to the surface of MWNTs, as shown in Fig. 6. Peaks located at 2920 cm^{-1}, 2850 cm^{-1}, 1460 cm^{-1}, and 1375 cm^{-1} are characteristic C–H stretching and deformation frequencies. The band at 1250 cm^{-1} is a characteristic vibration of aryl ethers while the one at 1710 cm^{-1} is characteristic of the carbonyl group (no indication of the acid to ester conversion could be obtained from this peak). Bands in the region 1100–1300 cm^{-1} are characteristic of C–O stretching vibrations in esters [14]. To assess the presence of residual epoxy rings in the DGEBA–MWNTs requires selection of a characteristic band that is
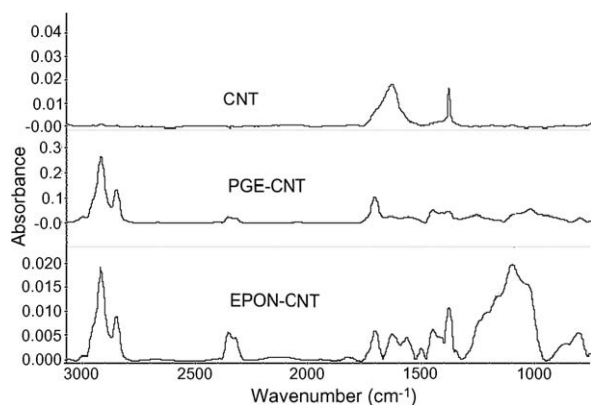
Fig. 6. FTIR spectra of neat and functionalized MWNTs (the peak at 2350 cm^{-1} was caused by adventitious CO_2 in the sample chamber).

not overlapped with other bands. A band that is typical of epoxy rings is located at 917 cm^{-1} [7]. The absence of this band in the FTIR spectrum indicates that most of the epoxy groups of DGEBA were consumed in the reaction, a conclusion similar to results reported by Eitan et al. [7].

The use of 4-dimethylamino pyridine (DMAP) as an initiator for DGEBA homopolymerization produced covalent bonds of PGE–MWNTs and DGEBA–MWNTs with the epoxy matrix through chain transfer reactions involving the secondary hydroxyls. While, in situ conversion of COOH–

MWNTs into DGEBA–MWNTs during cure did not produce uniform dispersions of nanotubes and was not effective. In the presence of a tertiary amine, epoxy-acid reactions are much faster than epoxy homopolymerization [10]. However, this reaction, which produced an in situ transformation of COOH-MWNTs into DGEBA–MWNTs, did not lead to uniform dispersion. In the absence of an adequate mixing stage, converting agglomerates of MWNTs to a uniform dispersion should require extremely long times. As polymerization proceeds and the matrix viscosity increases, migration of nanotubes will be increasingly inhibited and ultimately arrested by gelation. Therefore, in situ functionalization does not appear to be a suitable choice to obtain uniform dispersions of CNTs in epoxy.

All of the MWNT–epoxy composites were glassy at room temperature and exhibited a glass transition temperature of around 130 °C according to dynamic mechanical tests. Fracture surfaces of the cured epoxy and of MWNTs–epoxy composites with 1 wt% MWNTs obtained under cryogenic conditions, were examined by SEM (Fig. 7). Composites prepared with unmodified MWNTs and with COOH–MWNTs exhibited isolated regions of agglomerated MWNTs and other regions devoid of nanotubes (an interphase between both regions is shown in Fig. 7(c)). Both PGE–MWNTs and DGEBA–MWNTs were uniformly dispersed in the
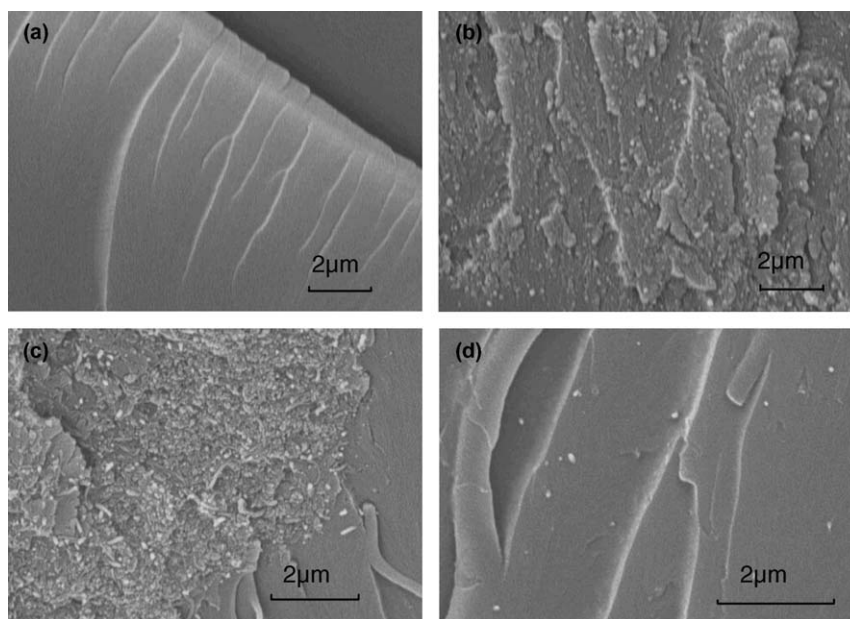

Fig. 7. SEM micrographs of fracture surfaces obtained under cryogenic conditions (1wt% CNT): (a) neat epoxy, (b) unmodified MWNTs–epoxy composite, (c) COOH–MWNTs–epoxy composite, (d) DGEBA-MWNTs-epoxy composites.

Table 1
Elastic modulus and flexural strength of the neat epoxy and MWNTs–epoxy composites

Material	wt% MWNTs	Elastic modulus (GPa)	Flexural strength (MPa)
Neat epoxy	0	3.48 ± 0.30	51 ± 15
Unmodified MWNTs-epoxy	0.5	3.06 ± 0.81	38 ± 7
	1	3.28 ± 0.52	39 ± 11
	3	3.15 ± 0.34	33 ± 13
COOH-MWNTs-epoxy	0.5	3.11 ± 0.24	50 ± 10
	1	3.10 ± 0.13	42 ± 7
	3	3.06 ± 0.20	26 ± 3
PGE-MWNTs-epoxy	0.5	3.48 ± 0.32	73 ± 12
	1	3.58 ± 0.29	83 ± 19
DGEBA-MWNTs-epoxy	0.5	3.52 ± 0.52	55 ± 7
	1	3.59 ± 0.41	58 ± 3
	3	4.02 ± 0.57	110 ± 5

epoxy matrix as was also demonstrated previously by their respective solubility in the epoxy. The SEM image, Fig. 7(d), shows MWNTs functionalized with DGEBA. For the particular concentration used to obtain this series of composites, the dispersed phase appears distant from the percolation threshold.

The two-step surface modification and the subsequent anionic homopolymerization yielded uniform MWNTs–epoxy composites with significant enhancement in flexural strength and a modest increase in the elastic modulus when compared to the neat epoxy. The monofunctional epoxide (PGE) was more efficient than the diepoxide (DGEBA) for functionalizing the nanotubes and led to higher values of flexural strength at the same loading of MWNTs. The measured elastic moduli (GPa) and flexural strength values (MPa) for the neat epoxy and for different MWNTs–epoxy composites are shown in Table 1. A non-uniform dispersion of nanotubes, as in the case of unmodified MWNTs and COOH-MWNTs, led to a notable decrease in elastic modulus and flexural strength of the composites compared to values for the neat epoxy. Composites exhibiting uniform dispersions of MWNTs showed significant increases in flexural strength and modest increases in elastic modulus. Compared with other more flexible epoxy systems [2–5], in which significant increases in both the flexural strength and the elastic modulus were observed, the relative small improvement for the elastic modulus in this study could be explained by the difficulty of the relative motion between MWNTs and the polymer chains/chain sectors in this rigid epoxy system at ambient temperature. At the same wt% of reinforcement, PGE–MWNTs exhibited a larger increase in flexural strength than DGEBA–

MWNTs. This can be attributed to the higher efficiency of surface functionalization in the case of PGE–MWNT that leads to more OH groups available to form covalent bonds with the epoxy matrix.

4. Conclusions

A two-step acid-epoxy functionalization of MWNTs coupled with anionic homopolymerization chemistry to build up the epoxy network was effective in achieving uniform dispersions of MWNTs in a stiff epoxy system. The resulting composites exhibited significant enhancement in flexural strength without any trade-offs in elastic modulus compared with the neat epoxy.

The findings underscore the significance of introducing suitable surface compatibility and reactivity with matrix system onto MWNTs to construct the nanocomposite network. Further improvements in mechanical and thermal performance are likely to be possible with optimized surface treatments tailored to specific polymer matrices. The addition of small amounts of CNTs affords myriad opportunities to design polymers with a broader range of enhanced properties for applications as adhesives, components, and composite matrices.

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