Carboxyl-terminated butadiene-acrylonitrile-toughened epoxy/carboxyl-modified carbon nanotube nanocomposites: Thermal and mechanical properties

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Abstract. Carboxyl-modified multi-walled carbon nanotubes (MWCNT–COOHs) as nanofillers were incorporated into diglycidyl ether of bisphenol A (DGEBA) toughened with carboxyl-terminated butadiene-acrylonitrile (CTBN). The carboxyl functional carbon nanotubes were characterized by Fourier-transform infrared spectroscopy and thermogravimetric analysis. Furthermore, cure kinetics, glass transition temperature (T_g), mechanical properties, thermal stability and morphology of DGEBA/CTBN/MWCNT–COOHs nanocomposites were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), universal test machine, thermogravimetric analysis and scanning electron microscopy (SEM). DSC kinetic studies showed that the addition of MWCNT–COOHs accelerated the curing reaction of the rubber-toughened epoxy resin. DMA results revealed that T_g of rubber-toughened epoxy nanocomposites lowered with MWCNT–COOH contents. The tensile strength, elongation at break, flexural strength and flexural modulus of DGEBA/CTBN/MWCNT-COOHs nanocomposites were increased at lower MWCNT-COOH concentration. A homogenous dispersion of nanocomposites at lower MWCNT–COOH concentration was observed by SEM.

Keywords: nanocomposites, thermal properties, thermosetting resin, carbon nanotubes, epoxy resin

1. Introduction

Epoxy resins are widely used as coatings, adhesives, insulating materials and matrices for fibrous composites for their rigidity, high temperature performance, chemical resistance and adhesive properties. However, the inherent brittleness due to the high crosslinking density becomes one of the biggest troubles in advanced application use in industries. Therefore, great efforts have been exerted in the modifications of epoxy resins for further improvement of multifunctional properties [1, 2].

Presently, reactive liquid rubber, thermoplastics, interpenetrating polymer networks (IPNs), thermotropic liquid crystal and nanofillers are used to toughen epoxies for improving properties of epoxy networks. The elastomeric toughening is the most frequently used and widely accepted among these methods. Recently, Tripathi and Srivastava [1, 3] reported that a two-phase morphology was observed and the best balance of mechanical properties were achieved with a concentration of carboxyl-terminated butadiene-acrylonitrile (CTBN) ranging between 15 and 20 phr (part per hundred resin) in the cured epoxy resin. Varley [4] effectively toughened the diglycidyl ether of bisphenol A (DGEBA) by both epoxy-terminated aliphatic polyesters and CTBN with a great improvement of the fracture properties whereas the addition of aminopropyl-ter-

minated siloxane showed no improvement due to the poor dispersion. Kishi *et al.* [5] found that though the CTBN/DGEBA/DDM (diamino diphenyl methane) resins indicated high damping performance and high adhesive strength to aluminum substrates, there was always loss of strength of the materials accompanied with the improvement of toughness. The work of Ratna and Banthia [6] showed that the tensile strength and flexural strength of the epoxy resins modified by carboxyl terminated poly(2-ethylhexyl acrylate) decreased rapidly with increase of the rubber. Similar observations have been reported by other authors [7, 8]. Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are considered as reinforcement for polymer matrix because of the remarkable physical, chemical and electrical properties with small dimensions and high aspect ratios [9–12]. In order to transfer the outstanding properties to the modified epoxy, functionalization of pristine CNTs is essential for getting strong interfacial bonding and proper dispersion [13–17]. Gojny *et al.* [18] studied the mechanical properties of epoxy matrix composites with different types of CNTs which exhibited an improved strength, stiffness and fracture toughness. Liu and Wagner [19] reported two epoxy matrices with widely different mechanical properties both were reinforced by CNTs. Sui *et al.* [20] reported that epoxy resins were reinforced and toughened more effectively by CNTs than CNFs [21]. However, the enhancement was not as significant as expected. Recently, Hsieh *et al.* [22] proved that the addition of CNTs increased the modulus of the epoxy. The measured fracture energy was increased, from 133 to 223 J/m^2 with the addition of 0.5 wt% of nanotubes.

To our knowledge, few studies have been carried out on the influence of CNTs on the rubber-tough-ened epoxy [23]. In present paper, CTBN and carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs) were first reacted with DGEBA to form adducts, which were then cured with a flexible curing agent, Jeffamine to further increase the toughness of the epoxy. The dynamic cure kinetics, thermal stability, glass transition temperature, mechanical properties, and morphology of carboxyl-functionalized MWCNT/epoxy/rubber nanocomposites were studied.

2. Experimental
2.1. Materials
The epoxy resin used in this study was DGEBA, E51, with an epoxide equivalent weight of 196 g/eq, from Wuxi Resin Factory (Wuxi, China). The curing agent was Jeffamine, T403, from Huntsman Corporation (Texas, USA). The elastomeric toughener used was a liquid CTBN rubber with an acrylonitrile content of 30–35%, from Lanzhou Petrochemical Company (Lanzhou, China). Chemical structures of DGEGBA, Jeffamine and CTBN are showed in Figure 1. MWCNTs with diameters of 40–60 nm and lengths of 5–15 μm were supplied by Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China).

2.2. Sample preparation
3 g MWCNTs were mixed with 100 mL nitric acid with a concentration of 5 mol/L and sonicated for 1 h in water bath, then the suspension reacted at 130°C for 10 h. After they were washed with deionized water until the filtrate reached a pH value of *ca.* 6–7, MWCNT–COOHs were dried in vacuum at 60°C for 3 day and collected then.

DGEBA and 15 phr (part per hundred resin) CTBN were mixed, then MWCNT–COOHs were added, the mixture was reacted for 2 h with mechanical
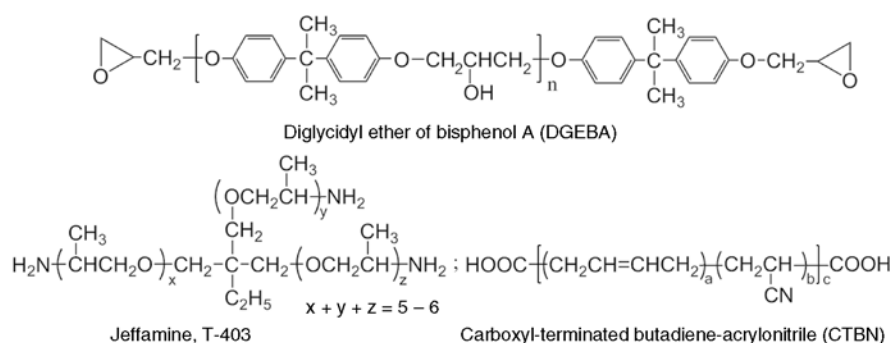

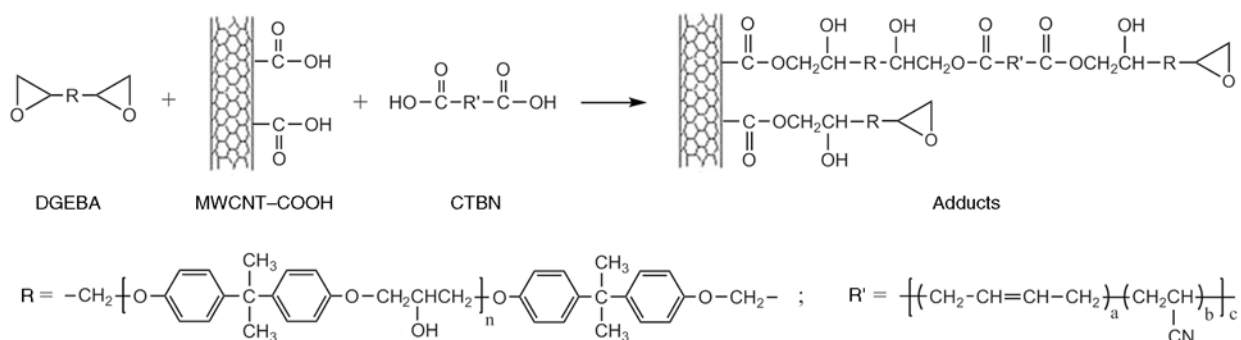**Figure 1.** Chemical structures of DGEBA, Jeffamine and CTBN

Figure 2. The reaction scheme between carboxyl groups in CTBN and MWCNT–COOHs and epoxy groups in DGEBA

stirring at 145°C and then sonicated for 1.5 h at 30°C, during which adducts could be formed among DGEBA, CTBN and MWCNT–COOHs, as shown in Figure 2. The adducts were placed in an oil bath at 75°C, then a stoichiometric amount of Jeffamine was added with continuous mechanical stirring until a homogeneous mixture was observed. Several DSC aluminum pans were filled with the reaction mixture. The mixtures (*ca*. 10 mg) were then cooled and stored in a freezer until they were required for the DSC measurements. Other mixtures were immediately poured into polytetrafluoroethylene molds and cured for 2 h at 80°C and 3 h at 125°C. DGEBA/CTBN/MWCNT-COOHs nanocomposites with 0, 0.5, 1, 2 wt% MWCNT–COOHs noted as MWCNT 0, MWCNT 0.5, MWCNT 1 and MWCNT 2, respectively.

2.3. Characterization

The FT-IR spectrum of MWCNT–COOHs was recorded on a Nicolet Avatar 360 FT-IR spectrometer (Thermo Scientific, USA) in the wavelength range of 4000–400 cm^{-1}, at a resolution of 4 cm^{-1}. MWCNT–COOHs were pressed into a pellet together with potassium bromide (KBr) powder. Studies on dynamic curing kinetics of epoxy nanocomposites were performed on Pyris 1 DSC (Perkin-Elmer, USA) under an argon flow of 20 mL/min. The samples for kinetic analysis were heated up from 50 to 300°C at heating rates of 5, 10, 15 and 20°C/min, respectively. The T_gs of the cured samples were tested using dynamic mechanical analysis (DMA; DMA + 450, 01 dB-Metravib, France). The measurements were taken under tension mode from –80 to 140°C with a frequency of 1 Hz at a heating rate of 2°C/min. All mechanical tests were performed on an Instron 4466 universal material tester (Instron, USA) at room temperature. The tensile tests were measured according to ASTM D638 at 5 mm/min. For the flexural test, rectangular specimens were cut with dimensions of $100 \times 10 \times 5$ mm according to ASTM-D790 and tested at a crosshead speed of 4 mm/min. Four specimens were tested in the mechanical measurements. TGA was performed at a Pyris 1 thermogravimetric analyzer (Perkin-Elmer, USA) with a heating rate of 20°C/min over a temperature range of 25–600°C under a nitrogen flow of 40 mL/min. Scanning electronic microscopy (SEM) images of the fracture surfaces were obtained on a Hitachi S-4800 field-emission scanning electronic microscope (Hitachi, Japan). The cured samples were fractured under liquid nitrogen, and then the fractured surfaces were vacuum-coated with a thin gold layer.

3. Results and discussion
3.1. Characterization of carboxyl-modified carbon nanotubes

Figure 3 shows the FT-IR spectrum of MWCNT-COOHs. The peaks at around 3435 and 1714 cm^{-1} could be respectively assigned to the O–H stretching vibrations and C=O stretching vibrations, so it
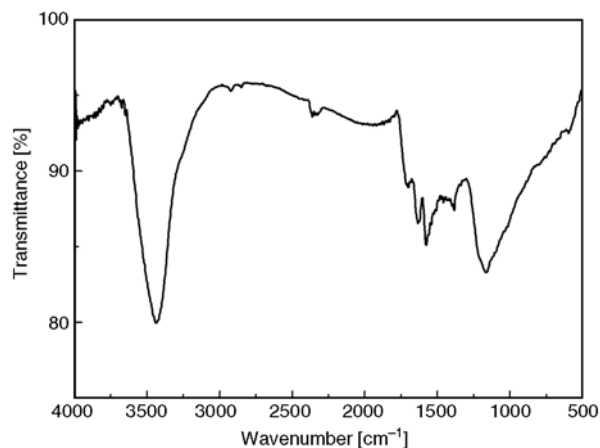

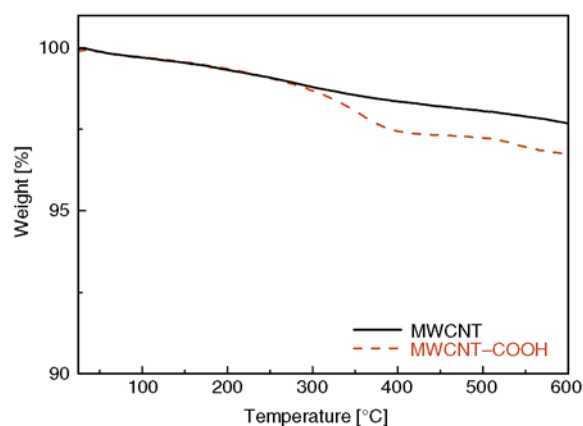**Figure 3.** FT-IR spectrum of carboxyl-modified MWCNTs

Figure 4. TGA curves of MWCNT and carboxyl-modified MWCNTs

is clear that MWCNTs were successfully modified with the introduction of the carboxyl functionalities. Besides, the peaks observed at around 1579 and 1384 cm^{-1} should be ascribed to the carbonic C–C stretch bonds [24].
The samples of MWCNTs and MWCNT-COOHs were studied with TGA (as shown in Figure 4). Compared with the pristine MWCNTs, carboxyl-functionalized MWCNTs displayed more weight loss between 300 and 600°C. This weight loss results from the losing of carboxyl groups on the surface of MWCNTs.

3.2. Cure behaviors

DSC is often used to study the effect of nanofillers on the cure behaviors of epoxy resin [11, 16, 25–27]. In present work, dynamic kinetic studies based on Kissinger and Flynn-Wall-Ozawa (FWO) models [26–28] were utilized to investigate the DGEBA/CTBN/MWCNT–COOHs nanocomposites. Both

models do not require prior knowledge of the reaction mechanism.
According to the Kissinger model [28], the activation energy can be obtained from Equation (1):

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_\alpha}{R} \tag{1}$$

where T_p is the peak exothermal temperature, β is the constant heating rate, E_α is the activation energy of the reaction, and R is the universal gas constant. The value of E_α can be obtained by plotting $\ln(T_p^2)$ versus $1/T_p$.
The Flynn-Wall-Ozawa (FWO) model [29, 30] yields a simple relationship between the activation energy E_α, the heating rate β, and the peak exothermal temperature T_p, giving the activation energy as shown by Equation (2):

$$\log\beta = A - 0.457\frac{E_\alpha}{RT_p} \tag{2}$$

Figure 5 shows DSC thermograms from dynamic heating experiments and conversion versus temperature curves for DGEBA/CTBN/MWCNT–COOHs nanocomposites conducted at a heating rate of 20°C/min, while the conversion is definited as the ratio of the heat generated up to time *t* to the total heat of the reaction. Clearly, the samples with MWCNT–COOHs reacted faster than the rubber-only toughened epoxy (MWCNT 0). Furthermore, the reaction rate of MWCNT–COOHs nanocomposites increased with the rise of MWCNT–COOH contents. The initial reaction temperature (T_i), exothermal peak temperature (T_p) and heat of curing (ΔH) of DGEBA/CTBN–COOHs nanocomposites at differ-
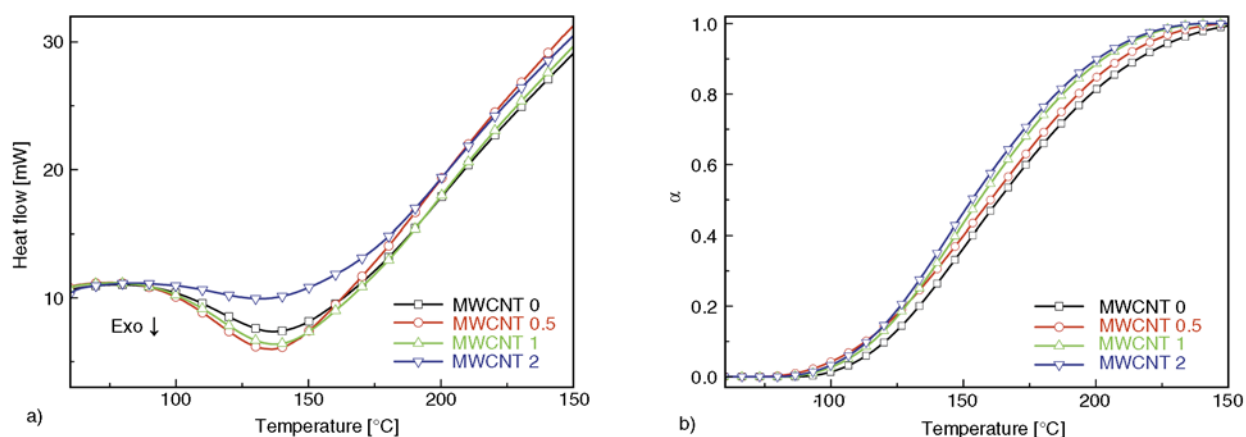

Figure 5. DSC curves (a) and relationship between conversion (α) and temperature (b) for DGEBA/CTBN/MWCNT–COOHs nanocomposites at a heating rate of 20°C/min

ent heating rates are listed in Table 1. It is observed that both T_i and T_p decrease with the increase of MWCNT–COOH contents, indicating that MWCNT–COOHs act as catalysts and facilitate the curing reaction and the catalytic effect increases with the MWCNT–COOH contents.

By applying the Kissinger and FWO methods, activation energies can be obtained from the slope of

Table 1. The initial temperature, peak temperature and heat of curing for DGEBA/CTBN/MWCNT–COOHs nanocomposites

MWCNT–COOH [wt%]	Heating rate [°C/min]	T_i [°C]	T_p [°C]	ΔH [J/g]
0	5	80.500	107.200	315.255
	10	81.100	121.200	313.661
	15	83.100	130.100	318.466
	20	87.700	137.200	315.875
0.5	5	78.600	103.300	313.303
	10	79.300	120.800	306.760
	15	81.200	127.300	313.697
	20	85.100	135.100	310.983
1	5	75.300	102.600	312.719
	10	78.000	118.100	308.868
	15	80.500	126.600	305.528
	20	81.200	134.500	299.297
2	5	73.400	100.000	310.877
	10	76.700	116.000	296.764
	15	78.600	125.300	291.877
	20	79.900	132.500	284.224

Table 2. Activation energies of DGEBA/CTBN/MWCNT–COOHs nanocomposites

MWCNT–COOH [wt%]	E_a [kJ/mol]	
	Kissinger	FWO
0	53.6	57.2
0.5	49.7	53.4
1	49.4	53.1
2	47.3	51.1

the lines as presented in Figure 6. Linear relationships were obtained, confirming the validity of the models for the systems under study. Table 2 summarizes the results obtained from the dynamic kinetic analysis. The activation energies calculated from the two models were in close agreement. It is obvious that E_α of nanocomposites decreased with the increasing of MWCNT–COOH contents. A decrease in activation energy implies that less energy of the reacting resin components is required and indicates an accelerating effect. This suggests that the addition of carboxyl-MWCNTs into rubber-toughened epoxy resin facilitates the curing reaction, which is consistent with the results of other workers [31, 32]. The high thermal conductivity of the MWCNTs is considered to be the origin for the decrease in activation energy [31].

3.3. Glass transition temperature (T_g)

The loss tangent ($\tan\delta$) as a function of temperature is shown in Figure 7. The temperature at which the $\tan\delta$ is maximum is defined as T_g. The T_g of MWCNT 0.5 was almost equal to that of MWCNT 0, but it decreased markedly with the increasing of MWCNT–COOH contents. One possibility is that the addition of MWCNT–COOHs causes over-stoichimetric active hydrogen which can react with the epoxy groups, since it is well known that the stoichimetric ratio of curing agent to epoxide group leads to maximum T_g [33]. Similar results were reported in fluorinated MWCNTs/epoxy nanocomposites [34]. The introduction of MWCNT–COOHs would increase the viscosity of the mixture significantly, resulting in the rapid decrease of the cure degree in the diffusion-controlled stage. Thus, T_gs of the MWCNT–COOHs nanocomposites are expected
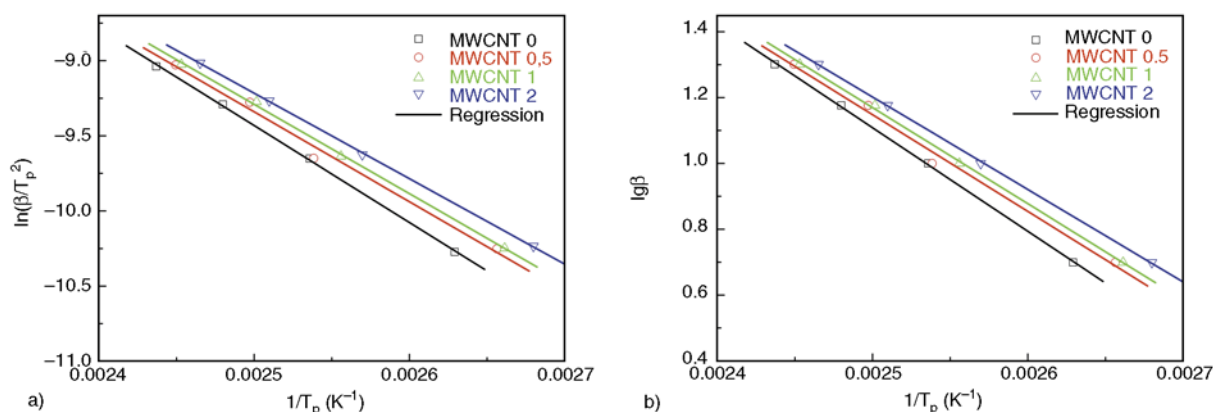

Figure 6. Relationship between $\ln(\beta/T_p^2)$ and $1/T_p$ (a) and between $\ln\beta$ (b) and $1/T_p$ (b) for DGEBA/CTBN/MWCNT–COOHs nanocomposites
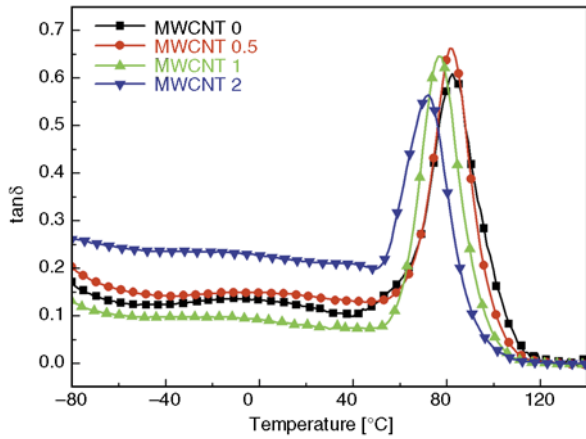
Figure 7. Temperature dependence of tanδ for the CTBN-toughed epoxy and DGEBA/CTBN/MWCNT–COOHs nanocomposites

to be lower than the rubber-only toughened one (MWCNT 0). Though MWCNTs could limit the mobility of the polymer chains to elevate the T_gs of the composites, the effect was counterbalanced by the poor dispersion of MWCNT–COOHs for MWCNT 1 and MWCNT 2 [26].

3.4. Mechanical properties

To evaluate the effects of MWCNT–COOHs on the mechanical properties of the toughened epoxy, tensile tests and flexural tests were performed, as showed in Figure 8a and 8b, respectively. It is known that the addition of rubber inevitably decreases the tensile strength of epoxy resin. With the addition of MWCNT–COOHs, tensile strengths of MWCNT 0.5 and MWCNT 1 and elongation at break of MWCNT 0.5 were greater than that of rubber-toughened epoxy (MWCNT 0). Moreover, with the increasing of MWCNT–COOH content, the tensile strength and elongation at break decreased gradually. As shown in Figure 8b, with the incorporation of CTBN, the addition of MWCNT–COOHs increased the flexural strength modulus of rubber-toughened epoxy. Furthermore, the flexural strength and modulus for DGEBA/CTBN/MWCNT–COOHs nanocomposites decreased with the increasing of MWCNT–COOH contents. The mechanical properties of nanocomposites depend on the dispersion of
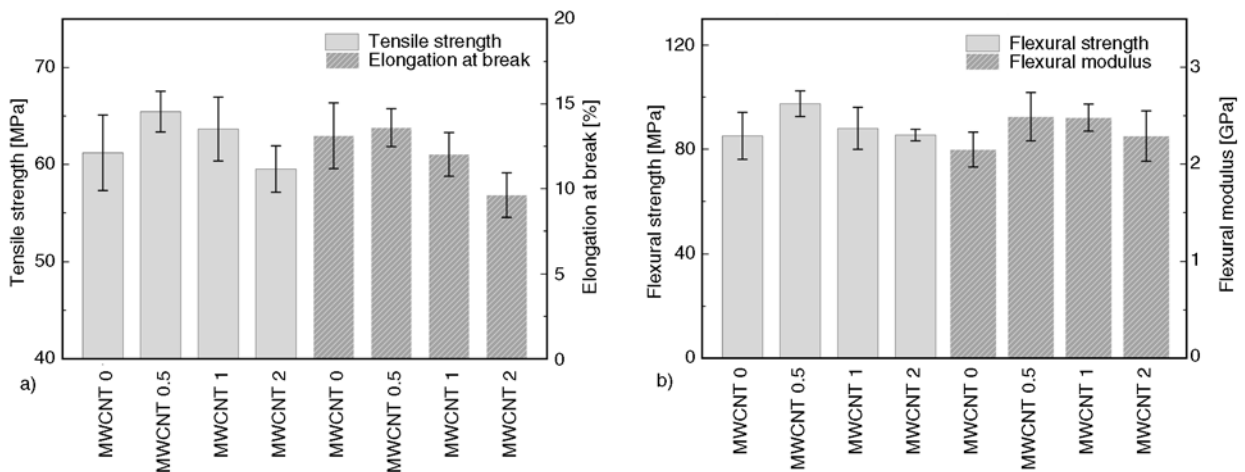

Figure 8. Tensile strengths and elongations at break (a) and flexural strengths and flexural moduli (b) for the CTBN-toughed epoxy and DGEBA/CTBN/MWCNT–COOHs nanocomposites
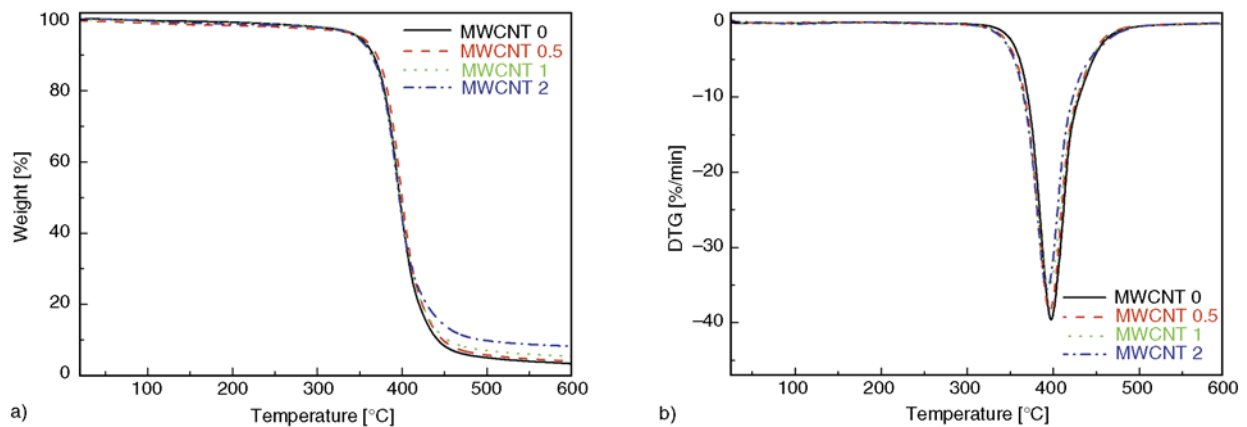

Figure 9. TGA (a) and DTG (b) curves for DGEBA/CTBN/MWCNT–COOHs nanocomposites

carbon nanotubes in the polymer matrix and the interaction between nanotubes and polymers [35, 36]. In other words, more homogeneous dispersion and better interface between the nanotubes and the epoxy matrix result in better mechanical properties. For MWCNT–COOHs, good dispersion can be achieved at lower concentration. However, higher nanotube concentration will cause higher viscosity

Table 3. TGA and DTG results for DGEBA/CTBN/ MWCNT–COOH nanocomposites

MWCNT [wt%]	IDT [°C]	T_{max} [°C]	Residue at 600°C [%]
0	349	397	3.2
0.5	352	395	3.9
1	350	395	5.3
2	347	393	8.2
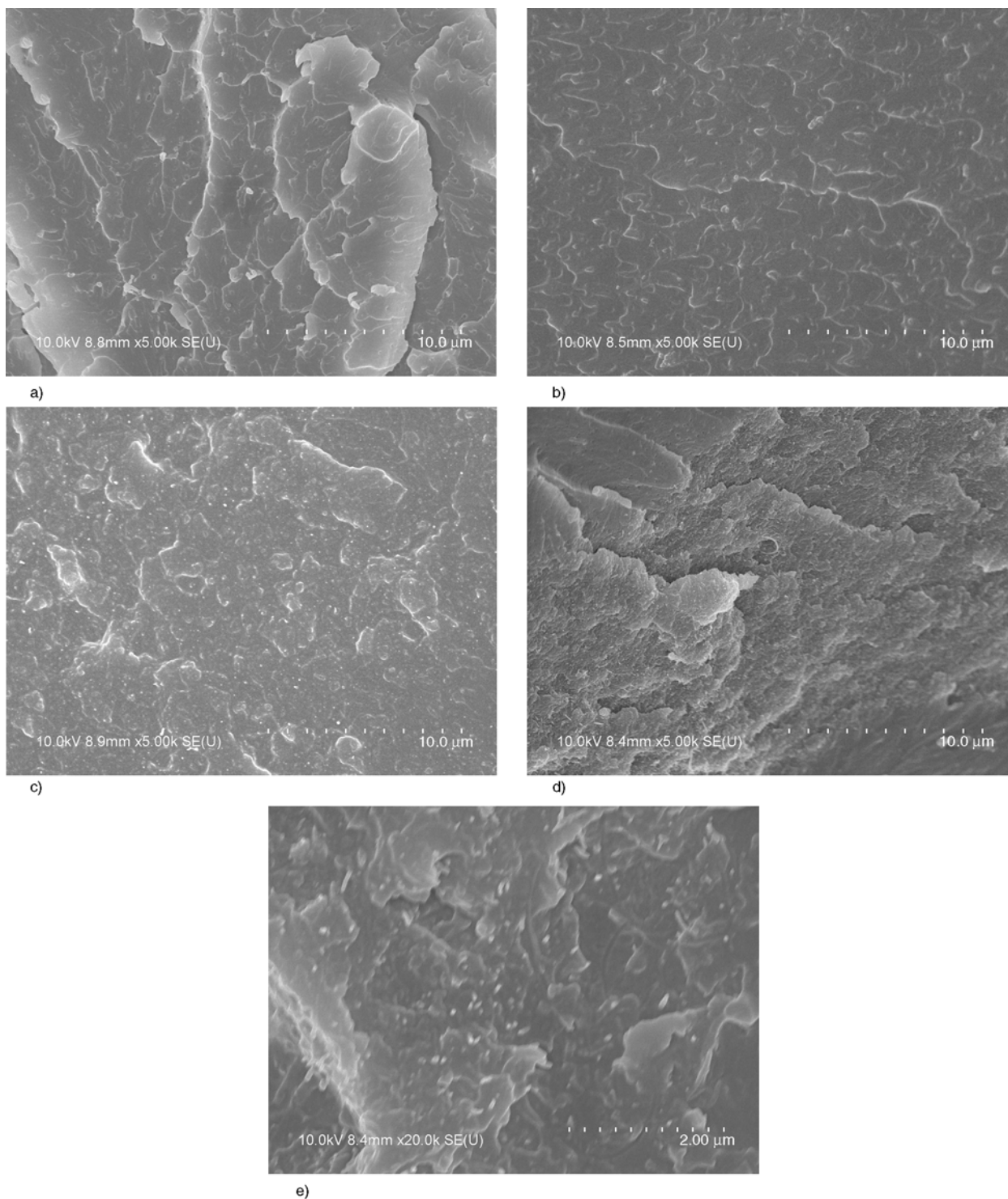
Figure 10. SEM images of cryo-fracture surfaces for (a) MWCNT 0, (b) MWCNT 0.5, (c) MWCNT 1 and (d) MWCNT 2; (e) high magnification image of (d)

and agglomerates with poor dispersion. The agglomerates present in poorly dispersed nanocomposites cause cracks to initiate and propagate easily. The generated cracks reduce the strength of the rubber-toughed epoxy nanocomposites.

3.5. Thermal stability

TGA and DTG curves for DGEBA/CTBN nanocomposites with different concentration of MWCNT–COOHs are presented in Figure 9. The initial decomposition temperature (IDT) which is set as the temperature at 5% weight loss, maximum rate of degradation temperatures (T_{max}) and residue at 600°C are summarized in Table 3. The negligible changes of IDTs and T_{max}s illustrate that MWCNT–COOHs do not affect the thermal stabilities of the resin matrices. The residues of the nanocomposites at 600°C increased with the growing concentration of MWCNT–COOHs. In Figure 9b, every curve showed a single peak at about 396°C, proving the strong interaction of the epoxy with CTBN and MWCNT–COOHs.

3.6. Morphology

SEM images of cryo-fracture surfaces for rubber-toughened epoxy and its MWCNT–COOHs nanocomposites are shown in Figure 10. Two-phase morphology was easily observed in MWCNT 0 (Figure 10a). MWCNT–COOHs dispersed relatively uniformly at a low concentration in the CTBN-toughened epoxy system (MWCNT 0.5, Figure 10b), while agglomerates were increased in both size and amount with the increasing of the concentration of MWCNT–COOHs, as shown in Figure 10c and 10d. These results indicate the existence of strong interfacial bonding between 0.5 wt% MWCNT-COOHs and CTBN-toughened epoxy in the nanocomposites. In contrast, 2 wt% MWCNT–COOHs have weak interfacial interactions with the rubber toughened matrix because of the agglomeration of MWCNT–COOHs. Many MWCNT–COOHs were pulled out from the fractured surface (Figure 10e), which phenomena have also been observed in our previous reports [17]. The poor dispersion of MWCNTs had significant influence on the glass transition temperature and mechanical properties of nanocomposites as discussed above.

4. Conclusions

Carboxyl-modified multi-walled carbon nanotubes were successfully prepared by treating MWCNTs with acid and then incorporated into the epoxy/CTBN matrix. Dynamic kinetic analysis showed that the activation energy of rubber-toughened epoxy nanocomposites decreased with the increasing of MWCNT–COOH contents, indicating carboxyl-functionalized carbon nanotubes accelerate the cure reactions of the rubber-toughened epoxy system. The incorporation of MWCNT–COOHs improved mechanical properties of the CTBN-toughened epoxy systems, whereas the improvement was not linear with the concentration of MWCNT–COOHs. The maximum tensile and flexural properties were obtained at MWCNT–COOH concentration of 0.5 wt% with uniform dispersion. Nevertheless, at higher concentrations, MWCNT–COOHs agglomerated in the viscous epoxy/CTBN system and resulted in the decreasing of mechanical properties. The glass transition temperature of rubber-toughened nanocomposites decreased with the increasing MWCNT–COOH contents.

Acknowledgements

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