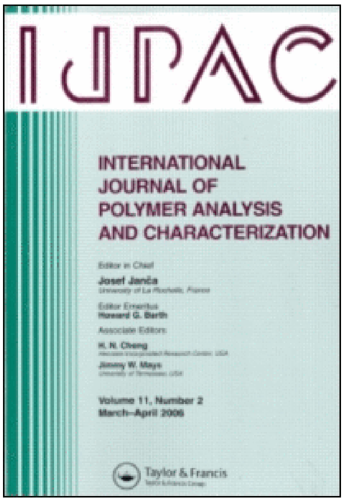

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THE EFFECT OF CURING CYCLE ON THE MECHANICAL PROPERTIES OF MWNT/EPOXY NANOCOMPOSITE

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Along with carbon nanotube (CNT) morphology, impurity, and fuctionalization, polymer curing cycle is another important factor in determining the mechanical properties of CNTlpolymer composite samples. Nanocomposite samples were prepared by mixing multiwall carbon nanotubes with epoxy resin. The main objective is the investigation of the effects of four curing cycles on the mechanical and thermo-mechanical properties of the conductive filler in the composite and the development of new nanocomposite materials based on epoxy resins with controlled structural and mechanical properties. The mechanical and thermo-mechanical properties of the resulting composite samples were evaluated by performing tensile and dynamic mechanical analyses (DMA) test. The results indicate that the mechanical properties of pure epoxy and composite samples have been affected by the conditions of the curing process. It seems that the effect of the reinforcement is more evident for a less cured resin.

Keywords: Curing cycles; Epoxy; Nanocomposites; Nanotubes; Mechanical properties; Thermo mechanical properties

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by the arc discharge method in 1991,[1] many research activities have been focused on CNT-related fields. Carbon nanotubes have excellent mechanical properties and are considered to be good reinforcing agents in the fabrication of composite materials. Nanotubes exist in the form of multiwalled nanotubes (MWNT), discovered by IiJima,[2] and single-walled nanotubes (SWNT), discovered by Bethune et al. in 1993.[3] MWNT have unique atomic structure, very high aspect ratio, and extraordinary mechanical properties, making them ideal reinforcing materials in nanocomposites.[4] Among various polymers, epoxy resin is the most common class of thermosetting resin used in various applications because of its high tensile strength and modulus, low curing shrinkage, good

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chemical and corrosion resistance, high adhesion, and dimensional stability. The main drawback of epoxy resins for structural applications may be their inherent brittleness. Thus, much effort has recently been devoted to reinforcement of epoxy matrices with CNTs. Nanotube-reinforced epoxy systems hold the promise of delivering superior composite materials with high strength, light weight, and good electrical conductivity for aircraft, space shuttle, and electronics applications.[5] In practice, however, some experimental results indicate that carbon nanotube/epoxy composites are weaker or only slightly stronger than neat epoxy.[6] Enhanced strength has also been reported by several investigators.[7,8] Nanotube epoxy composites have been fabricated using different purification and dispersion processes.[8–11] It has been observed that the curing of epoxy, its cross-linking, thermal contraction, and other physical/chemical properties are all affected by the presence of small amounts of SWNT and MWNT.[12–14] This study investigates the effect of various curing cycles on the mechanical and thermo-mechanical properties of MWNT/epoxy nanocomposite samples.

EXPERIMENTAL DETAILS

Materials

The multiwalled carbon nanotubes (MWNT) used in this study were supplied by Research Institute of Petroleum Industry (RIPI) of Iran. They were synthesized by chemical vapor deposition with an average diameter of 20 nm and a purity of >95 wt.%. Low-viscosity epoxy resin Ly564 (Araldite) and the hardener Hy560 Aradur were supplied by Huntsman Co. They are based on diglycidyl ether bisphenol-A and polyamine, respectively. The MWNT were purified by a 3:1 (vol/vol) mixture of concentrated sulfuric acid (98%) and nitric acid (65%) to remove impurities such as amorphous carbon, graphite particles, and metal catalyst.

Preparation of Pure Resin Specimen

Resin specimen was prepared by mixing Ly564 epoxy and Hy560 hardener (epoxy/hardener weight ratio = 100/27) thoroughly. This process was followed by placing the mixture under vacuum to remove air bubbles.

Preparation of Nanocomposites

First, 0.5 wt.% MWNT was mixed with epoxy at 80°C. The mixture was then sonicated (Bandelin HD3200, 20 KHz) for 2 h at 60% amplitude. After sonication, the hardener was added to the mixture and stirred for 10 min at 150 rpm, then put under vacuum to remove air bubbles.

Curing Cycles

Four curing cycles were used in this study: in A and B cycles the epoxy was hardened at 80°C for 4 h and 10 h respectively. In C and D cycles the systems were first cured for 24 h and 48 h at room temperature and post-cured at 80°C for 4 h and

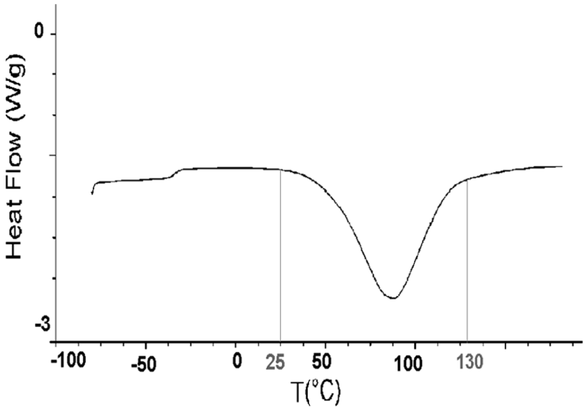


Figure 1. DSC scan of neat epoxy.

10 h, respectively. These curing cycles were selected based on the differential scanning calorimetry (DSC) result shown in Figure 1. This test was performed on the sample, which was cured with constant heating rate (5°C/min) up to 200°C. The curing started at room temperature and finished at 130°C.

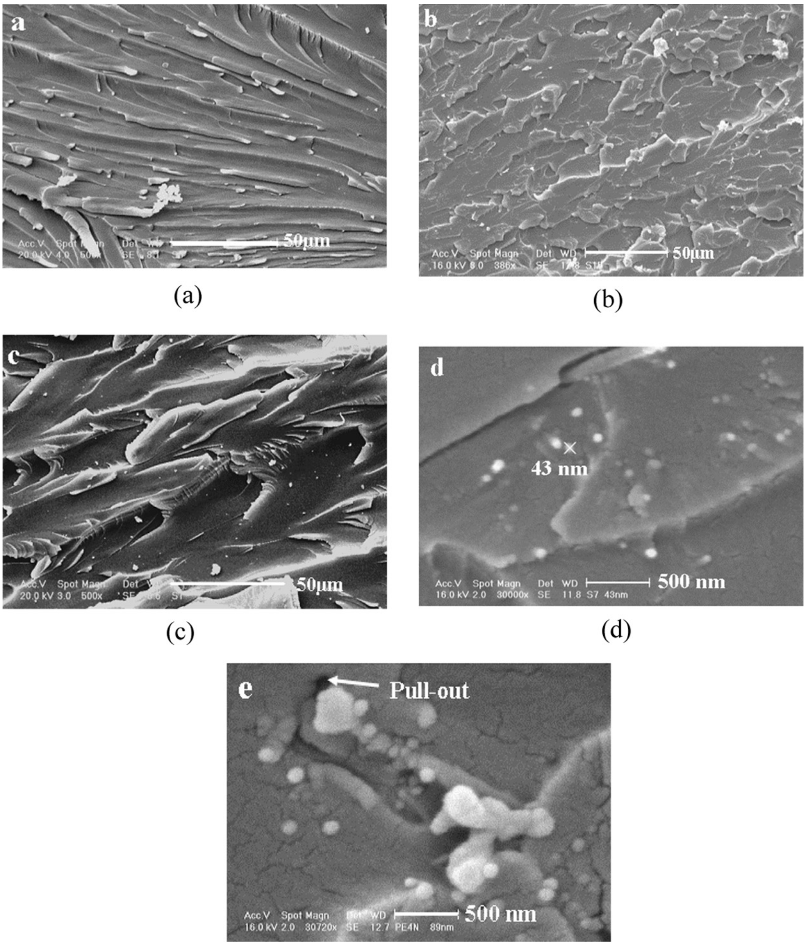
Analytical Methods

All MWNT/Ly564 nanocomposites and the neat resin samples were mechanically polished to minimize the influence of surface flaw, mainly porosity. Tensile tests were carried out at 25°C using a Hounsfield machine (model H100KS, Hounsfield static tension load cell of capacity 10 KN). An extensometer (Instron dynamic extensometer with 12.5 mm gauge) was used to record tensile strength, elongation, and modulus values. Four dog-bone-shaped specimens (ASTM D 638-IV) were used for each measurement. The samples were loaded to failure at a crosshead speed of 1.5 mm/min. The choice of this low loading rate was due to the brittle nature of composite samples. The investigation of the viscoelastic behavior was performed by dynamic-mechanical thermal analysis (DMTA) using a Netzch DMA 242 machine: For these measurements, rectangular specimens of 60 mm length, 9 mm width, and 2.5 mm thickness were prepared. The tests were performed in the tensile mode at a frequency of 1 Hz at the heating rate of 2°C/min. The kinetics of cross-linking and estimation of curing temperature was studied by DSC on a TA instrument (Q10). The cryogenic fracture surface analysis was performed by a scanning electron microscope (SEM, model LX 30 at 20 kV). The samples were coated with a thin layer of gold prior to the examination by SEM.

RESULTS AND DISCUSSION

Evaluation of the Fracture Surfaces

Nanotube dispersion within the matrix was examined by SEM. Figure 2 represents the fracture surfaces of neat epoxy and nanocomposite samples. As indicated in



(a) (b)

(c) (d)

(e)

Figure 2. SEM images of the fracture surface: (a) neat epoxy, (b) A-composite, (c), (d) C-composite, and (e) D-composite.

these figures, the fracture surface of the neat epoxy A cycle (Figure 2(a)) is flat, evidencing brittle fracture behavior. On the other hand, the fracture surfaces of (A) and (C) composites show quite different fractographic features. The fracture surface of (A) composite is significantly rougher than that of the neat epoxy, indicating a ductile type of fracture, as shown in Figure 2(b). Figure 2(c) shows the smooth fracture surface of (C) composite. When the curing time increases, the matrix and the fracture surface become stiff and smooth, respectively; this indicates a brittle fracture mode. Carbon nanotubes are observed as bright spots distributed rather evenly in the epoxy matrix (Figures 2(d) and 2(e)). A good dispersion is observed for the nanotubes in Figure 2(d). Pull out of nanotubes and a cavity of around 89 nm are observed between the fractured nanotubes (Figure 2(e)). It seems the pull out has increased fracture strain and fracture toughness in (D) composite (Table I).

Table I. Elastic modulus (E), strength (σ_{uts}), and ultimate tensile strain (ε_{ult}) of the examined materials

Material	E (Mpa)	σ_{uts} (Mpa)	ε_{ult} (%)
Epoxy (A)	3248	70.4	3.4
MWNT/epoxy (A)	3387	73	4.5
Epoxy (B)	3368	72.1	5.6
MWNT/epoxy (B)	3376	74.3	4.7
Epoxy (C)	3640	75.3	5.9
MWNT/epoxy (C)	3725	76.1	4.1
Epoxy (D)	3710	77	4.4
MWNT/epoxy (D)	3733	77	6.76

Mechanical Characterization

The mechanical properties of the pure epoxy and MWNT/epoxy composites following the four different cycles A, B, C, and D are given in Table I. The results show that there is an improvement in the mechanical properties of the pure resin with the increase in curing time. The observed increase in Young's modulus and tensile strength can be explained by the increase in the degree of cross-linking with the increase in time in the curing stage. According to Table I, the improvement in Young's modulus of epoxy samples with cycles A, B, C, and D with the addition of 0.5 wt.% MWNT were 3.7%, 1.2%, 4.4%, and 2.2% respectively. It is obvious that MWNT acts as reinforcing agent in the epoxy matrix for all cycles. However, the improvement becomes less significant with the increase in curing time (compare A, B and C, D). Similar results have also been reported in the literature.[12,13] The results in Table I show that the mechanical properties of pure epoxy and composite samples have been affected by the time of curing process. Tensile strength of pure epoxy resin was increased when it was reinforced with carbon nanotubes. The improvement in tensile strength of epoxy samples with cycles A, B, and C with the addition of 0.5 wt.% MWNT was 3.7%, 3%, 1.1% respectively. These results show that the reinforcement effect of MWNT diminishes with the increase in the degree of curing in the matrix, an observation that is in agreement with the previously reported data.[12] As indicated in Table I, the incorporation of 0.5 wt.% MWNT along with the application of a treatment such as curing cycle can improve the fracture strain by 53.6% (D cycle). Thus, proper curing after the addition of carbon nanotubes into polymer is very important in observing a reinforcement effect. It appears that the introduction of carbon nanotubes may have an effect on the initial curing rate of the composite. For example, an accelerating effect on the polymer cure rate by nanotube introduction has been reported for the epoxy system.[14,15] This acceleration effect was attributed to the higher thermal conductivity of carbon nanotubes.[14] As shown in Figure 3, the fracture behavior of composite samples cycles A, B, and C is brittle, whereas more ductility was observed in the case of D cycle sample. The comparison of tensile modulus and tensile strength obtained from cycles A to D of the neat epoxy with samples containing carbon nanotubes indicates that the increment of Young's modulus and tensile strength of the epoxy and nanocomposite is affected by the curing process.

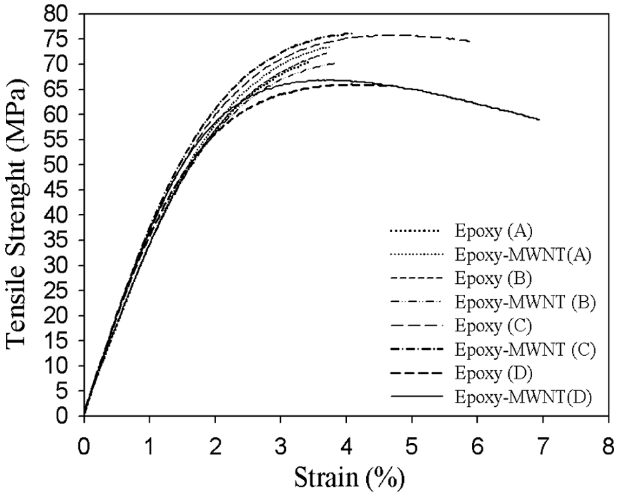


Figure 3. Stress-strain curves of epoxy and composite in four different cycles.

Thermo-Mechanical Behavior

The storage modulus of the nanocomposites treated by cycles A and C was investigated by DMTA. Figure 4 shows the results of dynamic measurement of storage modulus as a function of temperature. The addition of nanotubes to the epoxy had a slight effect on the rubbery regions. However, a strong increase was observed in the storage modulus in glassy regions and in the vicinity of the glass transition temperature (T_g). Improved interaction between the nanotubes and the epoxy matrix leads to stronger shift of the elastic properties of the epoxy system below the rubbery region. The behavior can be explained in terms of an interaction between the

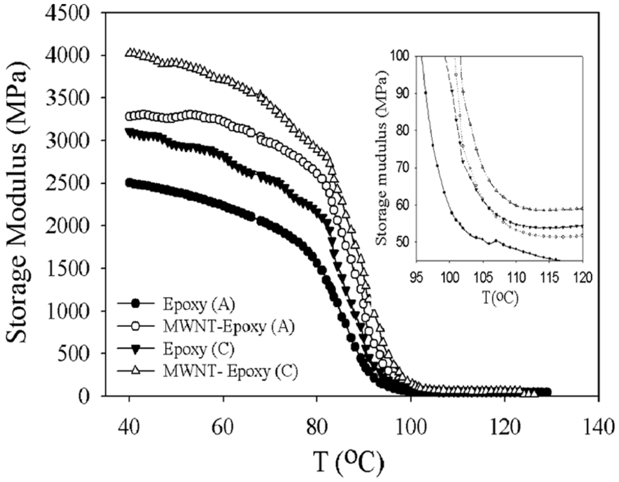


Figure 4. Storage modulus of neat epoxy and MWNT/epoxy composites for cycles A and C.

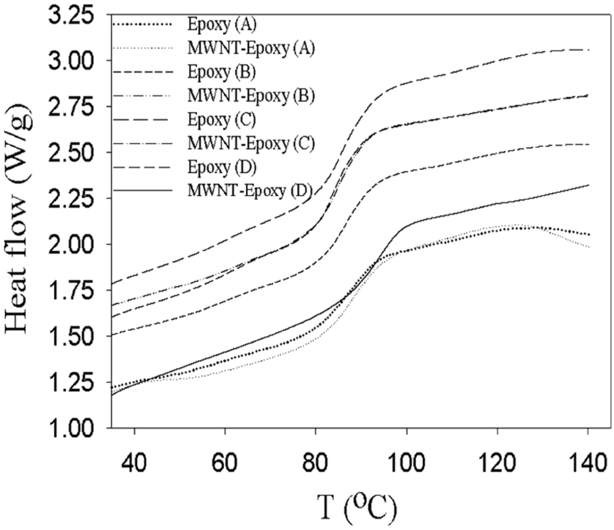


Figure 5. DSC curves of neat epoxy and MWNT/epoxy composites for cycles A to D.

nanotubes and the epoxy due to enormous surface area. This interfacial interaction reduces the mobility of the epoxy matrix around the nanotubes and leads to an observed increase in thermal stability.[16] For the whole range of temperatures, the nanocomposites of cycles A and C exhibit higher storage modulus than the epoxy. However, the increment of storage modulus composite A cycle above 45°C is more than that of the B cycle. The results of tensile and DMTA tests indicated that prolonging the curing time reduces the enhancement of mechanical and thermo-mechanical properties. This might be due to the fact that the introduction of carbon nanotubes has no effect on the maximum cure degree of epoxy, and by increasing the curing time, the nanotube effect decreases.

The cured samples were investigated by DSC to ensure a completed curing reaction and to exclude a possible influence of the degree of cross-linking on T_g. Figure 5 shows DSC curves measured for the neat epoxy and nanocomposites of 0.5 wt.% MWNT for cycles A to D. No exothermic post-curing peaks around

Table II. Values of T_g for epoxy and composite cycles A to D from DSC curves

Material	T_g (°C)
Epoxy (A)	85
Composite (A)	88
Epoxy (B)	92
Composite (B)	95
Epoxy (C)	90
Composite (C)	93
Epoxy (D)	90
Composite (D)	94

80°C were observed in the materials investigated. The T_g values obtained from the DMTA test are listed in Table II. The results show that the T_g point of the composites has been affected by the curing cycles. Comparing cycles A and B, epoxy and composite T_g has been increased by prolonging the curing time, but it seems that for cycles C and D, only composite T_g has been affected by the curing time.

CONCLUSION

The effect of four different curing cycles on the mechanical and thermo-mechanical behavior of MWNT/polymer composite samples was investigated. MWNT acted as reinforcing agent in the epoxy matrix in all of the cycles. However, enhancement efficiency was reduced with increase in curing time. It seems that the effect of the reinforcement is more evident for a less cured resin. The results demonstrated a high dependence of nanocomposite mechanical and thermo-mechanical properties on the curing cycle. The addition of CNTs also led to an increase in thermal stability. In addition, the best toughness was obtained using curing for 48 h at room temperature followed by a post-cure treatment for 10 h at 80°C.

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