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Effect of functionalization of multi-walled carbon nanotube on the curing behavior and mechanical property of multi-walled carbon nanotube/epoxy composites

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ABSTRACT

In this work, multi-walled carbon nanotubes (MWCNTs) were functionalized to fabricate MWCNT/epoxy composites by incorporating MWCNTs into an epoxy. Cure behavior of composites was investigated by differential scanning calorimetry. Thermo-mechanical behavior of the composite was then evaluated by dynamic mechanical analysis. Tensile strength, elastic modulus and maximum elongation were obtained by tensile test using the CMT-4204 universal testing machine. A field-emission scanning electron microscope was also used to characterize the fracture mechanism of composites and the dispersion state of MWCNTs in the epoxy. The results showed that the introduction of MWCNTs decreased the activation energy of the reaction and promoted the cure reaction. The addition of MWCNTs, especially amino-functionalized MWCNTs, clearly improved the tensile strength. The functionalized MWCNTs improved the interfacial bonding and made the dispersion of MWCNTs homogeneous in the matrix, giving the composites present a better mechanical property.

1. Introduction

Carbon nanotubes (CNTs) have excellent mechanical properties, such as high elastic modulus and high tensile strength [1–5]. They can serve as a promising reinforcement phase incorporated into a polymer matrix to improve its mechanical properties. In recent years, in order to research reinforcement effects on different polymer matrices, such as polyimide [6], epoxy [7,8], polyvinyl alcohol [9], and polyvinyl chloride [10] different CNT/polymer composites have been fabricated. In particular, as an important thermosetting polymer, epoxy resins with high tensile strength, good chemical resistance, high adhesion, low-weight, and low curing shrinkage in cure, have been applied in different industrial fields. However, cured epoxy resins are usually more brittle, and have poor fatigue resistance, heat resistance and impact resistance, which restrict their corresponding applications. CNTs as one of the most excellent reinforcements can be added into epoxy to improve its mechanical properties. One such example is that the effect of silane functionalized CNTs on the properties of epoxy-based composites studied by Kim et al. [11].

It is generally known that two main problems need to be solved in order to make the CNTs produce the maximum reinforcement effect in the polymer matrix [12,13]. The first problem is that the agglomeration owing to high Van der Waals force results in the inhomogeneous dispersion of CNTs in the polymer matrix. The other key problem is that weak interfacial bonding prevents stress transfer between CNTs and the polymer. The homogeneous dispersion of CNTs and strong interfacial bonding will improve the mechanical properties of CNT/polymer composites accordingly. Generally speaking, the functionalization of CNTs is a useful method to improve the dispersion of CNTs and enhance the interfacial bonding between CNTs and polymers [14]. Several approaches for functionalization of CNTs have been applied such as covalent functionalization [15,16] and non-covalent functionalization [17,18].

In this research work, multi-walled CNTs (MWCNTs) were used to obtain carboxyl-functionlized MWCNTs (COOH–MWCNTs) and amino-functionlized MWCNTs (amino-MWCNTs) by a series of chemical reaction. Epoxy-based composites filled with different MWCNTs were prepared. A tensile test, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were performed on neat epoxy and three different MWCNT/epoxy composites, respectively. At last, the fracture mechanisms of the

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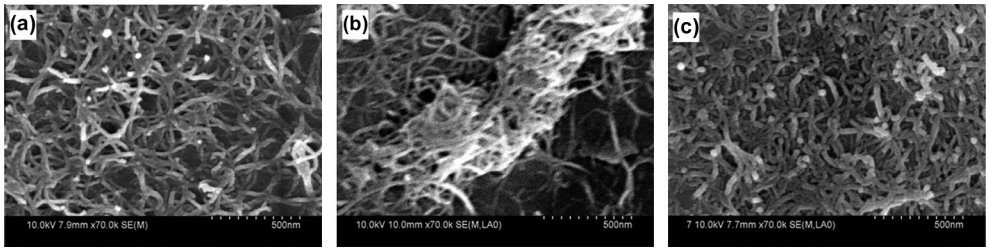

Fig. 1. Morphologies of (a) pristine MWCNTs, (b) COOH–MWCNTs and (c) amino-MWCNTs.

composites and dispersion of MWCNTs in the matrix were investigated through observing fracture surfaces of the materials.

2. Experimental details

2.1. Materials

The pristine MWCNTs used in this study were purchased from Nanocyl S.A., Belgium. They had a diameter of 10–20 nm and a length of 5–20 μm. The epoxy resin was bisphenol-A glycidol ether epoxy resin (DGEBA), purchased from Dalian Qihua Chemical Industry Co. Ltd, China. Triethylenetetramine (TETA), curing agent, was purchased from Tianjin Guangfu fine chemical Research Institute, China.

2.2. Fabrication of MWCNT/epoxy composites

COOH–MWCNTs and amino-MWCNTs were obtained by grafting carboxyl groups and amino groups on the surface of MWCNTs, respectively [19]. Firstly, 4 g pristine MWCNTs were treated with mixture acid with the volume ratio of 3:1 of concentrated sulfuric and nitric acid by sonicating at 40 °C for 10 h. The mixture was filtered and the residual substance was repeatedly washed with a mass of deionized water. And then, the sample was dried at 80 °C for 24 h in a vacuum oven and COOH–MWCNTs were obtained. Secondly, 2 g COOH–MWCNTs were dispersed in the mixture of 200 ml thionyl chloride ($SOCl_2$) and 20 ml dimethyl formamide (DMF), followed refluxed with magnetic stirring at 70 °C for 24 h. After reacting, the unreacted $SOCl_2$ was removed by the vacuum distillation. Finally, the acyl chloride functionlized MWCNTs were added into TETA and refluxed with magnetic stirring at 120 °C for 96 h. The mixture was filtered and the residual substance was repeatedly washed with ethanol until the last cleaning solution became clear and amino-MWCNTs were obtained.

Then, three different kinds of MWCNTs (pristine, COOH-, and amino-MWCNTs) were dispersed into the epoxy by a three-roller machine with water bath heating. Afterwards, TETA was gradually added into mixture to prevent, as far as possible, the creation of bubbles. Finally, the mixture was molded in a mould and cured at 40 °C for 0.5 h, 80 °C for 0.5 h, 110 °C for 1 h. The heating rate was 2 °C min^{-1} during the curing process.

2.3. Characterization

The MWCNTs were characterized by several methods. X-ray photoelectron spectroscopy (XPS) analysis was used to detect the element variation of the MWCNTs before and after functionalization. The microscopic morphologies of different MWCNTs were characterized by a field emission scanning electron microscope (FE-SEM), carried out on a Hitachi S-4800 at 10 kV. The curing reaction of the resins with and without MWCNTs was characterized through DSC (PerkinElmer) to study the curing behavior of the composites. The heating processes were scanned from 20 to 200 °C at a heating rate of 10 K min^{-1}. A CMT-4204 universal testing machine was used for the tensile testing at a crosshead speed of 2 mm/min (ASTM: D638-10). The tensile properties such as tensile strength, elastic modulus, and maximum elongation were determined through the tensile test. The fracture mechanisms of neat epoxy or composites and dispersion state of MWCNTs in the epoxy were observed using FE-SEM. Storage modulus (E') and mechanical dampening ($\tan\delta$) were evaluated by a DMA (NETZSCH DMA 242) with a three point bending mode. The dimensions of the sample were 50 × 10 × 5 mm. The heating rate was 3 K min^{-1} and frequency was 1 Hz under amplitude control.

3. Results and discussion

3.1. Morphology of MWCNTs

Fig. 1 presents morphologies of pristine MWCNTs, COOH–MWCNTs and amino-MWCNTs, respectively. As shown in Fig. 1a, the morphology of pristine MWCNTs is curly and they intertwine with each other. Also, the diameter of the pristine MWCNTs looks uniform and no obvious block is observed. After H_2SO_4/HNO_3 treatment, it is easy to observe that the diameter of the COOH–MWCNTs becomes a little smaller, owning to the oxidation of the outer layer of MWCNTs by strong acid. The MWCNTs severely intertwine with each other, which results in a bigger MWCNT block forming. This can be seen in Fig. 1b. From Fig. 1c, the most significant feature that we can observe is that the diameter of amino-MWCNTs is much bigger than that of pristine MWCNTs. Compared with pristine MWCNTs, the diameter of amino-MWCNTs changes from ~20 nm to ~30 nm. There are more defects created on the surface of the pristine MWCNTs after strong acid treatment and TETA is easily grafted onto the COOH–MWCNTs. The diameter is

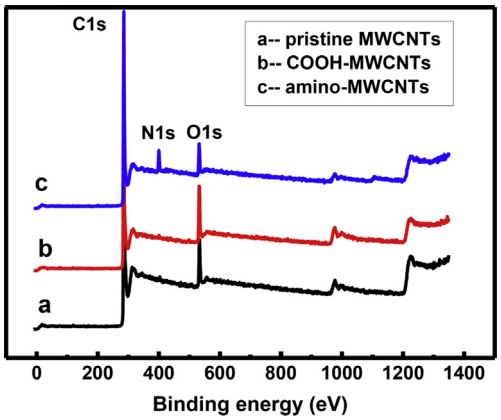

Fig. 2. General XPS survey spectra of (a) MWCNTs, (b) COOH–MWCNTs and (c) amino-MWCNTs.