Chemical Physics Letters 695 (2018) 34–43

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Mechanical properties and strengthening mechanism of epoxy resin reinforced with nano-SiO_2 particles and multi-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 3 December 2017
In final form 31 January 2018
Available online 2 February 2018

Keywords:
Epoxy composites
Multi-walled carbon nanotubes
Nano-SiO_2 particles
Mechanical properties
Strengthening mechanism

ABSTRACT

Nano-SiO_2 particles and MWCNTs were used to reinforce the EPs. The mechanical properties of the composites and the strengthening mechanisms of nano-SiO_2 and MWCNTs on the mechanical properties of epoxy composites were studied. The results show that the mechanical properties of the reinforced epoxy composites are greatly improved. Especially, nano-SiO_2/MWCNTs/EP composites exhibit the most excellent mechanical properties. The synergistic strengthening mechanisms of nano-SiO_2 and MWCNTs on the EP are the micro plastic deformation effect, micro-cracks and their divarication effect, and the pull-out effect of MWCNTs in EP matrix, which can reduce the extent of stress concentration and absorb more energy.

1. Introduction

Epoxy resins (EPs) have many advantages such as low density, good mechanical properties and high bond strength. They are widely used in structural adhesives, high-performance composites, electrical and electronic packaging materials and protective coatings etc [1–3]. However, epoxy resins have some essential disadvantages such as large internal stress, brittleness and poor impact resistance, so they are difficult to meet the application requirements under harsh conditions such as high load and strong impact, which limits their further application. Therefore, to further improve the mechanical properties of epoxy resins is an urgent problem to be solved.

In order to improve the mechanical properties of EPs, some research results were obtained by adding fillers to epoxy resin. The research results show that the filler in different scale (nano scale or micro scale) has a crucial effect on the mechanical properties of the epoxy composites. Cho et al. investigated the effect of particle size of glass beads and nano-alumina on the mechanical properties of polymeric composites. It is found that particle sizes at micro scale have little influence on the elastic modulus of the composite. However, the elastic modulus increases as the size of particles decreases to nano scale [4]. Because of the unique quantum size effect and surface effect [5], nanoparticles are desirable fillers to modify polymers and can improve the mechanical properties of epoxy composites [6]. As an inorganic filler, nano-SiO_2 particles have many favorable advantages such as inexpensive, nontoxic, biocompatible, chemical inertness, high thermal resistant and especially the ability to reinforce polymer matrix's mechanical properties, so they are widely used as fillers in polymer composites [7–9]. Preghenella et al. utilized nano-SiO_2 particles to modify epoxy resin and found that the dispersion of nano-SiO_2 greatly affects the mechanical properties of epoxy composites [10].

Carbon nanotubes (CNTs) have attracted considerable interest over the past two decades as they offer a unique combination of physical properties and chemical stability [11–13]. Generally, the mechanical properties of polymer composites added with carbon fillers depend on the intrinsic characteristics of the fillers, including morphology (size, aspect ratio, alignment, etc.) and their dispersion state in the polymer matrix [14,15]. CNT can tolerate 30% induced strain [16–19]. Due to the high elastic modulus of MWCNTs and the good interfacial interaction between MWCNTs and polymer matrix, the structural enhancement can be achieved when using MWCNTs in polymer composites. For example, Beg et al. found that the tensile strength and elastic modulus of nanocomposite increase by 22% and 20%, respectively, after adding MWCNTs [20].

However, the mechanical properties of epoxy composites reinforced with one single kind of filler are still not good enough. Especially, the strength and fracture toughness are still difficult to meet the needs of high load and strong impact as well as other harsh operating conditions. In order to further improve the mechanical properties of epoxy resins, the combination of two fillers are used

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https://doi.org/10.1016/j.cplett.2018.01.060
0009-2614/

to reinforce the epoxy resins, which is receiving more and more attention [21–27]. For examples, Li et al. studied the effects of hybrid carbon nanotubes (CNT) and graphite nanoplatelets (GNPs) on the mechanical properties of epoxy nanocomposites. The results show the quasi-static fracture toughness can be enhanced significantly by increasing the CNT content [26]. Yang et al. utilized nano-SiO_2 and EPDM to co-modify polypropylene, and found that the impact strength of ternary composites can reach 2–3 times higher than PP/EPDM binary blend [27].

At present, there is no report about the reinforcement of epoxy resin by the combination of nano-SiO_2 and MWCNTs. Therefore, in order to comprehensively utilize the advantages of nano-SiO_2 and MWCNTs to further improve the mechanical properties of epoxy composites, the epoxy composites reinforced by the combination of nano-SiO_2 and MWCNTs were prepared. Meanwhile, as comparison samples, the epoxy composites modified with nano-SiO_2 (nano-SiO_2/EP), and MWCNTs (MWCNTs/EP) were also studied. The synergistic reinforcing mechanisms of nano-SiO_2 and MWCNTs on mechanical properties of the epoxy composites were investigated, which provides a theoretical basis for their practical application in composites.

2. Experimental

2.1. Materials

Nano-SiO_2 particles with an average diameter of about 15 nm were provided by Shanghai Maikun Chemical Co., Ltd, China. The raw MWCNTs were provided by Shenzhen Nanotech Port Co., Ltd, China. The diameter of MWCNTs is from 15 nm to 25 nm and their length ranges from 1 μm to 2.5 μm. The epoxy resin (EP) was a bisphenol A epoxy resin (E-44) with an epoxy value of 0.44 mol/100 g, provided by Taizhou Huili Electronic Material Co., Ltd, China. The curing agent, polyether amine (D-230), was produced by Suzhou Chanco Industrial Co., Ltd, China.

2.2. Preparation of the composites

(1) Preparation of nano-SiO_2/EP composites

The addition contents of nano-SiO_2 particles are 1phr, 2phr, 3phr, and 4phr, respectively. The sample preparation procedures are as follows:

Firstly, the epoxy resin was degassed at 70 °C for 12 h. The required content of nano-SiO_2 particles were mixed with epoxy resin. For epoxy nanocomposites, high power dispersion methods such as ultrasonic and high-speed shear are the simplest and most convenient methods to improve the dispersion of nano fillers in the resin matrix. The mixture was placed in an ultrasonic bath apparatus (KQ-250DB ultrasonic treatment machine, Kunshan Ultrasonic Instruments Co., Ltd.) for ultrasonic treatment (40 kHz, 125 W) at 50 °C for 2 h. At the same time using electric stirrer (JJ-1A type, Changzhou Kaihang Instrument Co., Ltd.) stirring 12 h (the rotation speed of stirrer is 2500 rpm). Thereafter, 30phr curing agent (polyether amine, D-230) was added, the mixture was ultrasonic dispersed in ultrasonic bath (40 kHz, 125 W) for 30 min (temperature 40 °C) and stirring (speed 1500 rpm) at the same time. The mixture was vacuumed for 30 min and then poured into molds coated with release agent. All samples were kept at 25 °C for 24 h and then at 60 °C for 12 h. After curing, the nano-SiO_2/EP samples with different contents were obtained.

(2) Preparation of MWCNTs/EP and nano-SiO_2/MWCNTs/EP composites

The preparation of MWCNTs/EP and nano-SiO_2/MWCNTs/EP composites using the same procedures as above mentioned. In the MWCNTs/EP composites, the MWCNTs contents are 0.5phr, 1phr, and 1.5phr, respectively. In the preparation of nano-SiO_2/MWCNTs/EP, the MWCNTs were firstly mixed with the nano-SiO_2 according to the percent ratio shown in Table 1.

2.3. Characterization

The tensile and flexural properties of the samples were tested by CMT 5105 electronic universal testing machine. The tensile tests were carried out at the speed of 5 mm/min according to the ASTM D638-2014 standard, and the elastic modulus of the sample was measured using an electronic extensometer. The three-point bending tests were conducted according to the test standard of ASTM D790-2015, in which the bending speed is 2 mm/min. At least five samples were tested for each category.

The scanning electron microscope (SEM, Hitachi S4800) was used to observe the fracture surface morphologies of the samples. In addition, the transmission electron microscope (TEM, JEOL JEM-1011) was also used to examine the microstructure of the composites.

3. Results and discussion

3.1. Mechanical properties and strengthening mechanism of nano-SiO_2/EP composites

The effect of nano-SiO_2 on the mechanical properties of nano-SiO_2/EP composites is shown in Table 2. Fig. 1 shows the curves of tensile strength, elastic modulus and flexural strength of nano-SiO_2/EP composites. With the increase of nano-SiO_2 content, the tensile strength, elastic modulus and flexural strength take on an increase trend firstly and then decrease. When the content of nano-SiO_2 is less than 3phr, the tensile strength, elastic modulus and flexural strength improve with the increase of nano-SiO_2 content, and when the content of nano-SiO_2 is 3phr, they reach the maximum values. For example, the tensile strength increases to 64.75 MPa, which is 1.72 times that of neat EP. The flexural strength and elastic modulus are 1.45 times and 1.26 times of the neat EP, respectively. However, when the nano-SiO_2 content increases to 4phr, the tensile strength, elastic modulus and flexural strength decrease. Obviously, the proper addition content of nano-SiO_2 can greatly improve the mechanical properties of epoxy composites.

Fig. 2 illustrates the fracture surface morphologies of neat EP and nano-SiO_2/EP composites. As shown in Fig. 2a, the fracture surface of neat EP is smooth with few micro-cracks, which is a typical brittle fracture of thermosetting resins. With the addition of nano-SiO_2, the fracture morphology is changed and the fracture surface is obviously uneven as shown in Fig. 2b–e. Fig. 2b shows the fracture morphology of the sample with 1phr nano-SiO_2. Compared with neat EP, the fracture surface is obviously rough with a lot of micro-cracks that distribute radially and there are many micro-steps. The formation of these micro-cracks and micro-steps indicates the improvement of mechanical properties of the composite. Fig. 2c shows the fracture morphology of 2phr nano-SiO_2/EP sample, in which there exists a lot of micro-cracks (marked by arrow A) accompanied with some micro plastic deformation areas (marked by arrow B). The number of micro-cracks is more than that of Fig. 2b. Meanwhile, the propagating traces of the micro-cracks become curve and there are divergent phenomena, which can be inferred that much more energy is consumed in the fracture process.

When the nano-SiO_2 content reaches the optimum value (3phr), the fracture morphology of the composite is shown in Fig. 2d. There are much more micro-cracks with larger micro plastic deformation areas. The micro-cracks are closely arranged and their propagating directions interweave each other (marked by arrow A). Meanwhile, the addition of proper content of nano-SiO_2 causes