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Composites Science and Technology 66 (2006) 599–603
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness

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Received 11 August 2004; received in revised form 3 May 2005; accepted 16 May 2005
Available online 11 July 2005

Abstract

This paper systemically evaluates the different reinforcement roles of carbon nanotubes in those nanocomposites with different matrix stiffness while the curing process is controlled. Both mechanical test and microscope observation indicated that such reinforcement would gradually reduce while increasing the stiffness of matrix. However in the soft and ductile composites, carbon nanotubes show a significant reinforcement without fracture strain decreasing. The interface interaction is poor between carbon nanotubes and matrix in the stiff composite, and therefore, they have little contribution to the mechanical properties of composite. This research may help to propose a further positive solution for designing and fabricating carbon nanotube–epoxy nanocomposites.

Keywords: A: Polymer-matrix composites (PMCs); B: Curing; B: Mechanical properties; B: Microstructure

1. Introduction

Since carbon nanotubes [1] have proven their novel mechanical and electrical properties [2], researches on carbon nanotube/polymer nanocomposites have become a hot spot in the field [2,3]. Some previous investigations have revealed that the introduction of carbon nanotubes as a structural element in polymer matrix can improve their mechanical properties [4–6], and as conductive filler, they also can modify the electrical conductive property of polymers [7]. Therefore, the introduction of carbon nanotubes into polymers may improve their applications in the fields of reinforcing composites, electronic devices and more.

The recent researches have extensively focused on the epoxy resin-based carbon nanotube composites because of their wide applications in the electronics, aeronautics and astronautics industries [7–10]. However, the reinforcement role of carbon nanotubes in epoxy-based composites seems divergent. Some early research results just showed a barely stronger or weaker carbon nanotube–epoxy composites than the net epoxy [8,11,12]. Enhanced strength was also observed from several recent reports [10,13–15]. Carefully comparing these controversial results indicates that the stiffness of epoxy matrix seems to be a key point. Carbon nanotubes in a soft matrix seemed to easily take a significant role in the mechanical reinforcement [13–15]. However, there is no systemic investigation on the effect of the stiffness of matrix in the carbon nanotube nanocomposites. In this paper, we systemically evaluate the effect of the stiffness of epoxy matrix to the reinforcement role of carbon nanotubes by controlling the curing process. Mechanical test and microscope observation indicated that the reinforcement role of carbon nanotubes would gradually reduce while increasing the stiffness of matrix.

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0266-3538/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.compscitech.2005.05.020

2. Experimental

Carbon nanotubes were produced by a floating catalyst method, which was developed by Andrews et al. [16] for the commercial mass-production of aligned carbon nanotube arrays. Generally, a mixture of xylene (as carbon source) and ferrocene (dicyclopentadienyl iron, as catalyst source) with certain concentration (0.02–0.1 g/ml) was injected into a reactor at a reaction temperature of 650–850 °C, and a mixture of N_2 and H_2 (with total flowing rate of 1600 sccm and a ratio of 10:1) acted as the buffer gas. The growth time was about 30 min. Large amount of aligned multi-wall carbon nanotube arrays could be collected as small flakes from the wall of the quartz reactor tube. Fig. 1(a) displays a scanning electronic microscope (SEM) image of a piece of typical nanotube array, and the length of carbon nanotubes is about several tens of microns. After the carbon nanotube arrays were collected, they were directly dispersed in acetone by ultrasonic treatment for one hour, and the dispersed nanotubes were filtrated and dried. After that, we grinded them into carbon nanotube powder in an agate mortar. Fig. 1(b) shows an image of a dispersed and grinded carbon nanotube powder, and aligned carbon nanotubes became into loosely entangled ones. We found that it was much easier to disperse the rearranged nanotube powder into epoxy matrix than the as-grown aligned arrays by a mechanical mix method. TEM observation revealed that the diameter distribution of carbon nanotubes is in the range of 20–60 nm.

To prepare carbon nanotubes/epoxy composite, the nanotube powder (with a content of 0.5 wt%) was directly added into a liquid epoxy (Struers EpoxFix, bisphenol A-epichlorhydrine), and the solution was mechanically stirred for 5 min to form a homogeneous suspension. And then an epoxy hardener (Struers EpoxFix, triethylenetetramine) was mixed into the carbon nanotubes/epoxy suspension, and we softly stirred it for about 2 min. After that, we placed the mixture in a vacuum chamber for about 30 min to remove most of the bubbles induced from stirring. Finally, the composite suspension was poured into the dog-bone-like silicone mould with a gauge length of 30 mm, a width of 6 mm and a thickness of about 3 mm. Samples without carbon nanotube addition (matrix samples) were also fabricated for comparison.

As stated in Section 1, in this research, we tried to evaluate the influence of matrix stiffness on the reinforcement role of carbon nanotubes. It is well known that the degree of cure of pure epoxy and composite has great effect on their mechanical properties. Less hardener addition and shorter curing time suggests an incomplete cure, and consequently a more ductile matrix. Therefore, in our experiments, by changing the mixture ratio of epoxy hardener and the curing time that the matrix stiffness could be controlled. 10.7 wt% is considered as the normal hardener addition amount by the manufacturer, and 9–13 wt% as a hardener/epoxy ratio range of was employed. A range of curing time of 48–72 h was selected to obtain various stiffness of the composite matrix. Following this way, we produced a series of composite samples with different stiffness.

The as-prepared composite samples were then mechanically polished to form smooth surfaces. The thickness and the cross-section of the samples are carefully measured. Tensile tests were conducted on an Instron machine (model 4505, Instron static tension/compression load cell of capacity 5 kN with accuracy equal to or better than 0.025% of the cell rated output or 0.25% of the indicated load), and an extensometer (Instron dynamic extensometer with 12.5 mm gauge length with a travel of ±2.5 mm) was used to record the tensile strain of the samples. The samples were loaded to failure (or to the maximum limit of 2.5 mm of the extensometer) at a crosshead speed of 0.5 mm/min. Fracture surfaces of the composite samples were observed under a SEM after coating a thin layer of gold.

3. Results and discussions

Four pairs of typical stress–strain curves of the matrices (with pure epoxy) and of the composites with different stiffness are displayed in Figs. 2(a)–(d). The results indicate that carbon nanotubes take a more significant role in the composites with soft matrix than with hard

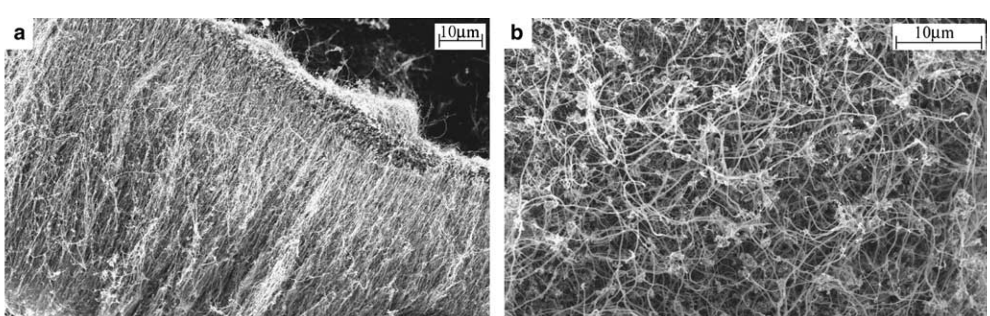

Fig. 1. SEM images of (a) as-grown aligned carbon nanotube arrays and (b) dispersed carbon nanotube powder.