Available online at www.sciencedirect.com
ScienceDirect
Composites Science and Technology 67 (2007) 3041–3050
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

The reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites

Jianfeng Shen, Weishi Huang, Liping Wu, Yizhe Hu, Mingxin Ye *

Department of Materials Science, Fudan University, The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Shanghai 200433, China

Received 16 November 2006; received in revised form 20 April 2007; accepted 25 April 2007
Available online 13 May 2007

Abstract

Functionalization with different amino groups of multi-walled carbon nanotubes was achieved and nanotube-reinforced epoxy nanocomposites were prepared by mixing amino-functionalized multi-walled carbon nanotubes with epoxy resin. Differential scanning calorimetry, thermogravimetric analysis and bending tests were used to investigate the thermal and mechanical properties of the nanocomposites. The results showed that different kinds of amino-functionalized multi-walled carbon nanotubes would have different effects on the thermal and mechanical properties of the nanocomposites. The reinforcement mechanism of amino-functionalized multi-walled carbon nanotubes in epoxy resin was discussed.

Keywords: A. Carbon nanotubes; B. Mechanical properties; B. Thermal properties; C. Stress transfer

1. Introduction

Epoxy resin is the most common class of thermosetting resin used in various applications because of their high tensile strength and modulus, low shrinkage in cure, good chemical and corrosion resistance, high adhesion and dimensional stability.

With unique atomic structure and very high aspect ratio, carbon nanotubes (CNTs) have extraordinary mechanical properties (such as high strength and unique flexibility), making them ideal reinforcing materials in composites [1–3]. CNTs incorporated composites represent a new frontier in materials science because the reinforcement scale has changed from micrometers to nanometers.

Processing of carbon nanotubes with and without surface modification and cure reaction of epoxy composites reinforced by single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have been reported. Breton et al. investigated the influence of microtexture, structure and surface chemistry of MWCNTs on the improvement of the elastic modulus of nanotubes-based composites [4]. Fidelus et al. reported that significant improvement (70% reinforcement) in tensile impact strength was obtained for the 0.5 wt% MWCNTs/epoxy system [5]. The research of Song et al. [6] proves that dispersion states of carbon nanotubes in epoxy composites were extremely important. Progress in reinforcing epoxy matrix with fluorinated single-walled carbon nanotubes has recently been reported [7].

However, the realization of nanotube-reinforced epoxy resin can only be achieved by solving following main problems: one is the lack of interfacial adhesion, which is critical for load transfer in composites – since the atomically smooth non-reactive surface of nanotubes built of rolled graphene sheets, lacking in interfacial bonding inhibits load transfer from the matrix to nanotubes across the nanotube/polymer interface. Another problem is the poor dispersion of nanotubes in the epoxy matrix, which is also significant for the fabrication of reinforced composites. Because of the

* Corresponding author. Fax: +86 021 65642622.
E-mail address: mxye@fudan.edu.cn (M. Ye).

0266-3538/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2007.04.025

fine size, high surface energy of CNTs and with intrinsic van der Waals forces, the as-received CNTs were apt to aggregate and entangle together spontaneously. In a CNTs/polymer composite, aggregation of CNTs may become a defect and cause the mechanical properties of the composite to deteriorate. Additional processing difficulties, as in the case of nanotube-reinforced epoxy polymer composites, come from the formation of high viscosity blends when the nanotubes are directly added at low shear rates. The high surface area of carbon nanotubes results in a high viscosity of the nanotube/epoxy mixture particularly when fabricating composites with high loading level of nanotubes, which makes the dispersion of nanotubes extremely difficult.

These problems can be overcome by using the functionalized nanotubes, which can provide multiple bonding sites to the organic/inorganic polymer matrix so that the load can be transferred to nanotubes and thus, inhibiting separation between the surfaces of polymer and nanotubes. Numerous methods for chemical functionalization of carbon nanotubes, either at the tips or sidewalls of CNTs, have already been reported. The chemical covalent bond mechanism has proved to be very useful in maintaining the stable bonds, and significant efforts have been directed towards the establishment of chemical functionalities on the surface of CNTs. Among them, amino-functionalized CNTs have been researched because amino group has a high reactivity, wealth of chemistry and can react with many chemicals, and thus can be directly incorporated into epoxy resin [8–15]. The hydrophobic nature of the as-received MWCNT surface becomes more hydrophilic after amine treatments, owing to the creation of amino functional groups, which are reactive with the functional groups in epoxy matrix.

In our work, we selected and prepared different amino-functionalized MWCNTs as reinforcing materials for epoxy resin. Comparing with SWCNTs, with smaller specific surface areas, MWCNTs show better dispersibility in polymer matrix, although their efficiency towards mechanical reinforcement is relatively lower than that of SWCNTs. In addition, high purity MWCNTs are available from a wide variety of sources at a fraction of the cost of SWCNTs. Serials of composites were prepared by incorporating homogeneously dispersed amino-functionalized MWCNTs into epoxy matrix. Furthermore, the influence of different kinds of amino-functionalized MWCNTs on the thermo-mechanical properties of the composites was presented. We found that the terminal amino groups covalently attached to the MWCNTs had a great effect on the ultimate properties of the composites, thus opening up new perspectives of reinforcing epoxy resin by selecting different amines to functionalize CNTs.

2. Experimental

2.1. MWCNTs

MWCNTs used in this study were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen,China). The MWCNTs synthesized by the chemical vapor deposition (CVD) process had an average diameter of 20 nm and length of 20–50 μm. The amino-fuctionalization and investigation of MWNTs would be published in other place [16,17]. Corresponding chemical reactions are illustrated in Fig. 1 and the exact compounds containing different amino groups are listed in Table 1.

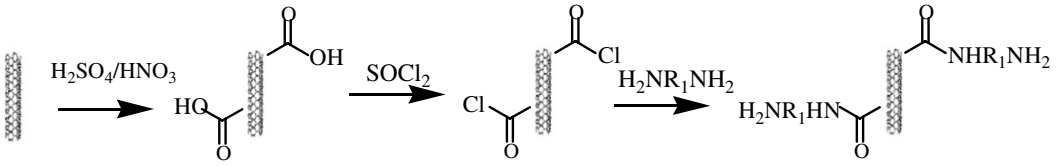
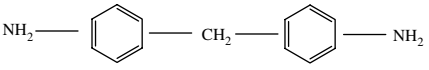


Fig. 1. The procedures used in this study for the functionalization of MWCNTs.

Table 1
Exact compounds for different functionalizations

Compound	R
Ethylenediamine (e-MWCNT)	$H_2NH_2CCH_2NH_2$
1,6-Hexanediamine (h-MWCNT)	$H_2NH_2CCH_2CH_2CH_2CH_2CH_2NH_2$
4,4′-Diaminodiphenylmethane (p-MWCNT)	
4,4′-Diamino-dicyclohexylmethane (c-MWCNT)