Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Materials Chemistry and Physics 94 (2005) 438–443
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Percolated network of entangled multi-walled carbon nanotubes dispersed in polystyrene thin films through surface grafting polymerization

Tian Shyng Lin, Ling Yu Cheng, Chih-Chun Hsiao, Arnold C.-M. Yang *

Department of Materials Science and Engineering, National Tsing Hua University, 101, Kuang Fu Road, Sec. 2, Hsinchu 30043, Taiwan

Received 10 December 2004; received in revised form 22 April 2005; accepted 18 May 2005

Abstract

Interpenetrating networks of entangled multi-walled carbon nanotubes (MWNTs) and polystyrene (PS) chains were prepared in thin films by solution casting from dilute solutions. The MWNTs were first surface grafted with PS chains to impart good interface compatibility and stereo hindrance against re-aggregation of the MWNTs in the solution phase. The grafting was accomplished by the reaction of 4-vinylbenzyl chloride with carboxylic acid groups previously attached to the nanotubes, followed by polymerization triggered by AIBN. The dispersion of the nanotubes was uniform, extending globally to form a percolated MWNT network, capable of withstanding large deformation, up to more than 25%, without fracture. The micro-necking of the fracture precursor of crazing was found to be strongly suppressed and only short and narrow crazes were formed in the stressed nanocomposites. Thus, the main energy dissipation mechanism of the composite upon external deformation shifted from craze widening to nucleation of new and short crazes that are much more resistant to fracture.

Keywords: Nanotubes; Percolated network; Surface grafting; Polymer thin films; Crazes; Entanglements; Interpenetrating networks

1. Introduction

The discovery of carbon nanotubes (CNTs) by Iijima [1] in 1991 had brought a widespread research enthusiasm for unveiling the fundamental properties, fabrication techniques, and novel applications of the nanotubes. It is now well-documented that CNTs possess quite unique and remarkable properties in respect of mechanical [2], electrical [3,4], thermal [5,6] and chemical behavior. For example, due to the high aspect ratio of their external shapes, nanotubes can form percolated networks even at very low filler fractions (<5 wt.%) to impart tremendous filler reinforcement effects. Intensive research is being focused on their potential applications such as field emission sources [7], AFM tips [8] and storage devices, hydrogen storage [9], nano-electronic or nano-photonic devices, and nanocomposite materials [10].

However, due to the large van der Waal forces stemming from large surface areas, inter-particle fusing by impurity amorphous carbon, and tube entanglements, CNTs tend to aggregate when introduced into a polymeric binder without proper pre-treatments. Once aggregation occurred, the intended percolated network would fail to form, and the resulted heterogeneities frequently hurt the very properties that were meant to be enhanced. Good dispersion generally requires proper surface treatments [11] as well as purification and disentanglement pre-treatment [12] of the highly intertwined nanotubes. There were extensive efforts in this regard [13–16]. Physical dispersing [10,17,18] (e.g., via van der Waals attraction, π–π interaction, etc.) to yield good dispersion of the as-produced nanotubes in aqueous solutions have been reported by Bandyopadhyaya et al. [19] and Fukushima et al. [20] although the effects intrinsically are of temporary nature. Star and Stoddart [21], and Hill et al. [22] Park et al. [18] and Mitchell et al. [23] had demonstrated significant progresses by chemical modifications of the single-walled nanotubes (SWNT) (via PMMA-grafted SWNT [15,16],

---

* Corresponding author. Tel.: +886 35720792; fax: +886 35722366.
E-mail address: acyang@mse.nthu.edu.tw (A.C.-M. Yang).

0254-0584/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2005.05.043

polypropylene/nano-carbon fiber, polystyrene (PS)/MWNT [14,23] and in situ polymerization of PI/SWNT [18]) in polymer matrices to exhibit good mechanical strength. None of them, however, dealt with highly diluted polymer solutions with pre-treated CNTs from which thin polymer films of well-dispersed percolated nanotubes could be produced by solution-cast. Thin films of novel properties are ubiquitous at the forefronts of scientific research and industrial applications. Furthermore, the molecular interactions between polymer chains and nanotubes usually can be most conveniently studied in thin films.

Therefore, in this paper, we focused on the development of the methods for stabilizing nanotube dispersion in dilute solutions, from which thin films of the nanocomposites could be obtained by spin-coating. The coupling agents to be grafted on the nanotube surfaces were selected to be polystyrene chains to give excellent compatibility with the PS surroundings and were long enough to provide stereo hindrance preventing the nanotubes from re-aggregating in the solution phase. The method used was based on the introduction of vinyl functional groups to the surfaces of CNTs by reaction of 4-vinylbenzyl chloride (CMS) with acid-treated MWNTs. The nanotubes were then polymerized in styrene to form polystyrene grafted-carbon nanotubes (p-MWNTs). The p-MWNT dispersed quite well in PS–toluene solutions and thin films of interpenetrated networks of PS and nanotubes could be made successfully by the spin-coating method.

2. Experimental procedures

The surface grafting of the MWNTs was carried out in three consecutive steps. First, the nanotubes were surface-treated by anchoring carboxylic acid groups onto the tube external surfaces (MWNTs–COOH). Then, the carboxylic acid groups in MWNTs–COOH were esterified by further reactions with 4-vinylbenzyl chloride to produce –COOR groups grafting on the tube surfaces (MWNTs–COOR). Finally, the grafted groups on the tube surfaces were put into the polymerization reaction, initiated with 2,2′-azobis-isobutyronitrile (AIBN), with styrene monomers. The surface grafting polymerization procedures were detailed in the following.

(1) *Preparation of MWNTs–COOH*: MWNTs synthesized via a chemical vapor deposition method (purchased from DESUN Nano Inc., Taiwan) had tube diameter of 10–30 nm and 5–15 μm in length. The as-received MWNTs were first purified by reflux for 48 h in 2.6 M nitric acid, followed by filtration with a PTFE membrane (0.2 μm pore size) and finished by repeatedly washing with deionized water. The purified MWNTs were then immersed in H_2SO_4/HNO_3 (mixture of 3:1 in volume) at 90 °C for 2 h and then vacuum-filtered through a 0.2 μm PTFE membrane. The solid was washed with deionized water again repeatedly until the pH of the filtrate reached 7. In this step, the nanotubes were oxidized by attachment of carboxylic acid groups on the MWNTs external walls. The tube lengths of the nanotubes were also reduced in this step [12]; therefore, the length of the treatment time was carefully controlled to retain optimal tube lengths.

(2) *Esterification of MWNTs–COOH with 4-vinylbenzyl chloride (CMS)*: The carboxylic acidified nanotubes (MWNTs–COOH) were then dispersed in toluene (10 mg of MWNTs–COOH in 10 ml toluene) with 68 mg of sodium ethoxylate at 40 °C by sonication continuously for 1 h to generate MWNT–COONa. Then, 1 ml of CMS was added into the solution and the mixture was again sonicated for another 2 h to produce the esterification product (MWNTs–COOR, $R = CH_2C_6H_4CHCH_2$).

(3) *Synthesis of polystyrene grafted-MWNT (p-MWNTs)*: To grow PS chains from the grafted functional groups on the CNTs, the esterification solution from the above procedure was added with 0.1 mg of AIBN and 1 ml of styrene monomer at 95 °C to initiate the polymerization reaction. The reaction batch was stirred continuously for 3 h. At the end, the majority of toluene in the solution was removed by low pressure distillation. Then, the polystyrene–MWNTs (p-MWNTs) were precipitated by adding methanol into the solution, and collected after filtration. The non-reacted or non-polymerized monomers (or oligomers) were herein washed and filtered out from the batch. The solid was then washed again in toluene by sonication and then vacuum-filtered through a 0.2 μm PTFE membrane. The chain lengths of the grafted PS on nanotubes were estimated from the SEC data of a batch without nanotubes but under the same polymerization conditions, to be around $M_n = 6300$ and $M_w = 7900$ (polydispersity = 1.26).

3. Results

3.1. FTIR

Fourier-Transform Infrared spectroscopy (FTIR) was used to identify the existence of carboxylic acid groups and the grafted polystyrene chains in the samples. The differences between the FTIR spectra, shown in Fig. 1a, of the as-received MWNTs, acid-treated MWNTs and p-MWNTs were noted. Two new peaks emerging at 1720 and 3400 cm^{-1} after the acid treatment corresponded respectively to C=O and –OH stretching, confirming the attachment of the carboxylic acid groups onto the MWNTs. The substitution of carboxylic acid group by ester group during reaction with CMS caused a decrease of height of the –OH peak at 3400 cm^{-1} and a shift of C=O peak from 1720 to 1680 cm^{-1}. Finally, after the graft polymerization, new peaks were observed to emerge in the frequency range from 2800 to 3200 cm^{-1} corresponding to sp^2 (=C–H) stretching (3000–3200 cm^{-1}) and sp^3 (–C–H)