Composites Science and Technology 91 (2014) 98–103

Contents lists available at ScienceDirect

Composites Science and Technology

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

Simultaneous reinforcement and toughening of polyurethane composites with carbon nanotube/halloysite nanotube hybrids

Ling Jiang [a], Chao Zhang [a], Mingkai Liu [a], Zhe Yang [a], Weng Weei Tjiu [b], Tianxi Liu [a,*]

[a] State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, PR China
[b] Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Singapore

ARTICLE INFO

Article history:
Received 6 October 2013
Received in revised form 23 November 2013
Accepted 27 November 2013
Available online 8 December 2013

Keywords:
A. Carbon nanotubes
A. Nanoclays
A. Hybrid composites
A. Polymer-matrix composites (PMCs)
B. Mechanical properties

ABSTRACT

In this work, three-dimensional (3D) hybrid nanofillers, composed of acid-treated multi-walled carbon nanotubes (a-CNTs) and silane-treated halloysite nanotubes (s-HNTs), have been successfully prepared through covalent bonding. By using simple solution-casting method, polyurethane (PU) elastomers reinforced with these s-HNT/a-CNT (HC) hybrid nanofillers have been fabricated. The morphology and mechanical properties of the resultant hybrid and PU composites are characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM), thermogravimetric analysis (TGA) and tensile tests. Tensile test data show that the tensile strength, Young's modulus and elongation at break of the resultant PU composite with merely 1 wt% HC hybrids are significantly improved by 140%, 35% and 68% respectively. This clearly demonstrates the synergistic reinforcement of one-dimensional CNTs and HNTs within the hybrid in improving the strength and toughness of PU composite. Therefore, the s-HNT/a-CNT hybrid thus prepared is an ideal agent for simultaneous reinforcement and toughening of PU elastomers.

1. Introduction

It is known that the mechanical properties of polymer/filler composites are mostly influenced by the dispersion state of the fillers as well as the interfacial interactions between the filler and the polymer matrix. It has been proved that the reinforcement of polymer composites can be achieved by adding various kinds of fillers, while few works have been focused on simultaneous reinforcement and toughening properties of elastomer composites. Hybrid nanomaterial, which is composed of two heterogeneous construction units with different properties, is one of the most reliable solutions for designing new class of efficient, functional, and multidimensional nanofillers [1]. By selecting different raw materials and modifying the hybridization process, taking into account the features and dimensions of building blocks or units, hybrid nanomaterials can be designed as co-dispersant for the two construction units themselves, thus enhancing their connection. This consequently improves the dispersion of the hybrid in the matrix, along with the enhancement of interfacial adhesion between the hybrid and the matrix, as well as combining the properties of both the discrete nanofillers and the host polymer matrix. Till now, hybrid nanofillers with different dimensions have been prepared, such as 1D/2D (e.g., CNT/graphene), 2D/3D (e.g., graphene/carbon black), 3D/3D (e.g. Au/Pt) core/shell nanomaterials, and so on. In particular, one dimensional (1D) carbon nanotubes (CNTs) are considered to be one of the most promising reinforcement candidates due to their excellent mechanical and thermal properties [2]. Various CNTs-containing hybrids with high performance had been reported, such as polypropylene grafted multiwalled carbon nanotubes (MWCNTs) [3], "pin" structural MWCNTs/Al_2O_3 [4], self-assembled DNA/single-walled carbon nanotubes [5], 1D CNTs/2D pyrolytic carbon [6], and so on. In our group, the hybridization of 1D CNTs/2D nanoclay had been achieved by the in situ growth of the CNTs into the interlayer galleries of clay. These CNT/clay nanohybrids were then used for fabricating nylon-6 composites which showed a dramatic enhancement in their mechanical properties [7]. Unique hybrids of 1D CNTs/2D graphene had also been prepared through their π–π stacking interaction and used for fabricating different polymer composites with desirable properties [8,9].

1D halloysite nanotube (HNT), $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$ [10], one of naturally occurring clay minerals, is a new kind of prominent nanofillers composed of multi-walled nanotubular-shaped crystalline nanostructures. HNTs can be used to fabricate complex and economically available polymer composites, especially for the purpose to improve mechanical and thermal properties [11]. At present, the approaches for fabricating 3D hybrid nanomaterials of 1D CNTs and 1D HNTs have rarely been reported. In this work, 3D intercross-linked hybrid of s-HNT/a-CNT (HC) has been

* Corresponding author. Tel.: +86 21 55664197; fax: +86 21 65640293.
E-mail address: txliu@fudan.edu.cn (T. Liu).

0266-3538/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2013.11.025

prepared for the first time by modifying low-cost HNTs with silane coupling agent (KH560) and subsequent grafting of acid treated multi-walled CNTs (a-CNTs). The obtained HC hybrids are then used to prepare polyurethane elastomer composites by using solution-casting method. The tensile strength, modulus and toughness of PU matrix are remarkably enhanced simultaneously with the incorporation of the 3D HC hybrids. In addition, the mechanisms of simultaneous reinforcement and toughening of the CNT/HNT hybrids are also being explored.

2. Experimental

2.1. Materials

MWCNTs, with a diameter of 10–20 nm, were supplied by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China. Halloysite nanotubes, with an outer diameter between 15–100 nm and approximate length of 500–1000 nm, were obtained from Zhengzhou Jinyangguang China Clays Co., Ltd. (China). The thermoplastic polyurethane (PU, Estane 58277) used in this study was a commercial polyester-type PU received from BF Goodrich Company. All other reagents were supplied from Sinopharm Chemical Reagent Co., Ltd. and used as received.

2.2. Preparation of acid-treated multi-walled carbon nanotubes (a-CNTs), modified halloysite nanotubes (s-HNTs) and s-HNT/a-CNT (HC) hybrids

a-CNTs were prepared by refluxing the pristine MWCNTs in concentrated nitric acid for 12 h at 120 °C, according to the procedures reported previously [12]. s-HNTs were synthesized by the reaction of silane coupling agent (KH560) with the hydroxyl groups of HNTs. Typically, HNTs (1.0 g) and KH560 (2 mL) were dispersed in toluene (50 mL) at 120 °C and stirred for 4 h. The resulting modified HNTs were then filtered, followed by subsequent washing with ethanol for several times, and finally dried in vacuum at 60 °C for 12 h to obtain epoxy-functionalized HNTs (i.e., s-HNTs).

In order to prepare HC hybrids, s-HNTs and a-CNTs were separately dispersed in DMF. Typically, 20 mg of s-HNT powder was dispersed in 70 mL of DMF and then sonicated for 60 min. The dispersion of a-CNTs in DMF with a concentration of 0.5 mg mL^{-1} was also prepared using similar method. Then, desired amount of each dispersions were extracted and mixed together, followed by sonicating for 30 min. After that, 0.4 g triethylamine was added into the mixture and subsequently refluxed at 120 °C for 6 h. Finally, the products were extensively washed with ethanol and dried via freeze-drying process to obtain the HC hybrid. For comparison purposes, mixture of s-HNTs and a-CNTs with equally desired quantity were prepared without any further treatment. This mixture was labelled as HCM.

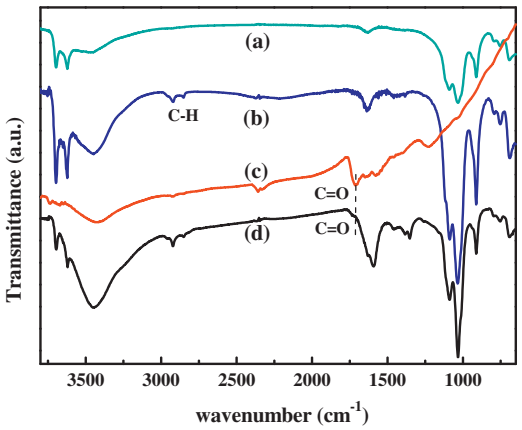
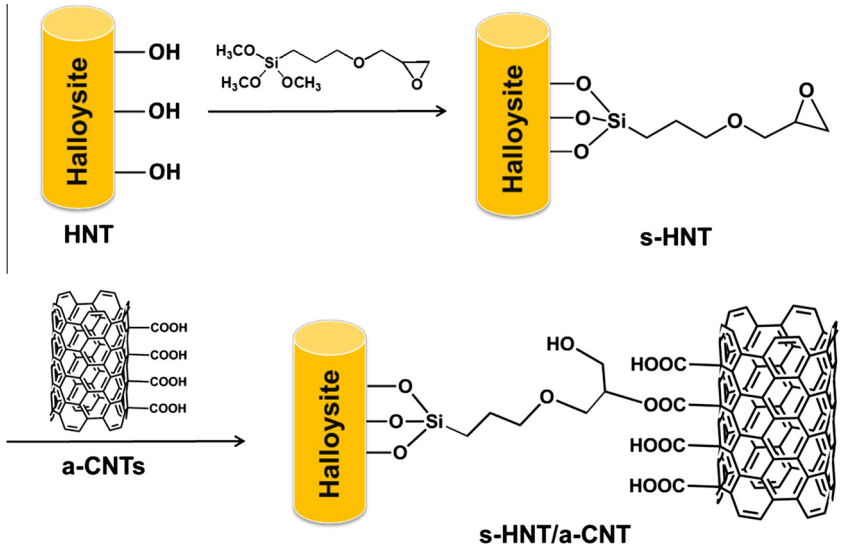


Fig. 1. FTIR spectra of (a) pristine HNT, (b) s-HNT, (c) a-CNT and (d) HC hybrid.

2.3. Fabrication of pristine PU and its composite films

To obtain the composite film containing 1 wt% HC hybrids, PU solution were first prepared by dissolving 0.5 g of polyurethane (PU) pellets in 10 mL of DMF at 95 °C. Then, 5 mg of the as-obtained HC hybrids were dispersed in 5 mL DMF and gradually added to the PU solution. After being stirred for 4 h, the mixture was poured into a culture dish and slowly evaporated at 80 °C until an equilibrium weight was reached. In addition, four parallel samples of neat PU as well as PU composite films, each being incorporated with 1 wt% of a-CNTs, HNTs and HCM respectively, were prepared in similar way. The thickness of the resulting films was about 0.2 mm.



Scheme 1. Schematic showing the modification of HNTs and the synthesis of s-HNT/a-CNT (HC) hybrids.