Applied Surface Science 316 (2014) 549–557

Contents lists available at ScienceDirect

Applied Surface Science

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

In situ polymerization of graphene oxide and cyanate ester–epoxy with enhanced mechanical and thermal properties

Fang Ren[a], Guangming Zhu[a,*], Penggang Ren[b], Yongkun Wang[a], Xiaoping Cui[a]

[a] *Department of Applied Chemistry, Northwestern Polytechnical University, Xi'an, Shaanxi 710129, PR China*
[b] *The Faculty of Printing and Packaging Engineering, Xi'an University of Technology, Xi'an, Shaanxi 710129, PR China*

ARTICLE INFO

Article history:
Received 14 June 2014
Received in revised form 23 July 2014
Accepted 24 July 2014
Available online 4 August 2014

Keywords:
Graphene oxide
Cyanate ester
Epoxy
Mechanical properties
Thermal stability

ABSTRACT

Uniformly dispersed graphene oxide (GO)/cyanate ester (CE)–epoxy (EP) composites were successfully synthesized by in situ polymerization. Both the results of FT-IR and XPS verified that epoxide groups on the GO sheets reacted with cyanate group (O—C≡N) in the resin. These results could provide excellent dispersion of GO and strong interfacial interaction between GO and CE matrix. TEM confirmed that GO tended to be a single layer. XRD and SEM indicated that matrix molecules could be inserted into the interplanar spacing of GO. The mechanical properties and thermal behavior of the composites were investigated in detail. It is observed that GO reinforced EP-CE composites demonstrated improved mechanical properties and better thermal stability than that of EP-CE matrix, which make them suitable for use in aerospace applications and structural composites.

1. Introduction

Graphene possesses extraordinary electronic, thermal and mechanical properties and, therefore, is the promising candidate as nanofillers in polymer composites. By incorporating within a polymer matrix, these atomically thin carbon nanosheets can significantly improve the physical properties of the host polymer at very low fillers loading. Homogeneous dispersion of graphene nanosheets (GNSs) in the polymer matrix and exact interface control are difficult to achieve due to the potent interlayer cohesive energy and surface inactiveness of the composites, which severely limit their application in the manufacture of polymer composites [1,2]. To solve these problems, various approaches to modify GNSs by chemical means or non-covalent functionalizes have been reported [3,4], among which graphene oxide (GO) can be easily synthesized [5]. There are plenty of oxygen-containing groups on GO surface, which not only allow the good dispersion in matrix, but also provide active sites to form chemical bonds, acting as an ideal interface between the GO and polymer [6,7]. In recent years, some works have been reported with respect to constructed the chemical bonding between the GO and polymer matrix, which would significantly increase the mechanical and thermal properties of composites. Li et al. [8] have reported that polyurethane/epoxy (PU/EP) composites in situ synthesized on the GO for the first time. Morphologic study shows that the GO was dispersed well in the PU/EP matrices and formed a strong interfacial interaction between the GO and the matrix due to the formation of chemical bonding.

Cyanate ester (CE) resin is superior to conventional EP as the next-generation thermosetting polymer matrix. The very low moisture absorption, good mechanical properties, good radiation resistance, long pot-life and cost-effective property make it suitable for use in many areas, such as electric packaging for microelectronic industries, matrix resins for aerospace applications and structural composites. In the aerospace industry, cyanate ester based composites are often used for engine cowlings and thrust reversers and for structural skins [9–11]. The cured CE exhibits excellent high-temperature properties, but because of highly cross-linked network structure it is brittle in nature. The mixture of CE and EP was reported for its excellent performance, such as good radiation resistance, long pot life and cost-effective property [12–14]. However, the pure mixture is normally brittle and has poor crack resistance. Therefore, it is essential to improve the mechanical properties of the matrix. Adding reinforcing nanofillers such as surface-treated silica [15], carbon nanotubes [16], and bentonite clay [17] to the thermosetting polymer matrix is an effective way to enhance toughness performance which can meet the application requirements.

---

* Corresponding author.
E-mail address: gmzhu@nwpu.edu.cn (G. Zhu).

http://dx.doi.org/10.1016/j.apsusc.2014.07.159
0169-4332/© 2014 Elsevier B.V. All rights reserved.

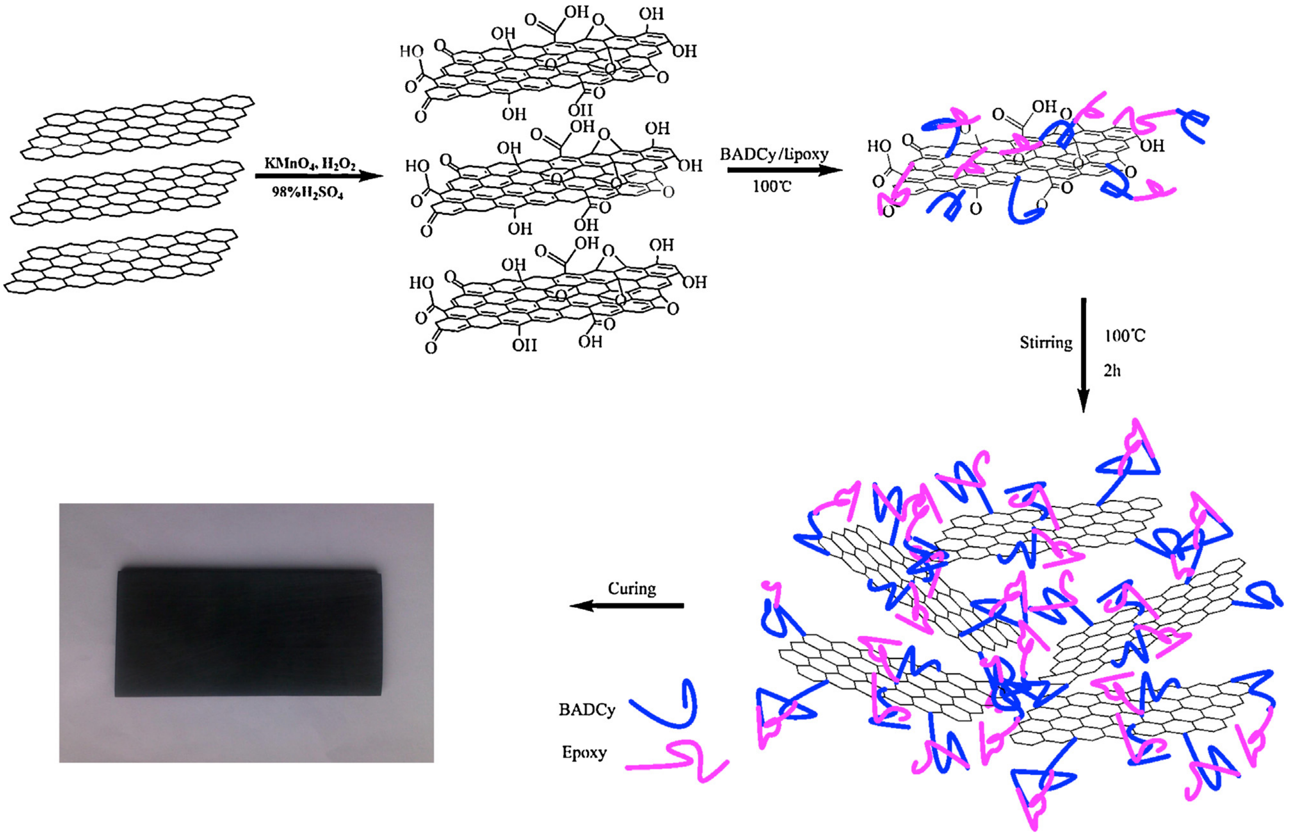

Fig. 1. Schematic for the process of GO/CE-EP composites.

Very recently, the enhancement of toughness on thermosetting materials by the incorporation of graphene has been studied [18–20]. EP has been reported to be successfully toughened by the incorporation of graphene [21–25]. The necessity of good dispersion and interfacial adhesion between graphene and EP were discussed in these reports. Furthermore, influences of graphene on the network structure, morphology and curing process of EP matrix are regarded critical in the toughening issue. Zaman et al. [21] synthesized two types of EP/Graphene platelets (GP) nanocomposites with different interface strength. The chemical modified GP (m-GP), which subsequently reacted with matrix molecules during curing, bridged with matrix, building a strong interface. However, little research has been done about interface reaction between CE and GO. Herein, inspired by Li' work, CE is selected as the host polymer to synthesize GO/CE-EP composites to investigate the effect of interface on the structure and properties of the composites. The differences between Li' work and our research are shown in Fig. S1 (Supplementary Information).

2. Experimental

2.1. Materials

Expanded graphite (expansion rate, 200 ml g^{-1}) was obtained from Qingdao Haida Graphite Co., Ltd. (Qingdao, China). H_2SO_4, $KMnO_4$, H_2O_2 and HCl were all analytical grade and supplied by Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Bisphenol A dicyanate ester (BADCy) was obtained from Shengda curatorial Co., Ltd. (Zhejiang, China). Bisphenol-A based epoxy (Epoxy E-51) with epoxide equivalent weight 184–200 g/equiv., was purchased from Lanxing resin Co., Ltd. (Wuxi, China). N, N-dimethylformamide (DMF) was purchased from Sigma–Aldrich and was used as purchased.

2.2. Preparation of GO/CE-EP resin composites

Graphite oxide was prepared as reported by modified Hummer's method [26]. Stable dispersions of GO were prepared by ultrasonic exfoliation (100 W) of the graphite oxide for 1 h in DMF. Here, the amount of GO added was considered as the amount of as-formed GO in the dispersion. A certain amount of the BADCy and E-51 (the weight ratio of CE and E-51 is 5:1) were mixed at 120 °C with magnetic stirring for 30 min. Then, the BADCy and E-51 mixture was added into the GO/DMF solution and stirred by a high-speed shear mixer at a speed of 10,000 rpm for 1 min, and sonicated for 30 min. And after, the solvent was evaporated off by heating the mixture in a temperature controlled oil bath pot at 120 °C with magnetically stirring at a speed of 300 rpm for 5 h. Stirring plays a crucial part in ensuring the uniform distribution of CE resin in the mixture when the solvent is evaporating off. After heating the mixture to eliminate most of the DMF, the mixture was placed in a vacuum oven at temperature of 100 °C for 12 h to ensure removal of residual solvent. After that, the mixture was cast into a mold for curing and postcuring with the sequence 120 °C/1 h + 150 °C/2 h + 180 °C/2 h and 200 °C/2 h. The GO/CE-EP composites obtained (all the process can be express as follow Fig. 1) were used for mechanical and dielectric testing.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} on IS10 Infrared Spectrometer (USA). X-ray diffraction (XRD) analysis was carried out in a D2 PHASER diffractometer operated at 30 kV accelerating voltage and 15 mA current. Scans were taken with 2θ from 5.8° to 30° and step size of 0.03° using a high resolution mode. X-ray photoelectron spectroscopy (XPS, Thermal Scientific K Alpha)