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Enhanced interfacial interaction between polycarbonate and thermally reduced graphene induced by melt blending

Bin Shen, Wentao Zhai *, Mimi Tao, Dingding Lu, Wenge Zheng *

Ningbo Key Lab of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang Province 315201, China

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ABSTRACT

Melt blending is the most economically choice to disperse graphene into polymer matrix because of its high efficiency, easy to scale up, and no solvent is involved. Therefore, it is meaningful to generate an enhanced interfacial interaction directly through melt blending of graphene and polymers. In this study, the effect of melt blending on the interfacial interaction between thermally reduced graphene oxide (TRG) and polycarbonate (PC) had been investigated. Ultracentrifugation of the melt-mixed PC/TRG composite solutions led to dark-colored supernatants, indicating the improved dispersion of TRG in some solvents, suggesting the existence of enhanced interfacial interaction between TRG and PC. The shift of C═O stretching vibration of PC (interacted with TRG) in the FT-IR spectra as well as the shift of absorption peak of phenyl groups in the UV–vis spectra suggested the formation of chemical bonding between the carbonate groups in PC chains and the carboxyl groups on TRG through transesterification and the formation of noncovalent π–π stacking interaction between PC and TRG during melt blending. Furthermore, the effect of melt blending on mechanical reinforcement of the PC/TRG composites was also evaluated.

1. Introduction

Graphene, characterized by an atomically thin two-dimensional sheet of *sp*^{2} atoms, is regarded as "the thinnest material in the universe" with tremendous potential applications [1–5]. For polymer/graphene composites, the well dispersion of graphene and the generation of strong interfacial interaction are two main issues for warranting excellent mechanical properties. Due to high aspect ratio of graphene, large interfacial areas are available for matrix-to-fillers' stress transfer, but an adequate interfacial interaction is necessary in order to achieve a good load transfer. The weak polymer/graphene's interfacial interaction prevents efficient stress transfer from polymer matrix to graphene. In order to overcome these hurdles, it is desirable to modify the graphene to enhance the interfacial interaction. At present, the main approach for modifying graphene is chemical covalent attachment of functional groups, which generally includes "grafting from" or "grafting on" strategies [6–11].

For the strategies mentioned above, the procedures are complicated, and the production efficiency is very low, which make these strategies unsuitable for abundant manufacture of polymer/graphene composites. Therefore, we propose that whether strong interfacial interaction can be achieved directly through melt blending (a highly scalable and environmentally friendly processing technique) of polymer and pristine graphene. Actually, simple melt blending can indeed induce some interfacial interaction between the nanofillers and the polymer components due to high temperature and strong shear forces [12,13]. For instance, Zhang et al. confirmed that melt blending could induce noncovalent π–π stacking interaction between polystyrene (PS) and the π-electrons of carbon nanotubes (CNTs) [14]. Similarly, Lu et al. studied the styrene–butadiene–styrene tri-block copolymer (SBS)/CNTs composite, and their results showed that there were π–π interaction between CNTs and SBS occurred during melt blending, leading to an improvement of the mechanical properties of SBS/CNTs composites [15]. Our previous study of PS/graphene composites had also shown that melt blending led to an enhanced interfacial interaction between PS and graphene due to the formation of π–π stacking interaction, which was indicated by the improved dispersion of graphene in solvents [16]. However, to the best of our knowledge, only noncovalent interfacial interaction induced by melt blending based on PS segments have been reported, and there is no research concerning the effect of melt blending on the interfacial interaction in other polymer/graphene composites. Addressing this question will help us understand the formation mechanism of the enhanced interfacial interaction and will be of great interest in both academic and industrial research.

The most used graphene in polymer composites is synthesized by thermal exfoliation and reduction of graphite oxide (GO) under heat treatment [17]. Compared with the defect-free graphene

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* Corresponding authors. Tel.: +86 0574 8668 5256; fax: +86 0574 8668 5186.
E-mail addresses: wtzhai@nimte.ac.cn (W. Zhai), wgzheng@nimte.ac.cn (W. Zheng).

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synthesized by chemical vapor deposition (CVD), thermally reduced graphene oxide (TRG) possesses not only rich π-electrons, but also multiple oxygen-containing functionalities, such as hydroxyl, epoxy and carboxyl groups on its surface [18]. We conjectured that these functional groups potentially allow TRG sheets to react with some functional groups in polymer chains during melt blending. Bisphenol-A polycarbonate (PC) is another most commonly-used commercial polymer due to its high toughness. The transesterification between the carbonate groups in PC and carboxy-CNTs under heat treatment has been reported [19–21]. Thus, we propose that the carboxyl groups on TRG sheets could react with the carbonate groups in PC through transesterification during melt blending as well, leading to the chemical bonding of PC chains to TRG sheets.

In this article, the main target is to investigate the effect of melt blending on the interfacial interaction between PC and TRG sheets. In order to achieve this purpose, the composites were first solution mixed and then subjected to melt blending for different times, in which the strong shear forces and high temperature was exerted on the melt. The resultant samples were then systematically assessed by various characterization techniques. The results indeed suggested an enhanced interfacial interaction between PC and TRG was generated due to the occurrence of transesterification as well as the formation of π–π stacking interaction. Furthermore, the effect of melt blending on mechanical reinforcement of the composites was also evaluated. It is anticipated that this work will explore a convenient gateway to achieving an enhanced interfacial interaction between polymers and graphene directly by melt blending, offering potential for practical application in polymer/graphene composites.

2. Experimental section

2.1. Materials

TRG sheets were prepared by low-temperature exfoliation and reduction of GO at 180 °C under ambient atmosphere according to our previous research [17]. The C/O ratio of TRG was ~8.0, measured with a Shimadzu Axia-Ultra DLD X-ray photoelectron spectroscopy. The specific surface area is ~700 m^2/g measured with a Micromeritics ASAP 2010 analyzer by the BET method using nitrogen adsorption. Bisphenol-APC was purchased from GE Plastics Inc. in the form of pellets. Poly(lactic acid) (PLA) (2002D) in pellet form was purchased from Nature Works LLC. Other reagents were obtained from Sinoparm Chemical Reagent (China).

2.2. Production of PC/graphene composites

TRG is a material with a low bulk density, and feeding large amounts of TRG into the polymer melt is difficult, especially in the case of high loading. Therefore, the PCG composites containing 3.0 wt% TRG were firstly prepared by solution mixing and subsequent melt-mixing (Fig. 1a). A typical procedure for the preparation of PCG composites is given below: The PC/$CHCl_3$ solution with 20 g of PC and 200 ml of $CHCl_3$ was added into a beaker containing 600 mg of TRG in 50 mL of $CHCl_3$ kept under sonication for 30 min. The mixture was constantly stirred for an additional 60 min and precipitated in excess *n*-hexane. The dried, premixed composites were melt-mixed at 240 °C in a mini-laboratory extruder (SJZS-10, Wuhan Rayzone Ming Plastics Machinery Co., Ltd.) with a speed of 40 rpm for different times, i.e., 0, 5, 10, 20 and 30 min, and the prepared PCG composites were coded as PCG0, PCG5, PCG10, PCG20, and PCG30, respectively. The dissolution of the composite was accomplished by adding appropriate $CHCl_3$ into a known amount of composite and stirring for 30 min. PCG films with thickness of about 100 μm were prepared by compression molding at 240 °C and were used for tensile tests. The PLA/TRG composite with 3.0 wt% TRG loading was first prepared by solution mixing and then melt blended at 180 °C for 30 min.

2.3. Ultracentrifugation and extraction

The same amount of PCG composite was dissolved in $CHCl_3$ under vigorous stirring, respectively. Then, the suspensions were centrifuged at 10,000 rpm for 60 min, and the supernatant solutions were decanted. After that, the supernatant solutions were vacuum-filtered through a 220 nm Teflon membrane, and the collected PC filtrate was dried at 80 °C under atmospheric pressure for GPC measurement. Moreover, the collected black solids were thoroughly washed by $CHCl_3$ through a dispersion-filtration-washing cycle to remove any free PC as mentioned in our previous study [8,22]. During each cycle of vacuum-filtration, several drops of filtrate were added into *n*-hexane from time to time, and the absence of cloudiness was used to indicate the complete removal of PC. Finally, the collected black solids were dried overnight at 80 °C.

2.4. Characterizations

Fourier transform infrared (FT-IR) measurements were performed on a Thermo Nicolet 6700 spectrometer. Transmission electron microscopy (TEM) was conducted on a Tecnai G2 F20 transmission electron microscope with an accelerating voltage of 100 kV. The samples for TEM measurements were prepared by placing one drop of sample dispersion in $CHCl_3$on carbon-coated copper grids. Thermal gravimetric analyses (TGA) were conducted at 20 °C/min from room temperature to 700 °C under a nitrogen flow (20 ml/min) using a Mettler-Toledo TG/DSC 1 analyzer (Switzerland). The ultraviolet–visible (UV–vis) spectra were recorded on a computer-controlled spectrophotometer (Perkin Elmer Lambda 950), using $CHCl_3$ as a reference solution. The scanned area was from 200 to 800 nm. Raman spectra were excited with a laser of 633 nm and record with Labram spectrometer (Super LabRam II system). GPC experiments were determined by Gel permeation chromatography (GPC, Waters Breeze 1515). THF was used as an eluent and the PS standard for calibration. Tensile testing was carried out according to ASTM D882-09 on an Instron testing machine at a crosshead speed of 5 mm/min. All samples were compression-molded to ~100 μm thick films and then cut into strips of ~150 mm × 10 mm using a razor blade. In cases, more than five samples were tested from which the mean and standard deviation were calculated.

3. Results and discussion

3.1. The enhanced interfacial interaction in melt-blended PCG composites

Various PCG composites with different melt-blending time were prepared by a two-stage blending procedure. The effect of melt blending on the interfacial interaction between PC and TRG was examined through dissolution in organic solvents. The PCG composites were soluble in organic solvents, such as $CHCl_3$, in which the PC matrix is soluble. Fig. 1b shows the photographs of supernatants decanted from the PCG composite solution (the concentration of TRG is about 1.2 mg/ml in all samples) after being centrifugated at 10,000 rpm for 60 min. Clearly, the supernatant obtained from PCG0 sample without melt blending is colorless and transparent, which indicated that no visible TRG was present in the supernatant. It is known that $CHCl_3$ is not a good solvent for TRG and the density of TRG is much higher than that of $CHCl_3$. Both of the two factors induced the occurrence of phase separation of the PCG suspension under strong centrifugal force. After being