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Polycarbonate toughening with reduced graphene oxide: Toward high toughness, strength and notch resistance

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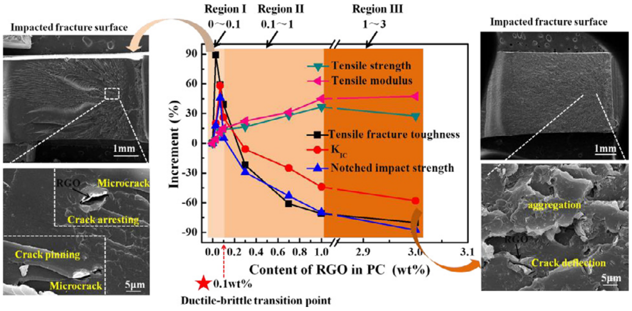
HIGHLIGHTS

- Reduced graphene oxide (RGO) was melt-processed into polycarbonate (PC).
- RGO can enhance the toughness, strength and notch resistance of PC greatly.
- The toughening mechanism was investigated.
- Microcrack, crack pinning, deflection and arresting were the toughening mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

The toughening effect of graphene sheets on polycarbonate (PC) was investigated to fabricate PC composites with excellent balanced toughness, notch resistance as well as strength. The reduced graphene oxide (RGO) was incorporated into PC matrix through melt compounding. A maximum toughening effect was observed in PC/RGO (PCG) composites with 0.03 wt% or 0.07 wt% RGO. Particularly, the tensile fracture toughness of PCG composites with 0.03 wt% RGO was enhanced by 89%. The notched impact strength and K_{IC} of PCG composite with 0.07 wt% RGO was increased by 46% and 58%, respectively. The point of 0.1 wt% was found to be the ductile-brittle transition point in PCG composites. Meanwhile, the yield strength of these novel materials was increased by around 12% as well at loading of 0.07 wt%. Microcrack, resulting from interfacial debonding between PC and RGO as well as breakage and pulling out of graphene layer, was proposed to be the main toughening mechanism contributing to the great enhanced fracture toughness and notch resistance. Apart from the microcrack, crack pinning, crack deflection and crack arresting were also found and proposed to be toughening mechanism in notch-fractured process. This work not only provides us a novel strategy to fabricate advanced PC nanocomposites but also gives us a deep understanding on the toughening role of graphene on polymers.

1. Introduction

Polycarbonate (PC) is a very attractive polymer used in many fields ranging from disk to helmet for astronauts due to its remarkable heat resistance, toughness, optical transparency, and electrical properties [1–3]. However, PC is very sensitive to the notches or cracks, which greatly limits its application in many high-end fields. It is therefore of great significance to enhance the notch resistance as well as the notch-fractured toughness of PC. It is well known that the notch sensitivity of PC is due to the change in stress state at the notch from plane stress to plane strain, resulting in the change in failure mechanism from shearing to crazing [4]. Generally, rubber is considered as the most effective method to toughen

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PC [5–7], which can induce cavitation, relieve the plane strain constraint at the notch and permit the matrix to deform by shearing. However, typically, 5–20 wt% of rubber is required, causing a dramatic reduction in strength and modulus. Apart from the rubber, rigid fillers, like carbon nanotube [8], SiO_2 [9] or nano-SiO_2 [10] have also been studied to improve the fracture toughness of PC. However, the increment in notch resistance or fracture toughness obtained with these rigid fillers is typically less than that with rubber.

Graphene, a two-dimensional material of numerous excellent properties [11–13], has attracted tremendous interest in scientific and industrial fields. Adding into polymers to improve the mechanical properties of polymers is considered one of the most promising applications of graphene [14–17]. However, compared with the role on reinforcing polymers, the toughening role of graphene on polymers has always been neglected. To the best knowledge, there was almost no report on the toughness of graphene/polymer nanocomposites before 2009. In the past few years, some studies have reported the toughening role of graphene on polymers. For instance, Rafiee et al. found that the fracture performance of epoxy composites with 0.1 wt% of pristine graphene was better than that with carbon nanotubes [18] and the increment in fracture toughness peaked at 0.125 wt% of graphene with a 65% increment [19]. Yong et.al [20] found that, graphene nanosheet can induce microcracks in epoxy filled with low loading graphene, resulting in an impressive toughening effect on epoxy matrix. However, up to now, there are still some challenging issues considering graphene as toughener to polymers. First of all, the matrices studied are too rare and most of the studies focused on the brittle thermosetting epoxy [18–23]. More comparative studies and modeling work are necessary to investigate the toughening ability of graphene on polymers. Then, the understanding of the toughening mechanism responsible for other polymers except epoxy is still insufficient. At last, most of the polymer nanocomposites toughened by graphene were fabricated through solution, in situ polymerization or layer-by-layer strategy using solvents or dispersions. They are not practical approaches to manufacture polymer/graphene composites environment-friendly and cost-effectively, placing great limitations on industrial implementation.

In this work, we sought to explore the toughening effect of graphene sheets on PC matrix and fabricate advanced PC nanocomposites with excellent toughness, notch resistance as well as strength. Reduced graphene oxide (RGO) was performed to prepare PC nanocomposite via melt compounding without any solvent. The notch resistance and notch-fractured toughness were evaluated based on notched impact mode and K_{IC}-test mode. The strength and tensile fracture toughness were explored through tensile fracture mode. Interestingly, an impressive toughening effect was observed at 0.03 wt% or 0.07 wt% of RGO loading in all three modes. Meanwhile, the strength of PC matrix was enhanced with the addition of low loading RGO. The corresponding toughening mechanism was proposed based on the fractographs of the composite samples and morphological evolution of RGO during the fracture process.

2. Experimental

2.1. Materials

Bisphenol-A Polycarbonate (PC-201, M_w = 31809, a density of 1.2 g/cm^3) was purchased from LG Chem (Korea) and vacuum-dried overnight at 110 °C before use. Paraffin oil (CAS: 8012-95-1, Kelong chemical reagent CO., LTD), being mainly composed of C16-C20 n-alkanes and with a density of 0.835 g/cm^3, was used as received. Reduced graphene oxide (RGO) were supplied by Changzhou Six element CO., Ltd. Table 1 summaries the specifications of RGO. Moreover, the other information about the RGO, including the original morphology (SEM images), Raman spectrum and XPS wide spectrum, can be seen in the Supplementary Materials (Figs. S1 and S2). The RGO were vacuum-dried overnight at 60 °C before use.

2.2. Preparation of PC/RGO composites

Firstly, PC pellets and RGO were physically blended together through paraffin oil, in a solid mixer (V5D, Feich machinery, China) at 60 r/min for 10 min. The weight ratio of PC and paraffin is 1000:1. The paraffin oil can make the RGO adhere uniformly around the PC pellets in advance, which is helpful for the dispersion of RGO in the melt-processed PC in the following process. Then PC and PC/ RGO composites (PCG) with a load varying from 0.03 to 3 wt% were prepared by melt compounding on a HaPu melt mixer at 260 °C. The melt mixing was performed by adding approximately half of the polymer quantity to the mixing bowl. When the polymer matrix melted and the torque started to decrease, the remaining composites were gradually added to the mixer. For all the materials the melt compounding was performed at a screw speed of 60 rpm for 20 min. The materials obtained via melt compounding were compression molded at 260 °C under 15 MPa, which were used as specimens for different characterizations. The as-obtained composites are coded using PCG and the RGO loading. For example, PCG-0.07 means the PCG composites with 0.07 wt%RGO.

2.3. Characterization

Scanning electron microscopy (SEM) images were taken using JSM-5900LV-SEM at a voltage of 5.0 kV. Prior to being analyzed, the samples were mounted on stubs and their surfaces were platinum coated. The dispersion of graphene in PC matrix was observed with a Tecnai G2F20S-TWIN transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. Ultrathin sections thinner than 100 nm were cryogenically cut with a glazing knife using a microtome and collected on 300-mesh copper grids for TEM observation. X-ray diffraction (XRD) measurements were conducted using a D8 Advance (Bruker) X-ray diffractometer using Cu Kα radiation (k = 1.5405 Å) with a scanning speed of 5°/min from 5 to 60°. The scanned area was from 190 to 600 nm. Raman spectra were measured on LabRam-HR (French Horiba, 532 nm). X-ray photoelectron spectroscopy (XPS) was conducted on K-alpha (Thermo Scientific).

Standard tensile test used dumbbell shaped sample was conducted at room temperature using tensile test machine (model CMT-4104) according to GB/T 1040-92. Tensile fracture toughness were evaluated based on the area under the stress-strain curve. Furthermore, due to the sensitivity of PC to the notch, the notched Izod impact test, K_{IC}-tests as well as *J*-integral tests were performed to evaluate the notch resistance and notch-fractured toughness of neat PC and its RGO composites. The notched impact test was performed following GB/1943–2007 with a XJU-22 impact test machine. Before the impact testing, a single-edge V-shaped notch with a depth of 2 mm was milled in all the rectangular bulk specimens ($80 \times 10 \times 4$ mm^3). The K_{IC}-tests as well as *J*-integral tests were performed according to ASTM D5045-99 and ASTM E813-89 [24], respectively (detail information can be seen in Support Information Fig. S3). All the mechanical property data with standard deviation was averaged using at least six specimens (seen in the Supplementary Material, Table S2). On the other hand, Polarized optical microscopy (POM, Leica, DM2500P) were performed to collect the initiation and propagation patterns of the crack or craze in neat PC and PCG composites after being tested through