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Reduced graphene oxide enhances the crystallization and orientation of poly(ε-caprolactone)

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ABSTRACT

Poly(ε-caprolactone) (PCL)/reduced graphene oxide (RGO) nanocomposite bars were prepared by injection molding, and the effects of RGO on the PCL matrix were investigated. Differential scanning calorimeter and polarized optical microscopy results demonstrated that RGO was an effective nucleation agent for PCL. Two-dimensional wide angle X-ray diffraction results showed that the incorporation of RGO can enhance the orientation degree of PCL crystals in the flow direction and did not influence the crystal structure of PCL. Two-dimensional small angle X-ray scattering results confirmed that the orientation of PCL chains in the flow direction was enhanced with the increase of RGO content, which was attributed to that RGO obstructed the motion of polymer chains. These results indicated that the incorporation of RGO can enhance the crystallization and orientation of PCL matrix, which was the major factor for the improvement of mechanical properties.

1. Introduction

In the development of composite materials, the filler decreases in size from macro- and micro- to the nanoscale. Nanosize reinforcing fillers have attracted great interests in the field of composite materials due to their inherent mechanical properties and high surface area. Polymer nanocomposites represent a new class of materials compared to conventional filled polymers or polymer blends because they can possess enhanced properties through nanoscale reinforcement [1]. In particular, the use of inorganic nanomaterials as fillers in the preparation of polymer/inorganic nanocomposites has attracted increasing interests owing to their unique properties and numerous potential applications [2,3].

It is well known that shear stress field can markedly affect the crystallization, orientation and the resulting mechanical properties of semi-crystalline polymer [4]. Traditional injection molding could lead to high orientation of the polymer chains under the intensive shear flow during the mold filling process. However, only small amount of oriented polymer chains are kept in the final injection-molded bars because of the sufficient relaxation of polymer chains in the slow cooling of melt [5]. Some new processing techniques such as dynamic packing injection molding (DPIM) [6], oscillation shear injection molding (OSIM) [7], vibration-assisted injection molding, shear controlled orientation injection molding (SCORIM) [8], and push pull processing [9] have been developed to suppress the relaxation of polymer chains and fabricate highly oriented injection-molded bars. Another approach for improving the mechanical properties of semi-crystalline polymer can be achieved by incorporating a small amount of nanofiller into the polymer matrix. It has been reported that shear stress conditions during the processing process will generate a certain level of nanofiller orientation [10], which will provide nucleation cites for oriented crystallization in some semi-crystalline polymers [11,12]. Interfacial crystallization is a novel route to enhance the interfacial adhesion between polymer and filler [13]. The formation of the interfacial crystalline layer could offer good interfacial action between the filler and polymer matrix resulting in significant enhancement in the final properties of the composites. Larin et al. prepared isotactic polypropylene (iPP)/carbon fibers (CF) composite filaments by melt mixing extrusion and melt drawing. The oriented CF aligned in the flow direction resulted in high degree of chains orientation and high degree of crystallinity, suggesting that the CF induced crystallization of surrounding iPP matrix after the cessation of stretching force and delayed relaxation of stretched polymer segments [14]. Kelarakis et al. also reported that the amount of shear induced oriented crystals increased with the modified CF concentration in iPP/modified CF composites, suggesting that the CF hindered the motion of polymer

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chains and increased their relaxation time [15]. Two-dimensional layered-silicate nanofillers can also improve the physical, mechanical, and thermal properties of polymer matrices [16]. These 2D layered nanofillers could effectively enhance the orientation of polymer chains since the polymer chains can be confined in the nanofiller network (exfoliated or/and intercalated) [17,18]. If the introduced 2D layered nanofiller can promote the crystallization ability and the orientation of polymer chains because of the interaction with polymer chains, the enhancement of mechanical properties will be more effective.

Graphene, which is an atomically thick, two-dimensional sheet, has attracted tremendous attention in recent years due to its unique mechanical, thermal and electrical properties [19,20]. The incorporation of graphene into polymers has drawn much attention as a route to obtain new materials with excellent properties [21–23]. The maximum improvements in final properties can be achieved when graphene is homogeneously dispersed in the matrix and the external load is efficiently transferred through strong polymer/graphene interfacial interactions [24,25]. It has been reported that graphene can significantly improve the crystallization behavior, thermal stability and mechanical properties of polymer matrix [26]. Cheng et al. reported that a small amount of graphene can dramatically improve the crystallization ability and thermal stability of PE [27]. Xu et al. investigated the effects of graphene oxide on the crystallization and conformational ordering of iPP [28]. They reported that the incorporation of graphene oxide could enhance the formation of long ordering segment in iPP crystallization [29] and combined effects existed with the presences of graphene and shear flow [30]. Surface-induce conformational order has also been reported in PLLA/graphene nanocomposites [31]. Effectively identify and utilize the contribution of graphene in reinforcing semi-crystalline polymers is necessary for better understanding the influence of graphene on polymer matrix.

In this work, reduced graphene oxide (RGO) was chosen since chemical/thermal RGO, as an efficient route, could be applied in the industrial production among all preparation methods. Poly(ε-caprolactone) (PCL) was selected as a model polymer to investigate the effect of space confinement and crystallization promotion of RGO on polymer matrix because PCL had planar zigzag confirmation and space lattice matching existed between PCL crystals and RGO. We emphasized on the effect of RGO on the crystallization and orientation of PCL injection-molded bars. GO was chosen as the comparison to confirm the orientation mechanism in these nanocomposites.

2. Experimental section

2.1. Materials

PCL was purchased from Shanghai Yizhu Co., Ltd. (Shanghai, China), with average weight $M_n = 42500\ \text{g mol}^{-1}$ and polydispersity index $M_w/M_n = 1.5$. Natural flake graphite was purchased from Qingdao Jiuyi graphite Co., Ltd. (Shandong, China) with mean particle size of 50 μm. Hydrochloric acid (HCl) (37%), sulfuric acid (H_2SO_4) (98%), potassium nitrate (KNO_3), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) (35%), n-hexanol and chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

2.2. Sample preparation

GO was exfoliated by ultra-sonication from graphite oxide which was produced by modified Hummers' method [32]. RGO was prepared by thermal exfoliation and reduction of GO [33]. PCL/RGO nanocomposites were prepared by solution mixing method with chloroform being a mutual solvent. The contents of RGO were 0.1 wt.%, 0.5 wt.% and 1.0 wt.%, respectively. Because GO cannot be dispersed in chloroform, PCL/GO nanocomposites were prepared by solution coagulation method [31]. GO was added to ethanol by ultra-sonication for 1 h and PCL was completely dissolved in chloroform. By dropping the pre-dispersed ethanol/GO suspension into the chloroform/PCL mixture, PCL/GO nanocomposites were precipitated. The contents of GO were 1.0 wt.%. The obtained nanocomposites were dried in vacuum at 50 °C for 2 days to remove the solvent completely. Neat PCL were prepared with the same procedure in order to eliminate experimental error. At last, the standard bars were prepared with HAAKE MiniJet II micro-injection molding machine. The melt temperature, mold temperature and injection pressure were preset at 90 °C, 30 °C and 650 bar, respectively.

2.3. Analytical methods

Differential scanning calorimetry (DSC) measurements were performed with Mettler Toledo DSC under nitrogen atmosphere. All samples were first heated to 90 °C at a heating rate of 10 °C/min, and equilibrated at 90 °C for 3 min to remove thermal history. Subsequently, the samples were cooled to −10 °C at a cooling rate of 10 °C/min.

Spherulitic morphologies of neat PCL and PCL/RGO nanocomposites were observed using a polarizing optical microscope (Olympus BX51) (POM) equipped with an Instec HCS601 hot stage. The samples were first heated to 90 °C at 50 °C/min on the hot stage and held for 3 min to erase thermal history. Then they were cooled to desired crystallization temperature at 100 °C/min. Here, the crystallization temperature was set at 39 °C.

Two-dimensional wide angle X-ray diffraction (2D-WAXD) experiments were carried out on the BL14B1 beam-line in the Shanghai Synchrotron Radiation Facility (SSRF). WAXD curves were collected from the 2D-WAXD patterns. The wavelength of the monochromatic X-ray was 1.24 Å. The 2D diffraction patterns were recorded in transmission mode at room temperature. The orientation level of various samples could be calculated by the Herman's orientation parameter *f*.

$$f = \frac{3\langle\cos^2\phi\rangle - 1}{2} \tag{1}$$

$$\langle\cos^2\phi\rangle = \frac{\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi\,d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi\,d\phi} \tag{2}$$

Therein, ϕ is the angle between the flow direction and the lamellae orientation. The value of standard Herman's orientation parameter *f* is 0 when the lamellae direction distribution is isotropic, and the value is 1 when the lamellae are in perfectly alignment.

Two-dimensional small angle X-ray scattering (2D-SAXS) experiments were carried out on the BL16B1 beam-line in the SSRF. The 2D patterns were recorded in transmission mode at room temperature and the sample-to-detector distance was 2000 mm.

Tensile test was performed on Instron 5567 at a tensile rate of 20 mm/min. The standard bars of 50 mm × 3 mm × 2 mm in size were prepared by HAAKE MiniJet II micro-injection molding machine. Five samples have been measured and the average values were calculated.

Dynamic mechanical analysis (DMA) was performed in tension mode on Mettler Toledo DMA at 1 Hz to examine thermal dynamic properties of the nanocomposites. DMA samples with 25 mm × 3 mm × 2 mm in size were tested from −80 to 30 °C at