The crystallization behaviors and rheological properties of polypropylene/graphene nanocomposites: The role of surface structure of reduced graphene oxide

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ARTICLE INFO

ABSTRACT

In this work, polypropylene (PP)/reduced graphene oxide (RGO) with various surface structures were fabricated. The crystallization behaviors and non-isothermal crystallization kinetics of PP/RGO nanocomposites were thoroughly studied. The results showed that the crystallization peak temperature, crystallization rate as well as crystallization degree of PP/RGO nanocomposites were greatly enhanced with the increase of reduced extent of RGO. Non-isothermal crystallization kinetics displayed that RGO with high reduction extent exhibited strong nucleation ability, which could decrease crystallization activation energy and accelerate the crystallization process. The rheological behaviors of the PP/RGO nanocomposites were also investigated. It was found that the non-newtonian behaviors of PP nanocomposites became stronger with the increase of reduction extent of RGO.

1. Introduction

Polypropylene (PP), a semi-crystalline thermoplastic polymeric material, has wide applications in the region of packaging, automobile, fibers and construction industries [1]. However, the unsatisfying mechanical and thermal properties of neat PP limit its capability as an engineering material. Compounded PP with nanoparticles is an effective, convenient and economical approach to satisfy the increasing demand of PP in practical application. In previous studies, nanoparticles such as Halloysite nanotubes (HNTs) [2], carbon nanotube [3], cellulose nanocrystals (CNCs) [4], nanoclay [5], graphene oxide (GO) [6] have been demonstrated as ideal reinforcing fillers for PP matrix, in virtue of their small dimension and high specific surface area [7].

Graphene is sp^2-hybridized carbon layer with the carbon atoms arranged in a two-dimensional honeycomb lattice [8]. It has the potential promise to become ideal nanofiller in the reinforcement of polymer, owing to its outstanding mechanical, thermal, electrical properties as well as easy processing [9,10]. Generally, the most effective route for the quantity production of graphene sheets is the chemical oxidation and exfoliation of graphite in solution, followed by reduction [11], which is referred to reduced graphene oxide (RGO). In the preparation process of graphene, the removal of oxygen-containing groups on the basal plane and edges of GO can be adjusted by varying reduction degree, leading to various surface structures and properties of

RGO. Recently, reports about the impact of reduction degree of RGO on the structure and morphology of itself and properties of polymer/RGO nanocomposites have sprung up. Bai et al. [12] reported that RGO improved the mechanical properties and thermal stability of silicone rubber (SR) nanocomposites, and the improvement enhanced with increasing reduction degree of RGO simultaneously. Liu et al. [13] found the dielectric constants of polyimide (PI)/graphene composites were significantly enhanced with the increase of reduction extent of RGO, and the mechanical properties of composites were best improved with the moderate reduction extent of RGO.

It is well recognized that crystallinity behaviors, i.e., the crystallization degree, crystallization temperature, crystallization rate as well as the crystallization morphology, are critical to the structure and mechanical properties of crystalline and semi-crystalline polymers [14,15]. Up to now, several studies have pointed out that graphene can act as a nucleation agent, promoting the crystallization process of polymer matrix. For example, Zhao et al. [16,17] investigated the crystallization behaviors of polypropylene/graphene composites. By the presence of graphene platelets, the overall crystallization rate was enhanced due to the heterogeneous nucleation. Cheng et al. [18] used solution crystallization to study RGO-induced polyethylene (PE) epitaxial crystallization, and the result showed that crystallization shifts to higher temperature during cooling and the crystallization rate are much faster for all PE/RGO nanocomposites compared with neat PE, indicating the superb capability of RGO nanosheets to induce
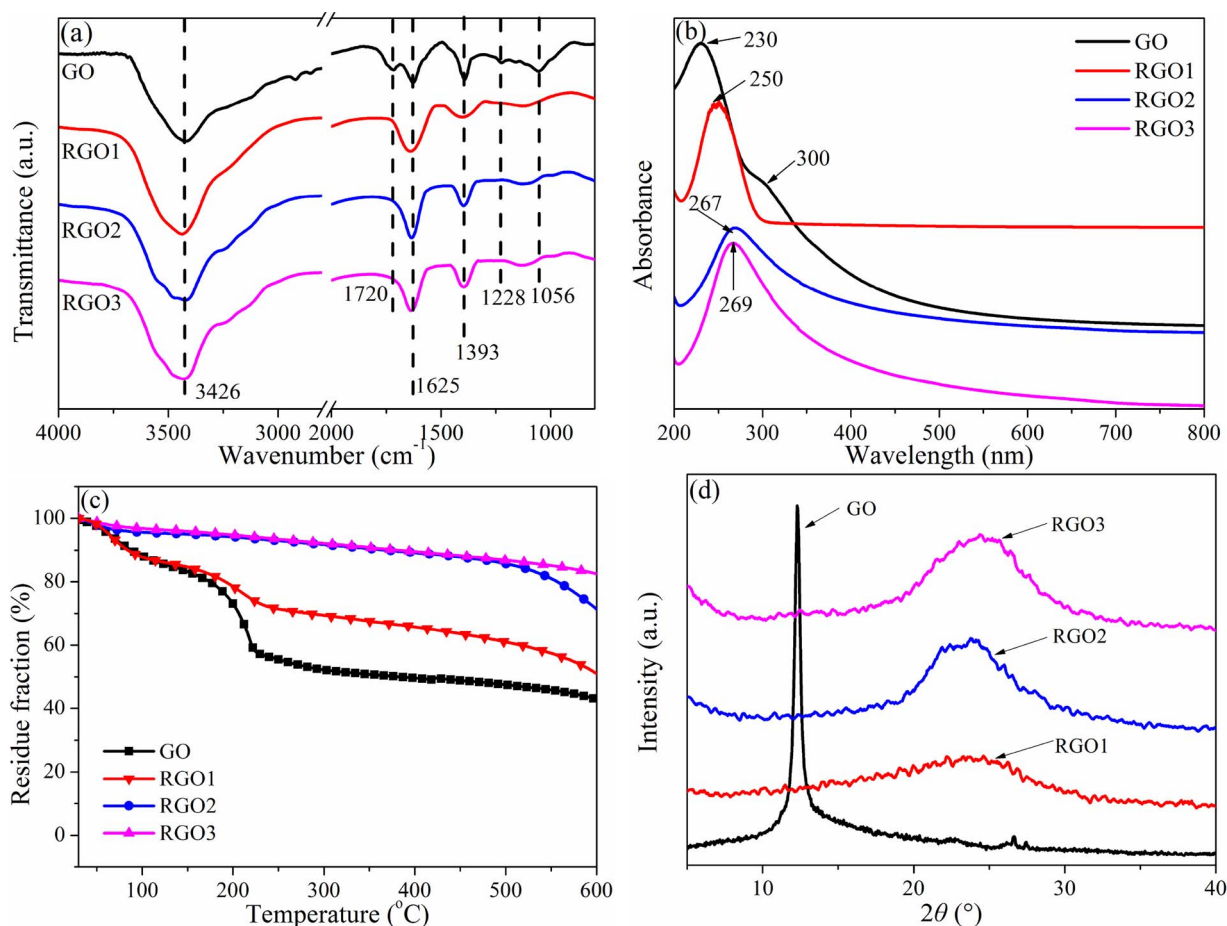

Fig. 1. Characterization of GO and various methods reduced RGO (a) FTIR; (b) UV-vis; (c) TGA; (d) XRD.

heterogeneous crystallization of PE. Also, the rheological properties of nanocomposites are very important to the process conditions for polymer product. However, to the best of our knowledge, the crystallization behaviors as well as rheological behaviors of PP nanocomposites influenced by RGO with various surface structures have rarely been systematically investigated.

In this work, RGO with various surface structures were synthesized via three different reduction agents, and were then used for the fabrication of the PP/RGO nanocomposites through melt blending method. The crystallization morphology, non-isothermal crystallization kinetics and rheological behaviors were investigated systematically, in order to explore the influence of surface structure of RGO on the crystallization behaviors and rheological properties of PP nanocomposites.

2. Experimental

2.1. Material

Polypropylene (PP, melt flow index = 21.7 g/10 min at 230 °C) was purchased from Sinopec-Yangzi Petro Co., Ltd, Nanjing, China. Natural graphite powder (particle size ≤ 30 μm, purity ≥ 99.85%), ascorbic acid, sodium borohydride (96 wt%), hydrazine hydrate (≥ 85 wt%), ammonia water (28 wt%) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Other starting materials used in this work were of analytical grade and used as received without further purification.

2.2. Synthesis of RGO and PP/RGO nanocomposites

GO suspension with a concentration of 1 mg/ml was prepared by the oxidation of natural graphite powder according to Hummers' method

[19], followed by the aid of ultrasonication for 2 h. GO was reduced by ascorbic acid as previously reported in the literature [20], which was named as RGO1. Meanwhile, GO reduced by borohydride sodium and hydrazine hydrate according to the reference [11], which were named as RGO2 and RGO3, respectively.

The resultant RGO and PP were dried in a vacuum oven for 24 h at 80 °C, and then the RGO and antioxidant were added into PP, which were mixed evenly using a high-speed mixing machine (modelCH-10DY) for 10 min. The formulation of blend was given as follows: PP 100 g, RGO 1 g, antioxidant 1 g. Melt blending was performed using a twin-screw extruder (TE-35, Gelan Machinery Co., Zhangjiagang, China) with a rotation speed of 200 rpm. The temperature along the barrel was increased gradually from 175 °C to 185 °C, 175 °C, 180 °C, 185 °C, respectively, and then was decreased to 180 °C. The obtained blend pellets were dried again at 80 °C in a vacuum oven before the injection molding, and then were molded into standard sample by injection-machine (JN55-E, Chen Hsong Machinery Co., Ltd, Ningbo, China). Pristine PP, PP/GO nanocomposites were also prepared for comparison, and the synthetic process was in agreement with PP/RGO.

2.3. Measurements

Fourier transform infrared spectra (FTIR) were conducted on a FTIR–8400S spectrometer (Shimadzu Corporation, Japan) in a transmission mode of KBr pellets with wavenumber ranging from 800 to 4000 cm^{-1} at a scanning resolution of 4 cm^{-1}.

Ultraviolet–visible spectroscopy (UV–vis) absorption spectra were performed on a UV–6100S spectrophotometer (Shanghai Mapada Co. Ltd., China) with scanning range from 200 to 400 nm at room temperature.