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Material Properties

Biodegradable graphene oxide nanosheets/poly-(butylene adipate-co-terephthalate) nanocomposite film with enhanced gas and water vapor barrier properties

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ABSTRACT

Poly-(butylene adipate-co-terephthalate) (PBAT) has captured significant interest by dint of its biodegradability, superb ductility, promising processing properties and good final properties, but the insufficient barrier performance limits its application, especially in packaging field. In the present work, improved barrier properties of PBAT films were obtained by introducing an extremely low amount of graphene oxide nanosheets (GONS). O_2 and water vapor permeability coefficients were decreased by more than 70% and 36% at the GONS loading of 0.35 vol%, respectively. The enhanced barrier performance was ascribed to the outstanding impermeability and well dispersion of GONS as well as the strong interfacial adhesion between GONS and PBAT matrix. Furthermore, tensile strength and Young's modulus of GONS/PBAT nanocomposite rise up to 27.8 MPa and 72.2 MPa from 24.6 MPa to 58.5 MPa of neat PBAT, respectively, showing a prominent increase of mechanical properties compared to neat PBAT. The incorporation of GONS also endowed PBAT matrix with an excellent thermal stability. These findings provide a significant guidance for fabricating high barrier films on a large scale.

1. Introduction

The widespread use of polymer films as food packaging is due to the advance that they are chemically and mechanically resistant, lightweight, heat-solderable [1,2]. However, overwhelming majority of polymeric packaging films (e.g., polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate),etc.) are produced from non-biodegradable fossil fuels. The use of biodegradable packages propagates aggressively due to the growing need to minimize the carbon footprint in the environment [3–5]. Various biodegradable polymeric materials have been successfully developed and put into applications [6–11]. Among them, aliphatic/aromatic copolymers are thought as one of the most important series because the synthetic biopolymers, in general, offer greater predominance over natural ones as they can be tailored to give a wider range of properties than materials from natural resources [12–20]. For instance, copolyesters of poly(butylene adipate-co-terephthalate) (PBAT) mainly derived from 1,4-butanediol, adipic acid, and terephthalic acid have been commercialized, and a tunable balance between the biodegradation and desirable physical properties for industrial applications has been spectacularly achieved [21–23]. In addition, excellent softness and ductility of make PBAT suitable for food packaging and agricultural mulch [11,24,25]. Nevertheless, the insufficient gas barrier properties of PBAT pose one serious technical challenge for the use as oxygen-sensitive and perishable commodities. To be specific, its barrier properties including both O_2 and water vapor barrier properties are seriously inferior to traditional fossil fuel films, such as polyethylene, polypropylene, polystyrene and poly(vinyl chloride) [26]. Therefore, an imperative task is to enhance the gas barrier performance of PBAT so as to make it competitive with the existing current petroleum-based polymers in

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the packaging field [27–32].

Graphene nanosheets (GNS), a monolayer of carbon atoms arranged in honeycomb networks, is found as the thinnest and strongest two dimensional material [33,34]. Due to unique graphitized planar structure, such as the extremely high specific surface area and large aspect ratios, GNS is well demonstrated to be highly effective barrier performance enhancers for carbon-based nanocomposites [35–37]. The GNS are generally recognized as "nanobarrier walls", generating increased tortuosity for gas molecular transport, which remarkably improves barrier properties of polymer films. The tortuosity of penetration path for diffusing molecules is principally influenced by the volume fraction and morphologies (i.e., aspect ratio, exfoliation, dispersion, orientation, etc.) of GNS in the matrix, as well as the interfacial interaction between fillers and polymer matrix. Complete exfoliation and uniform dispersion of GNS is desired to construct expected torturous paths to give rise to better barrier properties of GNS/polymer nanocomposites. Nevertheless, GNS is prone to agglomerate, which is detrimental to its uniform dispersion in polymer matrix. In contrast to GNS, graphene oxide nanosheets (GONS) is basically graphene bearing epoxide, hydroxyl, carboxyl groups and ketones, 6-membered lactol rings [38,39]. These chemical functional groups endow GONS with good interfacial interaction with polar polymers, which promotes complete exfoliation and homogeneous dispersion of GONS and improves the interfacial bonding notably. Hence, GONS are considered as forward-looking candidates for preparing high barrier polar polymer-based nanocomposite films [40–44]. For instance, Geim et al. prepared pure GONS membranes with a pronounced layered structure, revealing a complete impermeability to liquids, vapors, and gases, including helium [43]. With the addition of only 0.1 wt% GONS, the water-vapor-transmission-rate of polyimide nanocomposite films was significantly reduced from 181 to 30 *g* mil m^{-2} day^{-1} [44]. In our previous work, a remarkable improvement on barrier properties of GONS/poly(viny lalcohol) nanocomposite films was successfully obtained, wherein O_2 and water vapor permeability coefficients of poly(viny lalcohol) film were respectively decreased by about 98% and 68% at a GONS loading of 0.72 vol% [40].

The main objective of this study was to achieve an overall promotion of the barrier and mechanical properties of GONS/PBAT nanocomposites and to establish the relationship between microstructure and the performances of the nanocomposite. In the current study, a set of PBAT nanocomposites with low GONS loadings were fabricated through solution blending, wherein GONS were fully exfoliated and uniformly dispersed in the PBAT matrix. It was intriguing to found that O_2 and H_2O permeability coefficients were decreased by about 70% and 36%, respectively. Furthermore, the addition of low GONS loadings brought a prominent increase of 23% in the tensile modulus. These results could be ascribed to excellent barrier properties of GONS, its well exfoliation, uniform dispersion and strong interfacial adhesion between GONS and PBAT matrix.

2. Materials and methods

2.1. Materials

The biodegradable polymer, PBAT, was purchased from Chemical Company BASF (Germany) under the trade name of Ecoflex®-F. It possesses a density of 1.31 g/cm^3, a melt index of 3.5 g/10 min (190 °C/2.16 kg), and a glass transition and melting temperature of about −30 °C and 110–120 °C (DSC analysis), respectively. The modified "Hummers" method was adopted to prepare GONS from expandable graphite, which was purchased from Qingdao Haida Graphite Co., Ltd., China with an expansion rate of 200 ml/g. Details of preparation process were reported in our previous work [45]. Anhydrous N, *N*-dimethyl formamide (DMF) was purchased from Chengdu Kelong Chemical Reagent Factory, Chengdu, China. Other reagents were of analytical grade and directly used without further purification.

2.2. Preparation of nanocomposite films

Solution coagulation was employed to prepare a series of PBAT nanocomposite films containing various GONS loadings of 0, 0.1, 0.25 and 0.5 wt%. Taking the 0.25 wt% GONS/PBAT nanocomposite as an example. Adding 10 g of PBAT granules into about 200 ml of DMF solution with the aid of mild stirring for 30 min at 100 °C. 25 mg of GONS was dispersed into 250 ml of DMF solution with vigorous agitation and ultrasonic treatment for 2 h at room temperature, forming a stable and uniform GONS/DMF suspension. The transparent PBAT/DMF solution then mixed with the above GONS/DMF suspension for 15 min at 100 °C under vigorous agitation. Upon completion, the homogeneous GONS/PBAT slurry was immediately added into a large amount of vigorously stirred water and the coagulated materials precipitated continuously. Thereafter, the coagulations were isolated via filtration, washed with water, left in a drying oven at 60 °C to remove solvents, and further dried in a vacuum oven overnight at 60 °C. Finally, the composite powders were compression molded at 160 °C under a fixed pressure of 10 MPa. For comparison purposes, neat PBAT was prepared according to the same procedures. For the convenience of calculation, the weight content of GONS in the nanocomposites was converted to volume content by using the density of PBAT matrix and GONS as 1.31 and 1.80 g/cm^3, respectively [24]. Thus, the volume content of GONS incorporated into the PBAT matrix can be obtained as 0, 0.07, 0.18 and 0.35 vol%, respectively.

2.3. Characterization and measurement

Typical tapping-mode atomic force microscopy (AFM) measurement was performed using Nanoscope Multimode & Explore atomic force microscope (Veeco Instruments, USA) to present thickness and surface morphology of GONS. Samples for AFM images were prepared by depositing dispersion of GONS in DMF on a fresh mica substrate and allowing them to dry in air. To study the morphology of GONS in PBAT matrix, the nanocomposite samples were firstly cryo-fractured in liquid nitrogen, then the surfaces sputter-coated with gold were observed on a field emission scanning electron microscopy (SEM) (Inspect F, FEI, Finland) with an accelerated voltage of 10 kV. Two-dimensional wide angle X-ray diffraction (2D-WAXD) determination was carried out at the beamline BL15U1 of SSRF (Shanghai, China). The monochromated X-ray beam with a wavelength of 0.124 nm was focused to an area of 3 × 2.7 μm^2 (length × width), and the sample-to-detector distance was set as 173 mm. After 90 s exposure to the X-ray for the film samples (~100 μm), the 2D-WAXD images were collected with an X-ray CCD detector (Model SX165, Rayonix Co. Ltd, USA). Additionally, the WAXD intensity profiles for each 2θ were obtained by integration in the azimuthal angular range of a whole circle (0-360°) from the sample patterns employing the Fit 2D package, while background scattering was subtracted from the sample patterns. Crystallization behavior was investigated by differential scanning calorimetry (DSC) on a TA Q2000 instrument. The samples (around 5–6 mg) were heated from 40 °C to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Crystallinity (χ_c) of all the samples can be calculated as follows: