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Effect of oxidation degrees of graphene oxide on the structure and properties of poly (vinyl alcohol) composite films

Di Liu [a], Qibo Bian [a], Yan Li [a], Yaru Wang [a], Aimin Xiang [a], Huafeng Tian [a, b, *]

[a] School of Material and Mechanical Engineering, Beijing Technology and Business University, Beijing, 100048, China
[b] Key Laboratory of Carbohydrate and Biotechnology Ministry of Education, Jiangnan University, Lihu Road 1800, Wuxi, 214122, China

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ABSTRACT

In this work, graphene oxide (GO) was synthesized by the traditional Hummers method and the composite film of poly (vinyl alcohol) (PVA)/GO was prepared using solution casting method. Different oxidation degrees of GO were achieved by varying the content of oxidizing agent. The structure and properties of GO and PVA/GO film were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), tensile and oxygen barrier tests in detail. The natural graphite was well exfoliated and oxidized, and higher oxidation degrees and better layer structure of GO were achieved with higher loading of $KMnO_4$ oxidizing agent. For the PVA/GO composite film with the same content of GO, both tensile strength and elongation at break were improved with the increase of oxidation degrees of GO. In addition, a good improvement in the barrier properties of the PVA/GO composite film was also achieved. The oxygen permeability coefficient of composite film was reduced with the increase of oxidation degree compared with the neat PVA film.

1. Introduction

In recent years, advancement in nanoscience opens a wide range of application of nanoparticles towards automobile, construction, electronic and aerospace industries [1,2]. Owning to their structural features, such as the extremely tiny size, the special shape, the great surface area, nanoparticles exhibit great physiochemical properties and reflect their unique electrical, thermal, and mechanical properties [3–5].

Graphene, first experimentally discovered through mechanical exfoliation from graphite in 2004 by Angre Geim and Konstantin Novoselov, was regarded as the most exciting nanomaterial for its excellent mechanical properties with a modulus of over 1060 GPa [6–8]. As a derivative of graphene, graphene oxide (GO) was a layered nano filler produced by the oxidation of graphite. GO owns almost the same layer structure as graphene with only one-atom-thick planar sheet of sp2 bonded carbon atoms [9,10]. Compared with graphene, the layer structure of GO is heavily oxygenated, bearing hydroxyl, epoxide functional groups on their basal planes and carbonyl, carboxyl groups on the edge of sheets [11–13]. These reactive oxygen groups endowed GO a good candidate for use in the nanocomposite applications through chemical functionalizations [14,15]. When the GO sheet was incorporated into a polar polymer, great enhancement of properties could be achieved. For example, with 1% GO added into PMMA, there is an improvement trend in modulus, ultimate strength and thermal stability [16].

As a kind of biodegradable and eco-friendly material, polyvinyl alcohol (PVA) is widely used in paper coating, textile sizing and flexible water-soluble packing film, etc [17–19]. There bears massive hydroxyl groups on the main chain of PVA resulting in good water solubility in water, which allows for preparation of nanocomposites films in aqueous solutions through evaporation of water [20–22]. Dramatic enhancement of tensile strength, abrasion resistance and gas barrier properties of PVA film could be achieved through the introduction of nanofiller [23]. For example, PVA composite film with 5 wt% of MMT-Na^+ could give a significant decrease of oxygen permeability compared to the neat PVA film [24,25]. The mechanical properties could also be enhanced by incorporating cellulose nanofibrils and flax fabric [26,27].

In previous studies, PVA/GO composite films have been fabricated successfully [28]. The influences of GO content on the structure and properties of the composite films were investigated. The oxidation degrees of GO are the critical factors influencing the structure of GO, which would also influence the structure and

* Corresponding author. School of Material and Mechanical Engineering, Beijing Technology and Business University, Beijing, 100048, China.
E-mail address: tianhuafeng@th.btbu.edu.cn (H. Tian).

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properties. However, the influence of GO oxidation degree on the structure and properties of the composites was barely reported in the literature. In this study, GO with different oxidation degrees were synthesized by the traditional Hummers method and PVA/GO composite film was prepared by solution casting method. The influence of GO with different oxidation degrees on the structure and properties of PVA/GO composite film was investigated. We aim to pave a simple way to prepare eco-friendly PVA films with controllable mechanical and gas barrier properties.

2. Experimental

2.1. Materials

Poly (vinyl alcohol) (PVA 117) was obtained from Kuraray Co. Ltd. Concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$) and hydrochloric acid (HCl) were purchased from Beijing Chemical Works. Natural graphite powder, hydrogen peroxide (H_2O_2) and sodium nitrate ($NaNO_3$) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. All of these materials were directly used without further purification.

2.2. The synthesis of graphene oxide

According to the traditional Hummers method [29], graphene oxide was prepared from natural graphite powder by the oxidation with different content of $KMnO_4$ in the concentrated H_2SO_4. Natural graphite powder (2 g) and $NaNO_3$ (1 g) were added into the concentrated H_2SO_4 (46 mL). The mixture was stirred uniformly under ice bath. Then $KMnO_4$ was added gradually into the mixture. Two hours later, the mixture was heated up to 35 °C and maintained for 30 min. Then the mixture was heated up to 98 °C and stirred for another 20 min. The final mixture was filtered and washed successively with HCl aqueous solution and distilled water until the pH reached 7–8. After ultrasound and dialysis of graphene oxide solution, the final GO powder sample was obtained by vacuum freeze drying. The content of $KMnO_4$ was defined as 2 g, 4 g, 6 g, 8 g, and the corresponding GO samples were named as GO1, GO2, GO3, GO4, respectively.

2.3. Preparation of PVA/GO composite film

PVA powder was dissolved in distilled water at 90 °C for 2 h. GO was dispersed into the distilled water by ultrasound. Then the GO aqueous dispersion was added gradually into the PVA solution and stirred for 30 min. The final PVA/GO composite film was obtained by solution casting method. For all the composite film, the solid content of GO was set as 1 wt% compared with PVA.

2.4. Characterization

Fourier transform infrared (FTIR) spectroscopic measurements were performed using a Nicolet iN10 MX device (Thermo Fisher Scientific, US) with the wavenumbers ranging from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The morphology of the natural graphite and GO samples were observed using a scanning electron microscopy (Quanta FEG-250, FEI Co, US). All the samples were pre-treated by spray-gold before observing.

The component element ratio of GO sample was analyzed using an X-ray photoelectron spectrometer (ESCALAB 250, Thermofisher science Co, US). All the samples were pre-treated by freeze-drying.

X-ray diffraction (XRD) measurements was performed directly on the samples using a Rigaku D-Max-2500 VB^{2+}/pc device (40 kV, 40 mA, Rigaku Co, Japan) with Cu irradiation at a scanning rate of 10°/min in the 2θ range of 5°–40°.

Transmission electron microscopy (TEM) was performed on a Hitachi H-800 electron microscope (Hitachi Co, Japan) operating at an acceleration voltage of 100 kV.

The mechanical properties of composite films were analyzed using a testing machine (MTS systems China Co, Ltd) in tensile mode according to the ASTM D638 standard at room temperature with an extension speed of 50 mm/min and an initial gauge length of 40 mm. The samples were conditioned in a relative humidity of 35% for 2 days before testing. The data reported were averaged over at least five specimens.

The oxygen permeability of the composite film was measured using a BT-3 device (Toyoseiki Japan Co. Ltd). The test principle was using the partial pressure difference of oxygen among the film sample. The pressure of the upper cell was set as 100 MPa, while the opposite was set as vacuum. With time went on, the oxygen gas began to penetrate the sample film and the information of the relative gas pressure was recorded.

3. Results and discussion

3.1. Structure and morphology characterization of GO

The FTIR spectra of GO samples are shown in Fig. 1. For the natural graphite, few functional groups existed on the layer structure and no characteristic peak was observed on the FTIR spectra. While for GO1 and GO3, the peak at 1120 cm^{-1} corresponded to the C–O–C vibration. The characteristic peak of the aromatic carbon double-bond vibration and the stretching vibration of O–H was observed at 1619 cm^{-1} and 3420 cm^{-1}, respectively. All these peaks together indicated the existence of hydroxyl, epoxy and carboxyl groups on GO after oxidation [30]. In addition, compared with GO1, the peaks at 1734 cm^{-1} corresponded to the C=O stretching vibration was more apparent for GO3. The reason could be ascribed to the oxidation of graphite with strong oxidant $KMnO_4$ in the concentrated acid. With more $KMnO_4$ added during the oxidation process, more oxygen-contained groups might be produced on the sheet of GO, resulting in more polar character of GO.

To confirm the more polar character, the chemical composition of GO with different oxidation degrees were analyzed by XPS technique and shown in Fig. 2. The C_{1s} core level spectrum of

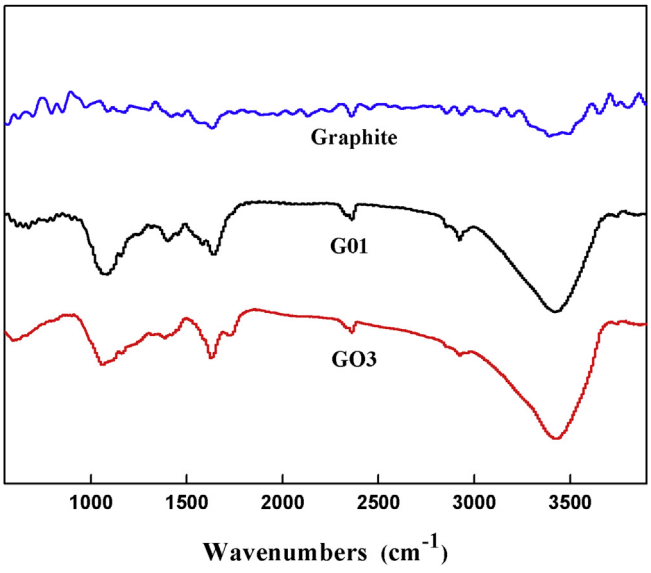

Fig. 1. FTIR spectra of GO samples.