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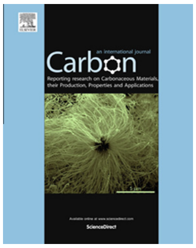

Uniaxial drawing of poly(vinyl alcohol)/graphene oxide nanocomposites

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ABSTRACT

The unique potential of graphene oxide (GO) was exploited in the nanocomposites by a simple uniaxial drawing (up to three times) of poly(vinyl alcohol) (PVA)/GO nanocomposites with a small amount loading of GO. From X-ray diffraction images, the PVA crystallites were found to be oriented parallel to the drawn direction. At the same time, exfoliated GO platelets were found to be aligned parallel to the film surface. Compared with the properties of the as-cast nanocomposites, those of the uniaxially drawn nanocomposites were found to be remarkably enhanced. For the mechanical properties, not only Young's modulus and tensile strength but also the toughness of the nanocomposites increased by the uniaxial drawing. It was revealed that 260% increase in toughness was achieved for the drawn nanocomposite with 1% w/w GO loading. Significant suppression of the swelling in water resulted in the excellent barrier properties against water, which exceeded that of the conventional high-barrier polymer, such as poly(vinylidene chloride). We revealed that this simple, fast and environmentally friendly process of uniaxial drawing exploits the excellent properties and high aspect ratio of GO in the nanocomposites.

1. Introduction

Among the composite materials, polymer nanocomposites have attracted a great deal of attention due to their high performances. The remarkable enhancements in various properties by the incorporation of a small amount of nanofillers have often been reported; therefore, they have been expected as alternatives for pure polymers or conventional micro-filler composites. Since Toyota Central R&D Labs., Inc., Nagakute, Japan, first reported the development of the nanocomposites composed of nylon 6 and clay [1–4], many kinds of nanofillers have been incorporated in polymer matrices [5–9]. In recent years, one of the most highly attractive nanofillers is graphene [10,11]. Graphene is a single-atom-thick layer of carbon which shows extremely high performances in its properties, such as mechanical, thermal and electronic properties [12–15]. In order to produce good interactions between graphene and polymer matrices, chemical modification of graphene has been widely conducted and rich varieties of graphene derivatives have been developed [11]. Chemically modified graphene derivatives are often processed from graphene oxide (GO), which is prepared during the chemical preparation of graphene through the oxidation of graphite [16]. GO possesses oxygen-containing functional groups on the base plane of graphene; thus, GO shows hydrophilic affinity [17,18]. Therefore, aqueous process for the preparation of nanocomposites can readily achieve the nano-dispersion of GO [19].

In our previous study, we selected poly(vinyl alcohol) (PVA), well known as a water-soluble polymer, as a matrix and prepared PVA/GO nanocomposites using a simple casting method through the aqueous medium [20] We revealed that

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the GO platelets were highly exfoliated and nano-dispersed in the polymer matrix, and the as-cast PVA/GO nanocomposites showed excellent properties. So far, several investigations into PVA/GO nanocomposites have been reported which have provided several methods of using water as a processing medium [21–24]. Zhao et al. prepared the nanocomposites with high content of GO using layer-by-layer assembly and showed the remarkable increases in elastic modulus and hardness [24]. The high-content PVA/GO nanocomposite was also prepared by vacuum-assisted self-assembly [25]. Both of these techniques brought the layered nanocomposites [26,27]. The strong interaction between polymer and filler was produced by these processes with the high in-plane alignment of GO, which results in the extremely high stiffness of the composites. Polymer nanocomposites reinforced by highly aligned layered nanofillers with high content were often investigated as artificial models of nacre, which is the composition of highly aligned inorganic aragonite platelets and protein. It was reported that the high stiffness comparable to that of nacre was achieved by a layer-by-layer process of PVA/clay nanocomposites [26]. However, it is difficult to control the amount of fillers by these methods, the filler content is necessarily high and intrinsically these are time/cost-consuming processes.

Generally, the alignment of the filler with high aspect ratio has a critical effect on the properties of composites [28,29]. For example, the alignment of the layered particles in the direction parallel to the film surface can produce the significant barrier properties [30]. In this study, orientation control of the PVA/GO nanocomposites was done by the uniaxial drawing of the as-cast nanocomposites. The casting method enables us to control the GO content to be 0–1% w/w. GO is expected to align parallel to the film surface by the simple uniaxial drawing. The effects of the uniaxial drawing on the structure and properties of the nanocomposites were investigated. This is an attempt to maximise the excellent properties of GO with a minimum content of GO.

2. Experimental

2.1. Materials

Graphene oxide aqueous suspension (1% w/w) was supplied by Mitsubishi Gas Chemical, Inc., Tokyo, Japan. GO in the aqueous medium was synthesised from graphite using the procedure based on Hummers' method [31]. The GO thickness was 0.8–1.0 nm with an average aspect ratio of 3000. The detailed information was given in our previous paper [19]. PVA powder ('Gohsenol NH-18', Nippon Synthetic Chemical Industry Co., Ltd., Osaka, Japan) was used with a degree of polymerisation of 1800 and a degree of saponification >99%.

2.2. Sample preparation

The PVA/GO nanocomposites were prepared by the solvent-casting method. The details of the nanocomposite preparation are described in our previous report [20]. The as-cast nanocomposites were put into an oven at 160 °C for 15 min, subsequently, uniaxially drawn. The draw ratio was fixed at three times and the thickness of the drawn films was 60 μm.

2.3. Characterisation

The X-ray generator (RINT2100, Rigaku, Tokyo, Japan) was operated at 40 kV and 20 mA. X-ray diffraction profiles were obtained by irradiating the samples by Ni-filtered CuKα radiation. The scanning speed was 1.0°min^{-1}, and the $2\theta/\theta$ scan data were collected at 0.02° intervals. X-ray diffraction images were taken with a flat camera.

The cross section of the uniaxially drawn PVA/GO nanocomposite with 1% w/w GO loading was observed using a field emission scanning electron microscope (FE-SEM) (JEOL JSM-7500F) at an accelerating voltage of 2 kV and emission current of 10 μA. Osmium tetroxide was deposited on the sample surface prior to observation.

Tensile test of the drawn PVA/GO nanocomposites were performed using Autograph AGS-1kND (Shimadzu Co., Kyoto, Japan). The cross-head speed was 2 mm min^{-1} and the initial length was 20 mm. More than 10 specimens were tested for each sample. The toughness (*K*) was calculated using the following equation:

$$K = \int_{\varepsilon=0}^{\varepsilon=\varepsilon_{\max}} \sigma \cdot d\varepsilon/\rho \ (\mathrm{J\ g^{-1}}) \tag{1}$$

where, σ is stress ($\mathrm{Pa = J\ m^{-3}}$), ε is strain (–) and ρ is density ($\mathrm{g\ m^{-3}}$).

The dynamic mechanical analyses were performed using a dynamic mechanical analyser, DVA-220S (ITK Co., Ltd., Osaka, Japan). A heating rate was 6 °C min^{-1} with a frequency of 10 Hz was employed under nitrogen flow.

Differential scanning calorimetry (DSC) was carried out using a differential scanning calorimeter (DSC-220CU, Seiko Instruments Inc., Chiba, Japan). The melting point temperatures (T_m) of the nanocomposites were determined as the endotherm peak temperature. The thermal decomposition temperature (T_d) was measured with a thermogravimeter (TG/DTA-220CU, Seiko Instruments Inc., Chiba, Japan). The T_d was defined as the temperature at which the substance had a 5 wt% thermal weight loss. DSC and thermogravimetry were performed under nitrogen flow with a heating rate of 10 °C min^{-1}. Thermal diffusivity (α) was obtained by Thermowave Analyzer TA3 (Bethel Co., Ltd., Ibaraki, Japan) under periodic laser heating. The α of the in-plane direction was measured at room temperature.

The swelling ratio was determined by immersing the specimens in distilled water at 30 °C and was defined as the weight gain of the specimens as follows:

$$\text{Swelling ratio} = W/W_0 \tag{2}$$

where, W_0 and W are the weight of the specimen before and after swelling, respectively. Then, the diffusion coefficient of water (*D*) was determined using the following equation: [32,33]

$$D = \pi\left(\frac{Qr}{4}\right)^2 (\mathrm{m^2 s^{-1}}) \tag{3}$$

where Q is the initial slope of the linear approximation obtained by plotting the swelling ratio versus the square root of the swelling time and *r* is the thickness of the specimens.