



Book reviews

Facile preparation of poly(vinyl alcohol)/graphene oxide nanocomposites and their foaming behavior in supercritical carbon dioxide



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ABSTRACT

In this study, we presented a novel polymer nanocomposite foam based on poly(vinyl alcohol) (PVA) and graphene oxide (GO) prepared via the supercritical fluid foaming technology. By using water as the benign solvent, GO sheets were fully exfoliated and homogeneously dispersed into PVA matrix with the assistance of mild sonication, and then the PVA/GO nanocomposite was obtained after thermal processing. The results indicated that the well-dispersed PVA/GO nanocomposite showed significantly improved mechanical strength, compared with neat PVA. In subsequent foaming procedure, GO sheets served as the reinforcing element for cell walls and played an effective role in stabilizing the cellular structure during cell growth. Benefiting from the heterogeneous nucleation of GO sheets, the nanocomposite foams exhibited smaller cell size and larger cell density, thus a remarkable enhancement in compressive strength was obtained for PVA/GO nanocomposite foams.

1. Introduction

Polymeric foams are found in various applications ranging from packaging [1], insulation [2], absorbents [3] and scaffolds [4] for tissue engineering because of their excellent properties; they are light-weight and exhibit high specific strength, good thermal and sound insulation qualities. However, compared to bulk polymers, foams have reduced mechanical strength and lower dimensional stability. If a sufficient number of pores smaller than the critical flaw size pre-existing in polymers can be produced, then the polymeric foams can be obtained without compromising the mechanical properties. Therefore, many efforts have been done to control the cell size. Recently developed polymer nanocomposite foams have received increasing attention in both research and practice [5–8]. Introduction of a small amount of nanoparticles (NPs) into polymer matrix will always provide significant improvement in a wide variety of properties, including enhanced mechanical strength [7], thermal stability [9] and barrier effect [10]. For instance, carbon-based NPs [6] and particularly carbon nanotubes [11–15] are usually used as the nanofillers to produce the nanocomposite foams with improved performance. Considering the nanometer dimension, the NPs are especially beneficial for reinforcing the thin cell walls of foam materials. Hence, the reinforced cell walls can effectively protect the cells from collapsing during cell growth [16]. Additionally, the NPs can act as nucleation sites to reduce the

nucleation energy that help to decrease the cell size and increase the cell density. It is believed that the well-dispersed NPs in polymer nanocomposites can produce great benefits in the foaming behavior and the final properties of foamed products.

Poly(vinyl alcohol) (PVA), a typical water-soluble polymer [17], is one of the few polymers which can be prepared via non-petroleum routes and possesses good comprehensive properties [18–20], such as good mechanical and thermal properties, excellent barrier property [21], favorable biocompatibility [22] and certain biodegradability under special circumstances [23]. Thus, porous PVA-based hydrogel are usually considered as the scaffold for tissue engineering applications [24,25]. The degradable PVA foam is suitable for use as the packaging materials [26]. In addition, PVA foam has also been extensively applied in wound healing [27], drug delivery [28] and heavy metal ions adsorbents [29]. However, as a result of the strong hydrogen bonding existing among PVA chains, the melting temperature of PVA is very close to its decomposition temperature, and the fabrication of PVA-based products has been mostly based on the solution method. In general, the porous PVA materials are prepared using repeated freezing-thawing processes [30,31]. PVA hydrogels obtained by this cyclic treatment are thermoreversible and show many useful properties like high mechanical strength, rubberlike elasticity, stability at room temperature and lack of toxicity [32–34]. However, the freezing-thawing method is an intermittent strategy and involves series of time-

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consuming procedures, which severely limits the production efficiency of porous PVA materials. Recently, Park et al. [35,36] prepared the PVA and PVA/microfibrillated cellulose (MFC) composites foams in a continuous extrusion process using supercritical carbon dioxide (CO₂) and water as co-blowing agent. The added MFC enhanced the melt strength and crystallinity of composite system, thus a uniform cell structure and a high cell density were created in the biodegradable PVA foams. Based on the theory of molecular complexation, Wang et al. [37,38] adopted water as both the plasticizer and blowing agent to develop the thermoplastic foaming of PVA. Neat PVA foam and a series of functional PVA-based composite foams, including biological PVA/hydroxyapatite (HA) composite foam [39,40], halogen-free flame retardant PVA/melamine phosphate (MP) composite [41] and inorganic flame retardant PVA/aluminum hydroxide (ATH) composite [42] foams, were successfully fabricated through continuous extrusion or intermittent molding foaming method. In our earlier work [18], a novel foaming strategy based on the thermal processing and supercritical fluid technology was proposed to prepare the microcellular PVA material. The foaming behavior of water plasticized PVA was systematically studied and the controlled porous structure was easily obtained by tuning the foaming parameters. Therefore, compared with the freezing-thawing method, the thermal foaming might be a practical, time-saving and cost-effective strategy to fabricate PVA-based foams.

Graphene, a two-dimensional carbon material, is considered to be one of most promising materials for high-performance applications. Since its discovery in 2004 [43], graphene has proved to have remarkable properties, such as superior mechanical strength, high thermal and electrical conductivities [44–46]. As a result of these intrinsic properties, graphene has been extensively applied in various polymer nanocomposite systems for improving their comprehensive performance [47–49]. But the optimum results can only be achieved when the graphene nanosheets are dispersed homogeneously or a strong interfacial interaction exists between graphene and polymer matrix. In order to exfoliate graphite more effectively, oxygen-containing sites are introduced into inter-layers of graphite to form graphite oxide using oxidization methods. Graphite oxide can be easily exfoliated into single layer graphene oxide (GO) in water with the assistance of mild sonication. In this way, researchers [50–52] produced the molecular-level dispersion of GO into PVA matrix through the simple water solution processing, and significantly enhanced properties were obtained for the PVA/GO nanocomposite. Various low-dimensional PVA/GO composite products, like nanocomposite films [53] and fibers [54] with improved performance, were successfully fabricated via the aqueous solution method. Besides, the PVA/GO nanocomposite hydrogel was prepared using the cyclic freeze-thawing method [55,56].

To the best of our knowledge, the thermal foaming of PVA/GO nanocomposite has not been previously reported in the literature. Therefore, the purpose of the present study is to prepare the PVA/GO nanocomposite foams based on thermal processing and supercritical fluid (SCF) technology. Firstly, GO was exfoliated and homogeneously dispersed into PVA matrix via the simple water solution processing in the presence of sonication. Then PVA/GO nanocomposite was foamed through batch foaming using supercritical CO₂ as the physical blowing agent. The effects of well-dispersed GO on the structure and some properties of PVA/GO nanocomposite were systematically studied. PVA/GO nanocomposite foams with fine cellular structure was successfully prepared and the compressive strength were also reported. It is believed that the reported nanocomposite foam may have great potential applications for use as the structural parts.

2. Experimental

2.1. Materials

Graphite powder was kindly supplied by Nanjing XFNano Materials Tech Co., Ltd. sodium nitrate (NaNO₃), Potassium permanganate

(KMnO₄), sulfuric acid (H₂SO₄, 98%) and hydrogen peroxide (H₂O₂) were purchased from Aladdin Chemical Co., Ltd. PVA, with a polymerization degree of 1700 and an alcoholysis degree of 99 was supplied by Sichuan Vinyllon Corporation (Chongqing, China). First, the PVA raw material was washed with deionized water until it had a pH of 7 to get rid of the residual sodium acetate (NaAc). Then, it was dried at 80 °C to achieve a constant weight. CO₂ (99.5% of purity) was provided by Taiyu Gas (Chengdu, China). The deionized water used was prepared in our laboratory.

2.2. Preparation of PVA/GO nanocomposite

First, GO was prepared from graphite using the modified Hummers method [57,58]. GO aqueous solution (2 mg/ml) was prepared with the assistance of mild sonication. Meanwhile, PVA particles (10 g) were dissolved in distilled water (90 ml) at 90 °C and the solution was subsequently cooled to room temperature. The GO aqueous dispersion was gradually added to the PVA solution and sonicated for additional 30 min at room temperature. Then this homogeneous PVA/GO solution was poured into a Teflon dish and kept at 60 °C for solvent evaporation until water content decreased to about 35%, thus the residual water acted as the plasticizing agent for PVA. Finally, the water plasticized PVA (WPVA)/GO were molded into plates (the thickness is 2.0 mm and diameter is 20.0 mm) using a Plate Vulcanization Machine (molding temperature is 165 °C and molding pressure is 15.0 MPa). Through the drying method, water content of the WPVA/GO sample was 27.5% by weight. The fabrication process is schematically shown in Fig. 1.

2.3. Preparation of PVA/GO nanocomposite foam

In this system, the plasticized PVA/GO nanocomposite was the foam matrix and CO₂ acted as the blowing agent. Firstly, the samples were saturated with supercritical CO₂ at constant temperature and pressure (the Syringe pumps was purchased from Teledyne ISCO, Inc., USA) in a stainless-steel autoclave (Beijing Century Senlang Experimental Apparatus Co., Ltd). After maintained for a fixed period of time, the supersaturated specimen was produced when the pressure was removed (pressure induced phase separation), resulting in the nucleation and growth of bubbles. The foaming processes were performed at 80–100 °C and 15.0 MPa with the depressurization rate of 5.0 MPa/s.

2.4. Characterization

2.4.1. Characterizations of PVA/GO nanocomposite

Atomic force microscopy (AFM) observation of GO were obtained using a DI Multimode V scanning probe microscope (Veeco, USA). Raman tests were conducted on a Labram HR spectrometer (HORIBA Jobin Yvon) using 532 nm laser excitation with a power of 1 mW. The obtained GO was dispersed in deionized water and then dip-coated onto a mica substrate. To study the dispersion behavior of GO in nanocomposite samples, Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 electron microscope at an accelerating voltage of 200 kV. The composite was cut into 80–100 nm thin section at a temperature of –100 °C using a LEICA EM FC6 frozen ultramicrotome, and the thin section was then placed on the copper grids. The tensile experiments of solid PVA and its GO nanocomposites were conducted on an Instron 5567 universal testing machine. The dog bone specimens were tested with a crosshead speed of 50 mm/min and the load cell was 10 kN with a gauge length is 10 mm. The specimen dimensions were 40 mm length, 2 mm width, and 2 mm thickness. The specimens used for mechanical tests were heat-treated at 80 °C under vacuum condition for 24 h to remove as much water as possible. The tensile experiments were repeated at least five times for exchange sample to confirm the average value. The fractured surfaces of samples after the tensile tests were further studied by scanning electron microscopy (SEM) using an Inspect F field-emission electron microscopy

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