



Fabrication of poly (vinyl alcohol)/graphene nanocomposite foam based on solid state shearing milling and supercritical fluid technology



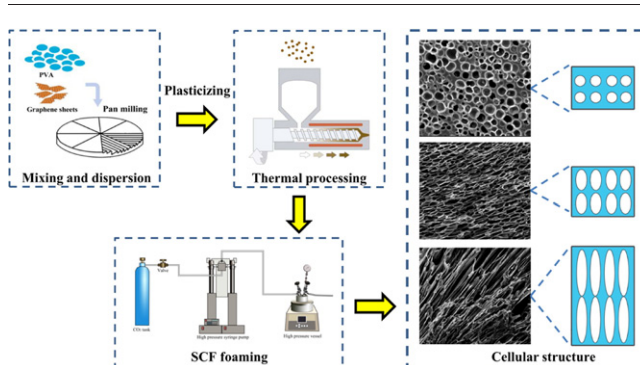
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HIGHLIGHTS

- The graphene sheets were effectively exfoliated and homogeneously incorporated into the PVA matrix.
- The well-dispersed graphene sheets served as the reinforcing element for cell walls to stabilize the cellular structure.
- Incorporation of graphene significantly improved cellular structure and compressive properties of the nanocomposite foam.
- The PVA/graphene nanocomposite foam with anisotropic mechanical properties was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Combining the nanocomposite and supercritical fluid (SCF) foaming technology develops an effective preparation method for new class of microcellular polymer nanocomposite foam, which has received much attention in both research and practice. In this paper, the poly (vinyl alcohol) (PVA)/graphene nanocomposites were successfully prepared at ambient temperature through the solid state shear milling technique, and made into foam material by using supercritical carbon dioxide as the physical blowing agent. The results indicated that graphene sheets were uniformly incorporated into the PVA matrix after milling, and graphene sheets did not reaggregate in the subsequent melting process. These well-dispersed PVA/graphene nanocomposites presented significant increases in tensile strength and thermal behavior compared to pure PVA. In the SCF foaming procedure, graphene sheets acted as the heterogeneous sites to facilitate the bubble nucleation process. More importantly, the embedded graphene sheets played an effective role of reinforcing the cell walls to stabilize the cellular structure during the cell growth stage, thus compressive properties of the nanocomposite foams were significantly enhanced. The bubbles tended to be elongated along the direction of CO₂ decompression at a relatively high foaming temperature and with fast depressurization rate.

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1. Introduction

Polymeric foams have been given increasing attention in both scientific and industrial applications because of their light weight, high specific strength, good thermal and sound insulation properties. In general, these excellent characteristics are provided by their unique porous structure and the final properties of foam products will always be

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strongly affected by relevant structure parameters (cell size, cell geometry and distribution). Recently, various advanced processing technologies have been developed to improve the cellular structure in obtained foam products. In order to increase the expansion space for the microcellular injection molding (MIM), some researchers proposed the foam injection molding machine enhanced with the breathing mold [1–3]. The gas counter pressure (GCP) [4,5] was also extensively employed in MIM, and it can improve the foamed part's surface quality by eliminating the surface defects caused by cell rupture. For batch foaming, the two-step depressurization [6,7] or the multiple soaking temperature method [8,9] was introduced to produce the foam products with bi-modal cell structure (BMCS). Compared with the mono-cellular foams, foams with BMCS have some superior properties [8,10]. Besides, a series of advanced extrusion foaming [11,12] and bead foaming [13,14] technologies have been developed. In summary, these developed polymeric foams provide improved mechanical and physical properties over conventional foams, but they require stringent processing conditions and high manufacturing cost. This severely restricts the large-scale application of polymeric foams for high-performance materials.

Nanocomposite technology has been regarded as a simple and effective method to prepare the high-performance polymer-based materials [15]. In this way, the creation of lightweight and high strength polymer materials can be realized through combining the foaming and nanocomposite technologies, thus enlarging the range of advanced applications for novel polymer-based composite materials [16]. But the optimum results can only be achieved when the multifunctional nanofillers are dispersed homogeneously or a strong interfacial interaction exists between the nanofillers and the matrix. Besides, the well-dispersed nanoparticles in the polymer matrix can play an effective role of heterogeneous nucleation agent during the fabrication of polymeric foams.

Poly (vinyl alcohol) (PVA), a typical water-soluble polymer, possesses good comprehensive properties, such as good mechanical and thermal properties [17–19], excellent barrier property [20], favorable biocompatibility [21] and certain biodegradability under special circumstances [22]. Thus, porous PVA is used as the scaffold for tissue engineering applications [23,24]. Biodegradable PVA foam can be considered as the suitable packaging material [25,26]. It has also been extensively applied in heavy metal ions adsorbents [27], wound healing [28] and drug delivery [29]. Carbon-based nanofillers and particularly graphene have recently attracted a great deal of interest due to their natural characteristics [30], such as high mechanical and electrical properties. PVA/graphene composite foam, combining the virtues of them, will be a promising material in various high value-added industries. But the big challenge in fabricating the high performance PVA/graphene foam is to obtain well-dispersed graphene in PVA matrix, or even better at the molecular level. The dispersion behavior of graphene particles will produce an important impact on the cellular structure and the final properties of the obtained foam products.

In the last decade, researchers have dedicated a great deal of effort to fabricate high-performance PVA/graphene composites. Liang et al. [31] reported a simple water solution processing method to achieve the molecular-level dispersion of graphene oxide (GO) into PVA, and significant reinforcement was observed for the nanocomposite due to the efficient load transfer between the nanofiller and the PVA matrix. But GO, fabricated through chemical exfoliation, will be endowed with damaged aromatic structure because of the introduction of various oxygen-containing groups on the basal planes and edges. As a result, these structural defects generate a deterioration effect on its original properties [32], for instance, GO is electrically insulating. Zhang et al. [33] prepared the graphene-reinforced PVA composite by incorporating GO into PVA aqueous solution and then reduced GO to graphene. On the contrary, Shen et al. [34] prepared graphene nanosheets firstly through the chemical reduction from GO, followed by the fabrication of the PVA/graphene nanocomposite by a simple solution-mixing method. The residual

oxygen-containing groups in graphene play a critical role in its homogeneous dispersion in water or organic solvent, as well as the favorable interaction between nanofillers and matrix. At present, researchers [35–37] usually adopt the solution method to prepare the PVA/graphene composite from the reduction of PVA/GO aqueous solution, and only low-dimensional products (film et al.) can be obtained. In view of this, developing a solid-state method for dispersing graphene in the PVA matrix will make a contribution to the fabrication of multi-dimensional products, especially for the PVA/graphene composite foam.

A solid-state shear milling process, pan milling, was developed in our group to prepare the polymer nanocomposites without any chemical modification. This method was based on self-designed pan-milling equipment, inspired by the traditional Chinese stone mill, which can provide strong shear and compression force in a solid state and hence have excellent dispersion and exfoliation effects for polymers and fillers. In our previous work, Poly (ethylene terephthalate) (PET)/montmorillonite (MMT) [38], Polyoxymethylene (POM)/carbon nanotubes (CNTs) [39] and polyamide 6 (PA6)/CNTs [40] were successfully prepared by solid state shearing milling. In addition, the pan-milling also realized the cutting of CNTs [40], the intercalation and exfoliation of talc [41], as well as the exfoliation and layer expansion of vermiculite [42]. Thus this solid state shearing milling technique can be considered as an effective way to prepare polymer nanocomposite materials. Based on these considerations, we propose a novel approach to fabricate the microcellular PVA/graphene materials, including the preparation of PVA/graphene composite by pan-milling and then foaming using supercritical fluid (SCF) technology.

Actually, the microcellular PVA foams with controlled porous structure have been successfully prepared through thermal processing and by using supercritical CO₂ as the blowing agent. The foaming behavior of PVA/CO₂ was investigated systematically as a function of saturation pressure, foaming temperature and saturation time [43]. To the best of our knowledge, few papers have focused on the fabrication of PVA/graphene foam. Therefore, the purpose of the present study is to prepare the PVA/graphene nanocomposite foams by combining the pan-milling technique and SCF foaming technology. Firstly, the graphene sheets were homogeneously dispersed into PVA matrix, which could further develop enhanced interfacial compatibility of the PVA/graphene nanocomposites after the co-milling process. Then the nanocomposite foams were prepared via batch foaming by supercritical CO₂ as the physical blowing agent. The influences of well-dispersed graphene sheets on the cellular structure and mechanical properties were systematically investigated in various conditions. It is believed that this work can provide an effective strategy for fabricating nanocomposite foam with controlled cellular structure.

2. Experimental

2.1. Materials

PVA, with a polymerization degree of 1700 and an alcoholysis degree of 99 was supplied by Sichuan Vinylon 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 natrium aceticum (NaAc). Then, it was dried at 80 °C to achieve a constant weight. Graphene was purchased from Deyang Carbonene Technology Co., Ltd. (Deyang, China). It is a commercial solution-based few-layer reduction of graphene oxide (layer number: 3–5) that is usually used for reinforcing polymers. Carbon dioxide (99.5% of purity) was provided by Taiyu Gas (Chengdu, China).

2.2. Preparation of the PVA/graphene composite

PVA pellets were first fed into the pan-mill through the hopper at a rotation speed of 20 rpm. The milled PVA materials were transformed into a fine powder and collected after five cycles of milling. The

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