Preparation of PMMA/graphene oxide microcellular foams using supercritical carbon dioxide

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Abstract. Microcellular foams have a widely applications in many industries due to their superior properties. In this paper, the polymethymethacrylate (PMMA)/graphene oxide (GO) microcellular foams were prepared by supercritical carbon dioxide as a friendly foaming agent. The effect of graphene oxide amount on cellular structure and mechanical strength of foams had been investigated. Microstructure characterization bases on scanning electron microscopy (SEM). The cell size and cell density were calculated via image analysis. It was found that the average foam cell size was decreased from 20.1 μm to 2.2 μm and the cell density was increased from 2.8×10^{8} to 3.3×10^{10} when 1.5wt.% GO sheets were added into PMMA matrix. In addition, the compression strength of polymeric foams was increased from 13 MPa to 39 MPa.

1. Introduction

Microcellular foams, typically characterized by cell sizes smaller than 10 μm and cell densities larger than 10^{9} cell/cm^{3} [1], have been attracted a great attention because of their great properties such as lightweight, thermal insulation, high strength and cost reduction [2]. Microcellular foams have potential applications in building, packaging, automotive and aircraft industries [3]. In the past studies, many kinds of polymer have been used to product microcellular foams such as polymethymethacrylate (PMMA) [4], polystyrene (PS) [5], polycarbonate (PC) [6], polypropylene (PP) [7] and polylactic acid (PLA) [8]. In recent years, with the development of microcellular foaming technology, polymer nanocomposite microcellular foams also have received widespread attention due to a small amount of nanoparticles can significantly improve a variety of properties without sacrificing the properties of polymer matrices [9]. These nanoparticels include nanosilica [10], carbon nanotube [11], grapheme [4, 5] and nanoclay [12]. Graphene, as a new multifunctional material, has been attracting enormous attention since it was first exfoliated mechanically from graphite in 2004 [13]. For a variety of excellent properties such as large theoretical specific surface area, high thermal conductivity and strength [13], graphene can be produced multifunctional nanocomposite microcellular foams. In this

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study, we fabricated PMMA/GO microcellular foams using supercritical carbon dioxide ($ScCO_2$). GO was used as a heterogeneous nucleation agent and a reinforcement. The effect of graphene oxide on cell sizes and cell density to microcellular foams was investigated.

2. Experimental

2.1. Raw materials

PMMA pellets were commercially available from Nantong Rayon Chemical Co. Ltd., China. The density of the PMMA is 1.19 g/cm^3 and the glass transition temperature (T_g) is 107^{o}C. Graphene oxide (GO) was obtained from Nanjing XFNANO Materials Tech Co. Ltd. The foaming agent is high-pressured CO_2 with a purity of 99.9%.

2.2. Preparation of PMMA/GO nanocomposites

The PMMA/GO nanocomposites were prepared by solution blending. Firstly, the GO sheets were dispersed in N, N-dimthylformamide (DMF) by ultrosonication for 4 h. The amounts of GO sheets were 0.5, 1.0 and 1.5 wt.% relative to PMMA. Furthermore, the PMMA particles were dissolved in DMF by heating. Then, the PMMA solution was mixed with the GO solution by ultrosonication for 4 h continually. Secondly, the solution blend was subsequently dropped into large amount of ethanol with strong agitation. Finally, the samples were dried in vacuum freeze-drying machine for 24 h to remove the solvent and then pressed into a flake by hot-pressing at 170^{o}C.

2.3. Supercritical CO_2 foaming process

The PMMA/GO microcellular foams were prepared by the batch foaming process. We also used molds to constrain foaming process (mold-limited foaming). The samples were placed in a mold with an inner height 3 mm and then the mold was placed in a stainless steel vessel filled with CO_2. The saturation conditions were 16 MPa, 80^{o}C and 8 h. After completed saturation, the pressure was quickly released within 1 s. The foam was then fixed using ice and water mixture bath after 30 s for foaming.

2.4. Characterization

The microstructures of PMMA/GO foam were characterized by scanning electron microscopy (SEM) with an accelerating voltage of 5 kV. The cell size and cell density were calculated via image analysis using Nano-Measure (Department of Chemistry, Fudan University) and more than 100 cells were tested. Then the cell density (N_f) was calculated according to [14]:

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2} \tag{1}$$

where, A is the area of the SEM micrograph (cm^2), n is the number of cells in the micrograph and M is the magnification factor.

The bulk density of PMMA/GO foam was measured based on drainage method by an analytical balance with an accuracy of 0.1 mg. The bulk density (ρ) was calculated as:

$$\rho = \frac{m_0}{m_0 - m_1} \times \rho_{water} \tag{2}$$

where, m_0 is the mass of the sample in atmosphere and m_1 is the mass of the sample in water and ρ_{water} is the density of water at room temperature.

The compression strength of PMMA/GO foam was measured by Universal Testing Machine (QJ-210A) at the loading speed was 0.5 mm/min. The typical dimensions of the specimens were 3 mm × 3 mm × 7 mm.

3. Results and discussion

3.1. Morphology of PMMA/GO foams

It is known that the nanoparticles can act as very effective heterogeneous nucleation sites due to the lowered energy barrier for nucleation. Nanoparticles especially suited for the production of microcellular foams of high a cell density and a small cell size [15]. In order to investigate the amounts of GO on the morphology of the microcellular foams, we produced microcellular foams with the GO amounts of 0 wt.%, 0.5 wt.%, 1.0 wt.% and 1.5 wt. %. The results showed in figure 1.

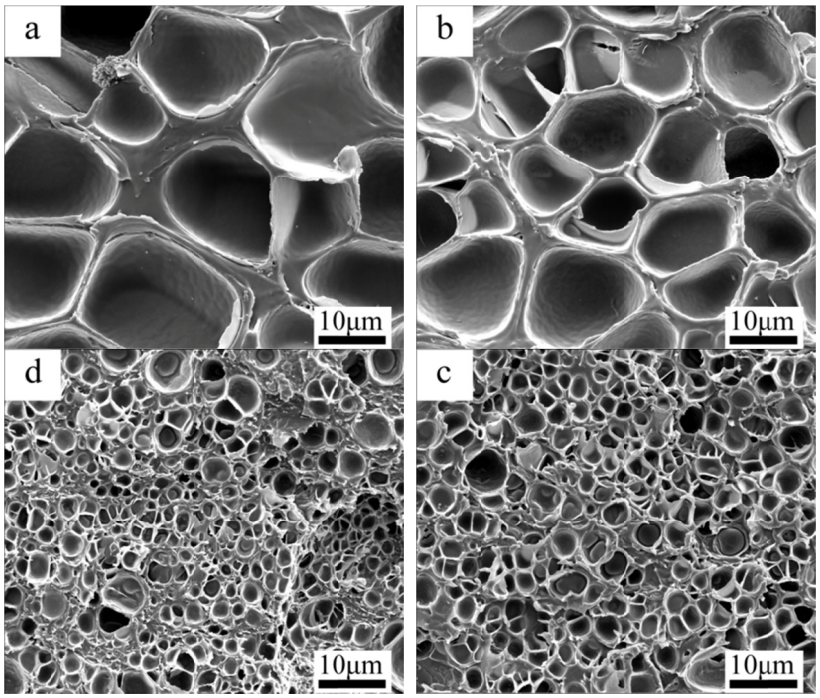

Figure 1. SEM images of PMMA/GO microcellular foams with different amounts of GO: a. 0 wt.%, b. 0.5 wt.%, c. 1.0 wt.%, d. 1.5 wt.%.

From the SEM images, it was found that average cell size decreased and cell density increased with the increasing GO content. It could be explained according to heterogeneous nucleation mechanisms [15]. GO sheets are heterogeneous nucleation sites, and more GO sheets could supply more nucleation sites and result in a higher nucleation rate. As it can be seen in figures 2 and 3, the average cell size were decreased from 20.1 μm to 2.2 μm and the average cell density were increased from 2.8×10^8 to 3.3×10^{10} with the 1.5 wt.% GO sheets compared with pure PMMA microcellular foam.

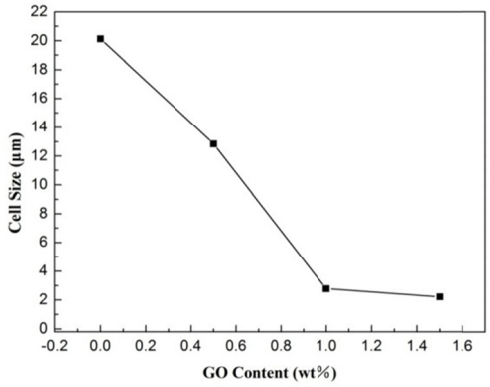

Figure 2. Variations of average cell size of PMMA/GO microcellular foam with different amounts of GO.

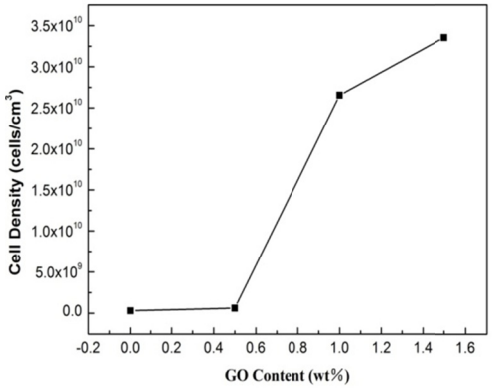

Figure 3. Variations of average cell density of PMMA/GO microcellular foam with different amounts of GO.

3.2. Compression properties of PMMA/GO foams

It is known to all that the problem of stress cracking could limit the application of PMMA. In order to investigate the effect of cell structure on mechanical properties of PMMA/GO foams, the compression properties of foams were tested. The result showed in figure 4. It was found that there is an obvious yield platform in the stress-strain curve of PMMA/GO foams. It showed that the foams have a great compression resistance capability due to the large number of cells with small size and high cell density. These cells could absorb a huge amount of energy when they were compressed. Moreover, the compressive strength has improved from 13 MPa to 39 MPa when the content of GO in PMMA matrix increased to 1.5wt.%. The density of PMMA/GO foams was showed in figure 5. It showed that the density of foams was increased with the increasing content of GO. The densities of foams also had an impact on compression strength. For the foams, the density increased means that the volume fraction of cell walls in pore structure increased. So it has strong bearing capacity to reply the compression.

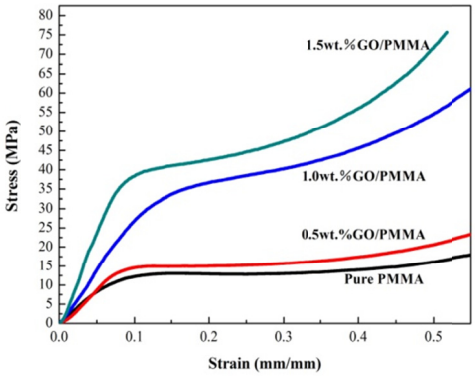

Figure 4. Compression stress-strain curves for PMMA/GO foams with different amounts of GO.

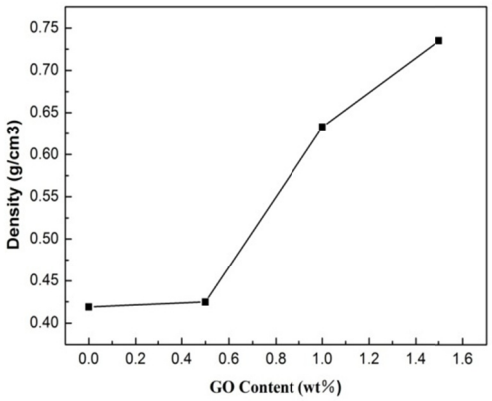

Figure 5. Variations of relative density of PMMA/GO foams with different amounts of GO.

4. Conclusion

In this work, the PMMA/GO microcellular foams were successfully prepared by superficial carbon dioxide foaming. The addition of GO sheets decreased the cell size and increased cell density in PMMA microcellular foam. With the increasing GO content, the average foam cell size was decreased from 20.1 μm to 2.2 μm and the cell density was increased from 2.8×10^{8} to 3.3×10^{10} when 1.5wt.% GO sheets were added into PMMA matrix. The compression strength of polymeric foams was increased from 13 MPa to 39 MPa, compared with the pure PMMA foam.

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