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Preparation of PMMA/CNT Microcellular Foam Using Supercritical CO_2

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Controlling the cell size and cell density of microcellular foams has an important influence on polymeric foams properties. By using nanoparticles in polymers and supercritical fluids as foaming agent, it is possible to create microcellular foams with controlled morphology. In this article surface modified carbon nanotube (CNT) was used to prepare Polymethylmethacrylate (PMMA) nanocomposite. Dry ice was used as the source of supercritical CO_2 in foam production. Microcellular foams were prepared form PMMA/CNT nanocomposites. The cell morphology was observed by scanning electron microscopy (SEM) and the cell size and cell density were calculated via image analysis. The effect of CNT on cell size and cell density of foams was investigated.

Keywords: Microcellular Foam, Carbon Nanotube, Nanocomposite, Supercritical CO_2, Dry Ice.

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1. INTRODUCTION

Microcellular foams are porous polymers generally have approximately 10 μm in diameter, with a cell density of 10^9 cells/cm^3. These foams offer some advantages compared to their solid analogs. They have superior properties to their non-foamed counterparts in terms of enhanced ratio of flexural modulus to density and impact strength. In the preparation of polymeric foams the polymer is saturated with CO_2 and thus the matrix is in a plasticized state. Rapid temperature reduction or depressurization results in CO_2 escaping from the material, which can cause nucleation, and as the T_g rises the foamed structure is "frozen". Recently, nanoparticles have been used for preparation of microcellular foams from polymer nanocomposites. These nanoparticles include multiwall carbon nanotube [1-4], clay [5-8] and nanosilica [9-10]. Nanoparticles have the role of nucleating agents in formation of microcellular structure, as they decrease the activation energy for generation of bubbles. In fact, dispersion of nanoparticles, followed by a surface modification, plays an important role in creation of microcellular architecture. They have been used to control the cell size of microcellular foam [1-8, 10].

In this study surface modification of multi-walled carbon nanotubes (MWCNTs) was carried out via an oxidization treatment by strong acids and a stable suspension of dispersed nanoparticles in acetone was made. This suspension was used to provide PMMA/CNT nanocomposites. Microcellular foams were prepared form PMMA/CNT nanocomposites by supercritical CO_2. The foaming agent was made via heating solid CO_2 (i. e. dry ice), in a pressure vessel. The effect of CNT loading on morphology of foams was investigated.

2. EXPERIMENTAL

2.1 Materials

The PMMA (Trade named acryrex CM-205) used in the study were from Chi Mei Incorp., Taiwan. Multi-walled carbon nanotubes (MWCNTs) with purity greater than 95% were purchased from RIPI, Iran. Carbon dioxide in solid state (i.e. dry ice) was from Vahe Iran Co. Concentrated nitric and sulfuric acids were purchased from Merck.

2.2 Preparation of PMMA/CNT Nanocomposite

PMMA was firstly dissolved in acetone to form a homogeneous solution. Functionalized CNT were sonicated in 20 ml acetone for 7 minutes and then the suspension was added to the polymer solution by magnetic stirring. The solution was further mixed with a homogenizer for 5 min. The polymer suspensions were sonicated again for a period of 15 min. The suspension was then added dropwise into a large volume of methanol. The solution was continuously stirred vigorously using a mechanical stirrer. The methanol solution was further separated from the precipitated solids by filtration. The precipitates were dried in a vacuum to remove the solvent.

2.3 Preparation of PMMA/CNT Foam

A self-designed foaming setup was used in this work. It consists of four main parts; a pressure vessel, an electric heater with a temperature controller, a pressure gauge and a release valve. The vessel was pressurized by heating dry ice. Samples were poured into the vessel and certain amount of dry ice, calculated by Van der Waals equation of state, was added into it. The vessel was sealed and the heater was switched on so that the temperature was reached to the adjusted one. Evaporation of dry ice led to pressurize the vessel. The pressure of the vessel which was always higher than the desired saturation pressure was adjusted using the release valve. After a period of 12 h at which temperature and pressure were kept constant, the pressure was then rapidly released and the foam morphology was fixed by cooling it with cold water.

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2.4 Structural and Morphological Characterization

Dispersion of CNT in polymeric matrix was studied by a PHILIPS–EM208 transmission electron microscope (TEM). The morphology of the prepared polymer nanocomposite and nanocomposite foams was observed with a LEO-440i scanning electron microscope (SEM) with an accelerating voltage of 100 kV.

Image analysis on the SEM micrograph was conducted to obtain the average cell size and cell density using Image J. The number of bubbles, n, in the micrograph was determined by software and the number of bubbles per unit volume, N, was calculated using the following equation:

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

where A is the area of the SEM image and M is the magnification factor.

3. RESULTS AND DISCUSSION

3.1 Preparation of PMMA/CNT Nanocomposite

Fig. 1 shows the TEM micrographs of PMMA/CNT nanocomposites prepared via anti-solvent precipitation with 1% CNT. A fine dispersion of nanoparticles is observed in nanocomposite structure. As shown earlier [2]., functionalization of CNT led to presence of some functional groups (hydroxyl, carboxyl and carbonyl) that resulted in stronger physical or maybe chemical interactions between CNTs and polymer molecules.

3.2 Preparation of PMMA/CNT Foam

For production of microcellular foams, supercritical carbon dioxide was provided from heating of dry ice. First of all, we had to calibrate the pressure vessel. Van der Waals equation of state (EOS) was used for first estimation of the amount of dry ice needed for pressurizing the vessel. Then, the calculated amount of dry ice was put into the vessel and pressurized by heating and a calibration curve was fitted to the experimental data for use in production of foams.

The influence of fillers and especially nanoparticles on the cell morphology of microcellular foams has been described in the literature [1-4, 8-12]. Following the sorption of supercritical fluid into the polymer phase, two phenomena have important roles in formation of foams structure that are nucleation and growth of gaseous bubbles in polymer. The effect of saturation temperature and pressure is dominant in the second stage i.e. growth of bubbles. While nanoparticles can promote the first stage i.e. the nucleation of bubbles. According to classical nucleation theory [13-14], two mechanisms, homogeneous and heterogeneous nucleation, for formation of bubbles have been proposed. The former occurs when a stable nuclei is generated from joining of molecules and making an embryo with larger size than its critical size. The latter occurs in the presence of particles, that is stable nucleus may be created at the polymer–particle interface through heterogeneous nucleation mechanism and grow to form bubbles. Indeed, presence of nanoparticles (nucleation agents) reduces the nucleation free energy and bubbles are generated more easily. In fact a fine dispersion of nanoparticles in the polymer matrix dominates the heterogeneous nucleation mechanism for bubbles generation.

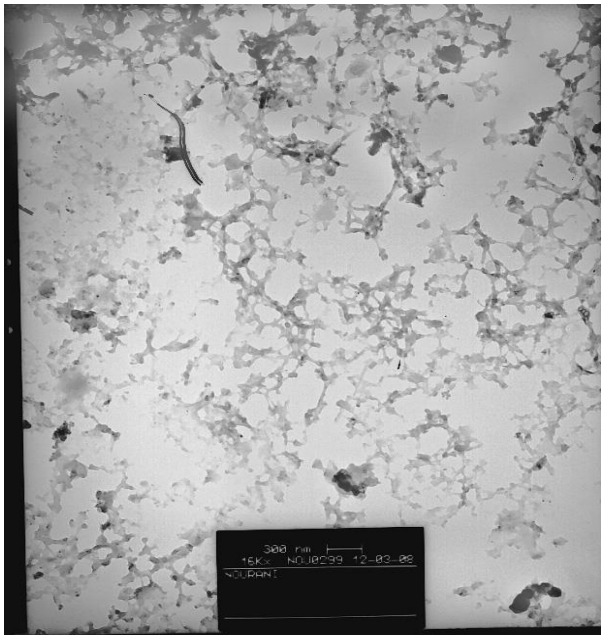

Fig. 1 – Transmission Electron Microscopy of PMMA/CNT nanocomposites

In the present study, to consider the influence of nanoparticles on the cells morphology of product, microcellular foams prepared from PMMA nanocomposites with different amount of nanoparticles while the saturation temperature and pressure were kept at 120ºC and 160 bar, respectively. SEM micrographs of foams prepared PMMA nanocomposites including 0 to 2 weight percent of CNT are shown in Figure 2. The effect of nanoparticles on cells density and average cell size of the foams is shown in figures 3 and 4, respectively. It is perceived that the presence of CNT in polymer led to formation of smaller cell sizes and higher cell densities of foams. Fine dispersion of nanoparticles in the polymer, as shown in TEM micrographs of nanocomposite in Fig 1, leads to generation of more embryos and hence stable nucleus at the polymer–particle interface through heterogeneous nucleation mechanism. More amount of CNT in the polymer results in more potential site for nucleation of bubbles. As more bubbles generate, a less amount of gas is available for bubble growth and a reduction in the cell size is observed.

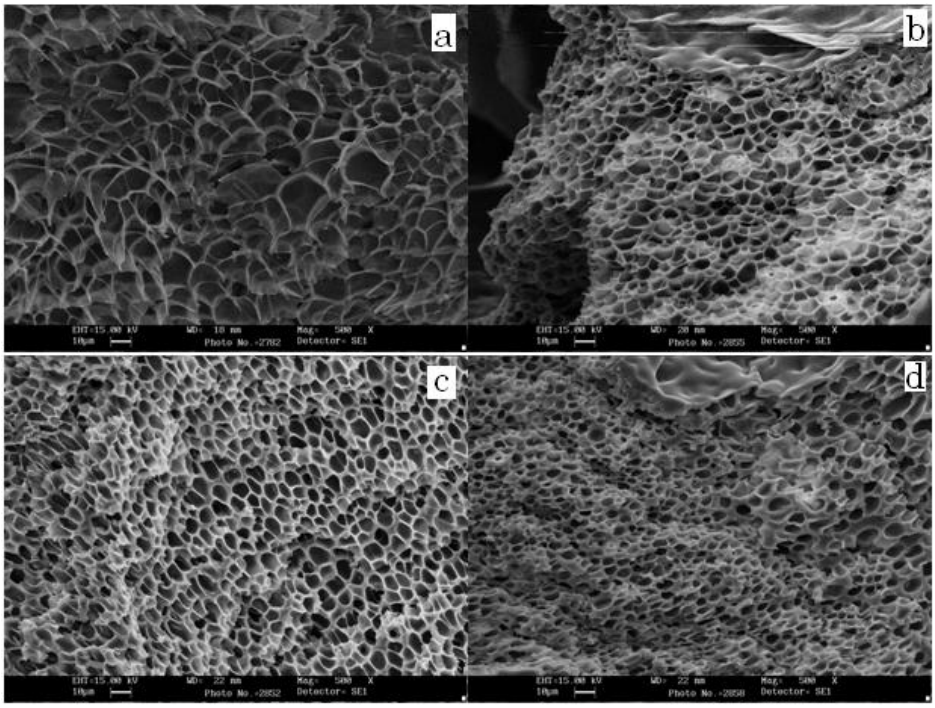

Fig. 2 – Scanning Electron Microscopy of microcellular foams prepared from nanocomposites with amount of 0 (a), 0.5 (b), 1 (c) and 2 (d) weight percent of CNT, The scale bar is 10 µm.

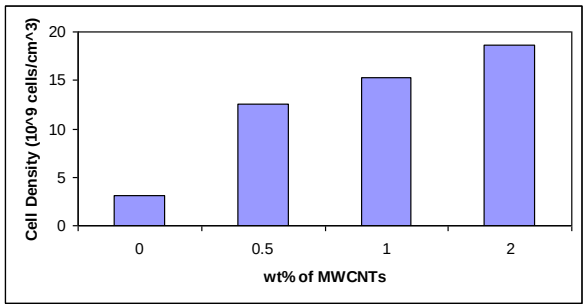

Fig. 3 – Effect of weight percent of CNT on cell density of microcellular foams

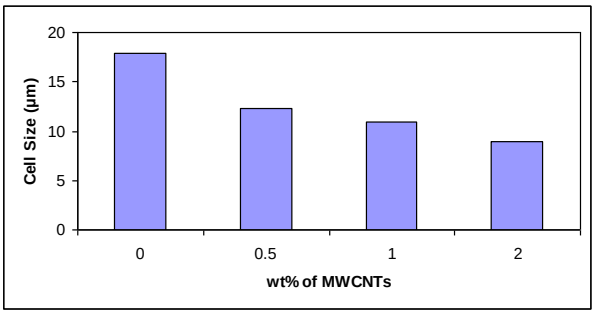

Fig. 4 – Effect of weight percent of CNT on average cell size of microcellular foams

4. CONCLUSION

In the present study, surface modified carbon CNT was used to prepare PMMA/CNT nanocomposite. TEM images showed that there is a fine dispersion of nanoparticles in nanocomposite structure. Supercritical CO_2 was used as a blowing agent in foam production from PMMA/CNT nanocomposites. SEM images of microcellular foams showed that the amount of CNT in nanocomposites results in smaller sizes and higher cell densities of microcellular foams.

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