

# Preparation of PMMA/MWNTs Nanocomposite Microcellular Foams by In-situ Generation of Supercritical Carbon Dioxide

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**ABSTRACT:** *Nanocomposites containing poly(methyl methacrylate) (PMMA) and surface functionalized Multi-Walled Carbon Nanotubes (MWNTs) were synthesized. The dispersion of MWNTs in PMMA was characterized using Transmission Electron Microscopy (TEM). The synthesized nanocomposites were successfully foamed using a simple method based on the in-situ generation of supercritical carbon dioxide (CO<sub>2</sub>). This method in contrast with conventional methods exempted from high-pressure pump and separated CO<sub>2</sub> tank. The effect of MWNTs concentration, saturation temperature and saturation pressure on cellular morphology of the prepared microcellular foams were studied by Scanning Electron Microscopy (SEM) and average cell size and cell density of the prepared foams were studied by image analysis. An increase in cell density, as well as a reduction in cell size, was observed with an increase in the concentration of carbon nanotubes. It was also observed that an elevation of saturation temperature from 90 °C to 100 °C, at constant saturation pressure, leads to a higher cell density and a lower average cell size. Furthermore, an increase in saturation pressure results in a decrease in average cell diameter as well as an increase in cell density. However, the effects of MWNTs concentration on both of average cell size and cell density were proved to be more striking than those of saturation pressure.*

**KEYWORDS:** *Nanocomposites; Carbon nanotubes; PMMA; Microcellular foam; Supercritical carbon dioxide.*

## INTRODUCTION

Polymer foams are important materials in a large spectrum of applications due to their numerous advantages, such as low density, light weight, high specific strength, reduced material consumption, enhanced thermal stability, good sound isolation and low thermal conductivity [1]. Hence, polymer foams have potential to be used in packaging, thermal insulation, acoustic

attenuation, damping of vibration, membranes for separation, absorbents and so forth. However, polymeric foams have lower mechanical properties and decreased dimensional and thermal stability, which limit their range of applications compared to the bulk polymers.

In recent years, polymer microcellular foams with the cell sizes smaller than 10 μm and cell densities greater

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1021-9986/2016/2/63-72

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than  $10^9$  cells/cm<sup>3</sup>, have attracted much attention [2]. Microcellular foams, compared to conventional plastic foams, exhibit superior mechanical and thermal properties such as higher fatigue life, impact strength, toughness and thermal stability. So, in recent years numerous polymers have been used for the microcellular foams production [3-5].

However, production of microcellular foams is challenging and the conventional methods of microcellular foams production require especial processing conditions and sophisticated expensive equipment such as separate CO<sub>2</sub> tank, refrigerator unit and high pressure pump. This greatly limits the processing of the foam products [6].

On the other hand, utilization of nanoparticles for production of polymer nanocomposites has attracted much attention in recent years, because of high potential to achieve great improvement in properties including dimensional stability, gas permeability, flame retardancy and mechanical properties by adding a small amount of nanoparticles in the polymer matrices [7-12]. Besides, polymer nanocomposite foams are a novel class of foams family where nanosized particles are used as nucleation sites. The incorporation of nanoparticles in polymeric foams offer several potential benefits and this topic has been discussed in detail in many papers [13, 14]. Nanoparticles due to the large surface area and aspect ratio and very close contact between particles and the polymer matrix may alter foam morphology and properties. They are very effective agents for heterogeneous nucleation that lead to higher cell density and apparently, nanoscale reinforcing materials are good candidates or improving the properties of polymeric foams [15]. Engineering the chemistry of nanoparticles surface makes it possible to achieve better dispersion and more favorable interactions between polymer, nanoparticle and gas bubbles which can decrease the nucleation free energy and leads to higher nucleation rate [16].

Most of the researches in microcellular foams area are focused on clay nanoparticles [17, 18], but Carbon NanoTubes (CNTs) are another kind of nanoparticles that has attracted tremendous interest in the research community because of the striking properties [19, 20]. The superior properties including large aspect ratio (>1000) and the nanometer dimensions make CNTs ideal reinforcing additive in a wide range of polymers. After CNTs dispersion in polymer mixture, polymer chains

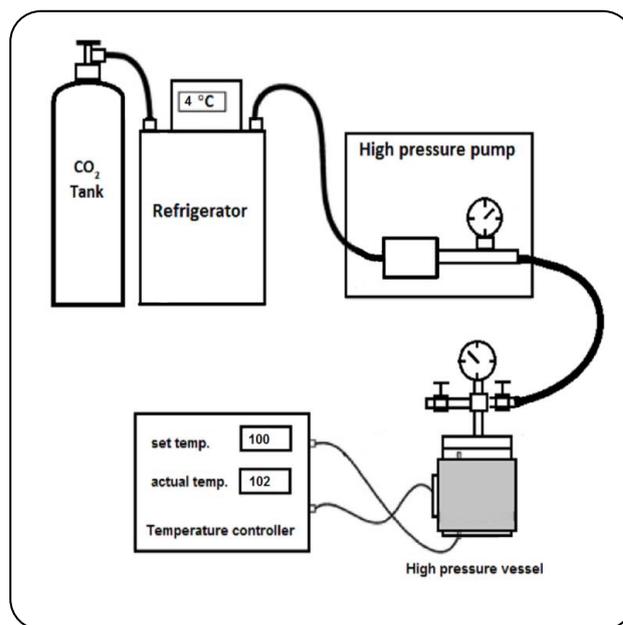


Fig. 1: Typical experimental set-up for fabrication of microcellular foams [23].

will wrap around the CNTs and the dispersion will be stabilized [21].

As a result, microcellular polymeric foams reinforced with CNTs will be a multifunctional material with superior properties. *Park et al.* studied Ethylene Vinyl Acetate (EVA) microcellular foam reinforced with CNTs and reported significant improvement in mechanical properties [22].

The basic processing method for all microcellular foams, as shown schematically in Fig. 1, is the use of thermodynamic instability phenomena [23]. A large amount of supercritical CO<sub>2</sub> which is an environmentally friendly, accessible and low cost blowing agent, is dissolved in the plastics. CO<sub>2</sub> in temperature above 31.5 °C and pressure beyond 73 bar shows supercritical behavior which leads to high penetrating coefficient and high solubility in polymer mixture. Dissolution of supercritical CO<sub>2</sub> under high pressure at the processing temperature creates a driving force for phase separation when the pressure is suddenly lowered [24, 25] which leads to achieving too many nucleation sites that is ideal for foaming process.

In the present article, a simple method for production of microcellular foams using in-situ generation of supercritical CO<sub>2</sub> from dry ice in a batch reactor is reported. When dry ice is sublimated at a certain

temperature, final pressure of the reactor can be predicted using semi empirical Van der Waals equation (Equation 1), in which  $V$  is the vessel volume (which was 150 mL in our study),  $T$  is adjusted temperature,  $n$  is the number of CO<sub>2</sub> mols and  $a$  and  $b$  are constants equations ( $a = 3.66 \text{ bar L}^2/\text{mol}^2$  and  $b = 0.0429 \text{ L/mol}$ ) [26].

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad (1)$$

This novel method can overcome the limitations of conventional methods so that this method is low cost, easy and free from separate CO<sub>2</sub> tank, high pressure pump and refrigerator unit. At the first stage, PMMA/MWNTs nanocomposites were prepared using surface modified MWNTs. Finally, the prepared nanocomposites were converted to microcellular foams and the morphology and properties of the prepared foams were studied in terms of variety of processing conditions such as MWNTs concentration and saturation temperature and pressure.

## EXPERIMENTAL SECTION

### Materials

PMMA (CM-205 grade) with MFI = 1.8 g/10 min and HDT = 100°C from CHIMEI, dry ice with density of 1.2 g/cm<sup>3</sup> and purity of 99% from Vahe Iran Co, sulfuric acid (98%) and nitric acid (68%) from Merck were used as received. MWNTs with purity of greater than 95% and an average tube diameter of 10-30 nm and tube length of 10 μm, were obtained from research institute of petroleum industry (Iran).

### Surface modification of MWNTs

The MWNTs were functionalized for better dispersion in polymer mixture [14]. Using sonication for 7 h in 40° C, 2 g of MWNTs was suspended in a mixture containing 150 mL of HNO<sub>3</sub> and 50 mL of H<sub>2</sub>SO<sub>4</sub> (3:1). MWNTs was separated from the system using a PTFE membrane and then washed with deionized water. The resulted surface modified MWNTs were placed in a vacuum oven at 80° C for drying.

### Preparation of PMMA/ MWNTs nanocomposites

According to the coagulation method described by Du et al. & Kashiwagi et al., which is considered to be an appropriate method for producing PMMA/nanoclay

nanocomposites, first, suspensions of the surface modified MWNTs with different concentrations of 0.5, 1 and 2 wt% were prepared by sonication in 20 mL of acetone [27-28]. Homogeneous PMMA/acetone mixture (25% wt of the polymer) was prepared using mechanical stirring for 24 h at 25°C. Then, each MWNTs suspension was added to certain amount of a prepared polymer solution and the mixtures were stirred vigorously using homogenizer (15000 rpm) and then, the mixture was sonicated again for 15 min to obtain a more homogenous suspension. Final suspension was added drop-wise into a large amount of methanol as a non-solvent and was vigorously stirred using mechanical stirrer to precipitate the nanocomposite. PMMA precipitated instantaneously due to its insolubility in the acetone/methanol mixture. The precipitating PMMA chains entrapped the MWNTs and prevented them from bundling again [27]. Finally, the precipitated product was separated from methanol by filtration and was dried in a vacuum to remove the solvent. Figs 2-A and 2-B show images taken from a prepared suspension of PMMA/MWNTs after 72 hour from its preparation and a precipitated PMMA/MWNTs composite, respectively.

### Preparation of polymer MWNTs nanocomposite foams

Microcellular foaming requires specific processing conditions, such as extremely high saturation pressure and high pressure drop rate, to create enough cell nucleation. In our method, a high pressure vessel equipped with a heater and a barometer and supercritical CO<sub>2</sub> were used for preparing microcellular foams. Fig. 3 shows schematic view of the used experimental set-up. In this foaming process, firstly dry ice and pure PMMA or the prepared polymer nanocomposite were poured into a saturation vessel and the vessel was quickly closed and heated until desired temperature was reached. After the temperature reached to the adjusted temperature, pressure of the vessel which was always higher than the desired saturation pressure was adjusted using a release valve. After that the temperature and pressure of the system were kept constant for a period of 12 h, the pressure was quickly released to atmospheric pressure which leads to cell nucleation and foaming. The foamed sample was pulled out from the vessel and immediately cooled in ice-water mixture to stabilize the desirable structure. For each series of processing conditions, at least three foam

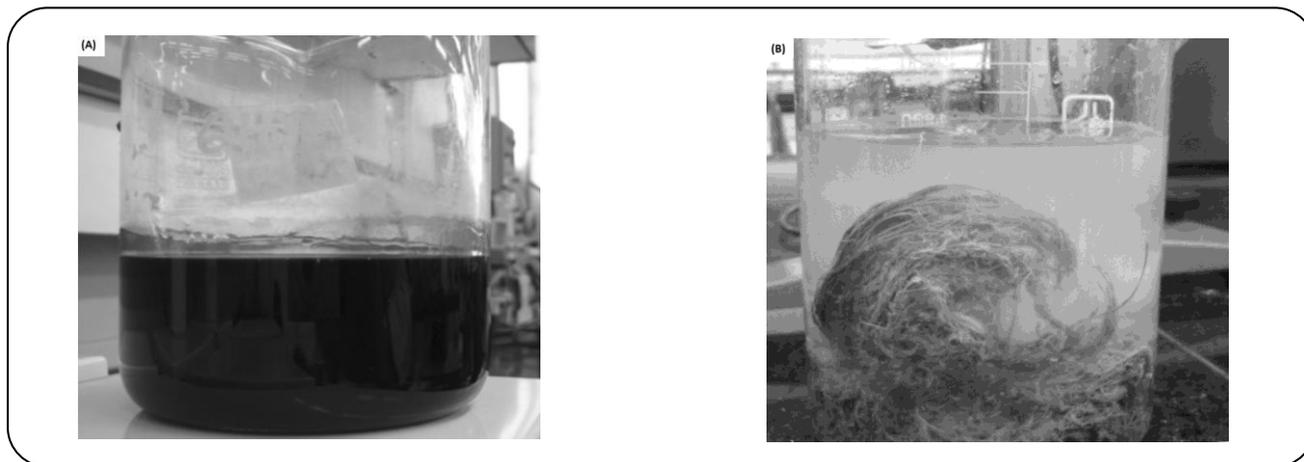


Fig. 2: A) A PMMA/ MWNTs suspension after 72 h from its preparation and B) a precipitated PMMA/ MWNTs composite sample.

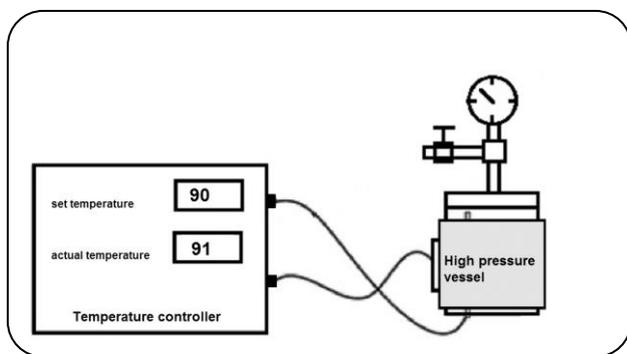


Fig. 3: A schematic view of the setup used for the foaming process of PMMA/MWNTs composites.

samples were prepared at the same conditions and average quantities obtained from the measurements were recorded. It should be noted that in order to determine the desired saturation time, several experiments at saturation times of 4, 8, 12 and 16h but at similar saturation temperature of 110°C (highest saturation temperature) and saturation pressures of 190 bar (highest saturation pressure) were carried out. Foam samples prepared at saturation times of 4 and 8 h were not completely expanded. So, these times were omitted as they were inadequate for complete saturation of the polymer with CO<sub>2</sub>. On the other hand, foam samples prepared at saturation times of 12 and 16 h had similar cell size and cellular morphology. So, the saturation time of 12 h was chosen for all remaining experiments.

#### Characterization

Transmission Electron Microscopy (TEM, Philips, EM208) was used for detailed nanocomposite

characterization. Samples for TEM were prepared by putting and drying a small drop of dispersion solution of the particles in distilled water on 100 mesh copper grid. The morphology of the prepared microcellular foams was observed by Field Emission Scanning Electron Microscopy (FESEM) using a Leo 440i unit. Specimens were obtained by fracturing the foam in liquid N<sub>2</sub> followed by coating with gold for 3 min. In order to determine the average cell diameter from SEM images of cross-sections, image processing software, Image-J was used. The average cell diameter is obtained by using Eq. (2) in which,  $D$  is average spherical cell diameter and  $d_{cell}$  is average diameter of craters on the cross-section [23].

$$D = \frac{4}{\pi} d_{cell} \quad (2)$$

Cell density (number of cells per cm<sup>3</sup>) of the prepared foams ( $N_f$ ) was obtained using Equation (3), in which  $A$  is area in SEM image on the order of cm,  $M$  is magnification factor and  $n$  is the number of cells in the SEM image [26].

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

## RESULTS AND DISCUSSION

### Effect of MWNTs surface functionalization on morphology of the prepared composites

An effective dispersion method is of great importance for attaining good dispersion of CNTs in polymer mixture. High power sonication is one of the usual

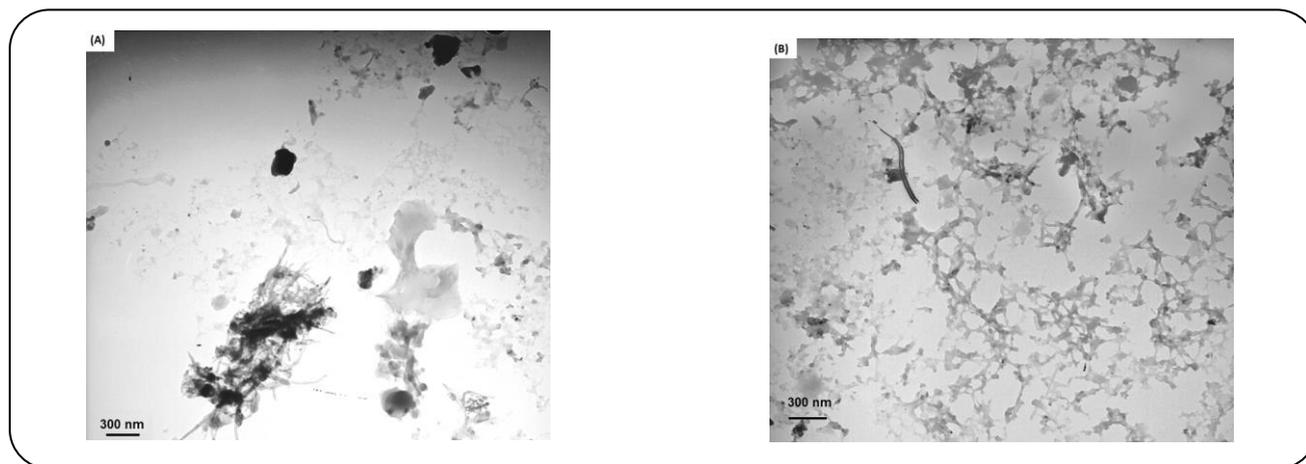


Fig. 4: TEM images of composite samples prepared by A) unmodified and B) surface modified MWNTs.

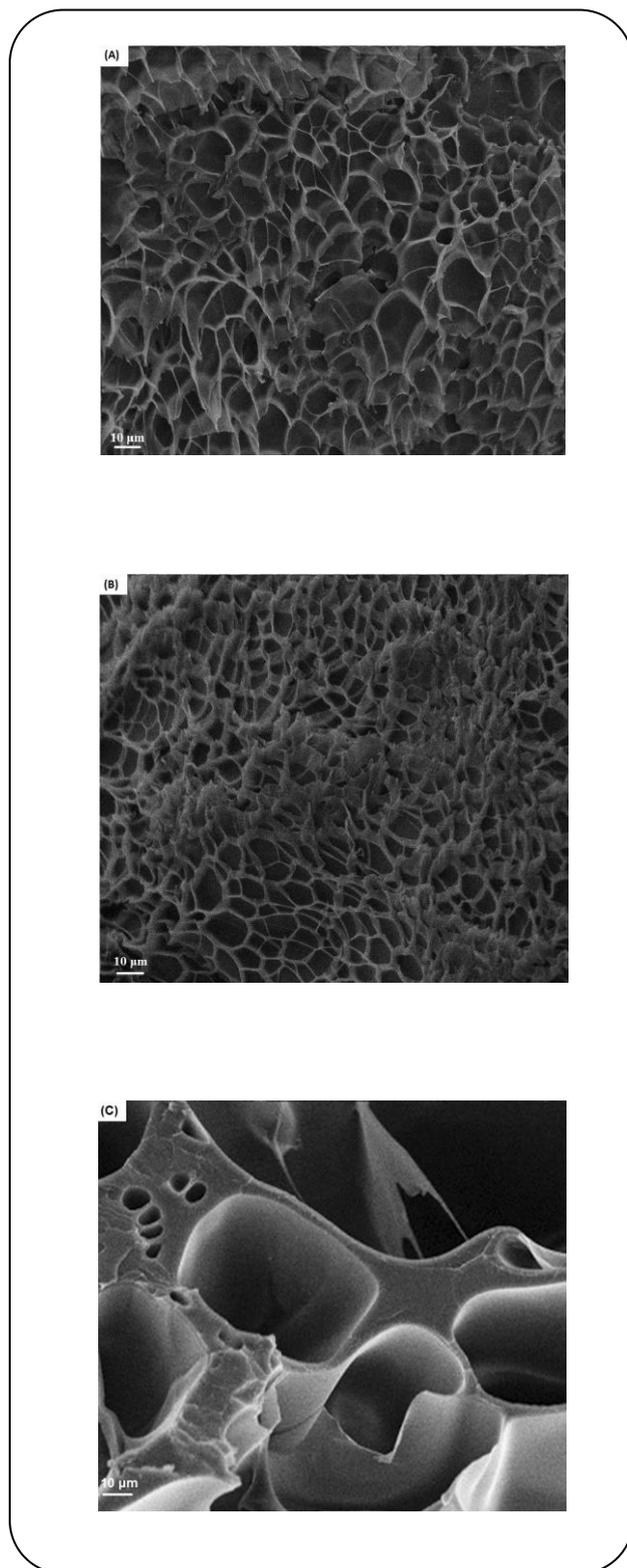
methods for dispersion preparation of nanocomposites. However, CNTs because of their large surface area and strong Van der Waals interactions incline to agglomeration. For better dispersion of CNTs in polymer mixture, surface functionalization is an effective method to increase the interaction between CNTs and polymers [14, 25, 29]. It is reported that using nitric acid, chemical groups such as carbonyl, hydroxyl and carboxyl groups were grafted on the CNTs surface. These functional groups lead to better chemical linkage between polymer and matrix and as a result, an improvement in physical properties. So, in the present work, surface functionalization of MWNTs using a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (with 3:1 volume ratio) has been done to improve the surface interaction between MWNTs and polymer matrix and hence, better dispersion of MWNTs in polymer system. TEM images showing the effect of MWNTs surface modification are presented in Fig. 4. As can be seen in Fig. 4-A, in a composite sample prepared with unmodified MWNTs, aggregates and agglomerates of nanotubes are present and the desirable dispersion is not achieved. However, in a composite sample prepared with surface modified MWNTs, as can be seen in Fig. 4-B, more uniform morphology with better dispersion is achieved.

#### **Analysis of the prepared foams**

##### *Effect of saturation/foaming temperature*

In our method foaming temperature was equal to saturation temperature, so, several points had to be considered in order to choose an appropriate temperature for both saturation and foaming stages. First, since  $31.5\text{ }^\circ\text{C}$

is critical temperature of  $\text{CO}_2$ , so the minimum saturation temperature should be higher than it. In addition, for better dissolution of  $\text{CO}_2$  in PMMA, the saturation temperature should not be far below its glass transition temperature ( $105\text{ }^\circ\text{C}$ ). On the other hand, during the formation of foam bubbles, the viscosity of polymer/gas system plays a main role in controlling morphology of the final microcellular foam and the viscosity in turn is controlled by foaming temperature [13]. After cell initiation stage, through propagation stage, the difference between foaming temperature and glass transition temperature ( $T_g$ ) of polymer is the driving force for cell growth and foaming. So, it seems that the temperature should be higher than the  $T_g$  to reach softening point, nucleation and growth but as the presence of supercritical fluid in the polymer mixture decrease the  $T_g$ , so, it is expected that foaming process could be carried out at lower temperatures. Furthermore, too high foaming temperature decreases the viscosity and hence facilitates cell growth resulting in a higher cell size and because of the presence of weak cell walls which are unable to prevent structural collapse, a lower average cell density will be achieved. So, it is likely that there is an optimum range for foaming process. In our study, saturation/foaming temperatures of  $90$ ,  $100$  and  $110\text{ }^\circ\text{C}$  were examined for preparation of neat PMMA foams, respectively. After that appropriate saturation temperature and pressure were determined for preparation of pure PMMA microcellular foams, effect of MWNTs concentration on cellular morphology of PMMA/MWNTs composites foamed at the desired processing conditions was evaluated.

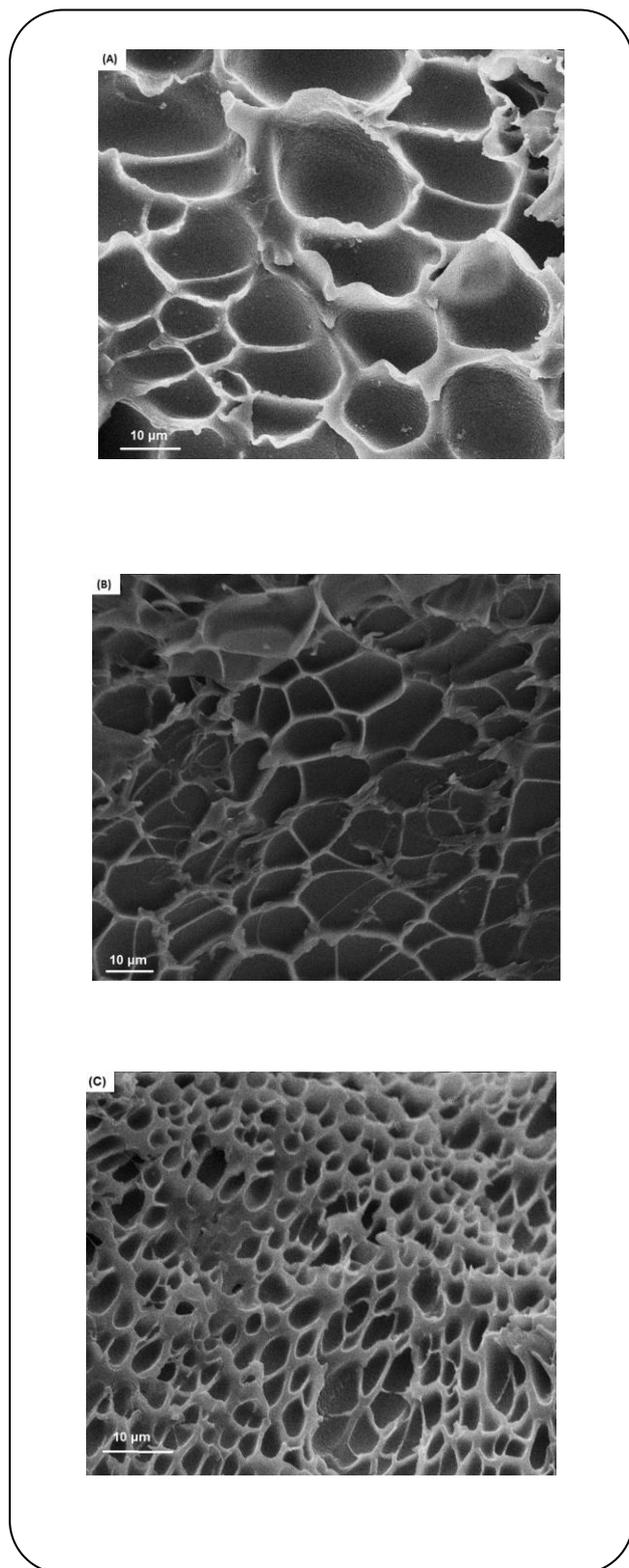


**Fig. 5:** FESEM images of the PMMA foam samples prepared at saturation temperature of A) 90°C, B) 100°C, C) 110°C. Saturation pressure and time were 160 bar and 12 h, respectively.

Morphology of the prepared PMMA foams was studied at saturation/foaming temperatures of 90, 100, 110°C and saturation pressure of 160 bar. Cellular morphology of the prepared microcellular foams was studied by FESEM and average cell diameter and cell density for the prepared foams were calculated using image processing software, Image-J, and Eqs. 2 and 3, respectively. The effect of saturation/foaming temperature on cellular morphology of the prepared foams is shown in Fig. 5. It is seen in the figure that elevation of saturation/foaming temperature from 90 to 100 °C at saturation pressure of 160 bar, leads to a decrease in average cell size. Accordingly, analysis of the FESEM images showed that average cell diameter and cell density change from  $11.9 \pm 2.4 \mu\text{m}$  and  $4.2 \times 10^9 \text{ cell/cm}^3$  to  $7.1 \pm 1.9 \mu\text{m}$  and  $8.3 \times 10^9 \text{ cell/cm}^3$ , respectively by increasing saturation temperature from 90 °C to 100 °C. This could be attributed to the fact that at saturation temperature of 90 °C and saturation time of 12 h, polymer/ CO<sub>2</sub> mixture has not been adequately soft, so, CO<sub>2</sub> was not so capable of nucleation and growth as in similar conditions at 100 °C. However, by increasing saturation temperature to 110 °C, as it can be seen in Fig. 5-C, the result is contrary and a significant increase in cell size and a partial collapse of the structure are observed. The phenomenon is due to lower solubility of CO<sub>2</sub> in the polymer at higher saturation temperature resulting in a slower rate of cell nucleation as well as lower viscosity of the system at elevated foaming temperature which makes cells growth easier. Furthermore, as the foaming temperature and the saturation temperature in our study were the same, foaming temperature in the latter case was 110 °C which was above the glass transition temperature of the polymer, so, the partial structural collapse of the foam prepared at 110 °C could be assigned to the drainage of the matrix polymer and the leakage of the CO<sub>2</sub> out of the foam before cooling in ice-water mixture. Eventually, according to the above results, desired saturation/foaming temperature for preparation of PMMA microcellular foams in this study was chosen as 100°C and was applied in the next experiments.

#### **Effect of saturation pressure**

Since 73 bar is critical pressure of CO<sub>2</sub>, so the minimum saturation pressure should be higher than it.



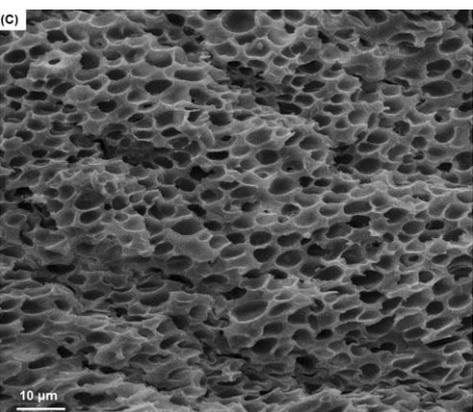
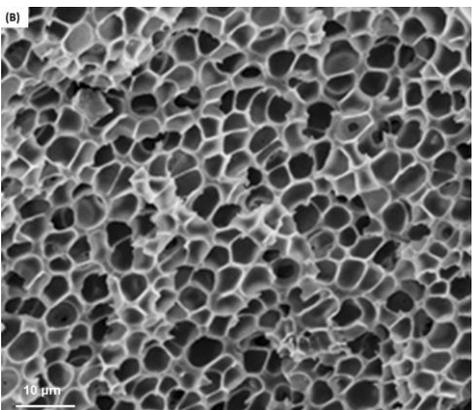
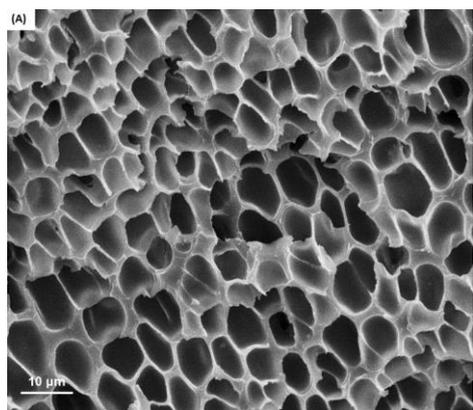
**Fig. 6:** FESEM images of the PMMA foams prepared at saturation pressure of A) 120 bar, B) 140 bar and C) 190 bar. Saturation temperature and time were 100°C and 12 h, respectively.

Hence, saturation pressures of 120, 140, 160 and 190 bar were examined in this study. Effect of saturation pressure on the final foam structure was studied for neat PMMA samples prepared at saturation temperature of 100 °C and saturation time of 12 h. FESEM images of the prepared foam samples at different saturation pressures are shown in Fig. 6. By comparison of the images shown in the figure and also in Fig. 5-B, it could be inferred that an increase in saturation pressure leads to a reduction in cell diameter. In addition, the calculated average cell diameter and cell density change from  $13.6 \pm 2.5 \mu\text{m}$  and  $6.1 \times 10^8 \text{ cell/cm}^3$  to  $6.5 \pm 1.5 \mu\text{m}$  and  $1.3 \times 10^{10} \text{ cell/cm}^3$ , respectively, by increasing saturation pressure from 120 bar to 190 bar. The phenomenon could be attributed to enhancement of the solubility of  $\text{CO}_2$  in polymer matrix with increasing saturation pressure, which in turn, causes to more nucleation sites when releasing of the pressure took place and consequently higher cell density will be achieved. On the other hand, amount of  $\text{CO}_2$  molecules allocated per each bubble is determined by the initial amount of bubbles nucleated. Due to the larger number of nucleation sites available at foaming mixture which was saturated at higher pressure, less  $\text{CO}_2$  molecules reach to each bubble during the growing process of bubbles and as a result, smaller cells will form.

Finally, as the results obtained at saturation pressure of 190 bar don't differ considerably with those obtained at 160 bars, appropriate saturation pressure for preparation of PMMA microcellular foams by our method was chosen as 160 bars and was applied in the next experiments.

#### **Effect of MWNTs concentration**

Effect of incorporation of MWNTs on cellular morphology of the prepared foams was studied. FESEM images of the PMMA microcellular foams at saturation temperature of 100°C, saturation pressure of 160 bar and saturation time of 12 h containing 0, 0.5, 1.0 and 2.0 wt% of MWNTs are shown in Fig. 5-B and Figs. 7-A to 7-C, respectively. As can be seen, addition of MWNTs into the polymer results in a finer and more uniform cellular morphology of the final foam, both of these effects are more pronounced in the case of the foams containing higher amounts of MWNTs. Furthermore, analysis of FESEM micrographs showed that incorporation of 2.0 wt% of MWNTs leads to a decrease in average cell diameter and an increase in cell density from  $7.1 \pm 1.9 \mu\text{m}$



**Fig. 7: FESEM images of the PMMA/MWNTs foams containing A) 0.5 wt%, B) 1.0 wt% and C) 2.0 wt% of MWNTs. Saturation temperature was 100 °C, saturation pressure and time were 160 bar and 12 h, respectively.**

and  $8.3 \times 10^9$  cell/cm<sup>3</sup> cell density, in the case of the neat PMMA foam, to  $4.3 \pm 1.1$  μm and  $2.1 \times 10^{10}$  cell/cm<sup>3</sup>, respectively. The observed increase in cell density and the decrease in average cell size could be explained by the classical nucleation theory which was suggested by *Colton & Suh* [23]. The theory predicts that incorporation of filler particles into a polymer matrix decreases the energy barrier for heterogeneous nucleation in foaming process, and hence, enhances the nucleation rate and decreases the nucleation time interval, so, almost instantaneous growth of cells is facilitated. Accordingly, more MWNTs with good dispersion lead to more and well-dispersed nucleation sites available at the foaming process. Thus, fine and narrow-distributed cell size can be obtained.

### CONCLUSIONS

In this work, PMMA/MWNTs nanocomposites containing different amounts of surface-modified MWNTs were synthesized precisely under controlled conditions. PMMA/MWNTs nanocomposites were converted to foam via a simple new batch foaming process using in-situ generation of supercritical CO<sub>2</sub> in a high pressure vessel. This method unlike the conventional methods is a facile and inexpensive method and exempt from especial processing conditions and sophisticated expensive equipment such as separate CO<sub>2</sub> tank, refrigerator unit and high pressure pump. It was observed that proper surface functionalization of MWNTs lead to better dispersion of MWNTs in PMMA and excellent nucleation efficiency of MWNTs in the nanocomposite foam. Effect of saturation temperature, saturation pressure and also MWNT concentration on the morphology and structure of the final foam was studied and optimum conditions for production of foams were attained. Cell density and average cell size as two important characteristics of microcellular foam were considered and FESEM images showed that at similar saturation pressure and time, an increase in saturation temperature from 90 to 100 °C increases cell density and decreases average cell size. In addition, by increasing saturation temperature beyond 100 °C, a contrary trend as well as a partial structural collapse is observed. It was also observed that both of enhancement of saturation pressure and incorporation of MWNTs lead to higher cell density and lower cell size however the effect of MWNTs concentration is more striking.

Received : Oct. 18, 2015 ; Accepted : Dec. 7, 2015

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