

Production of microcellular foam plastics by supercritical carbon dioxide

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Abstract—The production of microcellular plastic was studied in the polymethyl methacrylate (PMMA)-supercritical carbon dioxide and polycarbonate (PC)-supercritical carbon dioxide systems. The test pieces of PMMA and PC were put into a saturation vessel of which temperature and pressure were kept constant. Supercritical carbon dioxide at temperature between 303K and 393K and pressure between 100 bar and 250 bar was used as a foaming agent. After saturation of carbon dioxide, the pressure was quickly released to atmospheric pressure. The samples were immediately taken out from the vessel and heated in an oil bath. The fractured part of the sample was used for microstructure analysis with SEM. The effect of the saturation temperature, pressure of sorption and the foaming time on the cell mean size and cell density of the foam was investigated by considering the solubility of carbon dioxide in PMMA and PC. The foam morphologies of the foamed plastics were affected by solubility of carbon dioxide, which was directly related to saturation temperature and pressure. The cell density increased and, consequently, the cell size decreased with the solubility of carbon dioxide. The foaming time can be used a controlling factor to obtain the desired foam structure and the volume expansion ratio.

Key words: Supercritical Carbon Dioxide, Microcellular Foam, Polymethyl Methacrylate, Polycarbonate, Gas Solubility in Polymer

INTRODUCTION

Microcellular plastics have many more excellent mechanical and thermal properties than conventional foam plastics. This foam material has a cell mean size smaller than 10 μm and cell density greater than 10^8 cell/ cm^3 [Liang and Wang, 2000; Sumarno et al., 2000; Sun et al., 2002; Wang et al., 2001]. The cells are formed by bringing a plastic saturated by gas into thermodynamically unstable state, of which the gas solubility is rapidly reduced by decompression or heating process. Gases such as carbon dioxide and nitrogen as foaming agents replaced chlorofluorocarbons or volatile organics because of the necessity to develop an environmentally clean process.

Theoretical work [Colton and Suh, 1987; Goel and Beckman, 1994, 1995; Kumar and Suh, 1990; Ramesh et al., 1991] on the nucleation of cells in a microcellular plastic based on the classical nucleation theory has been done by a number of researchers. Colton and Suh [1987] extended the classical theory by considering the free volume effect of polymer. Kumar and Suh [1990] reported on experimental results of the cell nucleation for the polystyrene-nitrogen system. It was demonstrated that cell density increased with saturation pressure due to the increase of gas concentration in plastic. Ramesh et al. [1991] presented experimental and theoretical studies of the effect of various process conditions on cell morphologies. They reported that the cell growth rate increased with increase of the foaming temperature, because the viscosity of polymer solution was decreased and gas diffusivity was increased. The number of nucleated cells and cell density increased with increase of the saturation pressure, as reported by Kumar and Suh [1990]. Colias and Baird

[1996] investigated the deformation characteristics of polystyrene polymer by the presence of supersaturated nitrogen gas. The foamed plastic, resulting from their experiment, had cell size of 10 μm and nearly 25% volume expansion.

In the previous works mentioned above, the saturation process was usually carried out around room temperature, where the solubility of gases is relatively high, but it took very long time to reach saturation. Although the increase of saturation temperature can reduce the saturation time, the solubility of gas will drop due to the high temperature. Sun et al. [2002] reported foams having microcellular structures prepared from polyethersulfone and polyphenylsulfone saturated in a vessel with carbon dioxide at low pressure. The saturation time for all samples was over 70 hours. Recently, many researchers [Arora et al., 1998; Cooper, 2000; Goel and Beckman, 1994, 1995; Han et al., 2002, 2003; Krause et al., 2002; Lee et al., 2000; Liang and Wang, 2000; Mathieu et al., 2005] have studied the cell morphologies of polymer foam produced under the supercritical condition of absorbed gas, for the sake of high solubility in polymer and short sorption time, especially for materials which absorbed small amount of gas at low pressure and temperature in spite of quite long time.

Using supercritical carbon dioxide, Siripurapu et al. [2002] presented the foaming results of highly crystalline polyvinylidene fluoride (PVDF) and its blends with amorphous polymers in a continuous process. They reported the effects of blend composition and solubility of supercritical carbon dioxide on melt viscosity of the blend. Wang et al. [2001] investigated the microcellular structure of polystyrene-liquid crystalline polymer blends by using supercritical carbon dioxide. The research group of Masuoka [Sumarno et al., 2000] studied a batch-wise process for the production of microcellular plastics of polystyrene under the supercritical conditions of nitrogen. The effects of saturation temperature, saturation pressure and foam-

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ing method were investigated by considering the solubility of gas in polystyrene. They found that cell mean size was reduced and cell density increased with increase of gas solubility in polymer. The study of Liang and Wang [2000] extended the supercritical carbon dioxide foaming process to the polymers of high glass transition temperature, such as polyethylene terephthalate and polycarbonate. Lee et al. [2000] carried out their work on the morphology characterization of microcellular styrene-co-acrylonitrile foam processed in supercritical carbon dioxide. The effects of saturation temperature, pressure and swelling time on the cell size, cell density and bulk density of porous materials were studied. They concluded that higher pressure of carbon dioxide provided more molecules for foaming, generated lower interfacial tension and viscosity in the polymer matrix, and thus, produced lower cell size and higher cell density.

In this study, we investigated the morphologies of polymethyl methacrylate (PMMA) and polycarbonate (PC) foams produced with supercritical carbon dioxide. The solubility of carbon dioxide in polymers was examined at the supercritical condition. The effects of the process conditions such as the saturation temperature, pressure and foaming time on the expansion ratio, cell size and cell density of the foamed plastics was investigated.

EXPERIMENTAL WORK

Sheets of polymethyl methacrylate (PMMA, $M_n \approx 490000$) with thickness of 2 mm and polycarbonate (PC, $M_n \approx 25000$) with thickness of 3 mm were cut into 7×30 mm for the test pieces. Carbon dioxide (Daedong gas tech Co. 99.8%) as the blowing agent was used as received without further purification.

A schematic diagram of the experimental apparatus used in this work is shown in Fig. 1. Carbon dioxide was pre-cooled and pumped into sorption vessel (G), which was preloaded with several test pieces of PMMA and PC. The test pieces were placed on the glass wool packed loosely in the sorption vessel. A vessel with an internal volume of 300 ml was equipped with a heating jacket and a temperature controller. The pressure in the vessel was adjusted through back-

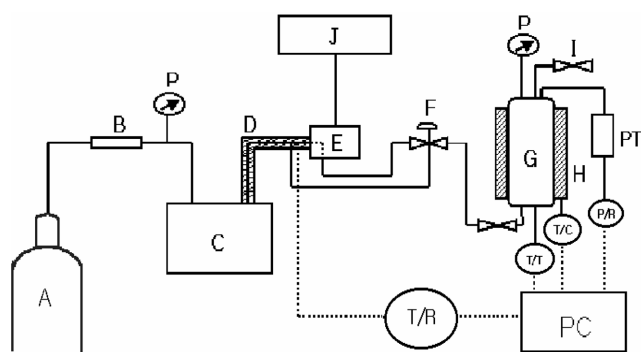


Fig. 1. Schematic diagram of experimental apparatus.

- | | |
|-----------------------------|----------------------------|
| A: CO ₂ cylinder | I: Valve |
| B: Filter | J: Air compressor |
| C: Cooling unit | PR: Pressure recorder |
| D: Insulation | PT: Pressure transducer |
| E: Air driven pump | TC: Temperature controller |
| F: Back-pressure regulator | TI: Temperature indicator |
| G: Sorption vessel (300 ml) | TR: Temperature recorder |
| H: Heating jacket | |

pressure regulator (F) and recorded in a computer. At the beginning, the vessel was flushed with low-pressure carbon dioxide from the gas cylinder (A) for about 3 minutes and then charged with the carbon dioxide up to a desired saturation pressure at a constant temperature. An air driven pump (E) was used for the compression to supercritical condition. After saturation of the test pieces, the pressure in the vessel was then released to the atmospheric pressure as quickly as possible. The test pieces were immediately taken out of the vessel after decompression. It took at least 2 minutes to take out them. The weights of some pieces were measured as a function of exposure time to know the gas sorption in the plastics, and the others were dipped in silicon oil bath at a constant temperature for a period of foaming time. Finally, those were immersed in ice water. Prior to the density measurement, the samples were exposed to the atmosphere for over 4 days, to ensure that the weight and volume of the samples were kept constant. A part of the foamed samples was fractured for microstructure analysis with a scanning electronic microscope (SEM). The image photographs of SEM were used to obtain the cell size and cell density. The cell density was calculated by the method suggested by Kumar and Suh [1990].

The bulk density of the test pieces was measured to determine their volume change before and after the foaming process. The buoyancy method using a pycnometer filled with water at 298 K was applied for the bulk density.

RESULT AND DISCUSSIONS

1. Equilibrium Sorption of Carbon Dioxide

The sorption amount in the test piece after taking out of the sorption vessel was decreased with exposure time in the atmosphere as shown in Fig. 2, which was represented as an example. The original sorption amount of carbon dioxide in the vessel was obtained by extrapolating the exposure time to be zero.

Fig. 3 shows the obtained sorption amount from Fig. 2 against the sorption time in the vessel to obtain the equilibrium sorption of carbon dioxide in PMMA and PC plastics. It was shown that it took at least 3 hours to reach the equilibrium sorption for PMMA and 5 hours for PC. As a result, the sorption measurement was carried

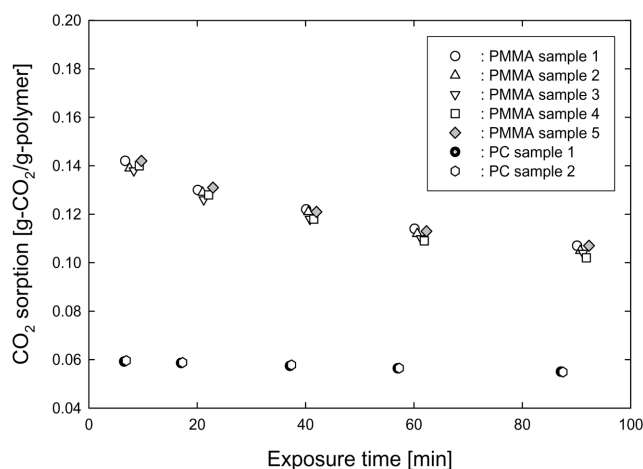


Fig. 2. Exposure time vs. CO₂ sorption in PMMA (at 323 K, 100 bar) and PC (at 393 K, 150 bar).

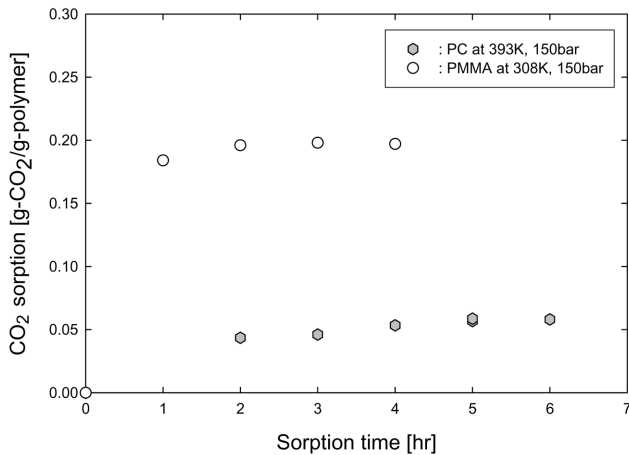


Fig. 3. CO₂ sorption in PMMA and PC vs. sorption time.

out over 3 hours for PMMA and over 5 hours for PC to ensure equilibrium sorption.

The experimental results of equilibrium sorption at various conditions of temperature and pressure are summarized in Table 1. Fig. 4 shows the relation of CO₂ solubility to the density of carbon dioxide that was calculated with the equation of state proposed by Huang et al. [1985]. The equilibrium sorption in PMMA and PC increased with the density of carbon dioxide.

2. Expansion Ratio of Volume

Some of the test pieces taken from the saturation vessel were immersed in hot silicon bath at 373 K in order to be foamed while a certain time as shown in Figs. 5 and 6 and right after, dipped in ice water to cool. After the foaming, they were exposed to the atmosphere for over 4 days to ensure that the weight and volume of the samples were kept constant. The expansion ratio in Figs. 5 and 6 is expressed as follows:

$$\text{Expansion ratio} = \frac{V_f - V_i}{V_i} \times 100\% \quad (1)$$

Where, V_i is the initial volume of the test piece and V_f is the volume

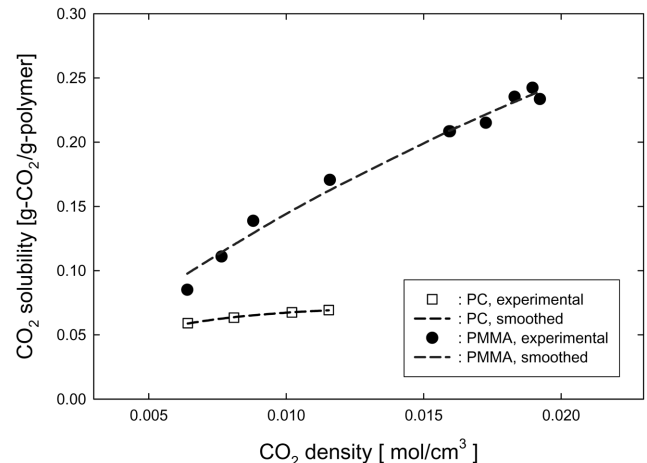


Fig. 4. Density of supercritical CO₂ vs. CO₂ solubility in PMMA and PC.

of the foamed piece. Figs. 5 and 6 show the results of expansion ratio for PMMA and PC test pieces, respectively. The expansion ratio increases until the foaming time has elapsed about 2 minutes for PMMA and 3 minutes for PC after foam beginning. After 2 or 3 minutes, it is almost constant regardless of the foaming time, as shown in Figs. 5 and 6. It was demonstrated that after enough foaming time-- over 2 or 3 minutes, the morphology of the test pieces would not be changed. Therefore, the SEM analysis of the cell size and cell density was examined only for the samples that were foamed over 2 or 3 minutes in an oil bath. It was observed from Figs. 5 and 6 that the expansion ratio decreased with increase of pressure. On the contrary, the sorption amount of gas in the sample piece increased with pressure. It means that the cell size became much smaller and consequently the cell numbers in polymer were much greater, as the saturation pressure increased. The results can be also seen in Figs. 7 and 8.

3. Effect of Saturation Temperature and Pressure on Cell Density and Size

Table 1. Equilibrium sorption of supercritical carbon dioxide in PMMA and PC

| Polymer | Temperature [K] | Pressure [bar] | CO ₂ density* [mol/cm ³] | Equilibrium sorption [g-CO ₂ /g-polymer] |
|---------|-----------------|----------------|---|---|
| PMMA | 303.5 | 150.2 | 0.0192 | 0.2335 |
| | 323.6 | 151.6 | 0.0159 | 0.2084 |
| | 343.6 | 151.2 | 0.0116 | 0.1706 |
| | 373.4 | 151.4 | 0.0077 | 0.1110 |
| | 393.9 | 151.1 | 0.0064 | 0.0851 |
| | 323.6 | 100.5 | 0.0088 | 0.1387 |
| | 323.4 | 151.4 | 0.0160 | 0.2084 |
| | 323.0 | 180.2 | 0.0173 | 0.2151 |
| | 323.8 | 221.7 | 0.0183 | 0.2353 |
| | 323.6 | 252.3 | 0.0190 | 0.2424 |
| PC | 393.2 | 151.1 | 0.0591 | 0.0064 |
| | 393.2 | 181.5 | 0.0634 | 0.0081 |
| | 393.2 | 221.0 | 0.0675 | 0.0102 |
| | 393.2 | 251.4 | 0.0693 | 0.0116 |

PMMA: Polymethyl metacrylate, PC: Polycarbonate *: Calculated by equation of state [Huang et al., 1985]

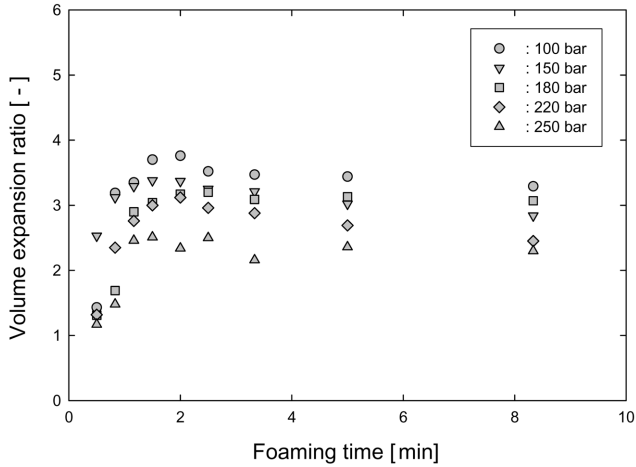


Fig. 5. Expansion ratio vs, foaming time for PMMA samples to be treated at 303 K and various pressures (foaming temperature=373 K).

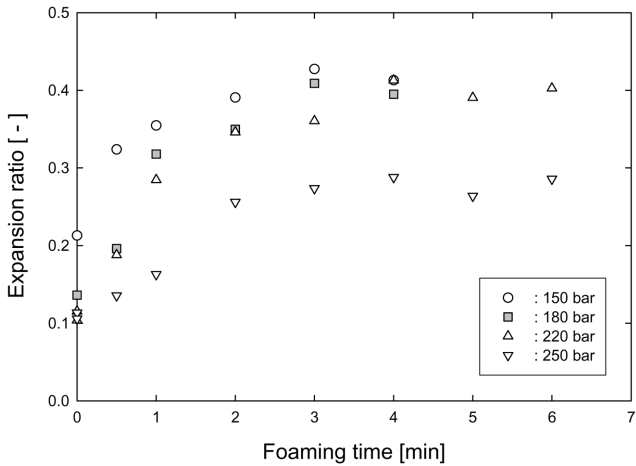


Fig. 6. Expansion ratio vs, foaming time for PC samples to be treated at 393 K and various pressures (foaming temperature=373 K).

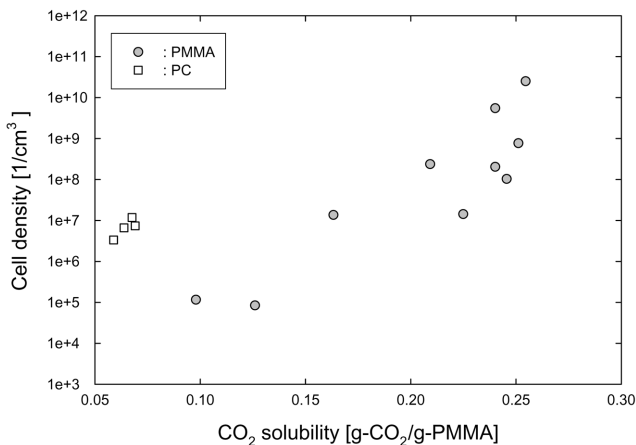


Fig. 7. Effect of solubility of CO₂ in polymers on cell density of PMMA and PC foams.

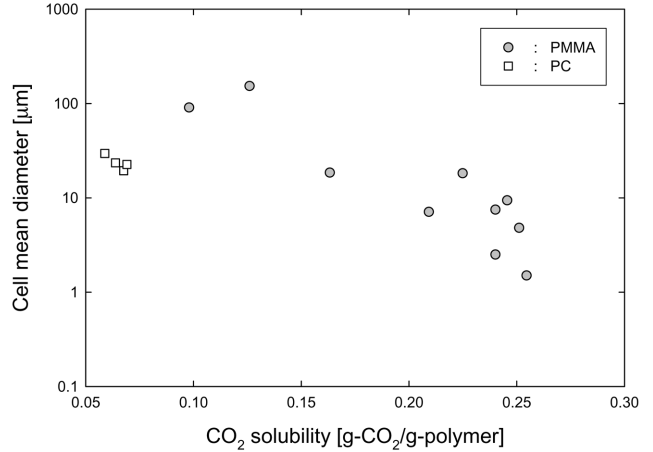


Fig. 8. Effect of CO₂ solubility in polymers on cell size of PMMA and PC foam.

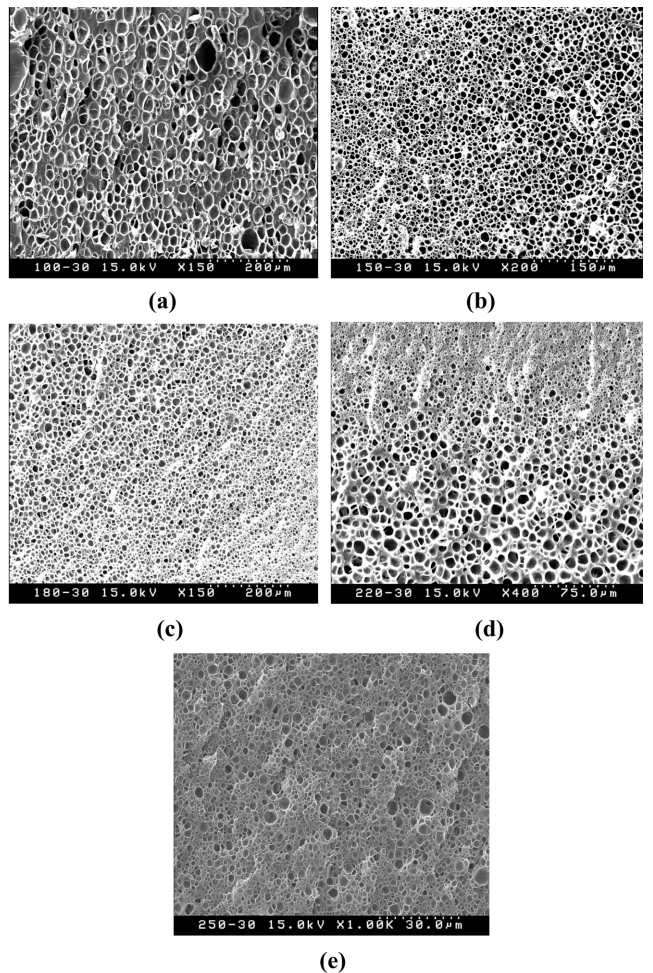


Photo 1. SEM photographs show the effect of saturation pressure on cell structure of PMMA foam produced at 303 K of saturation temperature and 120 sec. of foaming time. (a) 100 bar (b) 150 bar (c) 180 bar (d) 220 bar (e) 250 bar.

The cell density, N_0 , which means the number of cells nucleated per cm³ of original polymer, was determined as proposed by Kumar and Suh [1990]:

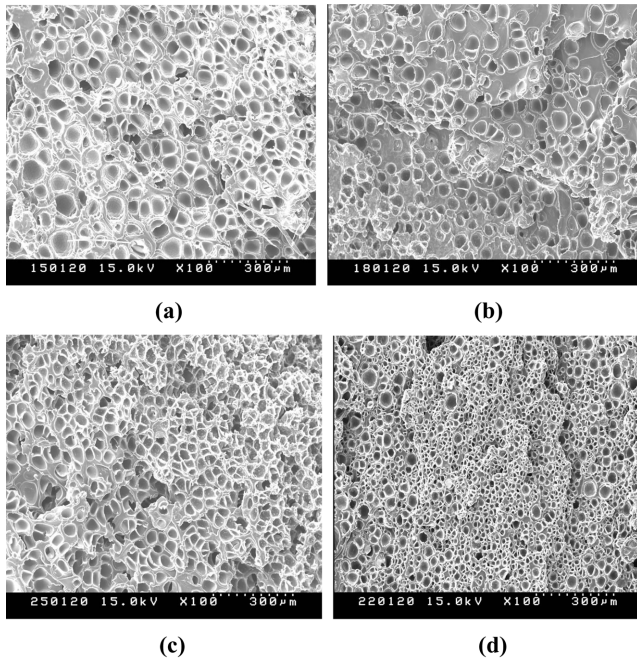


Photo 2. SEM photographs show the effect of saturation pressure on cell structure of PC foam produced at 393 K of saturation temperature. (a) 150 bar (b) 180 bar (c) 220 bar (d) 250 bar.

$$N_0 = \frac{N_f}{(1 - W_f)} \quad (2)$$

$$\text{Where, } W_f = \left(\frac{\pi}{6}\right) D^3 N_f \quad N_f = \left(\frac{nM^n}{A}\right)^{3/2}$$

N_f =number of cells per cm^3 of foam, n =number of cells in the micrograph, A =area of the micrograph (cm^2), M =magnification factor of the micrograph, D =cell mean diameter (cm) and W_f =volume occupied by the voids (cm^3).

The effect of CO_2 solubility on the cell structure was investigated in this work. It is shown in Figs. 7 and 8 that the cell density increased and cell mean diameter decreased with increase in the solubility of carbon dioxide for both PMMA and PC. The same results might be clear in the SEM images in Photo 1. Those represent the experimental results of PMMA at a saturation pressure of 150 bar, saturation temperature of 303 K and foaming time for 120 sec. It was observed that the cell density decreased and cell mean diameter increased with rising temperature. The relation of the solubility of carbon dioxide in polymers to the cell structure exhibited good agreement with the results of Figs. 7 and 8. It was shown in Photo 2 that the effect of the saturation pressure on the foam structures of PC was investigated at a saturation temperature of 393 K and a foaming temperature of 373 K. Variation of the foam structure with saturation pressure is presented in Fig. 8 with SEM images in Photo 2. The cell density increased and cell mean diameter decreased with increase of the saturation pressure, that is, with an increase in the gas solubility in PC.

CONCLUSION

PMMA and PC polymers were saturated with supercritical car-

bon dioxide in the temperature range of 343 K to 393 K and pressure range of 100 bar to 250 bar, and foamed in an oil bath at constant temperature. The effect of saturation pressure and temperature on the foam morphology of the polymers was investigated.

The solubility of carbon dioxide, which is related to the saturation temperature and pressure, consequently to the gas density, had a significant effect on the cell mean size and cell density of foamed plastics. As the gas solubility in plastics was increased, the cell density was increased and the cell size was reduced. The expansion ratio defined in Eq. (1) decreased with the increase in the pressure. It denotes that, as the pressure or the gas density is increasing, the foaming cells become smaller and are more uniformly distributed in the plastics and, as a consequence, the cell density is increased.

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