

Properties of Calcium Carbonate Filled and Unfilled Polystyrene Foams Prepared Using Supercritical Carbon Dioxide

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ABSTRACT: Foaming behaviors of four polystyrenes (PSs) filled and unfilled with various amounts of CaCO₃ using supercritical carbon dioxide were investigated. The PSs include three general purpose grades with different molecular weights (different melt index) and one high impact grade. By adjusting foaming conditions, foam density was determined for each investigated sample. In general, the sample with a lower molecular weight (i.e. higher melt index) yielded a lower foam density for the three general purpose PSs. With the addition of CaCO₃ filler, foam density would increase. The inclusion of rubber in high impact PS was found to complicate its foaming behavior. A qualitative correlation between

various types of filled/unfilled PSs and foam density was found in a certain range. An optimum foaming temperature range was required to obtain low foam density for each sample. The corresponding change in matrix modulus by employing various PSs and various filler contents apparently affected the resulting foam density. Although several factors were involved in foaming conditions, the addition of CaCO₃ filler played a significant role in reducing cell size and increasing cell density of the PSs foams investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2276–2284, 2006

Key words: polystyrene; supercritical CO₂; CaCO₃; foam

INTRODUCTION

In the past decade, researches on the preparation and characterization of microcellular polymeric foams have attracted considerable academic and industrial attention. Among the polymeric foams investigated, foam systems prepared through supercritical carbon dioxide (CO₂) have exhibited great promise for industrial applications because of their environmental friendly advantage over foams developed using isopentane or dichlorodifluoromethane, which produces global warming effects and is detrimental to our ecosystems. Nevertheless, the polymer foaming process using supercritical CO₂ ($T_c = 31^\circ\text{C}$, $P_c = 1070$ psi) requires high pressures, optimum foaming temperatures, efficient cooling devices, and so on to obtain fine cell structure. Martini-Vvedensky et al.¹ and Park et al.² have pioneered to carry out continuous and batch foaming processes on a large scale basis for high impact polystyrene (HIPS) and polypropylene (PP) systems. Other foaming researches on polymers, including polyethylene (PE),^{3,4} PP,^{5–7} polyethylene terephthalate, polycarbonate (PC),⁹ polysty-

rene (PS),^{10–17} and so forth, were also conducted to produce microcellular foams.

Regarding the PS system, Arora et al.¹⁰ investigated the foaming of PS using supercritical CO₂ to better understand the microcellular foaming mechanism. They found that higher foaming temperatures produced larger cells and reduced foam densities. Stafford et al.¹¹ pointed out that molecular weight and polydispersity did not significantly affect the foaming process of PS, but the addition of low molecular weight oligomers offered a way to control cell structure developed. Introducing suitable additives, such as zinc stearate, stearic acid, and carbon black into the PS matrix, and increasing CO₂ soaking pressures could yield the most desirable foams with a large number of small uniform cells. Doroudiani et al.¹³ conducted a statistical analysis on foaming results and showed that foaming duration was the most important factor in determining the foam density, whereas soaking pressure was the most important factor in determining the cell size and cell density. A continuous foaming process of PS was conducted via a two-stage single screw extruder by Han et al.¹⁴ Higher CO₂ concentrations and die pressures led to smaller cell size and greater cell densities.

To investigate the effect of additives on the foaming of PSs, wood fiber filled PS was foamed under various

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conditions by Doroudiani et al.¹⁵ It was found that fiber concentration was the most important factor in controlling the impact strength and tensile moduli of the composite foams. Extrusion of PS/clay nanocomposite foams was investigated by Han et al.¹⁶ The foam structure developed was compared with those of unfilled PS and PS/talc composites. With the addition of 5 wt % of intercalated nanoclay, cell size was reduced from 25.3 to 11.1 μm . As for exfoliated nanoclay inclusion, the nanocomposite foams exhibited the smallest cell size of $\sim 4.9 \mu\text{m}$. The nanocomposite foams possessed enhanced properties, such as higher tensile modulus, increased fire retardance, and better gas barrier properties. Furthermore, adding small amounts of fillers (e.g., carbon black, CaCO₃, or nanoclay particles) was found to prevent the demixing of PS/poly(methyl methacrylate) blend system when supercritical CO₂ foaming process was carried out.¹⁷

Apart from the aforementioned stringent processing conditions, cell nucleation, growth, and stability are primary concerns to accomplish a fine cell structure of polymeric foams. Several factors are involved in the cell nucleation process, such as matrix viscosity (modulus), surface tension, heat transfer rate, and so on. Cell growth kinetics was recognized to be governed by matrix viscosity and surface tension as well. Gent and Tompkins¹⁸ reported experimental results of the nucleation and growth of gas bubbles in crosslinked elastomers to depict the foaming process. While the cell size was bigger than 1 μm , surface tension effect could be neglected. Cell growth was thus mainly dominated by the matrix modulus. Since, modulus is time and temperature dependent, especially during foam formation, dynamic mechanical properties are thus rather important for obtaining a fine cell structure of foams.

To the best of our knowledge, few studies have been conducted on the correlation of matrix modulus and foaming behavior of CaCO₃ filled and unfilled PSs using supercritical CO₂ in a batch process. This research is an attempt to demonstrate this relationship qualitatively for three general purpose PSs with different molecular weights (different melt index) and one high impact PS. With the additions of various amounts of CaCO₃ filler, the filled PSs' moduli and resulting foams densities were determined and corre-

lated as well. Additionally, the cell structure of the foams was preliminary examined.

TERMINOLOGY

Supercritical Fluid: A substance in a state that is above its critical temperature (T_c) and critical pressure (P_c).

High Impact: High impact strength/resistance.

Morphology: The macroscopic form and structure of an entity.

Polydispersity: A common measure of molecular weight distribution, which is given by the ratio of M_w/M_n .

Melt Index: An indication of molecular weight grade, which is the weight (in grams) of a polymer extruded through a standard capillary in 10 min at a certain temperature under a standard weight (ASTM D1238).

EXPERIMENTAL

Materials

PSs used in this study are products of Chi-Mei Chemical Co. (Taiwan). Materials' characteristics of the four PSs denoted PS-H, PS-M, PS-L, and HIPS are listed in Table I. PS-H, PS-M, and PS-L represent high, medium, and low molecular weight grade of general purpose PS, respectively. HIPS is a high impact PS with ca. 10 wt % of butadiene rubber content. The density of each PS is around 1.05 g/cm³. CaCO₃ with a density of 2.53 g/cm³ and an average diameter of 3 μm was used as filler, and it was supplied from Yeng-Hsing Co. (Taiwan).

Preparations of filled samples and foams

The filled samples were prepared by thorough mixing of PS and CaCO₃ filler (2, 4, 6 phr) in a two-roll mill (Schwabenthan, Germany) at 150°C. The filled and unfilled PSs were then hot pressed to form 3, 5, and 9.5-mm thick sheets in a compression molding machine at 120°C, respectively. The supercritical CO₂ foaming process on the prepared sheets using a compressor (Seybert and Rahier) subjected to various pressures was carried out in a custom made cylindrical mold with a diameter of 250 mm and height of 130 mm. Foam boards were then obtained by releasing pressure

TABLE I
Material Characteristics of Polystyrenes Investigated

Sample	Melt index (g/10 min) ASTM D1238	Weight average molecular weight (g/mol)	Polydispersity	Glass-transition temperature (°C)
PS-H	2.2	280,000	2.4	106.6
PS-M	5	264,000	2.6	96.9
PS-L	8	253,000	3.2	94.4
HIPS	3	225,000	2.7	102.9

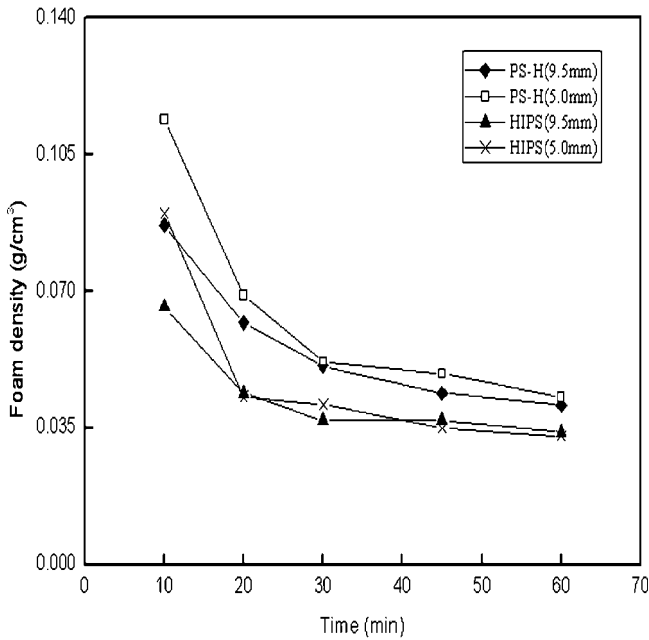


Figure 1 Foam density of PS-H and HIPS with two thicknesses subjected to different soaking times under 3500 psi at 135°C.

instantly (ca. less than 1 s) after various soaking times at different foaming temperatures.

Characterizations

The glass-transition temperatures (T_g s), as shown in Table I, of the neat PSs were measured using a DSC TA-

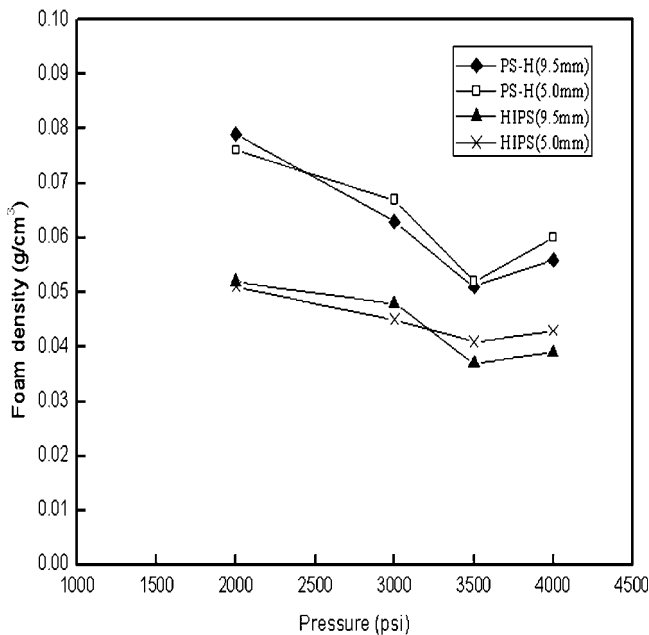


Figure 2 Foam density of PS-H and HIPS with two thicknesses subjected to different soaking pressures at 135°C for 30 min.

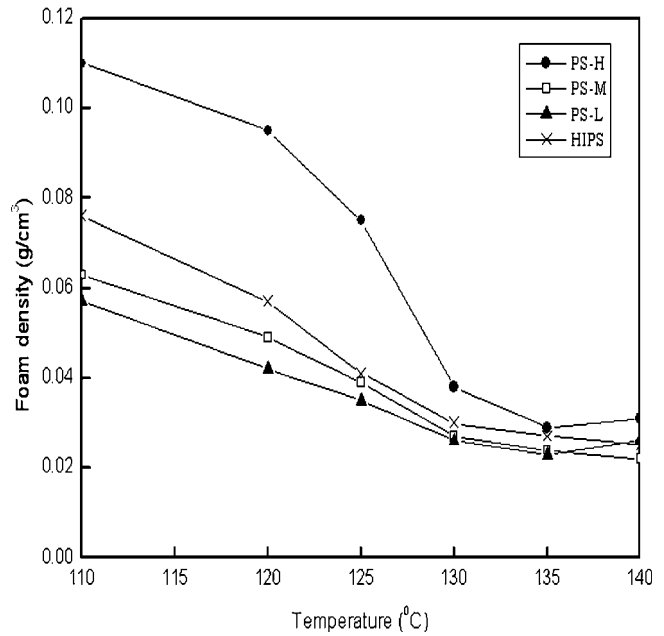


Figure 3 Foam density of unfilled PSs as a function of foaming temperature (under 3000 psi for 40 min).

2910 system. The heat flow and temperature of the instrument were calibrated using standard materials, such as indium and zinc. The dynamic mechanical properties of the compression-molded filled and unfilled PS specimens were measured using a Perkin-Elmer DMA 7e system. The measurements were carried out in a three-point bending mode at a frequency of 1 Hz from 30°C to 150°C at a heating rate of 10°C/

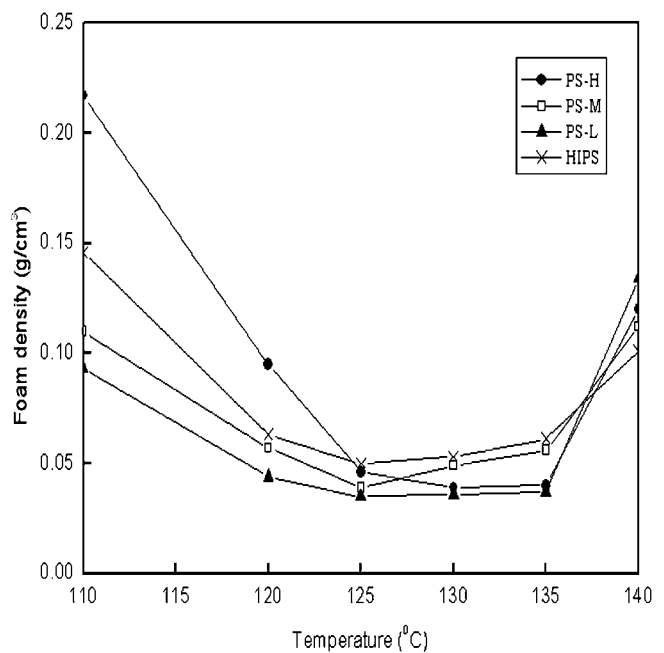


Figure 4 Foam density of 2 phr CaCO_3 filled PSs as a function of foaming temperature (under 3000 psi for 40 min).

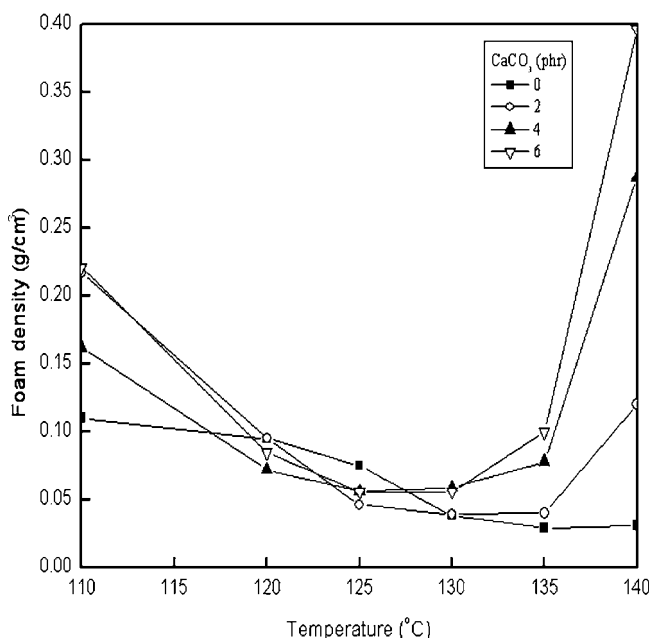


Figure 5 Foam density of filled PS-H as a function of foaming temperature (under 3000 psi for 40 min).

min in an air atmosphere. The dimension of tested specimens is $15 \times 5 \times 2 \text{ mm}^3$ with the deformation amplitude of $10 \mu\text{m}$.

Cell morphology of fractured foam specimens was elucidated using a scanning electron microscope (SEM, Cambridge S360). All specimens were sputtered with gold before characterization. Foam density of each

specimen was determined using a density analyzer (Precisa 180A). The density reported for each sample is an average value of two tested specimens. The densities measured for each set of two test specimens are within 10% of experimental error.

RESULTS AND DISCUSSION

Effects of soaking time and pressure on foam density

For a preliminary understanding of foaming behavior of the samples prepared, representative unfilled PS-H and HIPS boards with different thicknesses subjected to various soaking times and pressures were evaluated first. Figure 1 depicts the soaking time-dependent foam density. When soaking pressure and foaming temperature were fixed at 3500 psi and 135°C, foam density of the samples decreased considerably with increasing soaking time initially, and then leveled off at a soaking time longer than 30 min. Other foaming conditions showed a similar trend (not shown here for brevity) as well. It was thus determined that a minimum of 30 min was required to have a better supercritical CO₂ foaming efficiency under the foaming conditions we conducted. The effect of soaking pressure on the resulting foam density is illustrated in Figure 2. The result indicates a slight decrease in foam density with increasing soaking pressure for samples foamed at 135°C for 30 min. As the pressure was well above the P_c (1070 psi) of CO₂, the solubility of CO₂ in PSs was higher with increasing

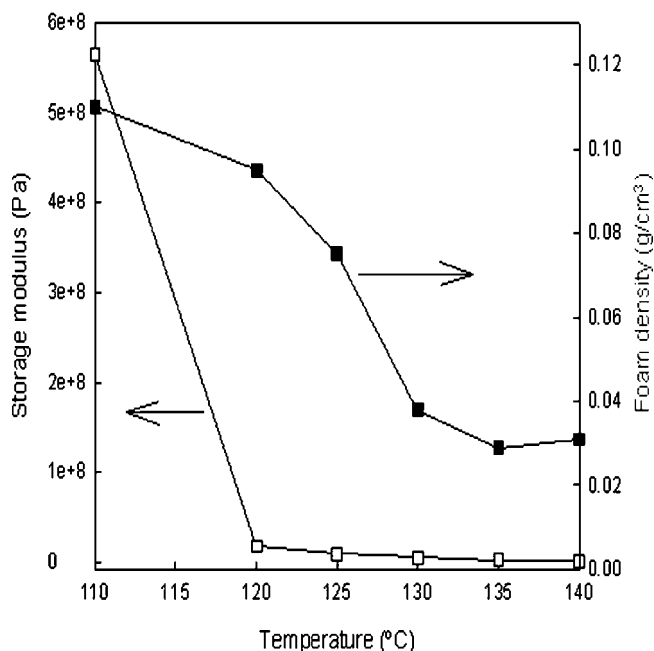


Figure 6 Correlation of foam density and matrix storage modulus for unfilled PS-H foamed (under 3000 psi for 40 min) and measured at different temperatures.

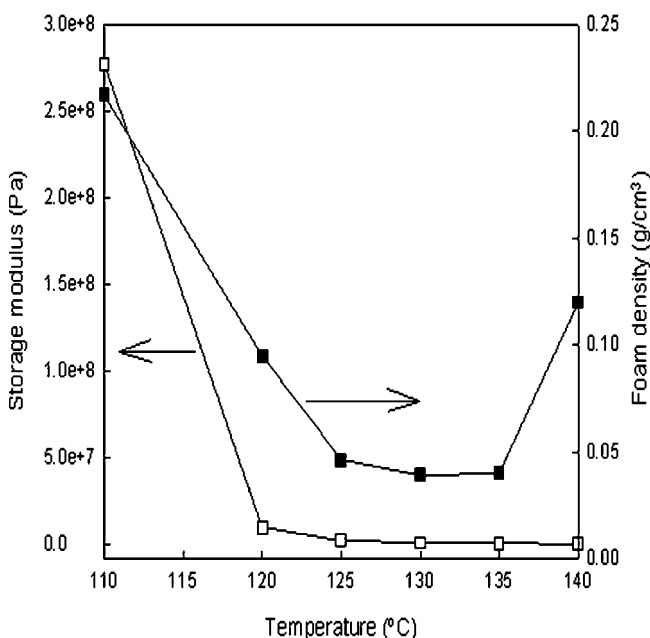


Figure 7 Correlation of foam density and matrix storage modulus for 2 phr CaCO₃ filled PS-H foamed (under 3000 psi for 40 min) and measured at different temperatures.

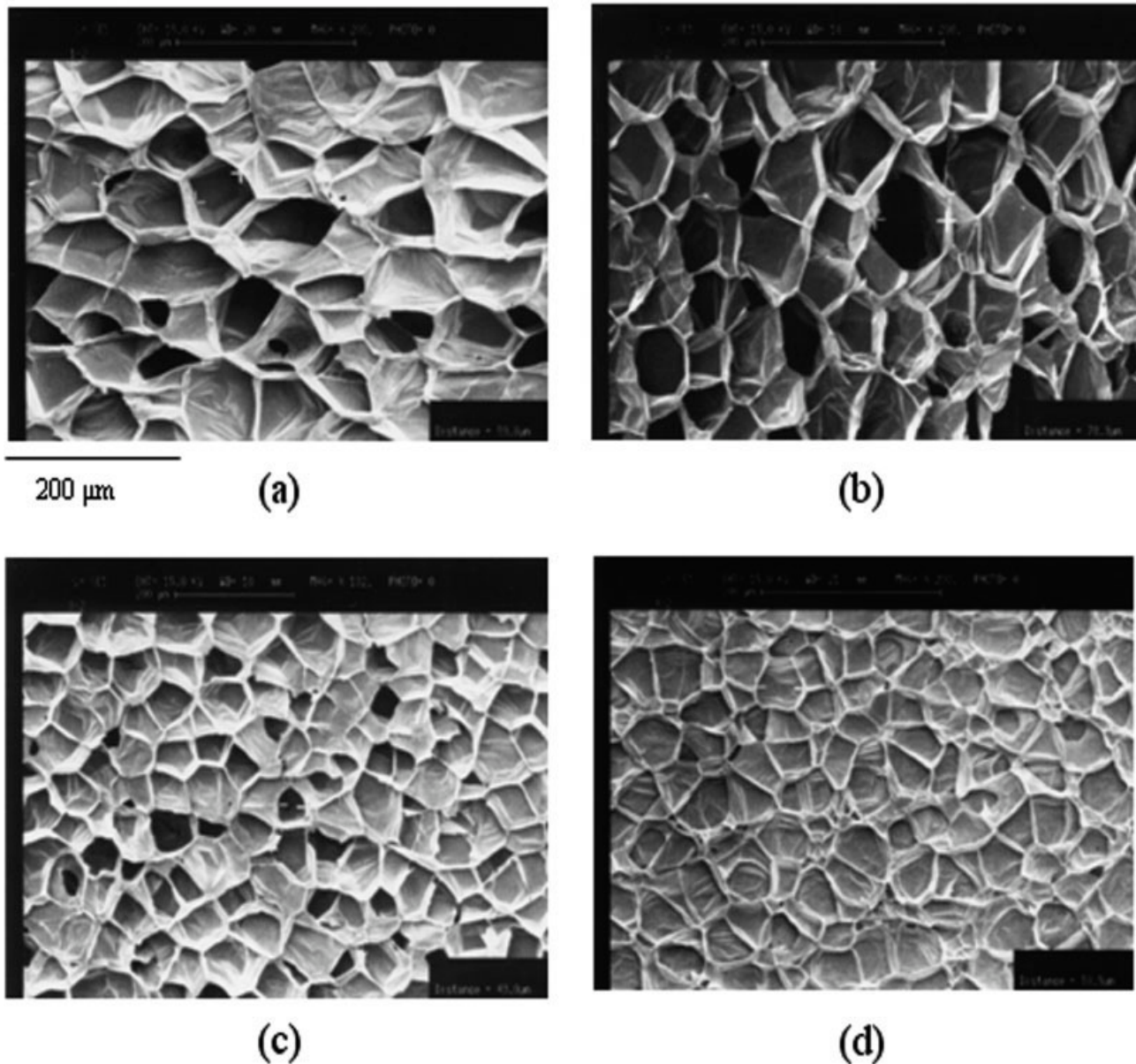


Figure 8 SEM fractured surface micrographs of unfilled PS foams (foamed at 135°C under 3000 psi for 40 min): (a) PS-H, (b) PS-M, (c) PS-L, and (d) HIPS.

pressure based on Henry's Law. Thus, a slightly higher foaming efficiency was anticipated to be observed. However, as the soaking pressure was above 3500 psi, a slight increase in foam density was noted. This behavior probably was due to a slightly higher pressure drop rate induced during foaming process from 4000 psi, which would more easily induce the cell rupture in comparison with a lower pressure imposed at 3500 psi under the same releasing time of less than 1 s. In addition, the foam density of PS-H was about 30% higher than that of HIPS within this region, which might be attributed to the combined effects of a higher molecular weight of PS-H and the rubber inclusion in HIPS. Meanwhile, from Figures 1 and 2, it is noted the effect

of sample thickness (5.0 mm vs. 9.5 mm) on the foam density was marginal, especially at soaking time longer than 30 min.

Effects of PS type and filler content on foam density

On the basis of previous foaming condition investigations, a soaking pressure of 3000 psi and soaking time of 40 min were chosen to evaluate the effects of PS type and CaCO₃ content on the foam density developed for 3 mm-thick samples. The foam densities of unfilled PSs foamed under various foaming temperatures are illustrated in Figure 3. While the foaming temperature was

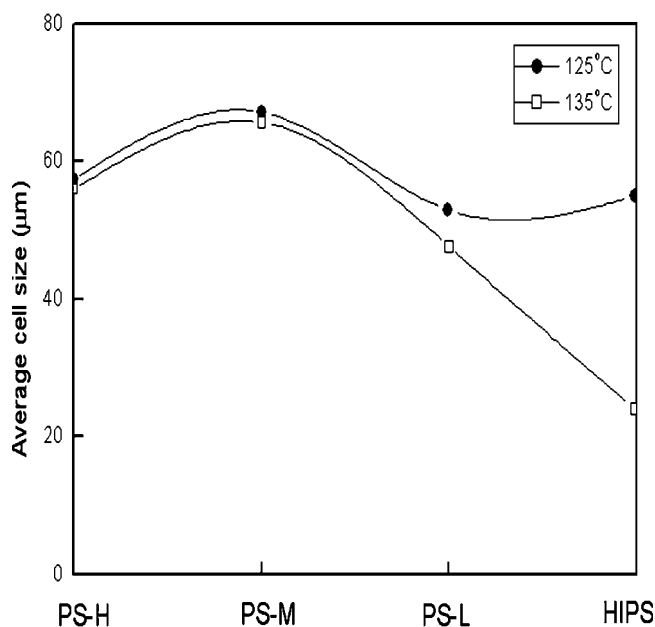


Figure 9 Average cell size of unfilled PS foams foamed at 125°C and 135°C, respectively (under 3000 psi for 40 min).

close to the T_g of each PS, the foam density was higher. This result indicates an inefficient foaming due to a higher melt strength/modulus of each matrix. As the foaming temperature increased, foam density decreased and leveled off at temperatures above 130°C for each PS. The lowest foam density obtained was around 0.022 g/cm³. In addition, it is noted that foam density basically decreased with a decrease in molecular weight (an increase in melt index) for the three general purpose PSs under a fixed foaming temperature. This observation is attributed to the fact that a higher molecular weight implies a higher melt strength/modulus (see the following results), which restrained foaming process and thus generated a higher foam density. Accordingly, to obtain a lower foam density, a lower molecular weight general purpose PS with a higher melt index is preferred in this study. Interestingly, it is noted that though the HIPS possessed a lower molecular weight but exhibited a higher foam density than those of PS-M and PS-L at the foaming temperatures investigated. As several factors including rubber content, polydispersity, melt index and so on were involved in the foaming mechanism, no conclusive explanation is given on the observation at this moment.

Figure 4 shows the foam densities of representative filled PSs (2 phr CaCO₃ filled) foamed under various foaming temperatures. The addition of CaCO₃ would expect to adjust the melt strength/modulus of PS matrix, and thus influenced the resulting foam density. Compared with the unfilled counterparts (cf. Fig. 3), a rise of foam density up to 2-fold was observed for the filled samples. This increase in foam density was attrib-

uted to the combined effects of incorporation of high density (2.53 g/cm³) CaCO₃ filler, and the possible CO₂ leakage at the interfacial region between the PSs and the fillers. Han et al.¹⁶ observed similar results on PS/CO₂/talc or nanoclay systems. They pointed out that CO₂ tended to accumulate within the polymer-filler interfaces during foaming process, which could justify the possible combined effects mentioned above. Nevertheless, the general role that CaCO₃ filler would play to promote cell nucleation should be taken into account (see later discussions on the cell morphology). Likewise, the intercalated or exfoliated nanoclays within the polymeric matrix could enhance cell nucleation but retard cell growth at the early stage of foaming.¹⁶ Again, shown in Figure 4, as the temperature is in the vicinity of each PS's T_g , foam density is higher. The effect of various filled-PS types on the foam density developed is similar to what was observed for unfilled systems within the T_g region. The lowest foam density was obtained at the foaming temperatures between 125°C and 135°C for each sample. The 2 phr CaCO₃ filled PS-L foam exhibited the minimum value of 0.035 g/cm³. Nevertheless, the foam density of each filled sample started to increase unexpectedly at the temperatures above 135°C. This result could be attributed to the facts of lower melt strength/moduli of PS matrix at higher temperatures causing cell rupture (opening) and the higher tendency of CO₂ leakage at the interfacial region between the PSs and the fillers. To illustrate the effect of filler content on the foam density, Figure 5 shows the foam densities of PS-H filled with various CaCO₃ amounts foamed at 3000 psi for 40 min under different temperatures. The foam density basically increased with the filler content, especially for foaming at higher temperatures. Furthermore, the incipient temperature for foam density started to increase at high foaming temperatures was lowered as filler content increased. These behaviors are rather interesting and indicate an optimum foaming temperature range existed for low density foams development. Nevertheless, more detailed study is necessary to elucidate these behaviors with respect to the filler type, matrix type, and so on.

Correlation of foam density with matrix dynamic mechanical property

It is recognized that melt strength/modulus of a polymeric matrix will influence its foaming behavior. Figure 6 reveals the correlation of foam density of unfilled PS-H foamed at 3000 psi for 40 min under various foaming temperatures and matrix storage modulus at corresponding test temperatures. A significant drop of storage modulus was observed at temperatures from 110°C to 120°C (around the T_g). Cell growth was thus expected to be facilitated due to aforementioned mechanisms proposed by Gent and Tompkins.¹⁸ Therefore,

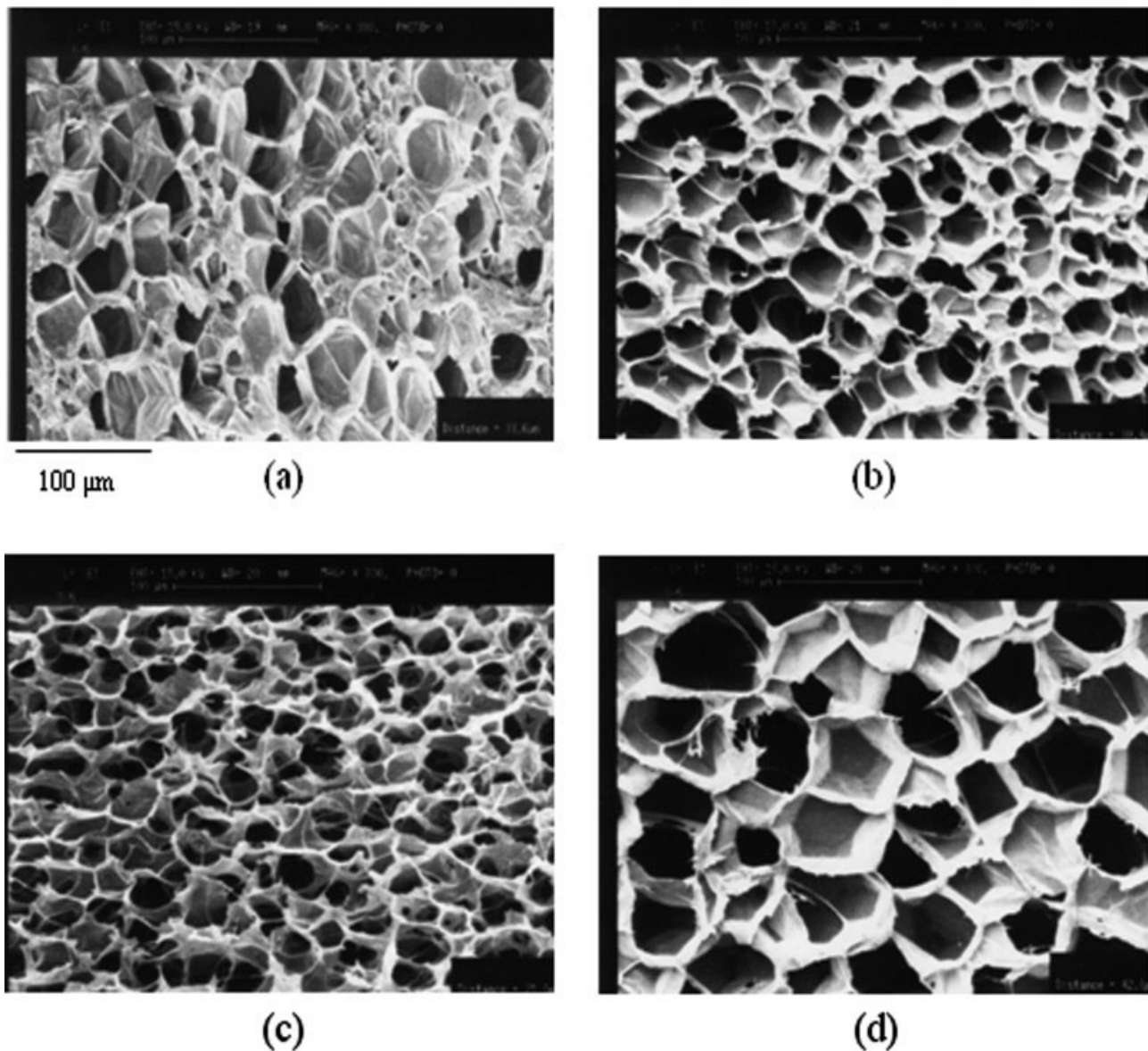


Figure 10 SEM fractured surface micrographs of 2 phr CaCO_3 filled PS foams (foamed at 135°C under 3000 psi for 40 min): (a) PS-H, (b) PS-M, (c) PS-L, and (d) HIPS.

foam density started to decrease because of the decline in matrix melt strength/modulus. Similar behaviors were also observed for other unfilled PS samples. Figure 7 shows the matrix modulus-dependent foam density of 2 phr CaCO_3 filled PS-H at corresponding test/foaming temperatures. The matrix storage modulus also dropped off significantly at temperatures from 110°C to 120°C , and then decreased smoothly at temperatures above 120°C . It was anticipated that cell nucleation would be limited because of a higher storage modulus around the T_g , which caused a higher foam density. The lowest foam density was found in the foaming temperature range of 125°C to 135°C . At higher foaming temperatures, foam density started to increase while the matrix storage modulus decreased

continuously. Based on these investigations, the change in matrix modulus apparently affected resulting foam density, yet other factors including the CO_2 leakage at the interfacial regions between PSs and CaCO_3 , pressure releasing rate, and cooling efficiency (rate) described earlier still played roles in controlling final foam density. Similar behaviors were also observed for other filled PS systems with various amounts of CaCO_3 included.

Cell morphology

Figure 8 shows the cell morphology of four fractured samples foamed at 135°C under 3000 psi for 40 min (scale bar: $200\ \mu\text{m}$). Observed holes with an average

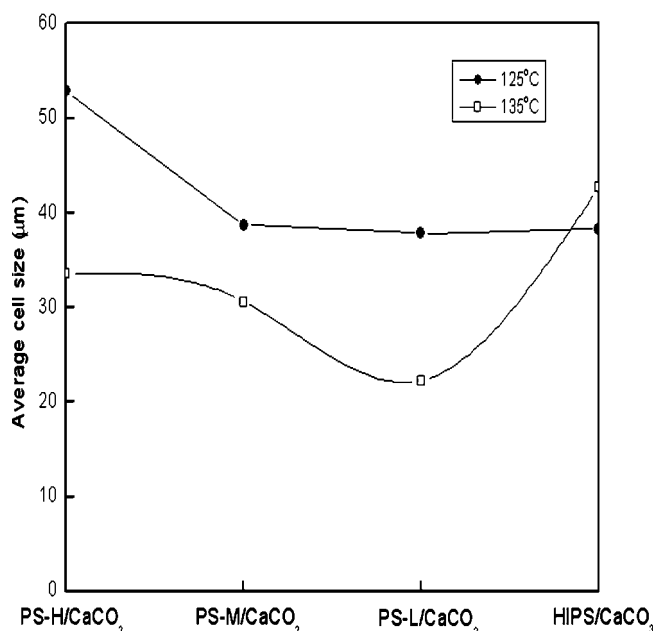


Figure 11 Average cell size of 2 phr CaCO₃ filled PS foams foamed at 125°C and 135°C, respectively (under 3000 psi for 40 min).

dimension of less than 70 μm represent the cell structure. It is noted that, among the samples, PS-L and HIPS foams exhibited slightly finer cell structures. As shown in Figure 3, foam densities of the four samples follow the order of PS-H (0.029 g/cm³) > HIPS (0.027 g/cm³) > PS-M (0.024 g/cm³) > PS-L (0.023 g/cm³). Since HIPS contains a certain amount of rubber, the foaming behavior within rubber domains was expected to be different from that of within PS matrix. Further investigations are necessary to have a better understanding of the simultaneous two-phase foaming mechanism. Results of the samples foamed at 125°C also revealed a similar trend on the cell morphology, but with a clearer difference in their foam density. The foam density is in the order of PS-H (0.075 g/cm³) > HIPS (0.041 g/cm³) > PS-M (0.039 g/cm³) > PS-L (0.035 g/cm³). To give a further comparison on the average cell size for the four unfilled PS foams, Figure 9 depicts the results of the samples foamed at 125°C and 135°C, respectively. As seen, cell size did not vary much with respect to the PS type, while foaming at 125°C. However, the variation on cell size existed for the samples foamed at a higher temperature of 135°C. It is illustrated that samples foamed at a higher temperature exhibited a smaller cell size.

With the addition of 2 phr CaCO₃ into the four PSs, cell size generally decreased along with increased foam density, which is illustrated in Figure 10 (scale bar: 100 μm). This behavior was due to the cell nucleation effect of the added CaCO₃ filler. However, a slightly larger cell size of filled HIPS foam was developed at foaming temperature of 135°C when compared with

that of its unfilled foam. The reason for this observation is unclear at this moment. Figure 11 compares the average cell size of the filled foams foamed at 125°C and 135°C, respectively. For the three general purpose PS systems, a higher foaming temperature as well as a lower molecular weight generated the foam with a smaller average cell size. The effect of foaming temperature on cell size developed was more obvious for the filled samples than previous unfilled samples. This result implies that though several factors were involved in foaming conditions, adding CaCO₃ did play a significant role in reducing cell size and increasing foam density for the PSs investigated here.

CONCLUSIONS

This study investigated the foaming of four PSs filled and unfilled with various amounts of CaCO₃ using supercritical CO₂. Suitable foaming conditions such as soaking pressure and soaking time were evaluated. By varying foaming temperatures, foam densities were determined for all developed foams. In general, a higher foaming temperature as well as a lower matrix molecular weight (higher melt index) generated a lower foam density for the general purpose PSs investigated. With the addition of CaCO₃, foam density increased, which might be attributed to the incorporation of high density filler and the possible CO₂ leakage at the interfacial region between the PS and filler. The inclusion of rubber in PSs (i.e. HIPS) was found to complicate the foaming behavior of PS. More detailed study is required and is in progress to unveil the reasons. Unexpectedly, for the filled PSs, the foam density was noted to rise after foaming at higher temperatures. The incipient temperature for foam density to rise at higher foaming temperatures was lowered as the CaCO₃ content increased. An optimum foaming temperature range was thus required to obtain a low foam density in all cases. The corresponding change in matrix modulus by employing various PSs types and various CaCO₃ contents apparently affected the resulting foam density. Although several factors were involved in foaming conditions, the addition of CaCO₃ did play a significant role in reducing cell size and increasing foam density for the PSs investigated.

References

- Martini-Vvedensky, J. E.; Suh, N. P.; Waldman, F. A. U.S. Pat. 4,473,665 (1984).
- Park, C. B.; Suh, N. P. *Polym Eng Sci* 1996, 36, 34.
- Rachtanapun, P.; Selke, S. E. M.; Matuana, L. M. *J Appl Polym Sci* 2003, 88, 2842.
- Zhang, H.; Rizvi, G. M.; Park, C. B. *Adv Polym Technol* 2004, 23, 263.
- Taki, K.; Yanagimoto, T.; Funami, E.; Okamoto, M.; Ohshima, M. *Polym Eng Sci* 2004, 44, 1004.
- Park, C. B.; Cheung, L. K. *Polym Eng Sci* 1997, 37, 1.
- Park, C. B.; Cheung, L. K.; Song, S.-W. *Cell Polym* 1998, 17, 221.

8. Xanthos, M.; Zhang, Q.; Dey, S. K.; Li, Y.; Yilmazer, U.; O'Shea, M. *J Cell Plast* 1998, 34, 498.
9. Gendron, R.; Daigneault, L. E. *Polym Eng Sci* 2003, 43, 1361.
10. Arora, K. A.; Lesser, A. J.; McCarthy, T. J. *Macromolecules* 1998, 31, 4614.
11. Stafford, C. M.; Russell, T. P.; McCarthy, T. J. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1999, 40, 551.
12. Colton, J. S.; Suh, N. P. *Polym Eng Sci* 1987, 27, 493.
13. Doroudiani, S.; Kortschot, M. T. *J Appl Polym Sci* 2003, 90, 1412.
14. Han, H.; Koelling, K. W.; Tomasko, D. L.; Lee, L. J. *Polym Eng Sci* 2002, 42, 2094.
15. Doroudiani, S.; Kortschot, M. T. *J Thermoplast Compos Mater* 2004, 17, 13.
16. Han, X.; Zeng, C.; Lee, L. J.; Koelling, K. W.; Tomasko, D. L. *Polym Eng Sci* 2003, 43, 1261.
17. Elkovitch, M. D.; Lee, L. J.; Tomasko, D. L. *Polym Eng Sci* 2000, 40, 1850.
18. Gent, A. N.; Tompkins, D. A. *J Appl Phys* 1969, 40, 2520.