

Preparation and Characterization of Microcellular Thin Polycarbonate Sheets

Banglong Xiang, Rong Guan, Quan Fang, Zhaoxin Xiao, Yajing Jiang

Faculty of Chemistry and Materials Science, Hubei University, Wuhan 430062, China

Received 3 September 2004; accepted 12 April 2005

DOI 10.1002/app.22705

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new method was developed for the microcellular processing of polycarbonate (PC) thin sheets by compression molding above PC's glass-transition temperature and below its melting temperature within a few minutes. The effects of the foaming time, foaming pressure, foaming temperature, and foaming agent active ratio on the cell size, cell density, and relative density were studied. The structures of the microcellular PC foam were controlled in the foaming process by carefully choosing the foaming parameters. In addition, the thermal, dynamic mechanical thermal, and electrical properties of the microcellular PC foam were investigated. A differential scanning calorimetry analysis showed that the microcellularly processed PC may have

a plastication effect. The variation of the storage modulus, loss modulus, and $\tan \delta$ under dynamic mechanical thermal analysis was in accord with the calorimetry analysis. The measurement of the electrical property demonstrated that the insulation ability of the microcellular PC thin sheet was obviously enhanced and the dielectric strength of the microcellular PC foam was decreased compared to the unfoamed PC. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1760–1766, 2006

Key words: polycarbonates; processing; compression; microcellular; foam

INTRODUCTION

Microcellular foam was invented at the Massachusetts Institute of Technology under the direction of Nam P. Suh.^{1–3} The cell size in microcellular foams is on the order of microns, generally between 1 and 10 μm , which is below the critical flaw size of polymer materials, so it will absorb the energy and increase the strength as additives (fillers) do when force is applied to microcellular foam.⁴ It is more interesting that, in many cases, these novel materials display high performance,^{5–7} implying that they have much potential for applications in daily life. Moreover, the tiny size and uniform distribution of the microcells make it possible to produce small-profile foaming parts for insulating purposes, such as microelectronic circuit board insulators, electronic signal-wire insulation, and read-only memory storage, which cannot be produced with traditional foaming processes.⁸ Therefore, the technology of microcellular foaming developed rapidly in the past few decades. At present, microcellular foams are produced by several techniques, such as phase separation, precipitation with a compressed fluid antisolvent, po-

lymerization, gas supersaturation, compression molding, and so forth.⁹

However, earlier research concentrated on gas supersaturation, such as the batch process, continuous extrusion, and the injection process; but high costs restricted their development. Until now, the research on microcellular foams has been mainly directed at polystyrene,^{10–18} polypropylene,¹⁹ poly(methyl methacrylate),²⁰ polyamide,²¹ polysulfone,^{9,22,23} poly(ether sulfone),^{23,24} poly(ether imide),²⁴ or their blends.^{25–31} Only a few studies have been conducted on the preparation of microcellular polycarbonate (PC) foam,^{5,32,33} one of the most important engineering plastics. Because of weak melt strength and melt elasticity, its foaming is more difficult than other plastics. In this study a microcellular PC thin sheet is prepared by a compression molding method invented by our group. Microcellular foaming by compression molding is between the glass-transition temperature (T_g) and the melting temperature (T_m) but close to the glass-transition temperature of PC; the foaming occurs in the solid state of the PC matrix. The advantages of using compression molding for microcellular processing of PC thin sheets are a short foaming time, simplicity, ease of operation, as well as being more economical. In addition, compared to conventional extrusion or injection molding to prepare a microcellular foam, this method is much easier to prepare thin sheets, because the conventional polymer foams that typically have cell sizes of 0.25 mm or larger are not

Correspondence to: R. Guan (rongguan@public.wh.hb.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50473026.

suitable for use in applications involved in thin wall products because of the excessive loss of strength. Thus, our method to prepare thin microcellular PC sheets is very theoretically and practically significant.

Until now, the focus of research was to investigate the influence of the microstructure,^{8–14,20–26,34,35} thermal properties,^{20,35} tensile strength,^{9,16,36} impact strength,^{5,15} compression strength, and any other mechanical properties. However, the electrical properties of microcellular PC sheets are also investigated in this article, which will facilitate their application in the electronics industry in the near future.

EXPERIMENTAL

Materials

A commercial-grade PC sheet with a thickness of 0.15 mm was used as received from GE. Low-density polyethylene (LDPE) pellets from Maoming Factory (Maoming, China) with a melt index of 2 g/10 min at 190°C were used as received. Commercial-grade azobisformamide (AC), a foaming reagent, and dicumyl peroxide (DCP) and zinc oxide (ZnO) were used without any further purification.

Foam preparation

The microcellular foam processing experiments were carried out as follows. We first mixed LDPE, AC, DCP, and ZnO in a two-roll mill as a gas source for PC foaming. Next, the PC sheets and the mixed LDPE were placed in a 250 × 250 × 2 mm mold and loaded in a hydraulic hot press under set experimental conditions.

Once the required foaming time and other conditions were reached, the mold was taken out of the hot press. Then, we unloaded the mold, quenched it at room temperature within 30 s, and removed the microcellular PC foam from the mold. Thus, the microcellular PC samples were ready for property characterization.

Foam characterization

Differential scanning calorimetry (DSC) analysis was performed in a NETZSCH DSC 204 differential scanning calorimeter at a scanning rate of 20°C/min under a nitrogen flow. To delete the thermal history effect during microcellular processing, a second heating scan was carried out at the same scanning rate and taken as the DSC analysis results.

Dynamic mechanical thermal analysis (DMTA) was done on a Rheometric DMTA III at a heating rate of 3°C/min and a frequency of 1 Hz in tension mode.

The cell size of the foamed samples was observed under an Olympus BX51 polarizing microscope (using

a 100× camera lens). The cell structure parameters, such as the average cell sizes and cell densities, were characterized using the method suggested by Kumar et al.³⁷ The cell diameter (D) is the average cell size measured from the photographs, which was usually more than 100 cells. The cell density (N_f), which is the number of cells per cubic centimeter of foam, is calculated as

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

where n is the number of cells in the photographs, A is the area of the micrograph (cm²), and M is the magnification factor. In addition, the cell density (N_0) based on the pristine unfoamed sample is calculated as

$$V_f = \frac{\pi}{6} D^3 \times N_f \quad (2)$$

$$N_0 = \frac{N_f}{1 - V_f} \quad (3)$$

where V_f is the void fraction of the foamed material.

The relative density was determined according to ISO 1183-1987. The mass of the sample in air and distilled water was measured with an analytical balance with an accuracy of 0.1 mg. The density of the sample (d) is calculated as

$$d = \frac{m_{\text{gas}}}{m_{\text{water}}} \times \rho_{\text{water}} \quad (4)$$

where ρ_{water} is the density of the distilled water at room temperature and m_{gas} and m_{water} are the mass of the sample in atmosphere and in distilled water, respectively. Then, the density of the foamed sample is divided by the density of the unfoamed sample to obtain the relative density.

The electrical properties were measured, including the insulating property, electrical resistivity, and dielectric strength. The investigation of the insulating property was carried out in a Zc-36 10⁷ Ω superhigh resistance instrument, following the method of volume resistivity and surface resistivity, with aluminum foil as the electrode material, a sample size of 50 × 50 mm, and a test voltage of 500 V at 23°C and 86% relative humidity (RH). The dielectric strength measurement was performed based on the strength test method of the working frequency electronics of insulation materials by continuously increasing the voltage at a rate of 1 kV/s at 23°C and 86% RH. The sample size was the same, and measurements were carried out separately in air and pure transformer oil.

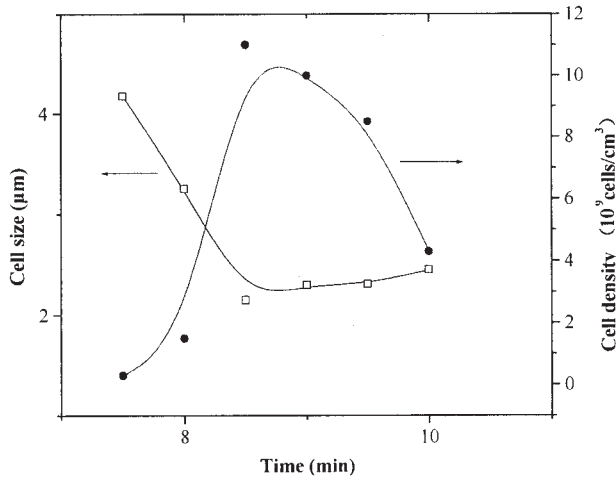


Figure 1 The effect of the foaming time on the cell size and cell density of microcellular PC foam with a pressure of 13.5 MPa at 413 K and a ZnO/AC ratio of 1 : 1.

RESULTS AND DISCUSSION

Processing parameter effects on microcellular PC foam

During the processing of microcellular PC foam, the cell size, cell density, and relative density are affected by the foaming temperature, foaming time, foaming pressure, and foaming agent active ratio.

Foaming time

The foaming time plays an important roll in the cell size, cell density, and relative density of microcellular PC foam. Results of this analysis are presented in Figures 1 and 2. They show that the cell size, cell density, and relative density of microcellular PC foam

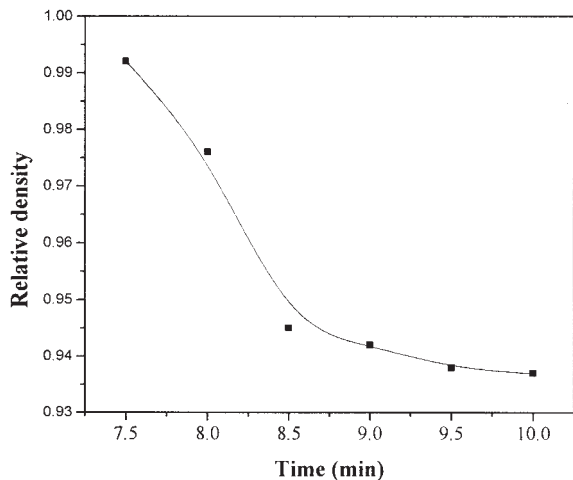


Figure 2 The effect of the foaming time on the relative density of microcellular PC foam with a pressure of 13.5 MPa at 413 K and a ZnO/AC ratio of 1 : 1.

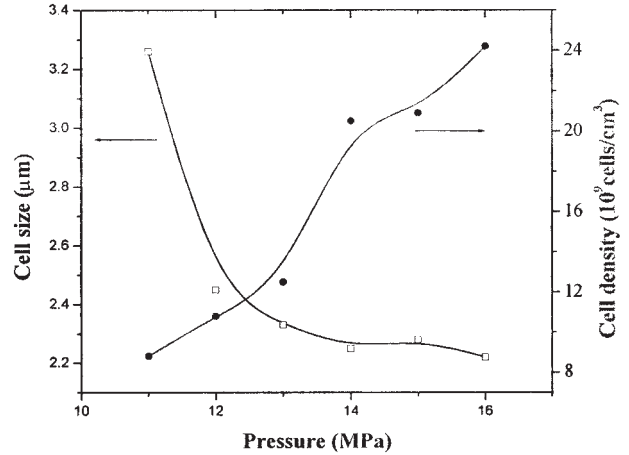


Figure 3 Effect of foaming pressure on the cell size and cell density of microcellular PC foam T=413K, t=8 min and ZnO : AC=1 : 1.

are a function of the foaming time. When the foaming time reaches 8.5 min, the minimum cell size and maximum cell density are obtained. After that, the cell size increases and the cell density decreases with increases in the foaming time. Therefore, the foaming time should not exceed 10 min when using compression molding to prepare a microcellular PC foam under our experimental conditions.

Foaming pressure

Foaming pressure is another effective controlling parameter for microcellular foaming. Figures 3 and 4 present the results for the cell size, cell density, and relative density of microcellular PC foam at different pressures and a constant foaming temperature (413 K), foaming time (8 min), and foaming agent active ratio (1). These curves exhibit a decrease of the cell size with increasing pressure and a change of slope at 13 MPa.

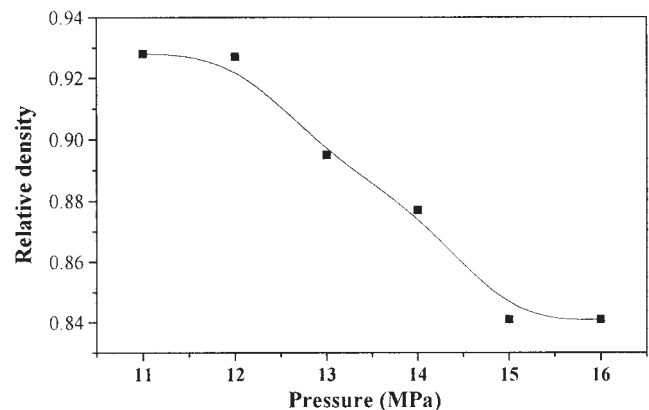


Figure 4 The effect of the foaming pressure on the relative density of microcellular PC foam at 413 K for 8 min with a ZnO/AC ratio of 1 : 1.

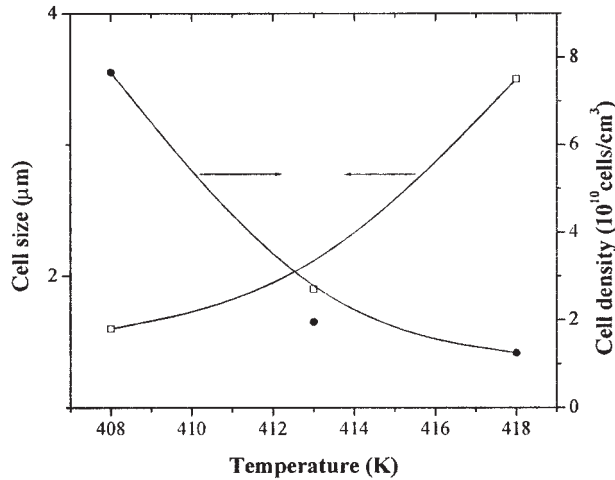


Figure 5 Effect of foaming temperature on the cell size and cell density of microcellular PC foam $t=8\text{min}$, $P=13.5\text{MPa}$ and $\text{ZnO} : \text{AC}=1 : 1$.

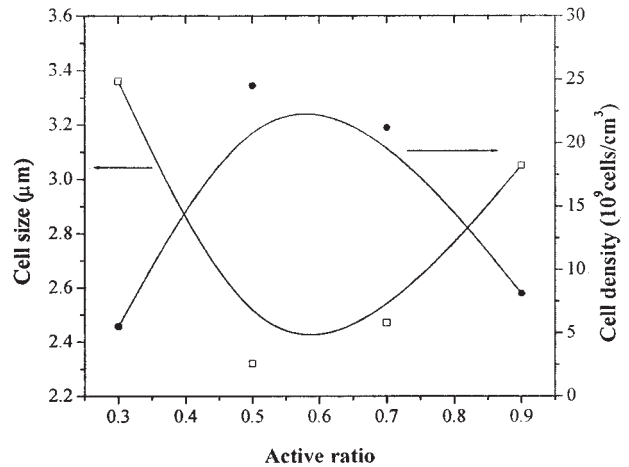


Figure 7 Effect of active ratio on the cell size and cell density of microcellular PC foam $t=8\text{min}$, $P=13.5\text{MPa}$ and $T=413\text{K}$.

It is evident from these figures that the foaming pressure plays a significant role in the cell size and cell density. When the foaming pressure is less than 11 MPa, no detectable cell structure can be observed because the produced gas largely escapes out of the mold rather than diffuses into the PC matrix to initiate nucleation. Increasing the foaming pressure causes the cell size to decrease (Fig. 3) and the cell density to increase (Fig. 4). Apparently, the increased pressure favors cell nucleation.

Foaming temperature

It has been reported that the foaming temperature is an important parameter to control the cell structure of microcellular PC foam. Figures 5 and 6 illustrate the effect of temperature on the cell size, cell density, and

relative density for microcellular PC foam. The cell size and cell density have an exponential relationship with the foaming temperature. From Figure 5 we can see that the cell size increases quickly with foaming temperature increases from 413 to 418 K. With the variation of the foaming temperature on a small scale, the cell size increases substantially and the cell density decreases as well.

In addition to the cell nucleation being depressed upon increasing the temperature, the foaming temperature can affect cell growth through the gas diffusion rate, the interfacial surface energy (i.e., surface tension), and the viscoelastic behavior of the polymer-gas matrix.

Foaming agent active ratio

Figures 7 and 8 explicitly show the influence of the

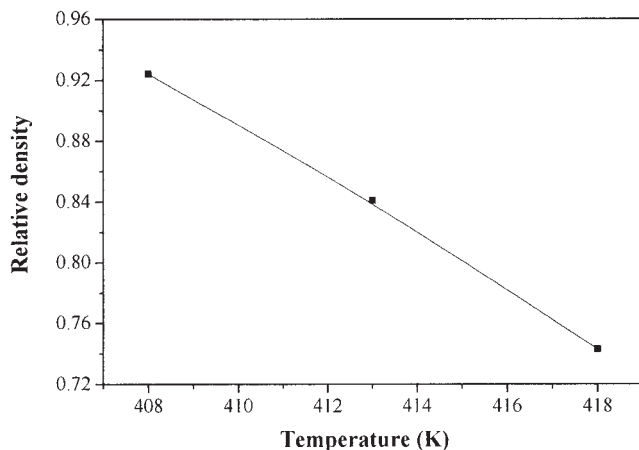


Figure 6 The effect of the foaming temperature on the relative density of microcellular PC foam at a pressure of 13.5 MPa for 8 min with a ZnO/AC ratio of 1 : 1.

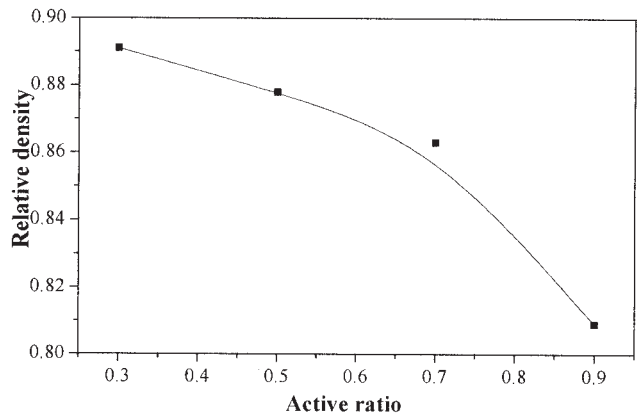


Figure 8 The effect of the active ratio on the relative density of microcellular PC foam at a pressure of 13.5 MPa for 8 min at 413 K.

TABLE I
DSC Data of Microcellular PC Foam

	Sample		
	A	B	C
T_g (°C)	152.65	151.73	150.02

active ratio (m_{ZnO}/m_{AC}) on the cell size, cell density, and relative density of microcellular PC foam. It is evident from the figures that the foaming agent active ratio has a larger effect on the cell size and cell density. With the increase of the active ratio, the cell size first decreases slightly and then increases, whereas the cell density first increases largely and then decreases. Apparently, 12% AC content can provide the gas needed to initiate the satisfied cell nucleation, and an active ratio of 0.6 can activate it. However, considering the experimental deviation, we actually selected 1 as the fixed active ratio throughout all our experiments.

The increase of the active ratio actually increases the rate of foaming agent degradation, increases the gas concentration, and reduces the foaming temperature and chain moving ability inside the PC, leading to cell size decreases and cell density increases. These are the reasons for the initial cell size increases and cell density decreases. When the active ratio is increased further, the rate of foaming agent degradation increases quickly and a lot of gas escapes through the gap of the mold before diffusing into the PC matrix, so the equilibrium time is shortened to a large extent. As a result, the cell size increases and the cell density decreases, as shown in Figure 7.

In the study of microcellular foaming processing of PC, it is usually assumed that the cell size is an indication of cell growth and the cell density is an indication of cell nucleation. Moreover, the cell density and cell size exhibit an explicit interaction. Because the PC used in our experiment is a nearly amorphous polymer, according to classical nucleation theory, the role of homogeneous nucleation is determined by processing parameters such as the foaming temperature, foaming pressure, and surface tension.³⁸ The growth rate of the cells is limited by the diffusion rate and the stiffness of the viscoelastic polymer-gas solution. In general, the cell growth is affected primarily by the time allowed for the cell to grow, the temperature of the system, the state of supersaturation, and the viscoelastic properties of the polymer-gas solution.¹⁹ Therefore, the structures of the microcellular PC foam could be successfully controlled through careful choices of foaming conditions.

Properties of microcellular PC foam

DSC

The thermal analysis data of microcellular PC foam at different foaming times throughout the heating scan

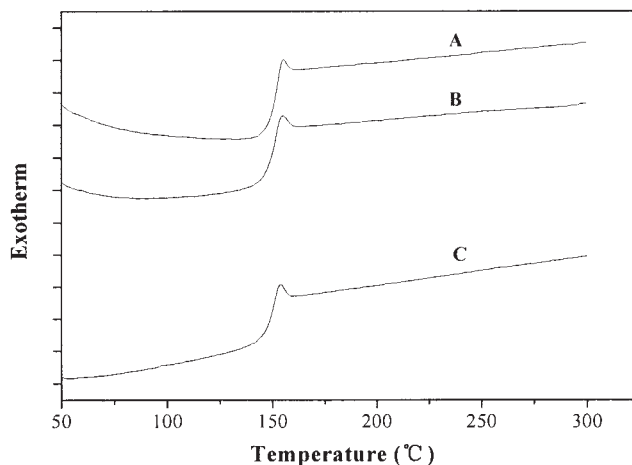


Figure 9 DSC curves of microcellular PC foam either unfoamed (curve A) or foamed at a pressure of 13.5 MPa at 413 K with a ZnO/AC ratio of 1:1 for 8 (curve B) or 9 min (curve C).

are listed in Table I. As shown in Figure 9, the glass-transition temperature (T_g) of the microcellular PC foam is lowered slightly with increasing foaming time, suggesting that the microcells may play the role of plastification.

DMTA

To confirm the DSC analysis results, DMTA is carried out to investigate the effect of the foaming time on the DMT behavior. From Figure 10 and Table II we can see that the $\tan \delta$ decreases with increasing foaming time, a result of the microcellular plastification effect. We have no doubt that the $\tan \delta$ variation is quite in accord with the T_g variation from the DSC analysis.

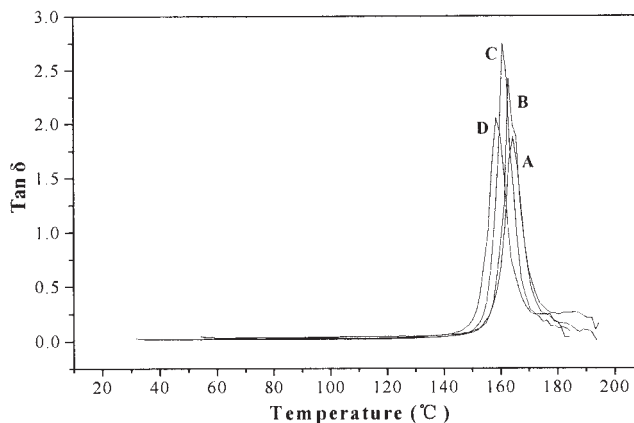


Figure 10 The effect of the foaming time on the $\tan \delta$ of microcellular PC foam either unfoamed (curve A) or foamed at a pressure of 13.5 MPa at 413 K with a ZnO/AC ratio of 1:1 for 8 (curve B), 8.5 (curve C), or 9 min (curve D).

TABLE II
Tan δ Data of Microcellular PC Foam

	Sample			
	A	B	C	D
Tan $\delta \approx T$ ($^{\circ}\text{C}$)	164.50	162.90	160.72	158.68
Peak of tan δ	1.87	2.43	2.75	2.03

The effects of the foaming time on the loss and storage moduli are shown in Figures 11 and 12, respectively. We can clearly see that the storage and loss moduli increase when the foaming time is less than 8.5 min and decrease when the foaming time is longer than 8.5 min. The larger cell PC foam has smaller slopes in the transition regions compared to the unfoamed PC. In other words, at a given temperature in the transition region the microcellular PC foam has a higher relative storage modulus compared to the unfoamed PC. This broadening of the transition region may provide for a higher design temperature for microcellular PC foam compared with the unfoamed PC. One possible reason for the increased slope in the transition region is molecular orientation in the cell walls of the microcellular PC foam. The cell wall orientation may be induced during foaming because of the biaxial extensional strain experienced by the cell wall material during cell growth. Such microcellular orientation could restrict the mobility of the polymer chain segments, thereby broadening the transition region. Another possible reason for the broad transition regions is the effect of increasing gas pressure in the cell during analysis heating. Although the cell gas pressure tends to lower the effective static tensile modulus, it may tend to increase the effective dynamic modulus through its effect on cell wall bending.⁵

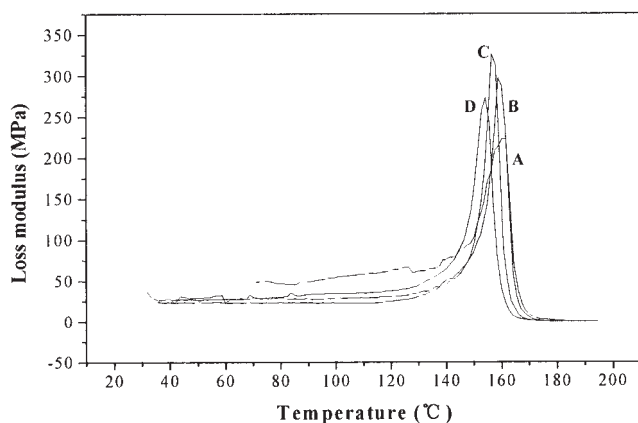


Figure 11 The effect of the foaming time on the loss modulus of microcellular PC foam either unfoamed (curve A) or foamed at a pressure of 13.5 MPa at 413 K with a ZnO/AC ratio of 1 : 1 for 8 (curve B), 8.5 (curve C), or 9 min (curve D).

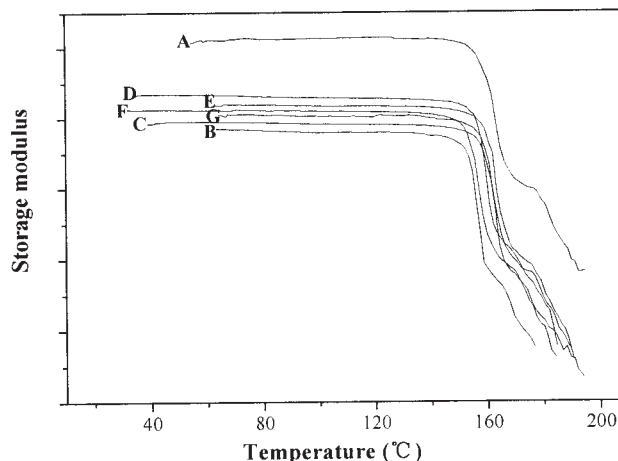


Figure 12 The effect of the foaming time on the storage modulus of microcellular PC foam either unfoamed (curve A) or foamed at a pressure of 13.5 MPa at 413 K with a ZnO/AC ratio of 1 : 1 for 7.5 (curve B), 8 (curve C), 8.5 (curve D), 9 (curve E), 9.5 (curve F), or 10 min (curve G).

Electrical properties

Considering the future applications of microcellular foam, such as in the electronics industry, several microcellular PC foam samples were selected to measure their electrical properties. It is evident from Table III that the microcellular PC has higher surface resistivity than the unfoamed PC. The volume resistivity of air is $5.86 \times 10^{15} \Omega \text{ cm}$ at room temperature, and the unfoamed PC value is $2.38 \times 10^{14} \Omega \text{ cm}$ from the measurements. Hence, the microcells introduced into the polymer matrix act as insulators; thus, it is reasonable to think that the volume resistivity of microcellular PC foam should be higher than the unfoamed PC. That is, the microcellular PC has better insulation properties. Moreover, the smaller cell size and larger cell density may lead to better insulation properties of microcellular PC foam. After microcellular processing, the dry and wet dielectric strength of PC sheets also changed, as listed in Table III.

CONCLUSIONS

A new method was developed for microcellular processing of thin PC sheets with a general hydraulic press above PC's T_g and below its T_m within a few minutes. This method is simple, easy to perform, and economical. The processing window to prepare microcellular PC was a foaming time between 7.5 and 10 min, a foaming pressure between 11 and 16 MPa, a foaming temperature between 408 and 418 K, and a foaming reagent active ratio between 0.3 and 0.9 under our experimental conditions.

The structures of microcellular PC foam (such as cell size, cell density, and relative density) were controlled

TABLE III
Effect of Cell Structure on Electrical Properties

Property	Sample						
	A	B	C	D	E	F	G
Cell size (μm)	0	4.12	3.27	2.15	2.29	2.30	2.47
Relative density (g/cm^3)	1	0.992	0.978	0.946	0.943	0.937	0.914
Surface resistivity ($\times E14\Omega$)	0.79	1.3	2.27	7.41	5.87	7.3	6.39
Volume resistivity ($\times E15\Omega \text{ cm}$)	0.238	1.34	1.89	5.86	5.55	4.9	1.8
Dielectric strength (kV/mm)							
Dry	91.6	84.1	83.0	89.1	76.5	88.8	83.1
Wet	85.0	85.1	82.3	83.8	77.0	87.8	83.9

in the foaming process by carefully choosing the foaming parameters (such as foaming time, foaming temperature, foaming pressure, foaming agent active ratio). After microcellular processing, PC's T_g only decreased a small amount. The DMTA results were in good agreement with the DSC analysis. Furthermore, the insulation ability of the microcellular PC was obviously enhanced and the dielectric strength of the microcellular PC was decreased compared to the unfoamed PC.

References

- Martini, J. E.; Waldman, F. A.; Suh, N. P. ANTEC'82, SPE Tech Pap 1982, 28, 674.
- Martini, J. E. M.S. Thesis, Massachusetts Institute of Technology, 1981.
- Martini, J. E.; Suh, N. P.; Waldman, F. A. U.S. Pat. 4,473,665, 1984.
- Shimbo, M.; Baldwin, D. F.; Suh, N. P. Polym Eng Sci 1995, 35, 1387.
- Collias, D. I.; Baird, D. G.; Borggreve, R. J. M. Polymer 1994, 35, 3978.
- Collias, D. I.; Baird, D. G. Polym Eng Sci 1995, 35, 1167.
- Collias, D. I.; Baird, D. G. Polym Eng Sci 1995, 35, 1178.
- Wang, J.; Cheng, X.; Yuan, M.; He, J. J. Polym Sci Part B: Polym Phys 2003, 41, 368.
- Sun, H. L.; Mark, J. E. J Appl Polym Sci 2002, 86, 1692.
- Arora, K. A.; Lesser, A. J.; McCarthy, T. J. Macromolecules 1998, 31, 4614.
- Stafford, C. M.; Russell, T. P.; McCarthy, T. J. Macromolecules 1999, 32, 7610.
- Spitael, P.; Macosko, C. W.; McClurg, R. B. Macromolecules 2004, 37, 6874.
- Sumarno, X.; Sato, Y.; Takishima, S.; Masuoka, H. J Appl Polym Sci 2000, 77, 2383.
- Doroudiani, S.; Kortschot, M. T. J Appl Polym Sci 2003, 90, 1412.
- Doroudiani, S.; Kortschot, M. T. J Appl Polym Sci 2003, 90, 1421.
- Doroudiani, S.; Kortschot, M. T. J Appl Polym Sci 2003, 90, 1427.
- Sumarno, X.; Sunada, T.; Sato, Y.; Takishima, S.; Masuoka, H. Polym Eng Sci 2000, 40, 1510.
- Han, X.; Koelling, K. W.; Tomasko, D. L.; Lee, L. J. Polym Eng Sci 2002, 42, 2094.
- Naguib, H. E.; Park, C. B.; Reichlet, N. J Appl Polym Sci 2004, 91, 2661.
- Mizumoto, T.; Sugimura, N.; Moritani, M. Macromolecules 2000, 33, 6757.
- Yuan, M.; Turng, L. S.; Gong, S. Polym Eng Sci 2004, 44, 673.
- Huang, Q.; Klötzer, R.; Seibig, B.; Paul, D. J Appl Polym Sci 1998, 69, 1753.
- Krause, B.; Mettinkhof, R.; van der Vegt, N. F. A.; Wessling, M. Macromolecules 2001, 34, 874.
- Krause, B.; Sijbesma, H. J. P.; Münüklü, P.; Van der Vegt, N. F. A.; Wessling, M. Macromolecules 2001, 34, 8792.
- Rachtanapun, P.; Selke, S. E. M.; Matuana, L. M. J Appl Polym Sci 2003, 88, 2842.
- Rachtanapun, P.; Selke, S. E. M.; Matuana, L. M. J Appl Polym Sci 2004, 93, 364.
- Rachtanapun, P.; Selke, S. E. M.; Matuana, L. M. Polym Eng Sci 2004, 44, 1551.
- Krause, B.; Diekmann, K.; van der Vegt, N. F. A.; Wessling, M. Macromolecules 2002, 35, 1738.
- Siripurapua, S.; Gay, Y. J.; Royer, J. R. Polymer 2002, 43, 5511.
- Wang, J.; Cheng, X.; He, J.; Yuan, M. Polymer 2001, 42, 8265.
- Wright, K. J.; Indukuri, K.; Lesser, A. J. Polym Eng Sci 2003, 43, 531.
- Wing, G.; Pasricha, A.; Tuttle, M.; Kumar, V. Polym Eng Sci 1995, 35, 673.
- Gendron, R.; Daigneault, L. E. Polym Eng Sci 2003, 43, 1361.
- Guo, G.; Rizvi, G. M.; Park, C. B.; Lin, W. S. J Appl Polym Sci 2004, 91, 621.
- Xu, Q.; Ren, X.; Chang, Y.; Wang, J.; Yu, L.; Dean, K. J Appl Polym Sci 2004, 94, 593.
- Nayak, N. C.; Tripathy, D. K. J Appl Polym Sci 2002, 83, 357.
- Kumar, V.; Suh, N. P. Polym Eng Sci 1990, 30, 1323.
- Baldwin, D. F.; Park, C. B.; Suh, N. P. Polym Eng Sci 1996, 36, 1437.