

Extrusion of Microcellular Open-Cell LDPE-Based Sheet Foams

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ABSTRACT: In this research, highly open-cell low-density polyethylene sheet foams are achieved with an annular die by applying various strategies for cell opening, i.e., (i) creation of a structural nonhomogeneity consisting of hard and soft regions with partial crosslinking, (ii) blending of a hard second-phase material (i.e., polystyrene phase) into the low-density polyethylene matrix, (iii) plasticization of the soft region with a secondary blowing agent, (iv) decrease of the cell wall thickness by increasing the cell density, and (v) decrease of the cell wall thickness by increasing the expansion ratio while cell

walls are soft. Although the higher surface-to-volume ratio of the sheet foams compared with filament foams made it challenging to prevent gas loss, highly open-cell (up to 99%) and microcellular (up to 3.5×10^{10} cells/cm³) foam sheets were successfully manufactured with high-pressure annular dies using the cell-opening strategies. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3376–3384, 2006

Key words: foam extrusion; blowing agents; crosslinking; blends; polyethylene

INTRODUCTION

Until recently, open-cell foams have been almost exclusively industrially manufactured with polyurethane thermoset materials.¹ Because the manufacturing technologies for open-cell thermoplastic foams have not been developed extensively, very few thermoplastic foams with exceptionally high open-cell contents are available.^{2–11}

Our previous studies have successfully demonstrated an open-cell foaming extrusion technology by achieving highly open-cell (up to 99%) filament foams with low-density polyethylene/polystyrene (LDPE/PS) blends while using CO₂ and butane as blowing agents and a small amount of crosslinking agents.^{12,13}

Numerous industrial applications of open-cell foams, such as filters, separation membranes, sound insulation panels, battery electrode supports, battery separators, and artificial bone tissues, require sheet foams rather than filament foams. In this study, the feasibility of producing a highly open-cell sheet foam was investigated using the five processing strategies established in our previous studies for a filament foam. If highly open-cell sheet foams can be manufactured at a low manufacturing cost without

compromising the desired functionality (i.e., permeability of gas or vapor, selective osmosis, or absorbing and dampening of sound), then more industry-friendly products will be made possible.

STRATEGIES FOR CELL-OPENING IN THERMOPLASTIC FOAMS

In our previous cell-opening studies, five major strategies have been applied to produce LDPE-based, open-cell foam structures for filamentary extrudates.^{12–14} The same strategies are applied to sheet foams in this work.

First, a structural nonhomogeneity consisting of hard and soft regions is created in the polymer matrix by using crosslinking.¹² Upon crosslinking at a high processing temperature, the polymer melts develop a nonuniform distribution of hard and soft regions over the polymer matrix. During cell growth, the soft regions are opened in the thinning cell walls and created interconnections between cells, while the hard regions hold the overall cellular structure instead of allowing the cells to completely coalesce with each other.

Second, a blended small amount of a second-phase, harder material (i.e., 10 wt % PS) further facilitates cell opening. Because of a poor bonding between the two phases and their different deformation behaviors, embedded PS phases seem to act as effective cell-wall-rupturing particles.¹²

Third, *n*-butane is introduced as a secondary blowing agent to soften the un-crosslinked sections of the

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cell walls (and thereby to open them) with its superior plasticizing effects.¹³

Fourth, the cell-wall thickness is reduced to increase the probability of cell opening by increasing the cell density. Since the cell-wall thickness (δ) decreases with the cell density (n) as shown in eq. (1), the cell walls can be more easily opened by increasing the cell-nucleation rate.

$$\delta = \frac{(\sqrt[3]{\varphi} - \sqrt[3]{\varphi - 1})}{\sqrt[3]{n}} \quad (1)$$

where φ is the expansion ratio. Various variables can be used to increase the cell nucleation rate, such as the pressure-drop rate, the nucleating-agent type and amount, the blowing agent type and amount, etc.^{14–18} The blending with PS would also increase the cell density, too.¹⁹

Finally, the cell wall thickness is further reduced to increase the chances of cell opening by increasing the volume expansion ratio while cell walls are soft. According to eq. (1), the cell wall thickness decreases as the volume expansion ratio increases for a fixed cell density. A high gas content and/or the optimization of temperature²⁰ can increase the expansion ratio. Since cell opening can start to occur in the initial expansion stage,^{20–22} the expansion ratio may decrease because of the fast gas loss that occurs with a high open-cell content. So the final expansion ratio may not be high once the foam has a high open-cell content.²³ Temperature control can be used to maximize the open-cell content. There is an optimum processing temperature to achieve the maximum open-cell content. At low temperatures, cell walls become too stiff for cell opening, and at high temperatures, the thickness of cell walls become too large for cell opening.^{12,14}

All these strategies have been empirically proven to be effective for cell opening. With proper combinations of these strategies, very high open-cell contents (up to 99%) were successfully achieved in the filament dies over a broad processing temperature spectrum.^{12–14}

COMPARISON BETWEEN SHEET FOAMS AND FILAMENT FOAMS

One of the major differences in producing sheet foams as opposed to filament foams lies in the different amounts of gas loss due to differing surface-to-volume ratios. The surface-to-volume ratio is a meaningful indicator for gas loss because the gas escapes through the surface of the extruded foam.²⁴ Because of the larger surface area of sheets for the same volume, sheet foams are more susceptible to gas loss. It is therefore more challenging to manufacture low-density sheet foams than filament foams.²⁴ A simple ratio analysis of gas loss can quantify the difference between filament-shaped and sheet-shaped

foams. For a filament die, the surface-to-volume ratio (ψ_f) is

$$\psi_f = \frac{\pi dl}{\pi \left(\frac{d}{2}\right)^2 l} = \frac{4}{d} \quad (2)$$

where d is the diameter of the filamentary die and l is the length of the extruded filament. On the other hand, for an annular die, the surface-to-volume ratio (ψ_a) is

$$\psi_a = \frac{2 \times \pi DL}{\pi DHL} = \frac{2}{H} \quad (3)$$

where D is the average diameter of annular die, L is the length of extruded sheet, and H is thickness of sheet. Thus,

$$\frac{\psi_a}{\psi_f} = \frac{d}{2H} \quad (4)$$

It should be noted that the surface-area ratio is the same as the ratio of surface-to-volume ratios for a constant volume flow rate.

$$\frac{S_a}{S_f} = \frac{2\pi DL}{\pi dl} = \frac{2\pi D \frac{Q}{\pi DH}}{\pi d \frac{Q}{\pi \left(\frac{d}{2}\right)^2}} = \frac{d}{2H} = \frac{\psi_a}{\psi_f} \quad (5)$$

In our case, the diameter of the filament die utilized in our previous studies^{12–14} to obtain microcellular foams was 0.457 mm (0.018"), whereas the common die gap size of annular dies, H , was 0.04 mm (0.0016"). Therefore, the ratio of annular-shaped and filament-shaped surface-to-volume ratios (or the surface area) is around 5.7. So the surface-to-volume ratio of the annular die is much higher than that of the filamentary die. As a result, it will be more challenging to prevent gas loss through large skinned area sheets and ultimately to produce highly open-cell microcellular sheet foams.

EXPERIMENTAL

Materials

The plastic material used in this study was commercially available LDPE resin (Novapol Polyethylene LC-0522-A) supplied by NOVA Chemicals (Calgary, Canada). The melt index (ASTM D 1238, 190°C/2.16 kg) was 4.5 g/10 min and the density (ASTM D 792) was 0.922 g/cm³. This polyethylene resin was biologically and chemically inert, which was suitable for biomedical applications such as tissue attachment and growth. The other polymer resin used in the study was PS from NOVA Chemicals (PS 101). The melt index (ASTM D 1238) was 2.2 g/10 min and the density of this PS was 1.040 g/cm³.

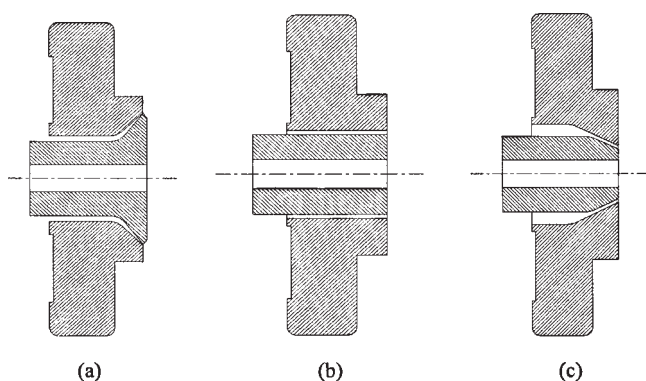


Figure 1 Schematic of an annular die with three different die lip designs: (a) divergent die, (b) straight die, and (c) convergent die.

The crosslinking agent was an organic dicumyl peroxide (Varox DCP-40C) supplied by R.T. Vanderbilt Company (Norwalk, CT). The melting or sublimation point of this chemical was 38°C (100.4°F) and the specific gravity was 1.6. This crosslinking agent was unstable and reactive with strong acids and strong oxidizers. The thermal behavior of this exothermic organic peroxide was examined using a DSC 2910 of TA Instruments, with a heating rate of 10°C/min. The onset temperature was around 150°C.

The nucleating agent employed in this study was talc (particle size range of 2–3 μm) supplied by Ingenia Polymers (Brampton, Canada). A fixed amount of 2 wt % was used throughout the experiments. The CO₂ and *n*-butane, supplied by Matheson Gas Product, were utilized as blowing agents. The CO₂ and *n*-butane were commercial grades with a minimum of 99.5 and 99% purity, respectively.

Setup

A single-screw foaming extrusion system was used in this study. The single extrusion system consists of

a 5 hp extruder drive with a speed-control gearbox, a 3/4" single-screw extruder (Brabender 05-25-000, South Hackensack, NJ), a mixing screw (Brabender 05-00-144, South Hackensack, NJ), two positive displacement devices (ISCO syringe pump 260D, Lincoln, NE), a gear pump (Zenith, PEP-II 1.2 cc/rev, Monroe, NC), a dissolution-enhancing device containing static mixers (Omega FMX8441S, Stamford, CT), two heat exchangers, and one of either medium, or high-pressure annular dies with various length and diameter (L/D) ratios. The general schematics of annular dies are shown in Figure 1. The extruder was used for plasticating the polymer resin. The gas-injection equipment, which was attached to the extruder at two separate points, was used for injecting the soluble amount of gases into the polymer melt. The gear pump controlled the polymer-melt flow-rate, which was independent of temperature and pressure changes. The dissolution-enhancing device ensured the homogeneity of the polymer/blowing agent solution. The heat exchangers provided uniform cooling for the polymer melt. Shaping and cell nucleation were accomplished in the annular die. Figure 2 shows a schematic of the overall setup.

Procedure

LDPE or LDPE/PS pellets, mixed with 2.0 wt % talc and a small amount of crosslinking agents, were first fed into the barrel through the hopper and were completely melted by the screw motion. The designated amounts of CO₂ (i.e., 8, 10, and 15 wt %) and/or *n*-butane (i.e., 0, 4, 6, and 8 wt %) were then injected into two separate points on the extrusion barrel by two positive displacement pumps. They were subsequently mixed with the polymer-melt stream in the barrel, and eventually dissolved in the melt. The single-phase polymer/gas solution went

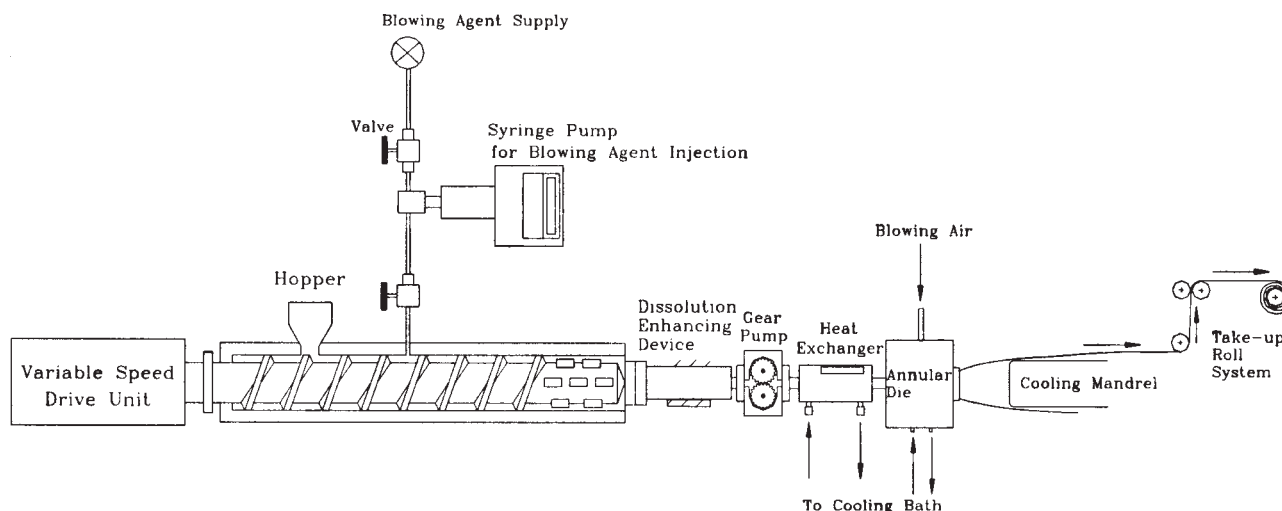


Figure 2 Schematic of a single extrusion system with an annular die.

TABLE I
Experimental Lists Using Medium and High-Pressure Annular Dies

Die type	LDPE (wt %)	PS (wt %)	Talc (wt %)	Crosslinking agent (wt %)	GMS (wt %)	CO ₂ (wt %)	Butane (wt %)	Die gap (mm)	Die length (mm)	Flow rate (g/min)	Thickness of sheet sample (mm)	
1	A	90	10	2	0.4	1.5	8	0	0.04	2.75	6	0.09–1.1
2	A	90	10	2	0.4	1.5	10	0	0.04	2.75	6	0.07–1.2
3	B	90	10	2	0.4	1.5	15	0	0.04	2.75	6	0.07–1.2
4	B	90	10	2	0.4	1.5	15	6	0.04	2.75	6	0.08–2.3
5	C	90	10	2	0.4	1.5	15	6	0.14	2.75	6	0.36–2.8
6	D	90	10	2	0.4	1.5	15	6	0.10	2.75	6	0.14–2.7
7	E	90	10	2	0.4	1.5	15	6	0.04	0.18	6	0.08–2.2
8	F	90	10	2	0.4	1.5	15	6	0.04	1.71	6	0.07–2.45

through the gear pump and was fed into the heat exchanger, where it was cooled to a preselected temperature. The cooled polymer/gas solution entered the die; foaming occurred at the die exit. All the

other materials and processing parameters including the screw speed, gear pump speed, barrel temperatures (i.e., 125–135°C) and blowing-agent content were fixed. Meanwhile, the synchronized melt and

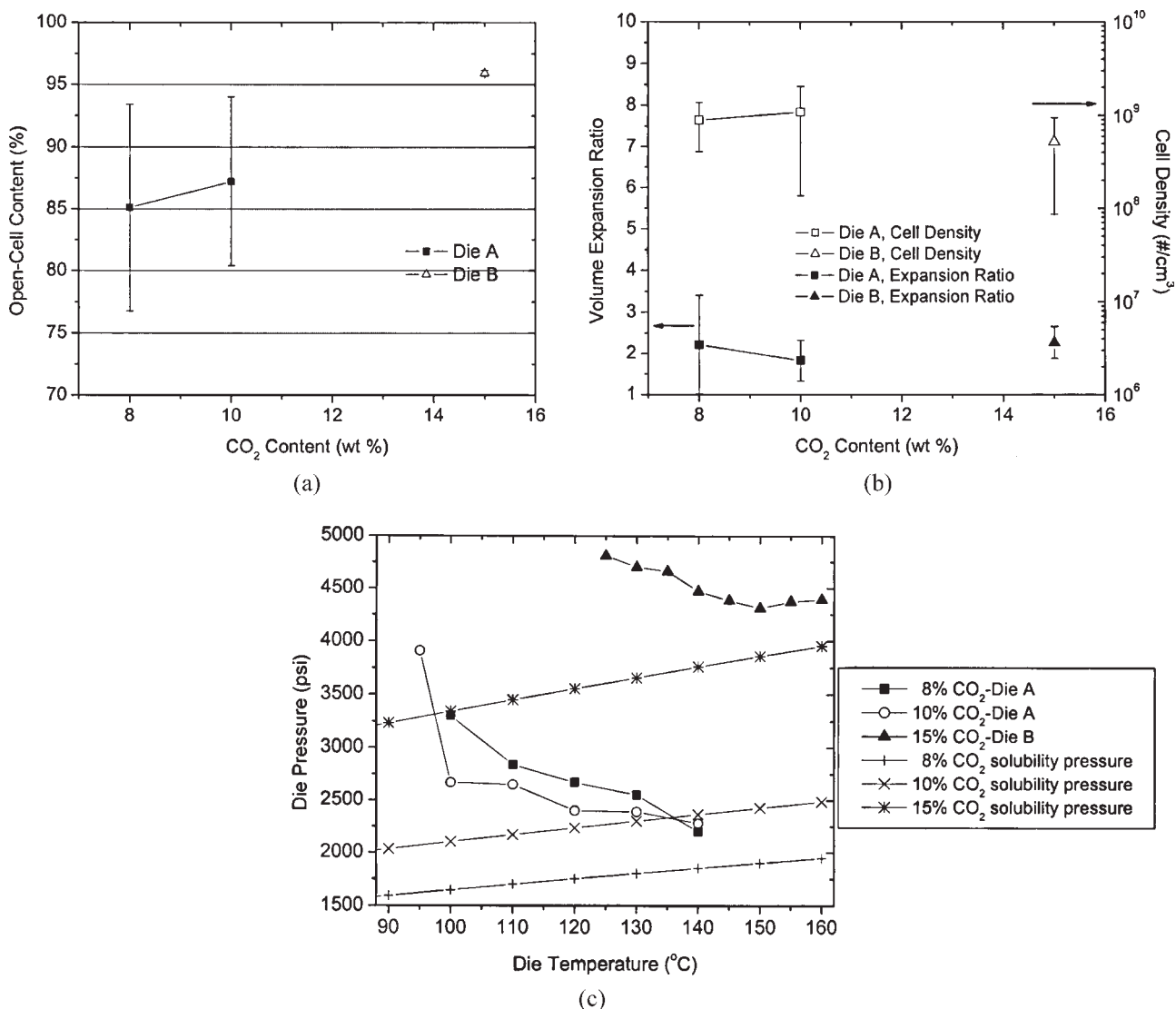


Figure 3 (a) Effect of CO₂ content on open-cell contents using a medium (Die A) and high-pressure (Die B) annular dies. (b) Effect of CO₂ content on cell densities and volume expansion ratios using a medium (Die A) and high-pressure (Die B) annular dies. (c) Effect of CO₂ content on die pressures using a medium (Die A) and high-pressure (Die B) annular dies.

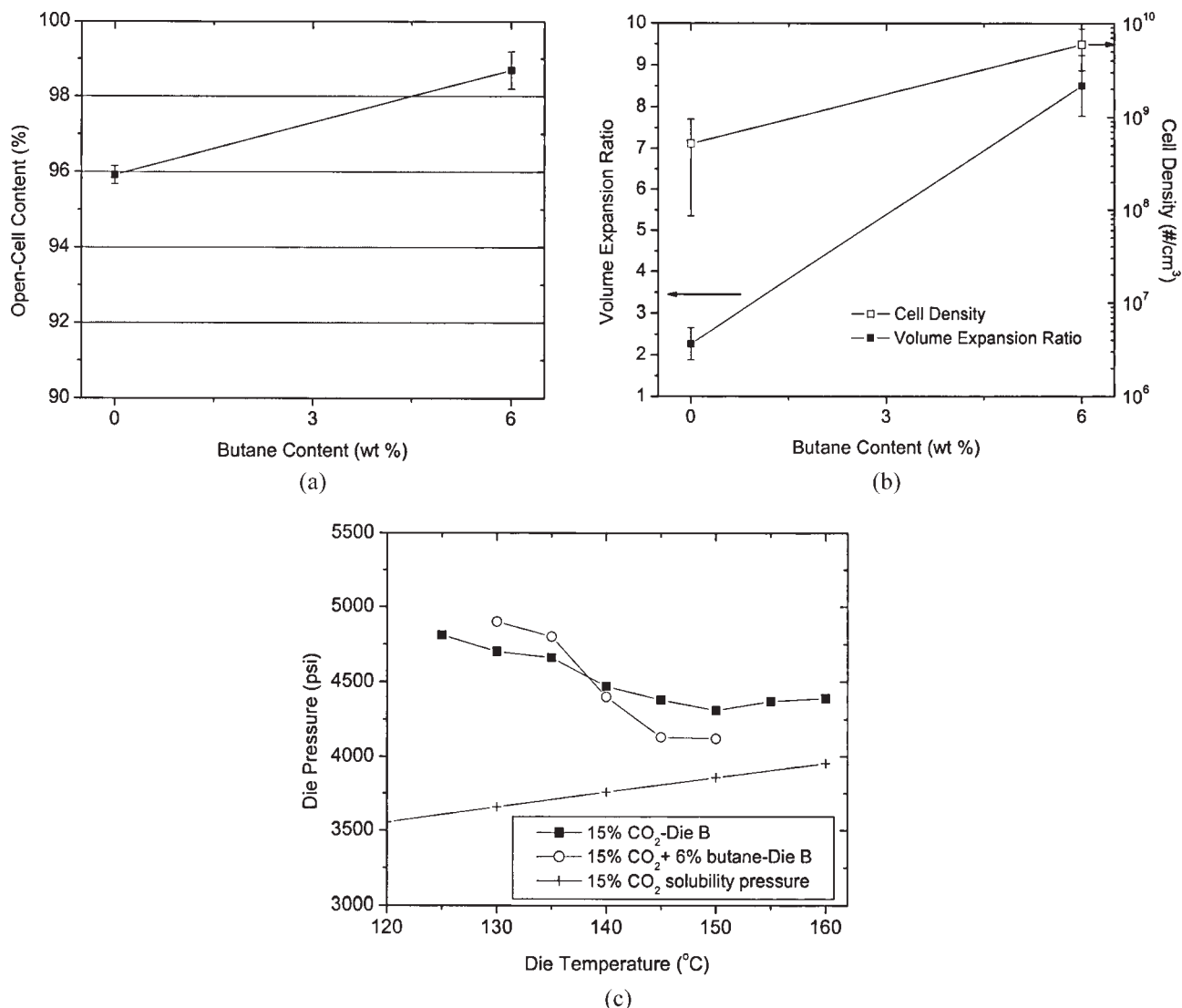


Figure 4 (a) Effect of butane content on open-cell contents using a high-pressure annular die (Die B). (b) Effect of butane content on cell densities and volume expansion ratios using a high-pressure annular die (Die B). (c) Effect of butane content on die pressures using a high-pressure annular die (Die B).

die temperatures were lowered step by step, and samples were randomly collected at each set temperature once the system reached the equilibrium state.

Depending on the cell sizes, the foam samples were characterized using an optical microscope (Wild Heerburgg, Switzerland) or a scanning electron microscope (SEM, Hitachi 510, New York, NY). The foam samples were dipped in liquid nitrogen and then fractured to expose the cellular morphology before the characterization of the foam structure. The open-cell content of the foam samples were measured using a gas pycnometer (Quantachrome, Boynton Beach, FL).

Open-cell content

The open-cell measurement is a porosity determination used to calculate the gas-accessible cellular volume of a material. The remaining volume is that

occupied by closed cells and cell walls. To obtain the open-cell content (OC), the geometric volume (V_{geo}) and the displacement volume (i.e., solid volume) (V_{disp}) of a foam sample should be determined. The geometric volume (V_{geo}) is determined by the measurements of the sample weight using a balance and a foam density based on the water displacement method described in ASTM D792-00. The displacement volume (V_{disp}) is determined by using a gas pycnometer. This device consists of two chambers, with known volumes, connected by a valve. One of the chambers, the calibrated sample chamber, can be accessed for the insertion of the test sample and is connected to a high-purity gas source. The pressure in the sample chamber is increased to a predetermined pressure and this value, P_1 , is noted. The valve between the two chambers is then opened and the second, lower pressure, P_2 , is again noted. The

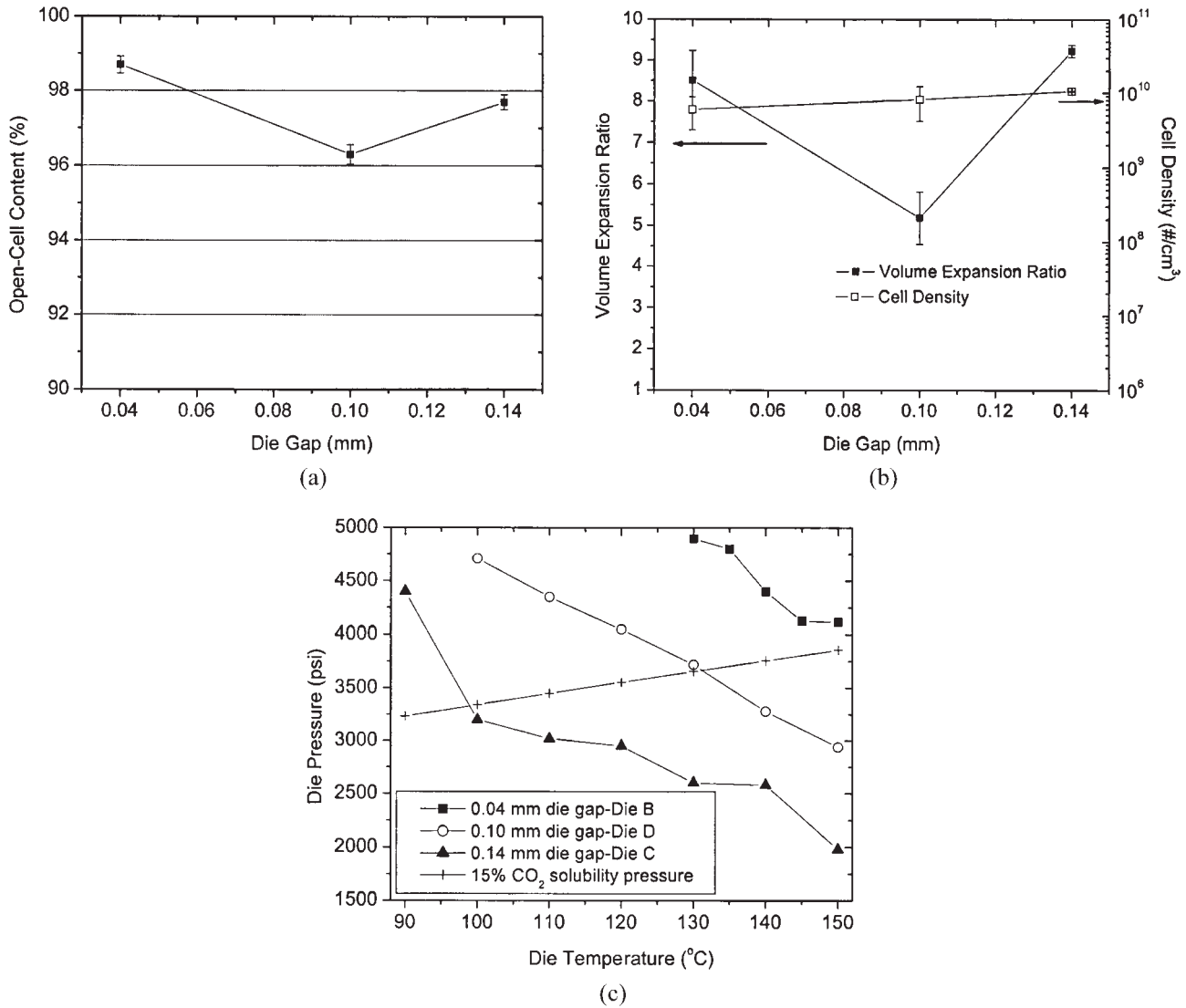


Figure 5 (a) Effect of die gap size on open-cell contents using high-pressure annular dies (Die B, C, and D). (b) Effect of die gap size on cell densities and volume expansion ratios using high-pressure annular dies (Die B, C, and D). (c) Effect of die gap size on die pressures using high-pressure annular dies (Die B, C, and D).

ratio of the pressure change, P_1/P_2 , is directly related to the volume of the sample chamber displaced by the specimen (i.e., due to the volume consisting of closed cells and cell walls). This displacement volume (V_{disp}) can be calculated as follows:

$$V_{\text{disp}} = V_{\text{chamber}} - \frac{V_{\text{exp}}}{\frac{P_1}{P_2} - 1} \quad (6)$$

where V_{chamber} is the volume of the sample chamber and V_{exp} is the volume of nonaccessible chamber. Finally, the open-cell content can be calculated as shown in eq. (5)

$$\text{OC} = \frac{V_{\text{geo}} - V_{\text{disp}}}{V_{\text{geo}}} \times 100 \quad (7)$$

The detailed open-cell content calculation procedure is described in ASTM D6226-98.

RESULTS AND DISCUSSION

To check the feasibility of producing open-cell microcellular sheet foams and to achieve desirable cell morphology, the die geometry should be designed to have a high pressure. Six different configurations of medium (i.e., Die A) and high pressure annular dies (i.e., Dies B, C, D, E, and F) were utilized in the experiments. Three different die lips were designed and manufactured in this laboratory²⁴; Die A is a divergent die [Fig. 1(a)], Die B, E, and F are straight dies [Fig. 1(b)], and Die C and D are convergent dies [Fig. 1(c)]. The die gap sizes and die land lengths of six medium and high pressure dies are listed in Table I. The materials used for these experiments were LDPE/PS (i.e., LDPE/PS = 90/10) blend with 2 wt % talc, 0.4 wt % crosslinking agent, and 1.5 wt % GMS. GMS has been used

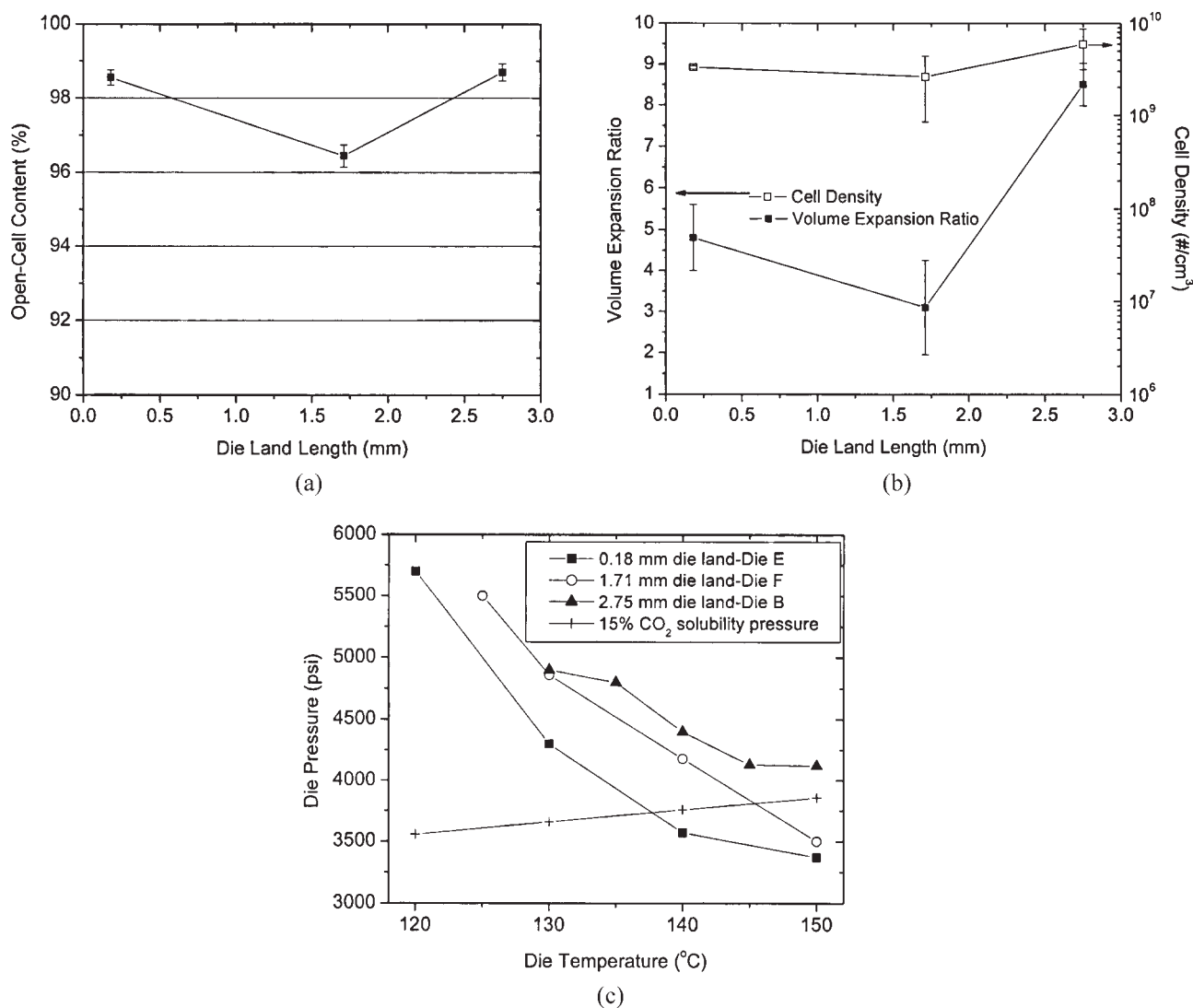


Figure 6 (a) Effect of die land length on open-cell contents using high-pressure annular dies (Die B, E, and F). (b) Effect of die land length on cell densities and volume expansion ratios using high-pressure annular dies (Die B, E, and F). (c) Effect of die land length on die pressures using high-pressure annular dies (Die B, E, and F).

as a butane retainer in the polymer melt to promote further volume expansion.^{25,26}

Effect of CO₂ contents

Die A was utilized for 8 and 10 wt % CO₂ experiments as shown in Figure 3(a–c). This medium-pressure annular die with an exit gap size of 0.04 mm and a land length of 2.75 mm built pressures from 2200 to 3310 psi (100 to 140°C) for the 8% CO₂ case, and from 2280 to 3910 psi (95 to 140°C) for the 10 wt % CO₂ case. According to the calculated solubility pressures shown in Figure 3(c), these pressures are all above the solubility pressure of CO₂ in LDPE melt, except for one data point in the 10 wt % CO₂ experiment at 140°C. This indicates that all the injected gas had been dissolved in the polymer melt

as a single phase and that the separation of gas and polymer melt was delayed to the cell nucleation stage right before the die exit (i.e., the end portion of the die land). Through this method, the final cell structure was more uniform and cell density increased.²⁴ The open-cell contents and cell densities increased as the CO₂ content increased from 8 to 10 wt %, but the volume expansion ratios were still below three folds, showing no increase with the CO₂ content. For the 15 wt % CO₂ experiment, a high-pressure annular die (i.e., Die B) was used successfully to dissolve the high gas content. The die pressure ranged from 4390 to 4810 psi, which is above the solubility pressure shown in Figure 3(c). Even though the die lip configuration had been changed to build a higher back pressure, the die exit gap and the die land length were kept the same as before

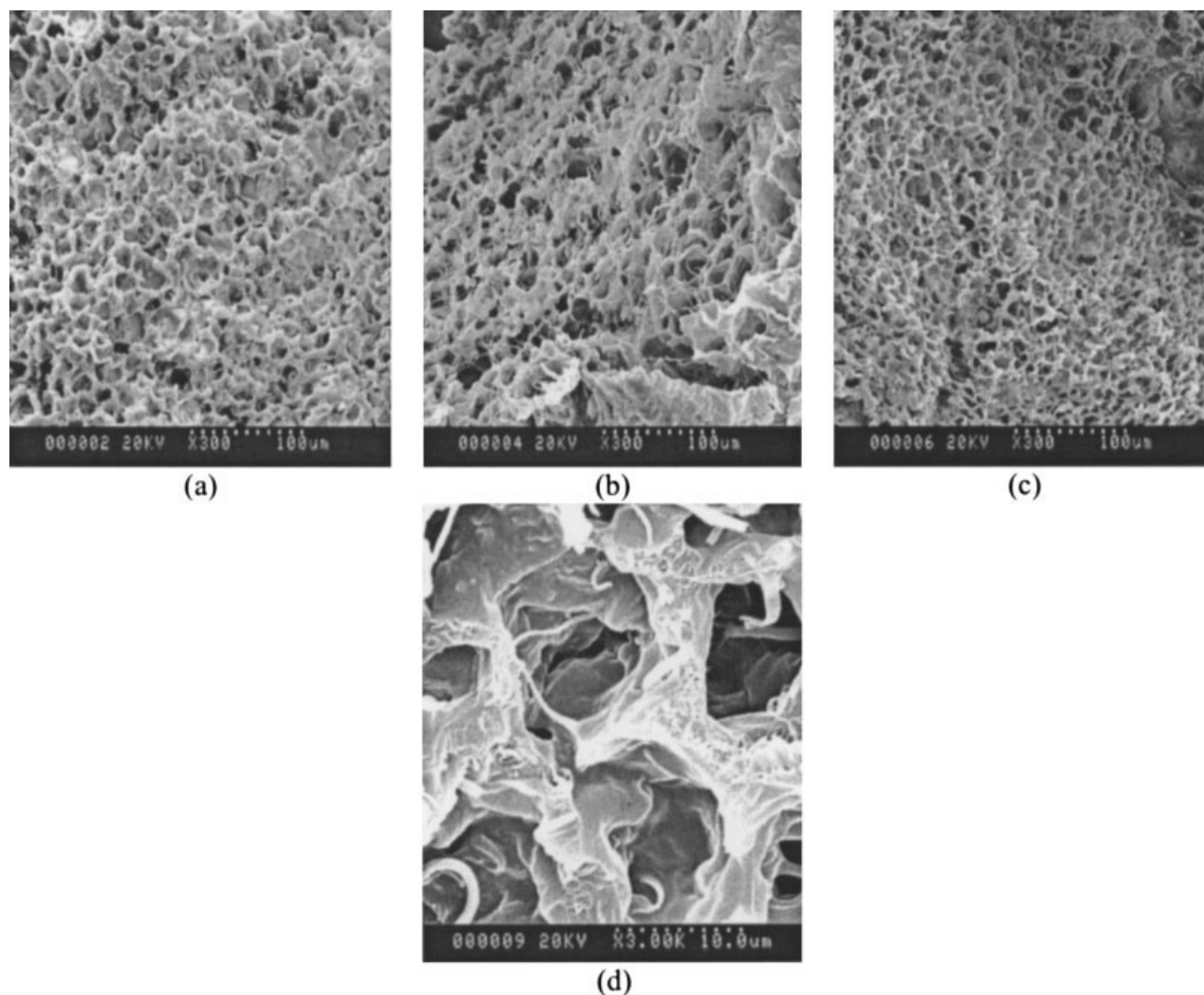


Figure 7 SEM Micrographs of sheet foam structure [(a): Die B, (b): Die C, (c): Die D, and (d) LDPE/PS blending structure].

(Table I). The average open-cell contents increased to almost 96% [Fig. 3(a)]. The cell densities were near 10^9 cells/cm³ and the volume expansion ratio was less than threefold.

Effect of added butane

Figure 4(a–c) show the open-cell contents, cell densities, volume expansion ratios, and die pressures of 15 wt % CO₂ experiments. One experiment was performed using only CO₂ as a blowing agent (i.e., 15 wt % CO₂) and the other was done with both CO₂ and butane as blowing agents (i.e., 15 wt % CO₂ and 6 wt % butane). The high-pressure annular die B was used, while keeping same die exit gap and land length for both experiments (Table I). Because of the plasticizing effect of butane in the polymer melt, the die pressure with butane addition decreased a little. The added butane increased the cell densities from 10^8 – 10^9 to 10^9 – 10^{10} cells/cm³ and the expansion ratio

from 2.3 to 8.5 fold. The open-cell contents were near 99% with the added butane.

Effect of die exit gap size

Figure 5(a–c) show the open-cell contents, cell densities, volume expansion ratios, and die pressures for experiments using three different high-pressure annular dies (i.e., Dies B, C, and D) with 15 wt % CO₂ and 6 wt % butane. All these dies had the same die land length of 2.75 mm, but had different die exit gap sizes as shown in Table I. As the exit gap size increased from 0.04 to 0.10, and to 0.14 mm, the overall die pressure decreased, revealing less back-pressure buildup. Both the open-cell contents and the volume expansion ratios of the experiment using the Die D (i.e., die exit gap = 0.10 mm) were the lowest, while the cell densities of three sets changed negligibly. The decreased open-cell content must have been caused by the decreased expansion ratio.

Effect of die land length

The open-cell contents, cell densities, volume expansion ratios, and die pressures for experiments using three different high-pressure annular dies (i.e., Dies B, E, and F) with 15 wt % CO₂ and 6 wt % butane are shown in Figures 6(a–c). All these dies had the same exit gap size of 0.04 mm, but had different die land lengths. As the die land length increased from 0.18 to 1.71, and to 2.75 mm, the die pressure increased as expected. The cell densities were in the range of 10⁹–10¹⁰ cells/cm³, showing insensitivity to the die land length. The open-cell contents and volume expansion ratio did not show any particular trend. Once the pressure is higher than the solubility pressure, an increased pressure does not affect the cell morphology.^{17,27}

The SEM micrographs of the foamed sheets at various processing conditions and die designs are presented in Figure 7.

CONCLUSIONS

In this paper, extrusion of microcellular open-cell sheet foams was successfully demonstrated using our previous strategies despite the high surface-to-volume ratios. These strategies include the following: (i) creation of a structural nonhomogeneity consisting of hard and soft regions with partial crosslinking, (ii) blending of a hard second-phase material (i.e., PS phase) into the LDPE matrix, (iii) plasticization of the soft region with a secondary blowing agent, (iv) decrease of the cell wall thickness by increasing the cell density, and (v) further decrease of the cell wall thickness by increasing the expansion ratio while maintaining softness of the cell walls. Microcellular (more than 10¹⁰ cells/cm³), open-cell (up to 99%) sheet foams have been successfully achieved with optimum processing strategies and conditions.

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