

# Preparation of Microcellular Poly(ethylene terephthalate) and Its Properties

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**ABSTRACT:** Engineering plastics poly(ethylene terephthalate) (PET) is relatively difficult to process microcellularly compared to general thermal plastics because of its low melting viscosity. A new method was developed to microcellularly process PET in this study with a general hydraulic press above PET's crystallization temperature and below its melting temperature within times of a few minutes. A processing window existed in which to prepare microcellular PET under certain foaming time, pressure, temperature, and foaming reagent content scope. The effects of foaming time, temperature, pressure, and foaming reagent content on the thermal, mechanical, and dynamic mechanical thermal properties of microcellular PET foam were investigated. Differential scanning calorimetry (DSC) analysis showed that

the transition temperature and crystallinity of microcellular PET had small changes with increasing foaming time. Under some processing conditions used in this study, the tensile strength and breaking extension of microcellular PET foam were both increased at the same time, indicating strengthening and toughening effects. The variation of storage modulus, loss modulus, and  $\tan \delta$  under dynamic mechanical thermal analysis was in accord with DSC analysis and mechanical measurements. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1956–1962, 2003

**Key words:** polyesters; mechanical properties; thermal properties; processing

## INTRODUCTION

Microcellular plastics are foamed thermoplastics materials with cell sizes generally between 5 and 100  $\mu\text{m}$ , according to Trexel Company, and depending on the materials and application, with a specific density reduction in the range of 5–98%.<sup>1–3</sup> Microcellular foam was invented at the Massachusetts Institute of Technology (MIT) under the direction of Professor Nam P. Suh.<sup>4</sup> The microcellular concept originated at MIT in response to an industry challenge to reduce the amount of material used in plastic productions without sacrificing toughness and other physical properties. The cell size in the microcellular is on the order of micrometers, which is below the critical flaw size of the polymer materials; therefore, it will absorb the energy and increase the strength as additives (fillers) do when force is applied to a microcellular foam. In many cases, microcellular plastics display high impact strengths, high toughnesses, high stiffness-to-weight ratios, high fatigue lives, high thermal stabilities, low dielectric constants, and low thermal conductivities.<sup>5–7</sup>

Until now, polystyrene, polyethylene, polypropylene, polyvinyl chloride, and others could be microcellularly processed via extrusion or injection molding. However, for engineering plastic poly(ethylene

terephthalate) (PET), microcellular processing was relatively difficult compared with the previously mentioned general thermal plastics because of PET's low melting viscosity when PET was processed via extrusion or injection molding. Baldwin et al.<sup>8</sup> prepared PET microcellular foam with the following method. They put some 2-cm<sup>2</sup> PET sheets in a pressure vessel charged with the saturation gas, 98% pure carbon dioxide, to a constant saturation pressure at room temperature; once the required saturation time was reached, the pressure vessel was discharged. Then, the PET specimens were foamed, unconstrained, in a glycerin bath for the allotted foaming time, and the specimens were quenched in a water bath to vitrify the microcellular structure. After this, Baldwin et al.<sup>8,9</sup> investigated the effects of four major processing variables (gas saturation time, gas saturation pressure, foaming time, and foaming temperature) on the microcell nucleation processes of amorphous and semicrystalline PET. They found that the cell density of PET increased with increasing gas saturation time and pressure, the foaming time had a relatively weak effect on the cell nucleation, and the foaming temperature near the glass transition influenced the density of the amorphous PET. The semicrystalline polymers had considerably higher cell densities than the amorphous polymers, which was attributed to the significant heterogeneous nucleation contributions in the amorphous crystalline interfacial regions. The amorphous foam experienced diffusional controlled cell growth,

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TABLE I  
The Average Size and Density of Microcellular PET

$T = 469 \text{ K}, P = 16 \text{ Mpa},$ and $AC = 12\%$			$T = 469 \text{ K}, P = 16 \text{ MPa},$ and $t = 3 \text{ min}$			$T = 469 \text{ K}, AC = 12\%,$ and $t = 3 \text{ min}$			$P = 16 \text{ MPa}, t = 3 \text{ min}$ $AC = 12\%$		
Time (min)	Cell size ( $\mu$ )	Density ( $\text{g}/\text{cm}^3$ )	Pressure (MPa)	Cell size ( $\mu$ )	Density ( $\text{g}/\text{cm}^3$ )	AC (%)	Cell size ( $\mu$ )	Density ( $\text{g}/\text{cm}^3$ )	Temperature (K)	Cell size ( $\mu$ )	Density ( $\text{g}/\text{cm}^3$ )
0	0	1.350	0	0	1.350	0	0	1.350	440	0	1.350
1	50	1.163	8	0	1.350	4	65	1.350	449	80	1.290
2	50	1.105	10	85	1.332	8	65	1.072	478	60	0.846
3	65	1.027	12	85	1.306	12	65	1.027	482	Vague cell structure	0.424
4	70	1.017	14	70	1.247	16	70	1.015			
5	70	0.814	16	65	1.027	20	70	0.974			

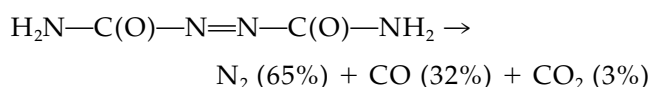
whereas the semicrystalline foams experienced viscoelastic controlled cell growth, and the longer the gas was allowed to diffuse into the cells, the larger the cell size was.

Although numerous aspects of microcellular processing have been studied over the last decade for general thermoplastics,<sup>10-15</sup> few studies exploring PET have been carried out, and very little work has been reported on the whole-property investigation of microcellular PET with a general hydraulic press to microcellularly process PET. The method that Baldwin used to microcellularly process PET<sup>8</sup> needed a longer processing time, usually more than 10 h, and a high-pressure vessel, whereas the method used in our study was a newly developed method for microcellularly processing PET with a general hydraulic press above PET's crystalline temperature and below its melting temperature ( $T_m$ ) within times of a few minutes. Thermal, mechanical, and dynamic mechanical thermal properties of microcellular PET under the different foaming times, pressures, temperatures, and foaming reagent contents were investigated.

## EXPERIMENTAL

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

The microcellular processing experiments were carried out as follows. First, LDPE, AC, and DCP were mixed in a two-roll mill as a gas source for PET foaming. Next, the PET sheets and the mixed LDPE together were placed in a 250 × 250 × 2 mm mold and were loaded in a hydraulic hot press under set experimental conditions. Under heating, the foaming reagent AC decomposes to produce gas:



Once the required foaming time and other conditions were reached, the mold was taken out of the hot press; we then unloaded the mold, quenched it at room temperature; and removed the microcellular PET foam from the mold. Thus, the microcellular PET samples were ready for property characterization. The average sizes and densities of the microcellular PETs are listed in Table I.

Tensile testing was carried out in a Shimadzu AG-A all-purpose testing machine (Japan) equipped with a computer, according to the ASTM D 638 standard method. The result was the average of five specimens for each sample. Differential scanning calorimetry (DSC) analysis was performed in a DuPont 2910 differential scanning calorimeter (Spring Grove, IL) at a scanning rate of 10°C/min under a nitrogen flow environment. To delete the heat history effect during microcellular processing, the second heating scan was carried out at the same scanning rate and taken as the DSC analysis results. The crystallinity of microcellular PET was calculated by measurement of the specific heat required for melting ( $\Delta H_m$ ) through integration of the melting peak and by division of this value by the heat of fusion of pure crystalline PET, that is, 125.6 J/g.<sup>16</sup> 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 a tension mode. The average size of microcellular PET was calculated on the basis of photos from a Leitz optical microscope (Germany) with a 100× camera lens. We obtained the density of microcellular PET by weighing a sample with known volume.

## RESULTS AND DISCUSSION

### DSC analysis for microcellular PET

Throughout the heating scan, the thermal analysis data of microcellular PET at different foaming times

TABLE II  
DSC Data of Microcellular PET (198°C, 16 MPa, 12% AC)

Foaming time (min)	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_m$ (g/J)	Crystallinity (%)
0	78.27	135.07	251.24	43.13	34.34
2	76.82	130.83	251.52	47.50	37.82
3	76.62	130.11	251.72	48.71	38.78
4	75.47	129.52	251.82	48.53	38.64
5	74.84	125.75	257.16	51.24	40.88

are listed in Table II. As shown, the glass-transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ), and  $T_m$  of microcellular PET decreased with increasing foaming time, suggesting that the microcellular cell played the role of plastification and led to  $T_g$ ,  $T_c$ , and  $T_m$  moving toward lower temperatures. This resembles Handa et al.'s<sup>17</sup> article, in which they indicated that high-pressure CO<sub>2</sub>, particularly supercritical CO<sub>2</sub> fluid, lowered  $T_g$  by up to 20–30°C or more. Although the gas produced by AC was a mixture of N<sub>2</sub>, CO<sub>2</sub>, and CO, it still had the plastification effect on PET: the longer foaming time was, the more gas diffused into the PET sample and the lower was  $T_g$ ,  $T_c$ , and  $T_m$ . However, the crystallinity of microcellular PET increased with increasing foaming time. This could also be explained as the microcellular plastification effect, which provided the PET chain with more moveability and made it easier to pack into crystal lattices, which led to an increase in crystallinity. Although the PET used in our experiment was a semicrystalline polymer, the crystallinity had no large effect on the microcellular PET properties, as the variation in crystallinity was small after microcellular processing.

#### Effect of foaming time on the mechanical properties

Figure 1 shows the effect of foaming time on the mechanical properties of microcellular PET. It was

apparent that the tensile strength and the breaking extension both increased with increasing foaming time when foaming time was less than 2 min and reached maximum at 2 min foaming time, showing strengthening and toughening effects at the same time. This means that by simply introducing the microcell into the PET sheet, the microcell toughened PET as a rubber does and strengthened PET as an inorganic filler does. When the foaming time was more than 2 min, the tensile strength and breaking extension of microcellular PET started to decrease. This was because the longer the gas was allowed to diffuse into the cells, the larger the cell size was, which is further proved in Table I. Therefore, the larger cell size (larger to some extent) decreased the tensile strength and breaking extension. In contrast to Baldwin et al.,<sup>8,9</sup> who found that the foaming time had a relatively weak influence on cell nucleation and cell growth for the amorphous and semicrystalline polyester because the gas in their samples was constant (meaning there was no effect on the mechanical properties), the foaming time in our experiment did have effects on the mechanical properties. Similar strong cell-size dependence on foaming time was reported for styrenic resins.<sup>1,18</sup> When the foaming time was longer than 5 min, both tensile strength and breaking extension decreased more and kept decreasing, so the foaming time was better when

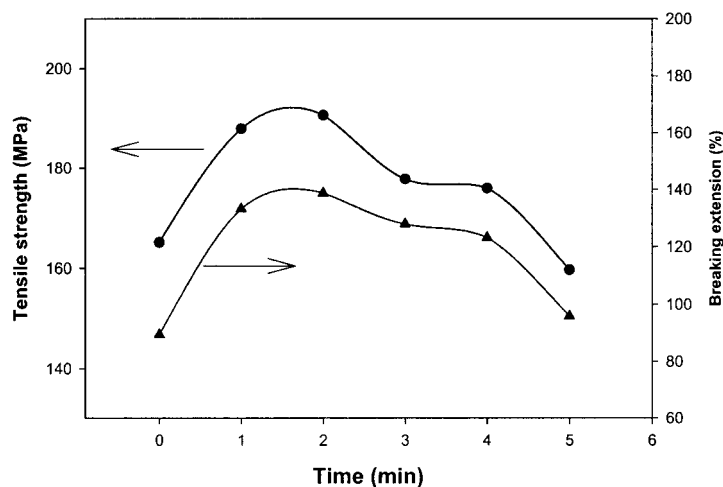


Figure 1 Effect of foam time on tensile strength and breaking extension ( $T = 469$  K,  $P = 16.0$  MPa, AC = 12%).

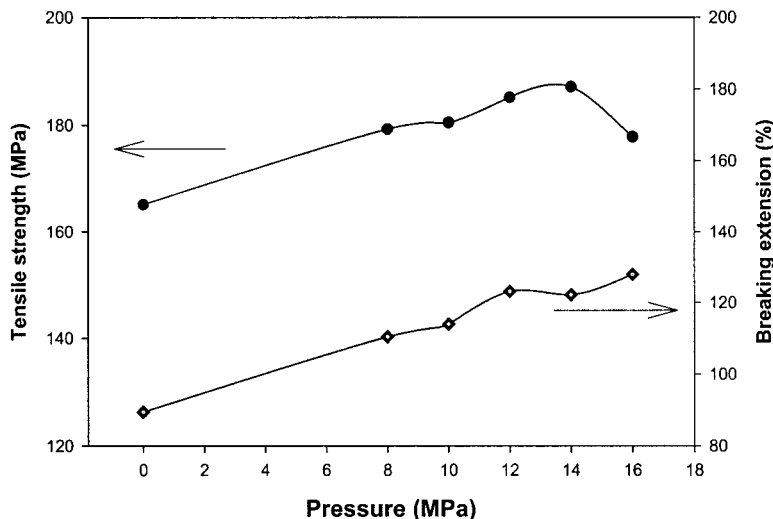


Figure 2 Effect of foaming pressure on tensile strength and breaking extension ( $T = 469$  K,  $AC = 12\%$ ,  $t = 3$  min).

it was shorter than 2 min under our experimental conditions.

**Effect of foaming pressure on the mechanical properties**

Figure 2 shows the effect of foaming pressure on the mechanical properties of microcellular PET. The tensile strength first increased and then decreased with increasing foaming pressure, whereas the breaking extension increased all the way. According to the Sanchez-Lacombe<sup>19,20</sup> equation of state and experimental data from Sato et al.,<sup>21,22</sup> the solubility of nitrogen in polymers increases linearly with pressure up to about 25 MPa. Therefore, increasing foaming pressure actually increased the foaming gas concentration inside of PET, and the net result was a cell-size decrease (Table I) and a cell density increase.<sup>8</sup> The larger the cell density was, the larger the breaking extension

was. This explains why the breaking extension increased with increasing foaming pressure under our foaming pressure scope. From Table I, we know that when the foaming pressure was smaller than 10 MPa, the PET sample showed no detectable cell structure. This means that the foaming pressure should exceed 10 MPa if one hopes to obtain microcellular PET foam.

**Effect of foaming temperature on the mechanical properties**

The effect of foaming temperature on the mechanical properties occurred in the temperature range between 449 and 510 K, as shown in Figure 3. When the foaming temperature was lower than 449 K, there was no detectable cell structure. One of the reasons was that the foaming reagent AC could not decompose completely at lower temperature; hence, there was probably not enough gas necessary to form microcellular

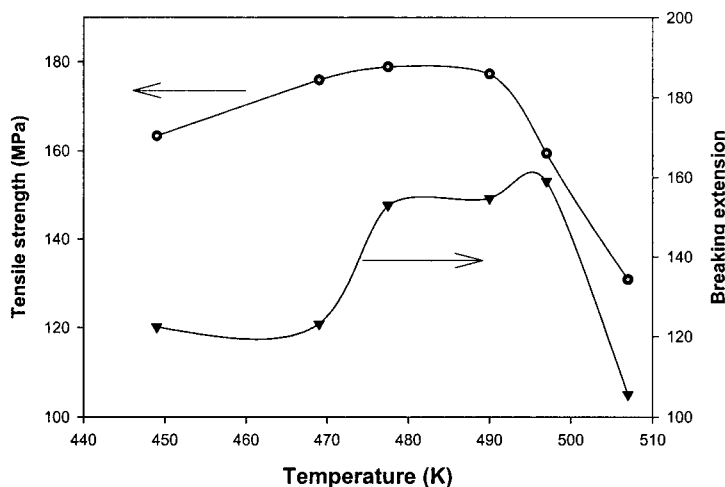


Figure 3 Effect of temperature on tensile strength and breaking extension ( $P = 16.0$  MPa,  $AC = 12\%$ ,  $t = 3$  min).

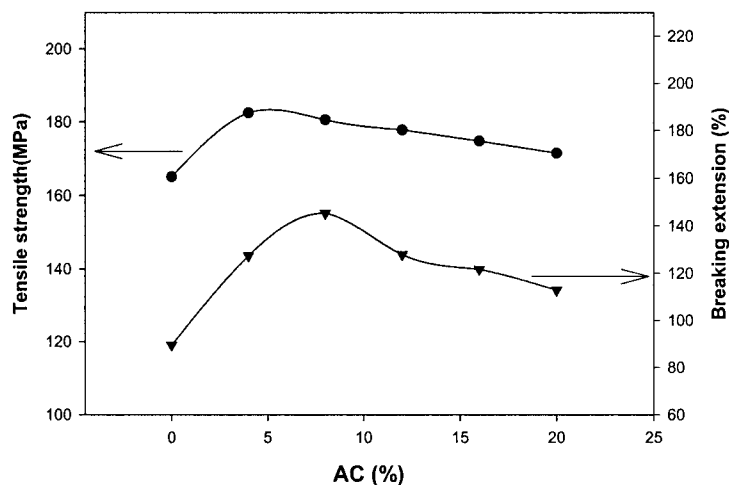


Figure 4 Effect of AC content on tensile strength and breaking extension ( $P = 16.0$  MPa,  $T = 469$  K,  $t = 3$  min).

PET. Another reason was that at lower foaming temperatures, the PET matrix stiffness may have been sufficiently large enough to prevent nucleated cells from growing to detectable size, even though the allotted foaming time should have allowed all of the available gas to diffuse into the cells. When the foaming temperature was higher than 510 K, a vague cell structure was observed under optical microscopy, suggesting that there was not enough matrix stiffness to fix the grown microcells and that some of microcells may have collapsed and melted. From Figure 3, it is clear that the tensile strength and breaking extension reached a high value around 475 K; that is, at this temperature, the size of microcell was reasonable, and its density was high, thus enhancing the mechanical properties of microcellular PET. A larger cell size and an ill-formed microcell structure decreased both the tensile strength and breaking extension (Fig. 3) when the foaming temperature was higher than 495 K. Therefore, a suitable foaming temperature for the microcellular processing of PET is around 475 K according to our experimental results.

#### Effect of foaming reagent content on the mechanical properties

To understand how much foaming reagent was needed to prepare microcellular PET and its effect on the mechanical properties of PET, we carried out our experiment with several foaming reagent contents at certain foaming temperatures, pressures, and times, determined from the experiments. The effect of foaming reagent content on microcellular PET is shown in Figure 4. The foaming reagent content had a relatively small effect on the tensile strength and a large effect on the breaking extension according to Figure 4. Similar to the effect of foaming time and temperature on the mechanical properties, the tensile strength and break-

ing extension reached higher values at certain foaming reagent contents. In this study, this was in the range 4–12%. Actually, when the foaming reagent content was 4%, there were only a few cells formed in the PET matrix; here, the breaking extension was not at its maximum value. However, when the foaming reagent content was more than 12%, the microcell size increased (Table I), which led to a decrease in tensile strength and breaking extension. To ensure there was enough gas available to form PET microcells, we actually selected the foaming reagent content at a level of 12% when we carried out most of our experiments to prepare microcellular PET samples.

#### Effect of foam density and cell size on the mechanical properties

From Table I, one can see that the foaming time, foaming pressure, foaming reagent content, and tem-

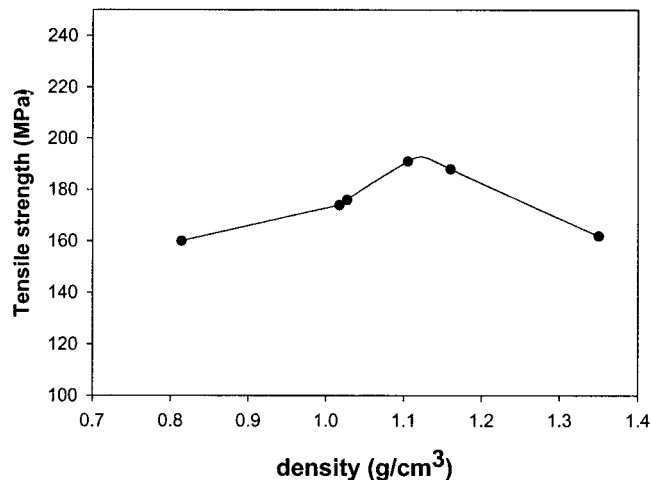


Figure 5 Effect of foam density on mechanical properties ( $T = 469$  K,  $P = 16.0$  MPa, AC = 12%).

**TABLE III**  
DMTA Data of Microcellular PET  
(198°C, 16 MPa, 12% AC)

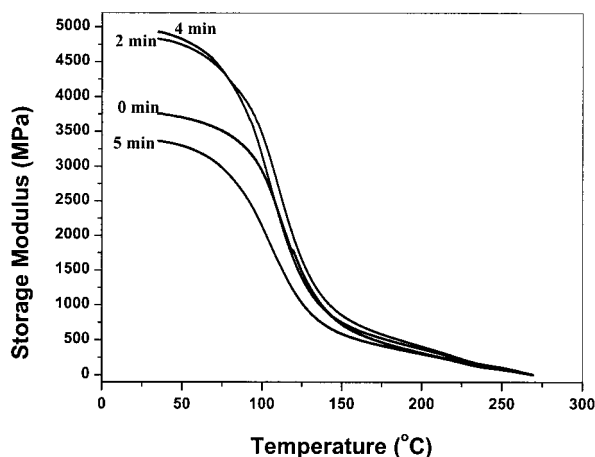
	Foaming time (min)			
	0	2	4	5
Tan $\delta$ (°C)	127.11	123.95	120.67	119.54

perature all reduced the foam density because increasing foaming time, foaming pressure, foaming reagent content, and foaming temperature actually increased the foaming degree. Figure 5 shows the effect of the density on the mechanical properties of microcellular PET foam within a foaming time of 5 min. The effect of the foam density on the tensile strength and breaking extension was similar to that of the foaming time on the mechanical properties, as shown in Figure 1. Similar effect of foam density on the tensile strength and breaking extension under different foaming pressure, foaming reagent content, and foaming temperature was observed.

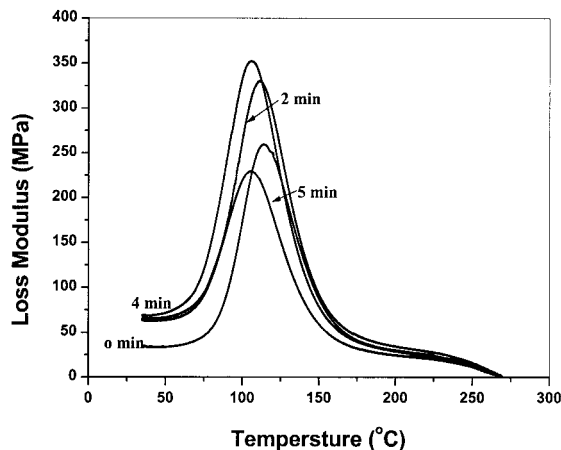
The effect of cell size, which represented the cell structure, on the mechanical properties can be seen indirectly from Figures 1–4 because the variation tendency was the same as the foaming time, pressure, reagent content, and temperature on the mechanical properties. The smaller the cell size was, the higher were the tensile strength and breaking extension.

**DMTA**

To confirm the DSC analysis and mechanical measurement results, DMTA was carried out to investigate the effect of foaming time on dynamic mechanical thermal behavior. From Table III, one can see that tan  $\delta$  decreased with increasing foaming time, a result of the microcellular plastification effect. We have no doubt that the variation of tan  $\delta$  was quite in accord with the  $T_g$  variation from the DSC analysis.



**Figure 6** Effect of foaming time on the storage modulus.



**Figure 7** Effect of foaming time on the loss modulus.

The effect of foaming time on storage and loss modulus is shown in Figures 6 and 7. One can clearly see that the storage and loss modulus increased when the foaming time was less than 4 min and decreased when the foaming time was longer than 4 min; such a variation tendency was similarly to the effect of foaming time on the mechanical properties, although the foaming time related to maximum strength shifted to longer foaming time.

Further research on the effect of the cell density on the mechanical properties will be carried out in near future.

**CONCLUSIONS**

A new method was developed to microcellularly process a PET sheet with a general hydraulic press above PET's  $T_c$  and below its  $T_m$  within the time of a few minutes. This method is simple, easy to perform, and economical. The effects of the processing parameters, foaming time, pressure, temperature, and foaming reagent content, on the properties of microcellular PET were investigated. There was a processing window in which to prepare microcellular PET, that is, at a foaming time between 1 and 5 min, at a foaming pressure larger than 8 MPa, at a foaming temperature between 450 and 500 K, and at a foaming reagent content between 6 and 12% under our experimental conditions. Within the microcellular PET processing window, the tensile strength and breaking extension both increased at some experimental conditions, showing strengthening and toughening effects at the same time.  $T_g$ ,  $T_c$ , and  $T_m$  of microcellular PET decreased, and its crystallinity increased with increasing foaming time. DMTA results were in good accord with DSC analysis and mechanical measurements.

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