

## Effect of Polytetrafluoroethylene on the Foaming Behaviors of Linear Polypropylene in Continuous Extrusion

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**ABSTRACT:** Linear polypropylene (PP) foams, blown in the continuous extrusion process using supercritical CO<sub>2</sub> as the blowing agent, exhibited poor cell morphology and narrow foaming window, because of their low melt strength. In this study, polytetrafluoroethylene (PTFE) was blended with PP resin with the aim of improving the foaming behavior of PP. It was found that the PTFE particles were deformed into fine fibers under shear or extensional flows during the extrusion process, which significantly increased the melt strength of PP from 0.005 N to 0.03 N (PP/PTFE with PTFE content of 4.0 wt %) at 230°C. The experimental results indicated that the presence of PTFE improved the cell morphology of PP foams and broadened the foaming window of PP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2253–2260, 2013

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### INTRODUCTION

Polypropylene (PP) has many desirable and beneficial properties such as high tensile modulus, high melting point, excellent chemical resistance, and easy recycling.<sup>1</sup> These prominent properties have made PP foams a substitute for other thermoplastic foams, such as polystyrene and polyethylene in industrial applications.<sup>2,3</sup> However, it is difficult to produce linear PP foams with a high expansion ratio because of their weak melt strength and melt elasticity. The formed cell walls of linear PP foams are not strong enough to endure any extensional force during bubble growth, and thus the bubbles tend to coalesce during foam processing.<sup>3,4</sup> Consequently, foamed PP products usually have a high open-cell content and nonuniform cell distribution<sup>5,6</sup> and thus are not good for practical applications. Meanwhile, the processing window of PP foaming is quite narrow.

Many methods have been used to increase the melt strength of PP resins with the aim to improve its foaming behavior, such as chemical or radiation crosslinking,<sup>7–9</sup> long chain branching,<sup>10,11</sup> and compounding.<sup>12–14</sup> Park and Cheung<sup>15</sup> found that high melt strength PP (HMSPP) presented excellent foaming behavior, that is, high foam expansion ratio, broad foaming window, and excellent cell morphology. Because of the price considerations, however, the actual usage of HMSPP in foaming area is limited. By introducing a small amount of crosslinked structure in PP chain, Zhai et al.<sup>6</sup> observed that the synthesized PP resins

possessed very broad foaming window, tiny cell size, and high cell density. Recently, the addition of nanoclays was verified by researchers as an efficient approach to significantly improve the foaming behavior of linear PP,<sup>14,16,17</sup> where various nanoclays such as montmorillonite and bentonite were used. The mechanism was attributed to the enhanced cell nucleation by nanoclays and the suppressed cell coalescence by the increased melt extensional viscosity.<sup>17–19</sup>

In this study, we present a new method to improve the foaming behavior of linear PP by adding a small amount of polytetrafluoroethylene (PTFE). It is reported that PTFE possesses many outstanding properties such as high melting point, marked solvent resistance, low yield stress, and low surface tension.<sup>20</sup> Furthermore, PTFE particles are found to be fibrillated easily under shear force even in solid state, which facilitates the increase in melt strength of polymer melts.<sup>21</sup> Using a continuous extrusion method, PP and PP/PTFE blends were foamed with 5 wt % CO<sub>2</sub> as a physical blowing agent. The expansion ratio and cell morphology of the prepared PP foams were investigated in relation to the die temperature as well as PTFE content. A suitable foaming window was obtained based on the foaming results of PP.

### EXPERIMENTAL

#### Materials

Linear commercial homopolymer PP (LPP), T30S with MFI of 2.8 g/10 min at 230°C /2.16 kg, was provided by Sinopec

Zhenhai Refining & Chemical Company (China). PTFE particle was supplied by Mitsubishi Rayon (Metablen A3000). The physical blowing agent, CO<sub>2</sub> (99% purity), was obtained from Ningbo Wanli Gas Corporation.

### Sample Preparation

The linear PP and PTFE were vacuum-dried at 80°C for 8 h before use. LPP/PTFE premix was prepared by dry-blending the LPP with the PTFE in a bag. The premix was subsequently melt extruded using the tandem single screw extruder at a temperature of 190°C. The PTFE content prepared for the master batch was 4 wt %. A series of blends with PTFE contents of 1, 2, and 4 wt % were obtained by diluting the master batch with LPP; they were coded as LPP/PTFE1.0, LPP/PTFE2.0, and LPP/PTFE4.0, respectively. The characteristics of the PTFE, LPP, and LPP/PTFE blends are shown in Table I.

### Extrusion Foaming

Figure 1 shows a schematic of the tandem extrusion system used in this study. It consists of a first extruder with screw diameter of 45 mm driven by a 25 hp drive motor (SIMO, Z4-132-3), and a second extruder with screw diameter of 65 mm driven by a 40 hp drive motor (SIMO, Z4-160-31), a ISCO syringe pump for injecting the blowing agent into the polymer melt, a heat exchanger that contains homogenizing static mixers, a filamentary die with a length of 40 mm and diameter of 3 mm, and a gear pump (Zenith, PEP-II). The first extruder is used for plasticizing the polymer resin and the second extruder provides mixing and cooling to completely dissolve the CO<sub>2</sub> in the polymer melt. During the extrusion process, the CO<sub>2</sub> content injected into the barrel, which was accurately adjusted and regulated by controlling both the gas flow rate of the syringe pump and the material feed rate, was fixed to 5 wt % throughout the experiment. When the uniformly mixed polymer/gas solution passed through the filament die, it would cause a sudden decrease in gas solubility in the polymer because of the rapid pressure drop. Consequently, numbers of bubbles were nucleated in the polymer and the foam structure was created with the bubbles growing. The foamed samples at different foaming temperatures were collected for observation of the cell morphology and measurement of the foam density.

### Characterizations

The melting point and crystallization temperature of the PTFE, LPP, and LPP/PTFE blends were determined by using an apparatus (Mettler Toledo DSC/TGA) calibrated with indium. Meas-

urements were performed with  $7.0 \pm 1.0$  mg samples in a dry nitrogen environment. The DSC heating and cooling rates of the DSC tests were fixed at 10°C/min over a temperature range from 50 to 200°C. To eliminate the effect of thermal history of the samples, only DSC data obtained from second heating were used.

The melt tension was evaluated at 230°C by a capillary rheometer (Rosand Corp. RH7-2) equipped with a balance and a haul-off device. The length and diameter of the capillary die were 16 mm and 1 mm, respectively. The extrusion speed was 1.6 cm<sup>3</sup>/min. The haul-off speed was 6 m/min and the melt tension was measured with balance.

The morphologies of LPP/PTFE blends were examined by a scanning electron microscope (SEM; Hitachi TM-1000) before foaming. Moreover, the dispersion state of PTFE in a molten PP was observed by an Olympus H-601 polarized optical microscopy (POM) equipped with an automated hot-stage at 200°C under crossed polars.

The foamed samples obtained at different temperatures were used for SEM (Hitachi TM-1000) observation and cell density measurement. All the foamed samples were freeze-fractured in liquid nitrogen and sputter-coated with gold before observation. The mass densities of the samples before ( $\rho$ ) and after ( $\rho_f$ ) foaming were measured by the water displacement method based on ISO 1183-1987. Cell size and density were determined from the SEM micrographs. The cell diameter was on average at least a size of 100 cells on the SEM micrographs. The cell density ( $N_0$ ), the number of cells per cubic centimeter of unfoamed polymer, was determined using eq. (1) as follows:

$$N_0 = \left[ \frac{nM^2}{A} \right]^{3/2} \phi \quad (1)$$

where  $n$  is the number of cells in the SEM micrograph,  $M$  is the magnification factor,  $A$  is the area of the micrograph (in cm<sup>2</sup>), and  $\phi$  is the volume expansion ratio of the polymer foam, which can be calculated using eq. (2) as follows:

$$\phi = \frac{\rho}{\rho_f} \quad (2)$$

## RESULTS AND DISCUSSION

### Phase Morphology and Melt Strength of LPP/PTFE Blends

LPP/PTFE blends with various PTFE contents were melt-blended by an extrusion system. Figure 2 shows SEM micrographs of the resultant LPP/PTFE blends. Compared to the pure LPP, it is interesting to find that some long fibers with diameter of 300–500 nm were present in LPP/PTFE blend matrix. As the PTFE content increased, the number of the fibers increased and the interlacement among them became notable. POM observation was carried out at 200°C to further detect the formation of PTFE fiber during melt compounding, where LPP/PTFE films were used and LPP resin was in the melt state. As indicated in Figure 3a, nothing was observed in LPP melt. In the case of LPP/PTFE blends, however, some fibers with a length of 400–800  $\mu$ m were found, and an increase in PTFE content increased

**Table I.** Characteristics of LPP/PTFE Blends

Sample	PTFE content (wt %)	Melting point (°C)	Crystallization temperature (°C)	Melt tension <sup>a</sup> (N)
PTFE	100	342	–	–
LPP	0	163	112	0.005 ± 0.001
LPP/PTFE1.0	1.0	164	117	0.01 ± 0.001
LPP/PTFE2.0	2.0	166	122	0.02 ± 0.002
LPP/PTFE4.0	4.0	166	123	0.03 ± 0.003

<sup>a</sup>Measured at 230°C.

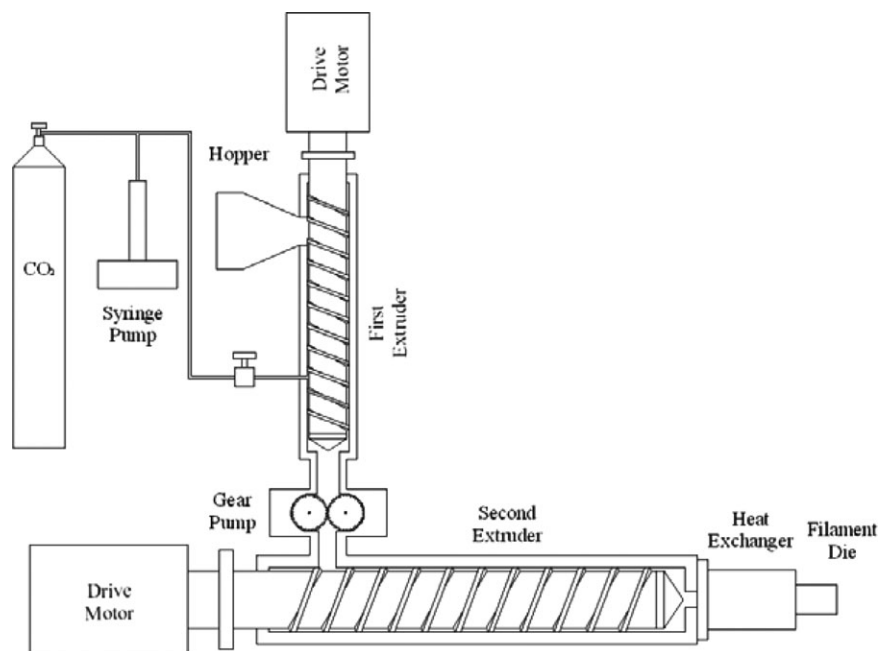


Figure 1. Experimental setup of tandem extrusion system.

the number of fiber. Both SEM and POM micrographs demonstrated that the PTFE particle deformed into fibrous shape, possibly resulting from the applied shear and extensional flow of extruder on the polymer melt.<sup>22–24</sup>

It is noted that the melting point of PTFE, that is, 342°C, was much higher than that of LPP (Table I), which means that

PTFE particle was in solid state during the blending. It has been known that PTFE has two transition temperatures at approximately 19°C and 30°C. Below 19°C, the shearing force causes PTFE particles to slide past each other, retaining their identity.<sup>25,26</sup> Above 19°C, PTFE exhibits a first-order transition from triclinic to hexagonal crystalline form. The cohesive force

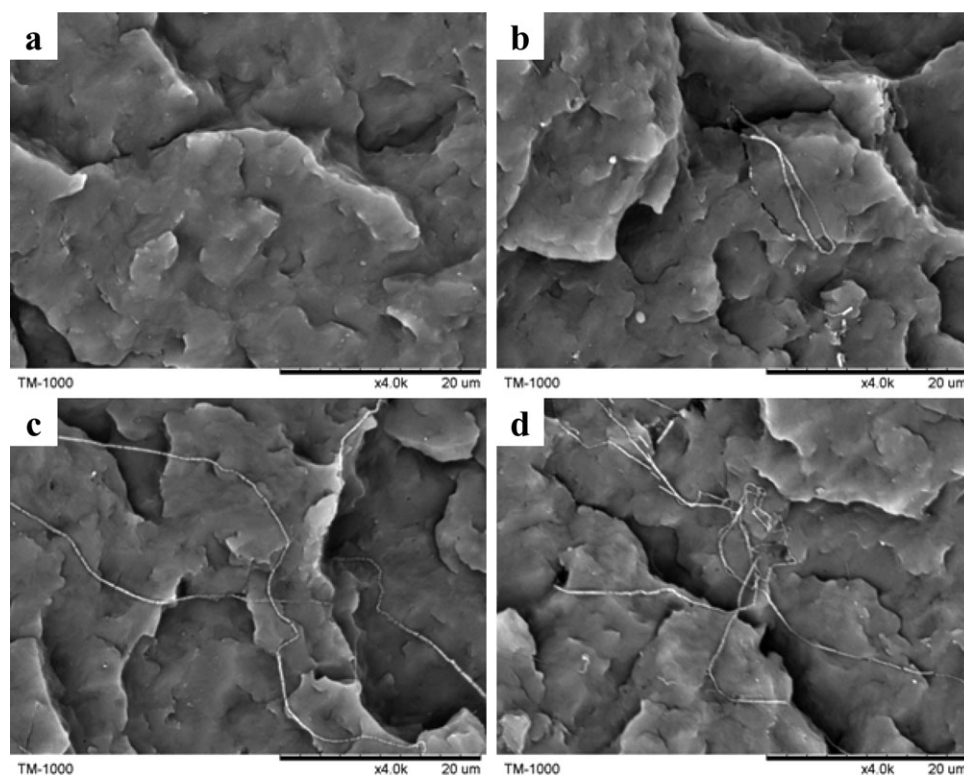
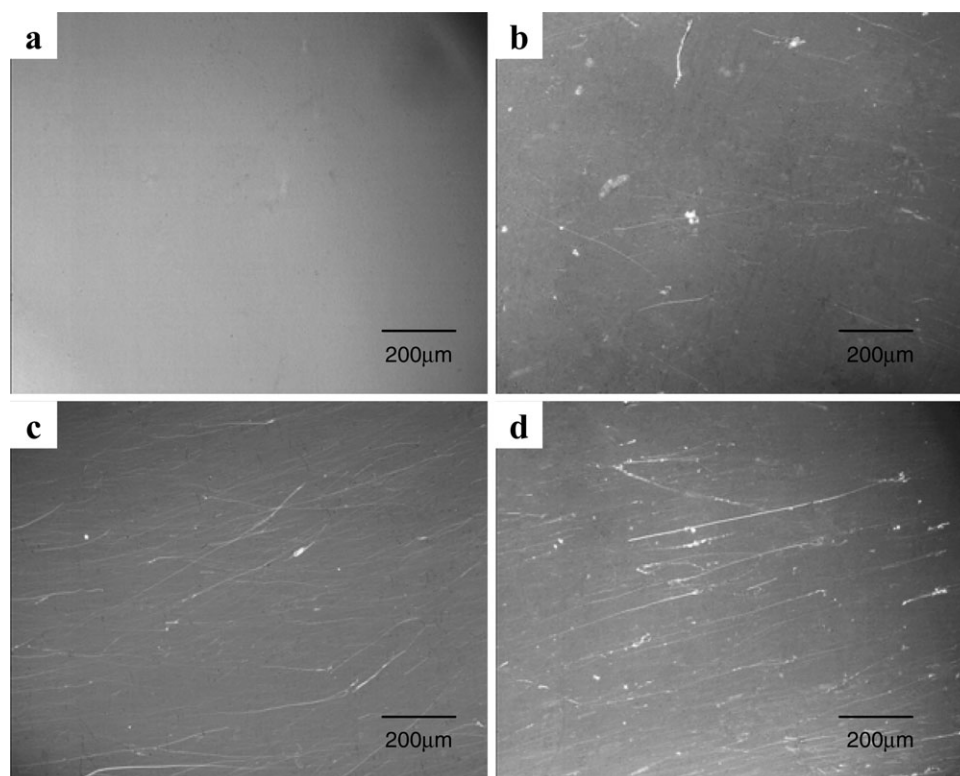


Figure 2. SEM images of (a) LPP; (b) LPP/PTFE1.0; (c) LPP/PTFE2.0; and (d) LPP/PTFE4.0.



**Figure 3.** Polarized optical micrographs at 200°C for (a) LPP; (b) LPP/PTFE1.0; (c) LPP/PTFE2.0; and (d) LPP/PTFE4.0.

between neighbor chains in the hexagonal crystalline is not strong enough.<sup>25,27,28</sup> Consequently, PTFE molecules are packed more loosely and shearing leads to the unwinding of crystallites, creating fibrils. In particular, a high degree of fibrillation can be achieved at temperatures greater than 30°C.<sup>29,30</sup> Ariawan et al.<sup>31</sup> investigated the flow behavior of PTFE during paste flow in an extrusion die and found that PTFE particles were interconnected and turned into a fibrous shape. Employing a rheometer as mixing devices, Ali et al.<sup>32</sup> observed that PTFE particles were agglomerated together by mechanical interlocking and then they were fragmented into fibers by hydrodynamic force with reorganization process of crystalline phase. In this study, the LPP/PTFE blends were extruded at temperatures above 150°C, and the PTFE particles in molten PP had high possibility of deforming into fine fibers. The effect of shear and extrusion flow on the formation of PTFE fibers during the extrusion foaming is under investigation.

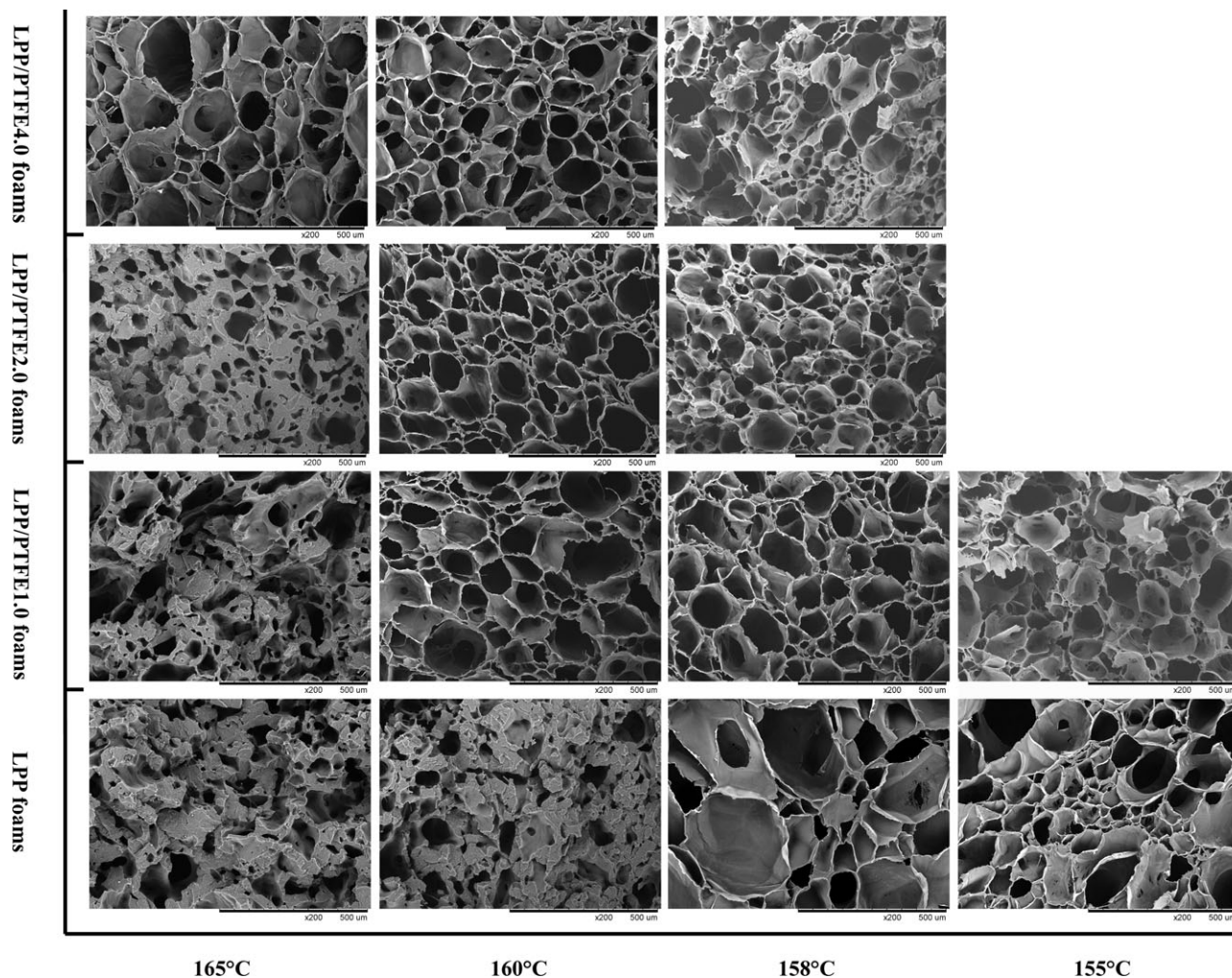
Influence of PTFE fiber on the melt strength of LPP was investigated at 230°C with a haul-off speed of 6 m/min, and the results are shown in Table I. It is seen that the melt strength of LPP was 0.005 N. With the introduction of PTFE, however, the melt strength of LPP increased dramatically up to 0.01 for LPP/PTFE1.0, 0.02 for LPP/PTFE2.0, and 0.03 for LPP/PTFE 4.0. These results suggested that PTFE could increase the melt strength of PP efficiently, possibly because of the formation of PTFE fiber.

#### Effect of PTFE Addition on the Cell Morphology of PP Foams

Figure 4 shows cell morphologies of LPP and LPP/PTFE blend foams obtained at different die temperatures. At high die tem-

peratures of 165–160°C, the pure LPP could hardly be foamed. The reason is that the melt strength of LPP was low, which caused most gas to escape and led to severe cell coalescence.<sup>4</sup> With the decrease of die temperature to 158°C, the expansion ratio increased as a result of the suppressed cell coalescence caused by the increased viscosity. However, poor foam morphology, namely, low cell density, large cell size, and nonuniform cell distributions, were still observed in LPP foams. This result demonstrated that the decreased die temperature did not effectively improve the melt strength of LPP and the serious cell coalescence was still present during LPP extrusion foaming. At the die temperature below 155°C, the LPP melt could not flow and a sudden increase in die pressure was observed; good foamed samples could not be obtained because of the occurrence of crystallization.

Extrusion foaming of LPP/PTFE blends was carried out to investigate the effect of PTFE addition on the cell morphology of PP foams. As shown in Figure 4, in the case of LPP/PTFE1.0 foams, the well-defined cell morphologies were observed at die temperatures of 160–158°C, indicating the positive effect of introducing PTFE on cell morphology. At higher PTFE contents, the cell morphologies of LPP/PTFE blend foams improved continuously, and higher cell densities, smaller cell sizes, and more uniform cell distributions were observed in LPP/PTFE2.0 and LPP/PTFE4.0 foams. It was noted that the pure LPP foams could hardly expand at 165°C, whereas LPP/PTFE4.0 foams had good cell morphology at the same die temperature. It was because the increased melt strength of LPP/PTFE could stabilize the nucleated bubbles.



**Figure 4.** SEM images of LPP and LPP/PTFE blend foams obtained at different die temperatures. CO<sub>2</sub> content injected to barrel is fixed to 5 wt %.

Dispersion of PTFE fiber in PP foams was further investigated by SEM observation. It is seen from Figure 5a1 and 5b1 that PTFE fibers grew from cell walls and presented a network-like structure. As indicated in Table I, the presence of PTFE increased the melt strength of PP, which facilitated the stabilization of cell structure and suppressed cell coalescence effectively during the foaming process.

#### Effect of PTFE Addition on the Cell Density of PP Foams

Cell density is a value to show the number of survived cells (per unfoamed unit volume) that undergo cell nucleation, cell collapse, and cell coalescence. It has been used by many researchers to study the cell nucleation process. Figure 6 shows the cell density of LPP and LPP/PTFE blend foams at different die temperatures. For LPP foams, the cell density of foams slightly increased with the decrease in die temperature, because of the increased melt strength of PP melt at low die temperature. For the LPP/PTFE blend foams, the cell density increased with increasing content of PTFE. When the PTFE content was above 2 wt %, the cell density did not show any die temperature dependence, which indicated that the cell coalescence had been

suppressed efficiently and most of the nucleated bubbles were survived during the followed cell growth process.

Figure 7 summarizes the cell density and cell size of foamed samples as a function of PTFE content obtained at 160°C. It was shown that the average cell diameter decreased remarkably from 300 μm for neat LPP foam to 130 μm for LPP/PTFE1.0 foam, and then leveled off at higher PTFE contents. On the other hand, the cell density increased from  $6.82 \times 10^6$  cells/cm<sup>3</sup> of pure LPP foam to  $1.64 \times 10^7$  cells/cm<sup>3</sup> of LPP/PTFE4.0 foam, possibly contributed to the improved cell nucleation.

#### Effect of PTFE Addition on Foam Expansion

The expansion ratio is an important parameter describing the amount of gas that is retained and used during foam expansion, and the expansion ratio usually includes the contributions of cell nucleation, opening, and growth. Figure 8 shows the expansion ratios of LPP and LPP/PTFE blend foams at various die temperatures. It was found that all the foams with different PTFE contents exhibited a low expansion ratio of about 1.5 at high die temperatures of 170–180°C. With decreased die temperature, the expansion ratio increased rapidly until the matrix was too rigid to enable the bubble to grow. The maximum

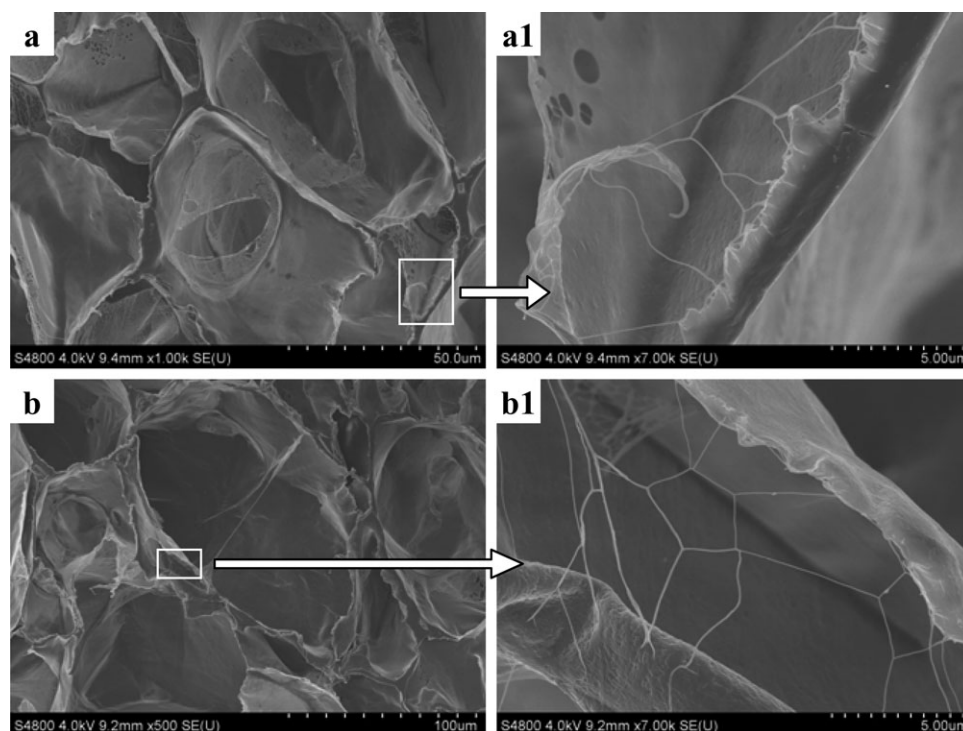


Figure 5. Dispersion of PTFE in LPP/PTFE2.0 (a,a1) and LPP/PTFE4.0 (b,b1) foams.

expansion ratio of LPP foam was 15.5, which was obtained at a die temperature of 158°C. With the introduction of 1.0 wt % PTFE, however, the expansion ratio of LPP/PTFE blend foam slightly decreased to 15.1 at 159°C. With further increasing the PTFE content, LPP/PTFE2.0 and LPP/PTFE4.0 exhibited a gradually decreased expansion ratio at the foaming scopes, and the maximum expansion ratio decreased from 15.1 for LPP/PTFE1.0 to 13.0 for LPP/PTFE2.0 and to 11.2 for LPP/PTFE4.0. Meanwhile, the die temperature suitable for foaming shifted to higher temperature sections. For example, the temperature of the maximum expansion ratio for LPP foams was 158°C, whereas it reached up to 163°C for LPP/PTFE4.0 foams. This

result indicated that the introduction of PTFE facilitated foam expansion even at high die temperature because of high melt strength of LPP/PTFE blends.

A foaming window is a critical parameter by which the foamability of polymer resin can be evaluated. In general, a broad foaming window facilitates foam processing, whereas a narrow foaming window tends to make higher demands on the foaming system, particularly on the temperature control system. Unlike amorphous polymers, crystalline polymers have a viscosity that is weakly temperature dependent before crystallization occurs, resulting in a narrow foam-processing temperature range. Figure 9 shows a suitable foaming window for LPP and LPP/PTFE blends with respect to the die temperature, which was decreased from 170 to 154°C. The suitable foaming window in

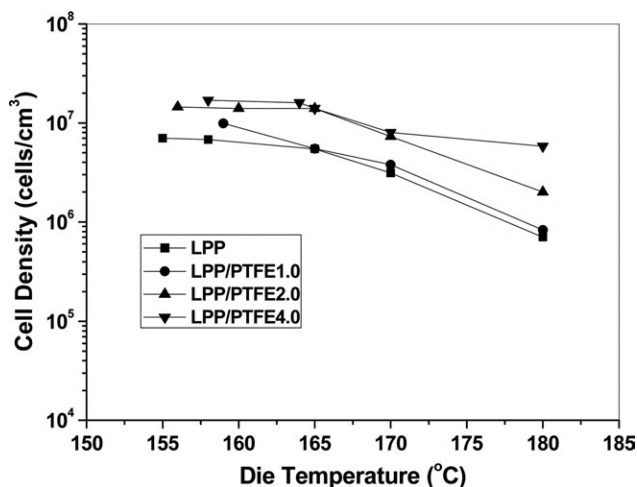


Figure 6. Effect of die temperature on foam cell density of LPP and LPP/PTFE blend foams with different PTFE content.

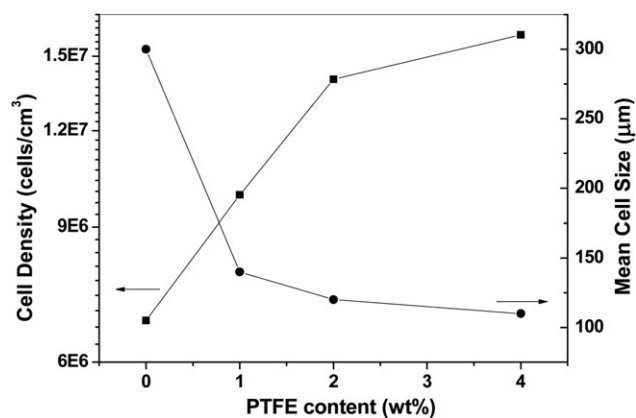
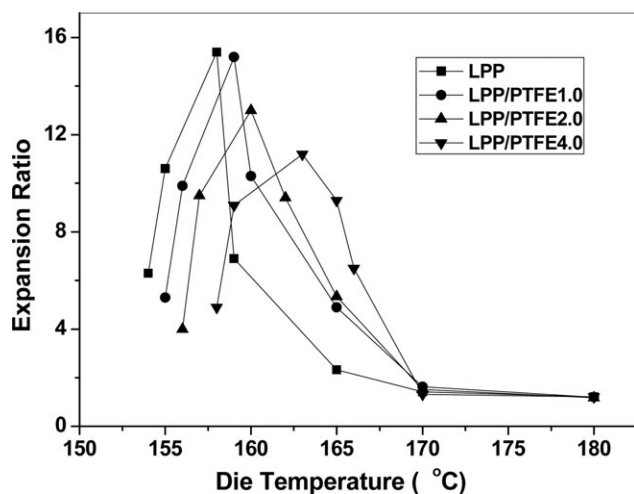


Figure 7. The cell size and cell density of LPP and LPP/PTFE blend foams obtained at 160°C.

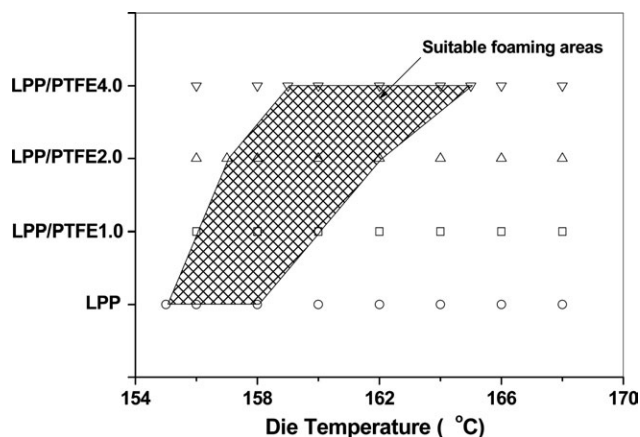


**Figure 8.** Effect of die temperature on foam expansion ratio of LPP and LPP/PTFE blend foams with different PTFE content.

this figure means the foams obtained in those foaming areas had a well-defined cell structure with very thin walls and uniform cell distributions. In the case of pure LPP, good foamed samples could be produced at a die temperature of about 155–158°C. This result indicated that the suitable foaming window for pure LPP was only 4°C. Table I shows that the crystallization temperature of PP increased with rising PTFE addition. Therefore, the minimum suitable foaming temperature for LPP/PTFE blend foams elevated with the increased PTFE content. With the introduction of 1 wt % PTFE, the temperature suitable for foaming increased to 5°C (from 156 to 160°C). At higher PTFE contents of 2 and 4 wt %, broader foaming windows of about 6 and 7°C, respectively, offered good foamed samples. These results verified that the addition of a small amount of PTFE broadened the foaming window of LPP.

## CONCLUSION

In this study, LPP and LPP/PTFE blend foams were fabricated by extrusion foaming, and the cell structure evolution of LPP



**Figure 9.** Suitable foaming window of LPP and LPP/PTFE in fabricating foams with well defined cell morphology.

foams with PTFE content and die temperature were investigated. This research led to the following conclusions:

- i. In the foaming process, the solid PTFE deformed into fine fibers which showed a network-like structure. These fibers were uniformly dispersed in the LPP matrix and increased the melt strength of LPP.
- ii. The introduction of small amounts of PTFE effectively stabilized the cell structure and suppressed the cell coalescence, which led to the preparation of LPP/PTFE blend foams with good cell morphologies and high cell density.
- iii. The addition of PTFE broadened the suitable foaming window from 4°C for LPP to 7°C for LPP/PTFE4.0.

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