

# Effect of Long-Chain Branches of Polypropylene on Rheological Properties and Foam-Extrusion Performances

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**ABSTRACT:** The effect of modifying polypropylene by the addition of long-chain branches on the rheological properties and performance of foam extrusion was studied. Three polypropylenes, two long-chain-branched polypropylenes and a linear polypropylene, were compared in this study. The modification was performed with a reactive-extrusion process with the addition of a multifunctional monomer and peroxide. The rheological properties were measured with a parallel-plate and elongational rheometer to characterize the branching degree. The change from a linear structure to a long-chain-branched nonlinear structure increased the melt strength and elasticity of polypropylene. Also, there was a significant improvement in the melt tension and sag resistance for branched polypropylenes. Foam-

ing extrusion was performed, and the effect of the process variables on the foam density was analyzed with Taguchi's experimental design method. For this study, an  $L_{18}(2^{13}5)$  orthogonal array was used on six parameters at two or three levels of variation. The considered parameters were the polypropylene type, the blowing agent type, the blowing agent content, the die temperature, the screw speed (rpm), and the capillary die length/diameter ratio. As a result, the most significant factor that influenced the foam density was the degree of long-chain branching of polypropylene. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1793–1800, 2005

**Key words:** foam extrusion; poly(propylene) (PP); reactive extrusion; rheology

## INTRODUCTION

A foamed or cellular plastic is characterized by a decreased apparent density, which is due to the presence of numerous voids or cells dispersed throughout its mass. Foamed plastics have great advantages, such as reduced weight, energy absorption, and low thermal conductivity. In particular, foams made from polyolefins keep the properties of polyolefins, such as toughness, flexibility, and resistance to chemicals and abrasion, and they are environmentally friendly. The most commonly used material for polyolefin foam production is polyethylene (PE). The advantages of PE foam are its economy, good temperature stability, high chemical resistance, and wide processing window. Also, it can be used at higher temperatures than polystyrene foam. Polyolefin foam processing is reviewed in ref. 1.

The use of polypropylene (PP) foam has been considered in industry recently.<sup>2–4</sup> PP is superior to PE in some ways. It has a high melting temperature ( $T_m$ ),

stiffness, and the capability of static load bearing, which is the shortcoming of PE. Also, PP foam can offer good temperature stability and high chemical resistance, just as PE can. The application of PP to the foam process has been limited, however, because of its weak melt strength and melt elasticity, which make foaming PP difficult in comparison with other plastics. When the melt strength and melt elasticity are weak, the cell wall separating the bubbles cannot be strong enough to keep the extensional force, and they are apt to rupture easily. As a result, foamed PP usually has a high open-cell content and deteriorated quality.

The addition of long-chain branches to the PP backbone may be an alternative for improving its melt strength and foaming processability. The branched structure can stabilize the bubble growth and retard cell coalescence or rupture. Several possible methods have been introduced for branching PP. Widely used methods include high-energy irradiation and reactive extrusion with a multifunctional monomer and peroxide.<sup>5–14</sup> Also, many results have been published on the foaming of branched PP.<sup>15–18</sup>

Two long-chain-branched PPs with a linear PP were compared, and the effects of the structural modification on the rheological and thermal properties were investigated in this study. The modification was performed through a reactive-extrusion process with a multifunctional monomer and peroxide. The rheologi-

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cal properties were measured with a parallel-plate and elongational rheometer to characterize the degree of branching both qualitatively and quantitatively.

Also, foaming extrusion was performed, and the effects of PPs or process variables on the foaming performance were analyzed. The foaming-extrusion process was not simple, and it was hard to select the main process parameter. From the many variables, five main process variables were selected along with the branching degree of PP; they were the blowing agent (BA) type, the BA content, the die temperature, the screw speed (rpm), and the capillary die length/diameter ( $L/D$ ) ratio. The usual traditional analysis (one-at-a-time experimentation) holds all factors constant but one and records the results as that single factor varies. That is time-consuming and expensive and is unable to analyze the effects of a factor with respect to various levels of other factors. Taguchi's experimental design method, instead of the traditional approach, was used in this study.<sup>19–21</sup> From this analysis, it was possible to obtain the contribution of the processing and material parameters to the foaming extrusion in a systematic way.

## EXPERIMENTAL

### Materials

Homopolypropylene (melt index = 3.0, 230°C, 2.16 kg) from Hyosung Corp. (Seoul, Korea), named PP1, was modified by a reactive-extrusion process with the addition of a small amount of peroxide and a multifunctional agent. The peroxide and multifunctional agent were dialkyl peroxide (2,5-dimethyl-2,5-bis-*t*-butylperoxy) hexane from Elf Atochem (King of Prussia, PA) and trimethylolpropane triacrylate from Aldrich Chemical Co. (St. Louis, MO), respectively.

Reactive extrusion was performed in a twin-screw extruder ( $L/D = 18$ , diameter = 25 mm) at 60 rpm. The temperature profiles were 160 (feeding zone), 190 (melting zone), and 210°C (metering zone and die). The concentrations of the multifunctional monomer and peroxide were 1.5 phr and 200 ppm for PP2 and 2.5 phr and 300 ppm for PP3, respectively. The gel contents were measured by Soxhlet extraction in boiling xylene for 24 h, and no significant macrogel was formed for PP2 and PP3.

### Thermal property measurements

The thermal properties of the samples were measured with a TA Instrument 2910 differential scanning calorimeter (New Castle, DE). The temperature and heat-flow area were calibrated with indium before the analysis. The samples (ca. 10 mg) were sealed in an aluminum pan and heated or cooled in a nitrogen atmosphere. Initially, the samples were heated from

TABLE I  
Characteristics of Three PPs

	$T_m$ (°C)	$T_c$ (°C)	MW	Polydispersity
PP1	169.4	108.3	260,000	8.2
PP2	168.0	122.4	250,000	7.6
PP3	167.6	124.2	250,000	7.5

room temperature to 200°C at a rate of 10°C/min and cooled at a rate of 10°C/min to obtain the crystallization temperature ( $T_c$ ). They were reheated to 200°C to obtain  $T_m$ . The characteristics of the PPs are listed in Table I.

### Rheological property measurements

An ARES rotational rheometer (TA Instrument) was used to measure the complex modulus and complex viscosities of PPs. The frequency range was 0.1–500  $s^{-1}$ , and the temperature was 230°C. The measurements of the dynamic viscosity were performed with a parallel-plate fixture (diameter = 25 mm), with a gap distance of 1.5 mm, and the strain was kept at 10% to ensure linear viscoelasticity. The measurements were conducted under a nitrogen atmosphere to prevent degradation. The steady-shear experiments were performed at low shear rates (from 0.01 to 0.2  $s^{-1}$ ) to fit the Cross model.

The extensional viscosities were measured in a silicone oil bath with a Meissner-type rheometer. Rodlike samples with a diameter of 3 mm and a length of 170 mm were prepared. After being immersed for 2 min in a silicon oil, the molten samples were stretched by one side of a rotary clamp. The force ( $f$ ) and strain were measured with time, and the extensional viscosity ( $\eta_e^+$ ) was calculated as follows:

$$\eta_e^+ = \frac{f \exp(\dot{\epsilon}t)}{\pi R_0^2 \dot{\epsilon}} \quad (1)$$

where  $\dot{\epsilon}$  is the extensional rate,  $t$  is the time, and  $R_0$  is the initial radius of the rod. The measuring temperature was 190°C, and the elongational rates were 0.05, 0.1, 0.2, and 0.3  $s^{-1}$ .

The melt tension was measured with a capilograph with a 2.095-mm-diameter orifice at 230°C. The extrusion rate was 20 mm/min, and the take-up velocity was 3.14 m/min. The sagging degree was compared to measure the sag resistance of the specimen. The test samples were prepared by compression molding, and the dimensions of the sample strips were 1 mm  $\times$  20 mm  $\times$  200 mm (thickness  $\times$  width  $\times$  length). Once the predetermined oven temperature (170°C) was reached, each specimen was placed in the oven by the clamping of each end, and the sagging length at the center of the sheet with time was measured.

### Foam-extrusion procedure

Foam extrusion was performed with a chemical blowing method. Azodicarbonamide (Unicell-D2500, Dong Jin Semichem Co., Seoul, Korea) and sodium bicarbonate (Unicell-C114, Dong Jin Semichem Co.) were used as organic and inorganic chemical blowing agents (CBAs), respectively. Foaming was performed in a twin-screw extruder ( $L/D = 18$ , diameter = 25 mm). The temperature profiles were 160 (feeding zone), 190 (melting zone), and 230°C (metering zone). PP pellets were fed through the hopper and melted from the barrel heat and the friction. CBA was then injected and mixed with PP. CBA released gas at a certain decomposition temperature, and the gas dissolved in the polymer. A regular static mixer was installed between the mixer and the die to enhance the diffusion of BA. Shaping and foaming were performed in the sheet die with a 1-mm thickness and a 20-mm width. The die temperature was varied from 170 to 210°C. When the melt exited the die, a solubility drop of BA in the polymer led to bubble formation. To analyze the effects of the process variables on the foaming performance by Taguchi's experimental design method, we determined six factors that influenced the foam density. They were the PP type, the BA type, the BA content, the die temperature, the screw speed (rpm) and the die  $L/D$  ratio.

The morphology of the foamed cell structure was examined with scanning electron microscopy (SEM; S-2500C, Hitachi, Tokyo, Japan) at 25 kV. The samples were gold-coated before the examination.

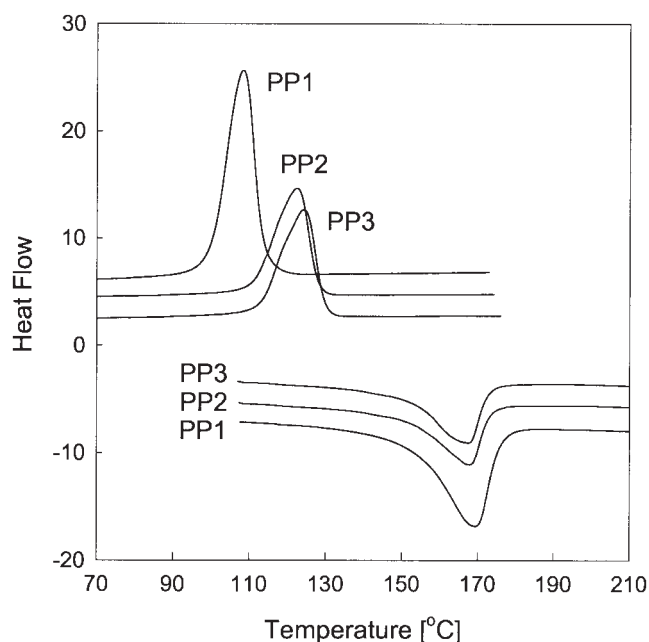


Figure 1 DSC melting and cooling behaviors of three PPs.

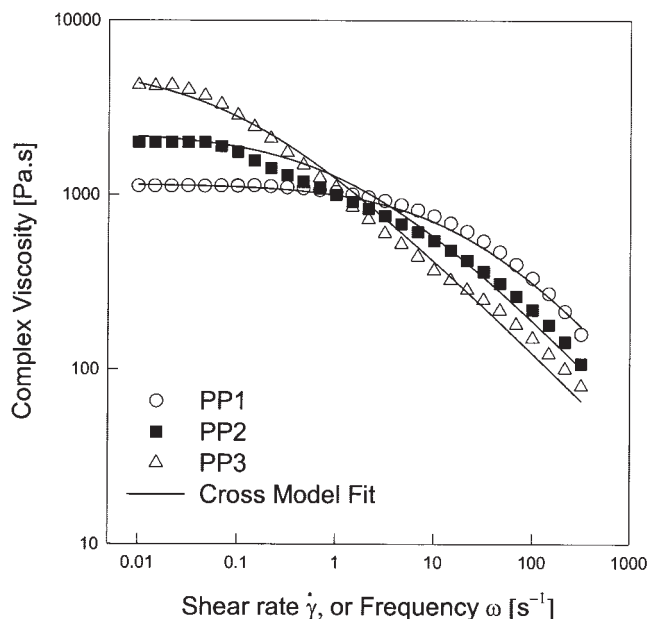


Figure 2 Complex viscosities of three PPs and curve fitting by the Cross model at 230°C.

## RESULTS AND DISCUSSION

### Thermal properties

Figure 1 shows the results for the melting and cooling behaviors. Three PPs had similar  $T_m$  values, but PP2 and PP3 showed somehow lower and broader  $T_m$  peaks. This was due to the introduction of chain defects and irregularities induced by the branching and grafting.<sup>10</sup> The level of crystallinity, which could be reflected by the heat of fusion, was further reduced by the noncrystallizing structure in the chain. Also, PP2 and PP3 had higher  $T_c$  values than PP1. The branching or crosslinking unit considerably increased the nucleation density of PP, and it accelerated the crystallization.

### Rheological properties

Figure 2 shows the complex viscosities of three PPs. Data at low frequencies (up to 0.2 rad/s) were obtained from steady-shear experiments and were overlapped by the Cox–Merz rule. The two modified PPs, PP2 and PP3, had high zero-shear viscosities ( $\eta_0$ ) and showed shear-thinning behaviors at low frequencies. On the other hand, PP1 had a long Newtonian plateau and low  $\eta_0$  values. The high  $\eta_0$  values were mainly due to two reasons: a broad molecular weight (MW) and the existence of long-chain branches. The latter was thought to be the main reason for this result because the three PPs had similar MWs, as shown in Table I.

The storage moduli for various PPs are compared in Figure 3. PP2 and PP3 showed, at low frequencies, a

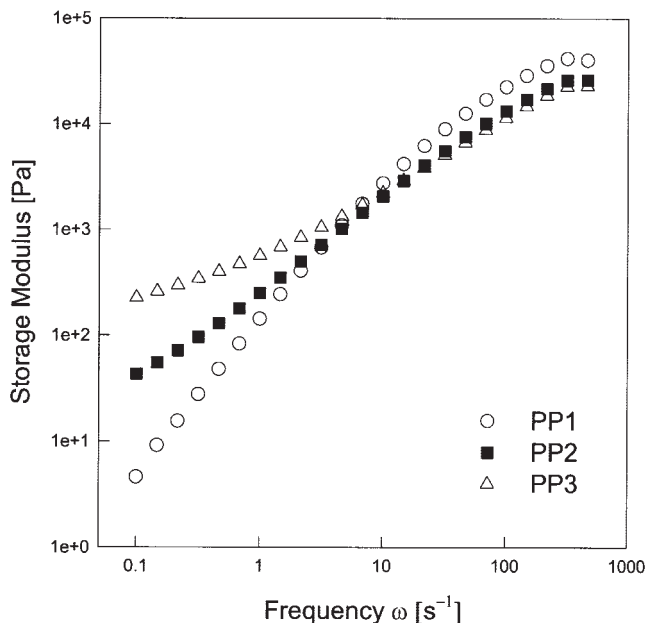


Figure 3 Storage modulus versus the frequency of three PPs at 230°C.

plateau behavior that could not be observed for PP1. Hingmann and Marczinke reported similar behavior with long-chain-branched PP.<sup>22</sup> The physically connected structure increased the relaxation time of branched PP2 and PP3 and the dynamic storage modulus. At high frequencies, however, the elastic energy was dominated by MW of the polymer rather than the chain structure; PP1 showed a somehow higher storage modulus. Figure 4 presents Cole–Cole plots for

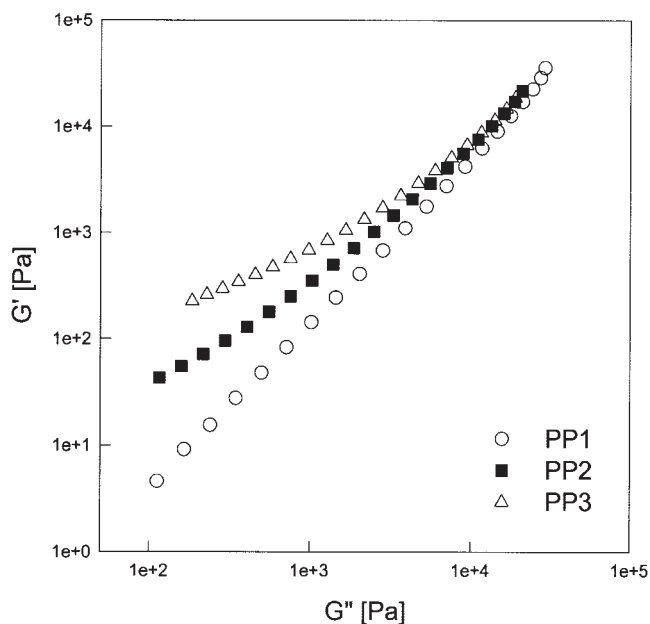


Figure 4 Cole–Cole plots of three PPs at 230°C ( $G'$  = storage modulus,  $G''$  = loss modulus).

TABLE II  
Rheological Characteristics of Three PPs Measured and Calculated from the Cross Model Fit

	$\eta_0$ (Pa · s)	$\tau_0$ (s)	Activation energy (kcal/mol)	RPI	Melt tension (gf)
PP1	950	0.08	4.53	3.7	1.5
PP2	2600	0.33	6.16	5.1	7.8
PP3	5600	0.91	8.17	5.5	10.5

three PPs. Behavior similar to that shown in Figure 3 can be observed. PP2 and PP3 showed highly elastic behavior at low frequencies, whereas PP1 had no plateau behavior and lay in a straight line. These rheological results clearly showed that PP2 and PP3 had long-chain-branched structures. Of the two, PP3 had the higher degree of branching.

Calculated parameters from the measured rheological properties are summarized in Table II.  $\eta_0$  and the characteristic relaxation time ( $\tau_0$ ) were fitted by the Cross model as follows:<sup>23</sup>

$$\eta = \frac{\eta_0}{[1 + (\tau_0 \dot{\gamma})^m]} \quad (2)$$

where  $\eta$  is the viscosity,  $\dot{\gamma}$  is the shear rate, and  $m$  is related to the power-law index. As the branching degree increased,  $\eta_0$  and  $\tau_0$  increased. The activation energy was obtained by the measurement of the storage modulus at different temperatures (200, 210, 220, and 230°C) and then was shifted to 200°C with the

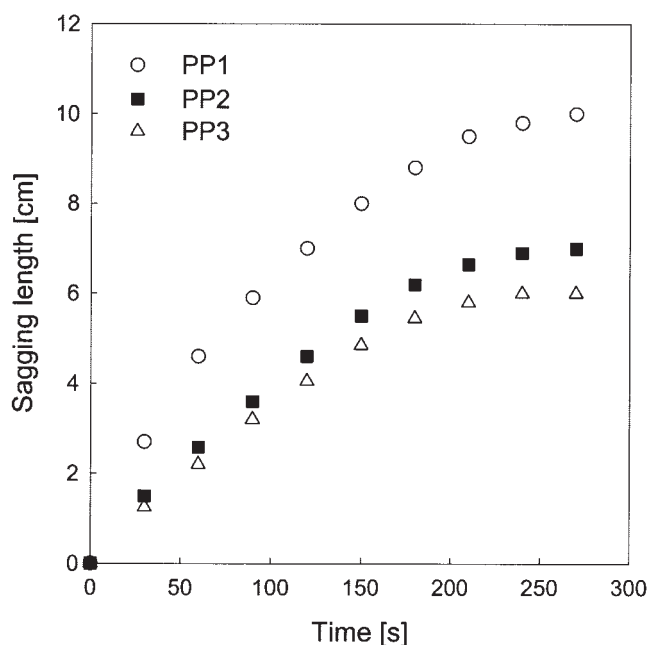
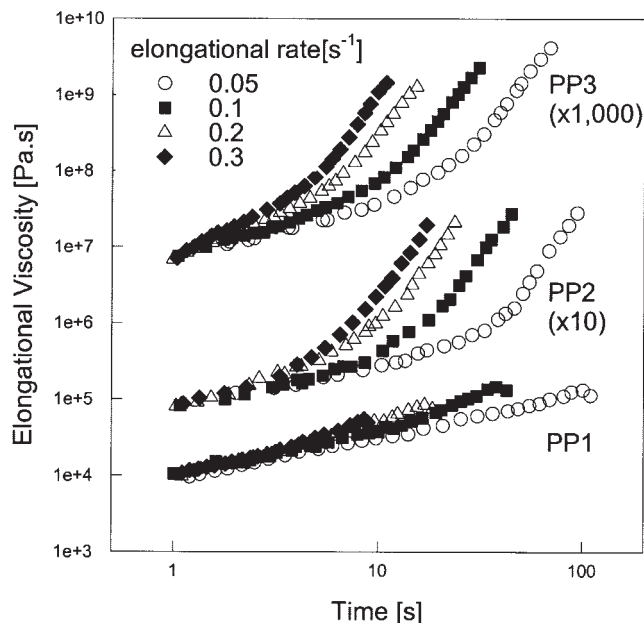


Figure 5 Comparison of the sagging length of three PPs with time at 170°C.





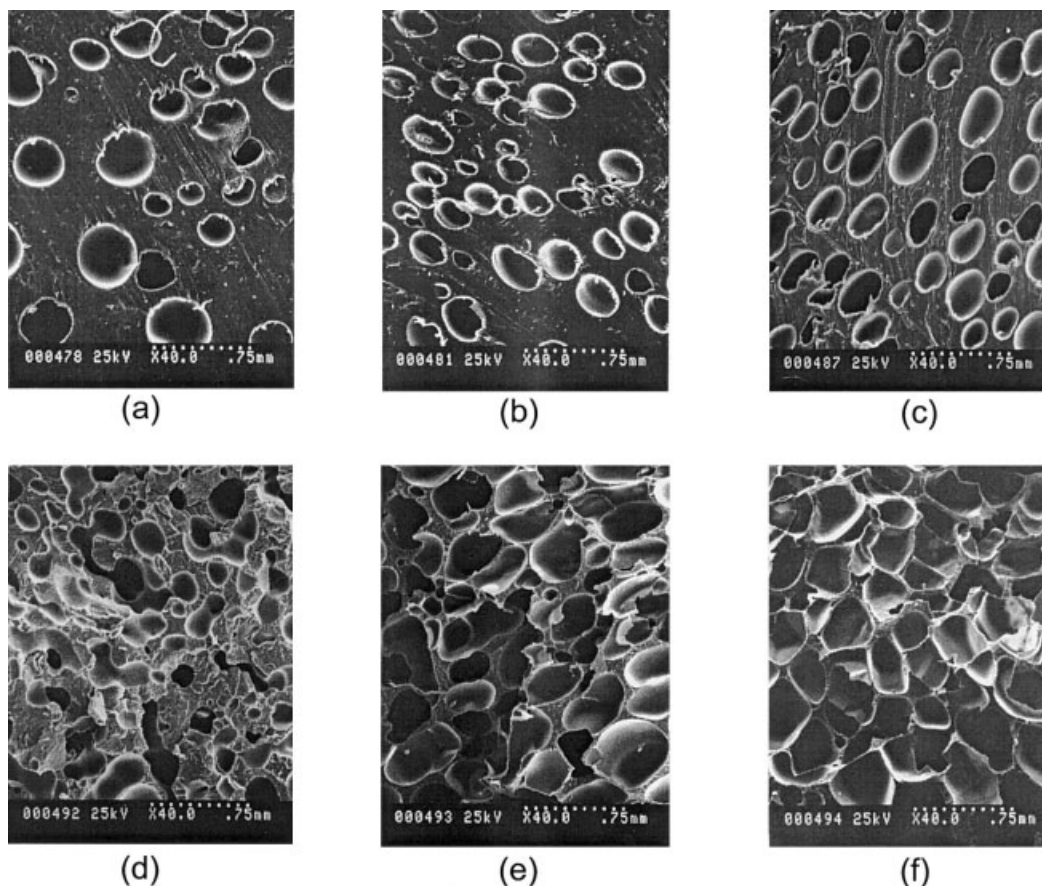
**Figure 6** Elongational viscosities of three PPs at various elongational rates at 190°C.

time-temperature superposition principle.<sup>24</sup> Linear PP (PP1) had the lowest activation energy, whereas branched PP (PP3) had the highest value.

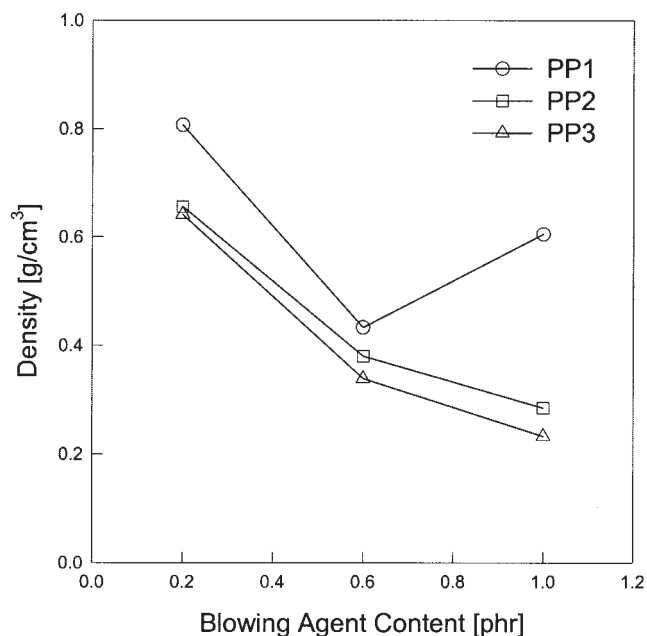
The rheological polydispersity index (RPI) is defined as  $10^5/G_c$ , where  $G_c$  is the crossover modulus (storage modulus = loss modulus) in pascals.<sup>25</sup> RPI is directly proportional to the molecular weight distribution (MWD) or the degree of long-chain branching. As the three PPs had similar MWs and MWDs, as shown in Table I, RPI represents the branching degree in this system in a quantitative manner. The RPI value shows a similar behavior with the other parameters.

The sagging behaviors of PPs with time are represented in Figure 5. PP1 showed a greater sagging length than PP2 and PP3. This greater sagging of PP1 was due to its poor melt tension, as listed in Table I. The sagging degree was in inverse proportion to the melt tension.

Figure 6 shows the elongational viscosities for three PPs. The elongational viscosity of a polymeric material in the molten state is strongly dependent on its structure and is clear evidence of a branched structure for polymers.<sup>26,27</sup> In comparison with PP1, PP2 and PP3 showed noticeable elongation hardening. The higher



**Figure 7** SEM morphologies of three PPs with CBA contents at 190°C and a screw speed of 40 rpm: (a) PP1, 0.2 phr CBA; (b) PP2, 0.2 phr CBA; (c) PP3, 0.2 phr CBA; (d) PP1, 1.0 phr CBA; (e) PP2, 1.0 phr CBA; and (f) PP3, 1.0 phr CBA.



**Figure 8** Foam densities of three PPs with various CBA contents. The die temperature was 190°C, and the extrusion screw rate was 40 rpm.

the elongational rate was, the shorter the time was when nonlinearity happened. Also, the elongation hardening was more severe in PP3 than in PP2.

### Foam-extrusion results

Figure 7 shows SEM images of three PP foams with various BA contents. Organic CBA was used here. The die temperature was 190°C, and the screw speed was 40 rpm. When the CBA concentration was 0.2 phr, a foamed structure was not fully developed, and thick cell walls were observed. When 1.0 phr CBA was added, PP2 and PP3 had well-developed and uniformly foamed structures, whereas PP1 had many small open cells. The measured densities of the foamed materials are presented in Figure 8. Even at a low CBA concentration, PP2 and PP3 had lower densities. As the CBA concentration increased, the foam density decreased. When the CBA concentration was 1.0 phr, however, the density of PP1 increased again. This was due to the linear structure and low melt

**TABLE IV**  
 $L_{18}(2^13^5)$  Orthogonal Array

	BA	Resin	BA content	Die temperature	Screw speed (rpm)	Die L/D ratio
Case 1	1	1	1	1	1	1
Case 2	1	1	2	2	2	2
Case 3	1	1	3	3	3	3
Case 4	1	2	1	1	2	2
Case 5	1	2	2	2	3	3
Case 6	1	2	3	3	1	1
Case 7	1	3	1	2	1	3
Case 8	1	3	2	3	2	1
Case 9	1	3	3	1	3	2
Case 10	2	1	1	3	3	2
Case 11	2	1	2	1	1	3
Case 12	2	1	3	2	2	1
Case 13	2	2	1	2	3	1
Case 14	2	2	2	3	1	2
Case 15	2	2	3	1	2	3
Case 16	2	3	1	3	2	3
Case 17	2	3	2	1	3	1
Case 18	2	3	3	2	1	2

strength of PP1. The low melt strength and elongational viscosity caused the rupture of the cell wall during expansion at a high CBA concentration and, as a result, increased the density.

### Experimental design analysis

To analyze the effect of the main processing parameters on the performance of foaming systematically, we applied experimental design analysis. The considered factors are listed in Table III with selected levels. An  $L_{18}(2^13^5)$  orthogonal array was used as a basis for the experimental design in this study, and all 18 cases are listed in Table IV. Two cooling methods were used to consider the effect of the process noise: cold-water cooling after die exit and air cooling. It should be emphasized that the object of comparing the two cooling media was not to investigate the effect of the cooling speed but to impose external noise on the system. Therefore, detailed operation data, such as the temperature or bath length, are not important and are not mentioned here. Each sample was measured five times to ensure the reproducibility of the measure-

**TABLE III**  
Factors and Levels for Taguchi's Experimental Design Method in Foaming Extrusion

	Factor					
	CBA	Resin	BA content (phr)	Die temperature (°C)	Screw speed (rpm)	Die L/D ratio
Level 1	Organic	PP1	0.2	170	20	10
Level 2	Inorganic	PP2	0.6	190	40	20
Level 3	—	PP3	1.0	210	60	30

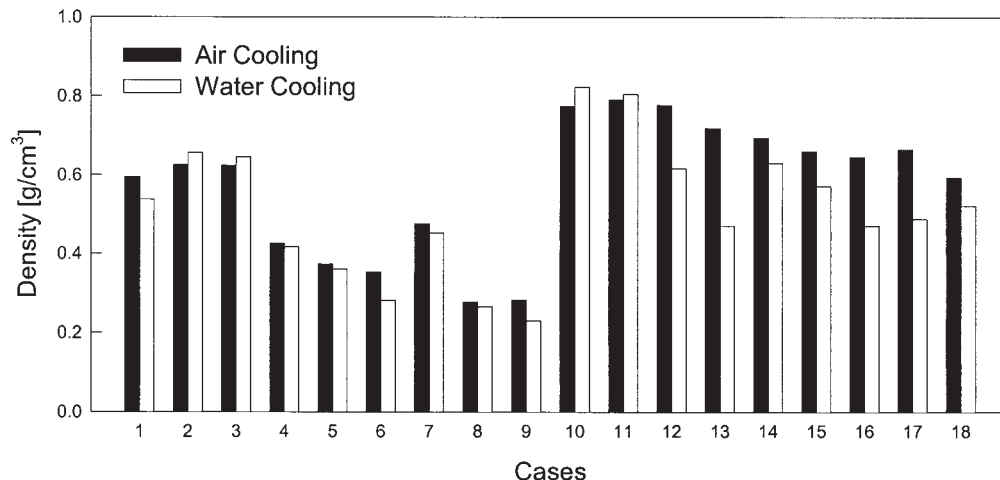


Figure 9 Foam densities of various cases.

ment. The measured foam densities for the 18 cases are presented in Figure 9. The foam densities varied from 0.2 to 0.8 g/cm<sup>3</sup> with the processing conditions. Also, the effect of the process noise was significant in some cases. The maximum density difference due to the process noise reached 0.25 g/cm<sup>3</sup> for case 13.

The signal-to-noise (S/N) ratio for each process variable is presented in Figure 10. This result was analyzed with an analysis of variance. The S/N ratio means how the signal, that is, the foam density, is stable versus the process noise. It was calculated by the smaller-is-better characteristic because better quality was obtained when the density was low. A higher value of the S/N ratio meant that the variation of the output signal was stable with the given process noise. In that case, the factor and level had robustness in the

process. For a smaller-is-better characteristic, as the goal was reducing both the mean value and the variation, the S/N ratio was calculated as follows:

$$S/N_i = -10 \log \sigma^2 = -10 \log \left[ \frac{1}{n} \sum_{j=1}^n y_{ij}^2 \right] \quad (3)$$

where  $S/N_i$  is the S/N ratio of the  $i$ th factor,  $\sigma^2$  is the variance,  $n$  is the number of measurements, and  $y_{ij}$  is the signal.<sup>19</sup> The most significant factor influencing the foam density was the chain structure of PP. PP1 had a poor S/N ratio, whereas PP3 had a superior S/N ratio. The second significant factor was the type of BA. Organic BA showed higher S/N values than inorganic BA. This was due to the high amount of gas evolution

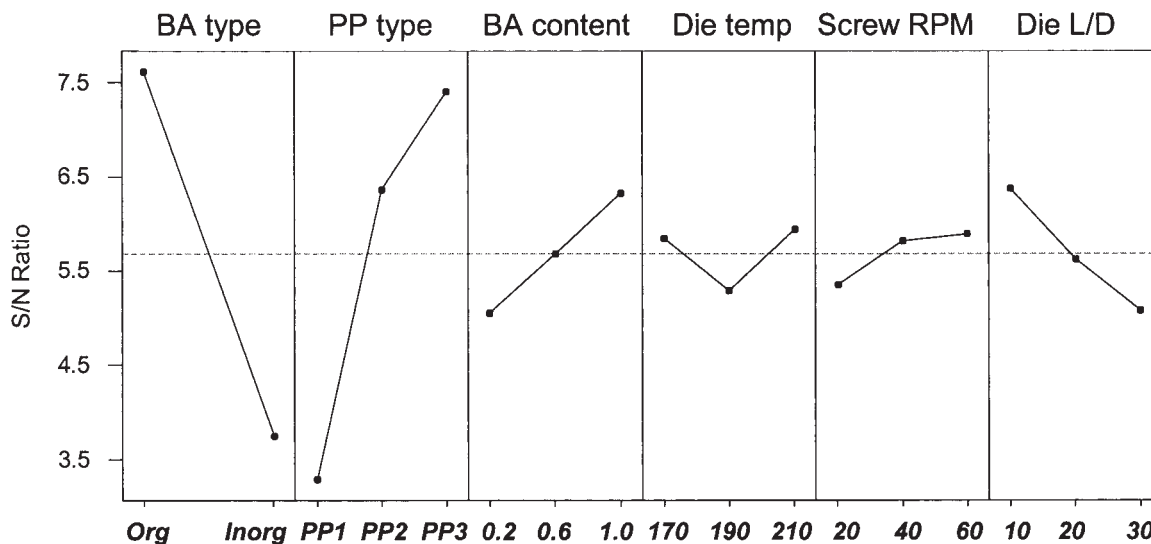


Figure 10 Main-effect plot for various factors and levels.

of organic CBA. The gas evolution volume of organic CBA was 225–245 mL/g, whereas that of inorganic CBA was 120–140 mL/g. The third factor was the die  $L/D$  ratio. A lower  $L/D$  ratio led to a higher S/N value. The rapid pressure drop led to a rapid drop of gas solubility, which induced thermodynamic instability and promoted a higher nucleation rate.<sup>28</sup> The next one was the BA content. A higher BA content evolved more gas to dissolve in the polymer. The last two factors were the screw speed (rpm) and die temperature. A high screw speed increased the pressure, and more gas could be dissolved at a high pressure. This explained the high S/N ratio with the screw speed (rpm). As for the die temperature, a low die temperature led to a low foam density. The S/N ratio from Figure 10, however, shows similar behavior with the die temperature. We believe that some interactions between the parameters are involved in the variation of the die temperature.

### CONCLUSIONS

The rheological and thermal properties were investigated for three PPs: one had a linear structure, and the others had branched structures. A reactive-extrusion process was used to modify PP from a linear structure to a branched structure. According to the complex viscosity measurements, the branched PPs had higher  $\eta_0$ , activation energy, RPI, and  $\tau_0$  values. Also, the extensional hardening, sag resistance, and melt tension of branched PPs were significant in comparison with those of linear PP. The effects of PPs on the foaming performance were investigated under various processing conditions. When PPs had long-chain-branched structures, the foam density became lower. The foams were apt to collapse in a linear structure because of the low melt strength. From an analysis with Taguchi's experimental design method, it was determined that, of the various processing variables, the long-chain branching of PP was the main factor affecting the foam density.

### References

1. Park, C. P. In *Handbook of Polymeric Foams and Foam Technology*; Klemmner, D.; Frisch, K. C., Eds.; Hanser: New York, 1991.
2. Cheung, L. K.; Park, C. B.; Behraves, A. H. *Soc Plast Eng Annu Tech Conf Tech Pap* 1996, 42, 1941.
3. Nojiri, A.; Sawasaki, T.; Koreeda, T. U.S. Pat. 4,424,293 (1984).
4. Alteepping, J.; Nobe, J. P. U.S. Pat. 4,940,736 (1990).
5. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E. *Polym Eng Sci* 1988, 28, 170.
6. Chiang, W. Y.; Yang, W. D. *J Appl Polym Sci* 1988, 35, 807.
7. Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J., Jr. U.S. Pat. 4,916,198 (1990).
8. Chodak, I.; Lazar, M.; Capla, M. *J Polym Sci Part A: Polym Chem* 1991, 29, 581.
9. Kim, B. K.; Kim, K. J. *Adv Polym Technol* 1993, 12, 263.
10. Wang, X.; Tzoganakis, C.; Rempel, G. L. *J Appl Polym Sci* 1996, 61, 1395.
11. Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. *J Appl Polym Sci* 1996, 60, 617.
12. Panzer, U. Presented at SPO 98, Houston, TX, 1998.
13. Yu, Q.; Zhu, S. *Polymer* 1999, 40, 2961.
14. Sugimoto, M.; Tanaka, T.; Masuduchi, Y.; Takimoto, J.; Koyama, K. *J Appl Polym Sci* 1999, 73, 1493.
15. Bradley, M. B.; Phillips, E. M. *Soc Plast Eng Annu Tech Conf Tech Pap* 1990, 36, 717.
16. Naguib, H. E.; Xu, J. X.; Park, C. B.; Hesse, A.; Panzer, U.; Reichelt, N. *Soc Plast Eng Annu Tech Conf Tech Pap* 2001, 47, 1623.
17. Andreassen, E.; Borve, K. L.; Rommetveit, K.; Redford, K. *Soc Plast Eng Annu Tech Conf Tech Pap* 1999, 45, 2104.
18. Gaylord, N. G.; Park, J. P. Pat. WO 91/13933, designated state AT, BE, CA, CH, DE, DK, ES, FR, GB, GR, IT, JP, KR, LU, NL, SE (1991).
19. Taguchi, G. *Introduction to Quality Engineering*; APO: Tokyo, 1986.
20. Del Vecchio, R. J. *Understanding Design of Experiments*; Hanser: Munich, 1997.
21. Skourlis, T. P.; Mohapatra, B.; Chassapis, C.; Manoochhri, S. *Adv Polym Technol* 1997, 16, 117.
22. Hingmann, R.; Marczinke, B. L. *J Rheol* 1994, 38, 573.
23. Dealy, J. M.; Wissbrun, K. F. *Melt Rheology and Its Role in Plastic Processing*; VNR: New York, 1990.
24. Ferry, J. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
25. DeMaio, V. V.; Dong, D. *Soc Plast Eng Annu Tech Conf Tech Pap* 1997, 43, 1512.
26. Wagner, M. H. *Korea-Aust Rheol J* 1999, 11, 293.
27. Baird, D. G. *Korea-Aust Rheol J* 1999, 11, 305.
28. Park, C. B.; Baldwin, D. F.; Suh, N. P. *Polym Eng Sci* 1995, 35, 432.