Compounding and Injection Molding of Polybutene-1/Polypropylene Blends

G. Kalay, C. R. Kalay

Materials Science Program, Faculty of Engineering and Natural Sciences, Sabanci University, Orhanli, 34956 Tuzla, Istanbul, Turkey

Received 28 February 2002; accepted 14 June 2002
Published online 12 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11617

ABSTRACT: The effect of shear-controlled orientation injection molding (SCORIM) was investigated for polybutene-1/polypropylene blends. This article reports on the methods and processing conditions used for blending and injection molding. The properties of SCORIM moldings are compared with those of conventional moldings. SCORIM is based on the application of specific macroscopic shears to a solidifying melt. The multiple shear action enhances molecular alignment. The moldings were investigated with mechanical tests, differential scanning calorimetry studies, and polarized light microscopy. The application of SCORIM improved Young's modulus and the ultimate tensile strength. The gain in stiffness was greater for higher polybutene-1 content blends. A drastic decrease in the strain at break and toughness was observed in SCORIM moldings. The enhanced molecular orientation of SCORIM moldings resulted in a featureless appearance of the morphology. Interfacial features due to segregation were visible in the micrographs of SCORIM moldings. Both conventional and SCORIM moldings exhibited form I′ in polybutene-1. This article explains the relationship between the mechanical properties and micromorphologies. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 806–813, 2003

Key words: poly(propylene) (PP); blends; injection molding; mechanical properties; structure-property relations

INTRODUCTION

Polybutene-1 (PB-1) is compatible with both polypropylene (PP) and polyethylene (PE). However, although it is compatible in all proportions with PP, it can only be blended with high-, medium-, and low-density PE in limited proportions. The blending of PB-1 with PE improves stress crack resistance, toughness, and melt processing characteristics.[1] Blends of PB-1 and low-density PE, for example, have gained importance as peel-seal layers in the packaging market. PB-1/low-density PE blends as peelable films also demonstrate the importance of matching the components by their rheological properties because the dispersion quality is a key to optimum performance.[2] In PB-1/PP blends, it is desirable to match the components according to their viscosities at anticipated shear rates because PB-1 is shear-thinning. The blending of PB-1 and PP can be achieved with a dry blended feed in conventional extruders. The addition of PB-1 to PP improves the weld line strength, impact strength, and flow characteristics in molded products.[1]

The blending of PB-1 in PP decreases the flexural modulus while increasing the optical properties and heat-seal properties.[3] It is known that PB-1 acts as an internal lubricant in PP and, therefore, helps to improve processability.[3] Crucial for the blending of PB-1 and PP is the difference in crystallization observed in the two polymers. PB-1 crystallizes at a much lower temperature and at a very low speed with respect to PP.[4,5]

Wasiak and Wenig[6] examined the core crystals in PP/PB-1 blends crystallized from an oriented melt by small-angle X-ray scattering and wide-angle X-ray diffraction (WAXD). The WAXD measurements indicated a decrease in the lateral dimension of the core crystal for both components. They also reported calculations of the scattering power through a three-phase model for the electron densities that indicated a nonproportional distribution of crystalline and amorphous phases in the blends. Lee and Chen[7] reported on injection-molded and compression-molded PB-1/PP blends, finding that the tensile strength and elongation of the injection-molded blends exhibited a positive synergism due to the mutual interference between the two components with respect to crystal modification and the plasticization effect of PB-1 on PP. They postulated that the heat generated during tensile testing by necking might melt the PB-1 crystals, promoting the chain mobility of the PB-1 molecules. The tensile modulus and strength of the samples were

Correspondence to: G. Kalay (gkalay@sabanciuniv.edu.tr).
Contract grant sponsor: European Commission (through the Brite-Euram Programme for the Decrypo Project); contract grant number: BE 95-2067.

TABLE I
Processing Conditions for the Conventional and SCORIM Moldings of the PB-1/PP Blends

	CMPB10PP-A	SCPB10PP-A	CMPB30PP-A	CMPB30PP-B	SCPB30PP-A
Injection pressure (bar)	50.4	100.8	100.8	100.8	100.8
Holding Pressure (bar)	56.7	75.6	56.7	81.9	66.8
Injection time (s)	0.36	0.31	0.3	0.3	0.3
Holding pressure time (bar)	30	37	30	30	49
Cycle time (s)	60	58.7	56.4	106	72.8
Mold temperature (°C)	40	40	40	40	40
Melt temperature (°C)	210	210	210	210	210
Average cavity pressure (bar)	400	380	300	400	380

reported to linearly decrease with increased PB-1 content.

The research presented in this article was aimed at exploring the effect of different processing techniques on the properties of PB-1/PP blends. Conventional molding and shear-controlled orientation injection molding (SCORIM)[8] were used to produce moldings. SCORIM enhances molecular alignment, which results in more highly oriented moldings and, therefore, improved properties.[9] The two homopolymers, PP[10,11] and PB-1,[12] were previously found to respond positively to the application of macroscopic shears during SCORIM processing.

EXPERIMENTAL

Materials

The grade of isotactic polypropylene (iPP) used for the blending was Daplen KS10, supplied by Borealis AG (Linz, Austria), with a weight-average molecular weight (M_w) of 404,000, a number-average molecular weight (M_n) of 59,000 and a polydispersity (M_w/M_n) of 6.9. The melt-flow index of the material was 8 g/10 min. The PB-1 used was PB0300, supplied by Shell Research SA (Louvain-la-Neuve, Belgium). PB0300 was characterized by M_n = 98,600, M_w = 391,800, and M_n/M_w = 4.0. The melt-flow index and density of PB0300 were 4.0 g/10 min and 0.915 g/cm^3, respectively

Compounding

A Betol twin-screw extruder was employed for the blending work. The melt temperature and screw speed were 205°C and 180 rpm, respectively. Two compositions were prepared: 90/10 (w/w) iPP/polybutene (PB) and 70/30 (w/w) iPP/PB. The blends were then granulated.

Injection molding

One set of conventional moldings (CMPB10PP-A) and one set of SCORIM moldings (SCPB10PP-A) were produced with the 90/10 PP/PB blend. Two sets of conventional moldings (CMPB30PP-A and CMPB30PP-B) and one set of SCORIM moldings (SCPB30PP-A) were produced with the 70/30 PP/PB blend. All the moldings were produced at a melt temperature of 210°C. The numbers 10 and 30 used in the sample names stand for the weight percentage of PB; for example, SCPB30PP-A means a 70/30 PP/PB blend produced by SCORIM. Table I summarizes the general processing conditions. The moldings were stored for 1 month under room conditions before testing.

Tensile testing

The tensile testing was carried out on an Instron 4505 series tensile testing machine. The crosshead speed of 5 mm/min was applied up to a strain of 1.5%, and then 50 mm/min was applied until failure. An Instron 2630 resistive extensometer was used with a gauge length of 10 mm. Young's modulus and the secant modulus at a 0.8% strain were calculated. A toughness value was also quoted in the results. It was calculated as the energy at the break point divided by the product of the cross-sectional area of the sample multiplied by the gauge length. For necking, this value represents a lower limit estimate calculated from the original area of the sample.

Microtomy and light microscopy

Thin sections approximately 10 μm thick were prepared with a Leitz rotary microtome. A tungsten carbide-hardened steel knife of a small included angle was used to cut thin sections. The knife and the specimen were maintained at room temperature. Sections were cut from planes parallel to the injection direction. The thin sections were mounted in immersion oil and contained between a glass slide and a cover slip. A soft brush was used to obtain the sections before they curled. Then, the samples were examined with a Leitz polarized light microscope.

Differential scanning calorimetry (DSC)

A PerkinElmer DSC-7 was used in the measurements of the DSC thermograms. Samples (ca. 10 mg) were

TABLE II
Tensile Test Data for the Conventional and SCORIM Moldings of the Two Sets of PB-1/PP Blends

	CMPB10PP-A	SCPB10PP-A	CMPB30PP-A	CMPB30PP-B	SCPB30PP-A
Young's modulus (MPa)	2083 (214)	2894 (226)	1233 (91)	1285 (62)	2020 (126)
0.8% secant modulus (MPa)	1789 (112)	2503 (133)	1141 (55)	1163 (61)	1816 (79)
Displacement at maximum load (mm)	4.0 (0.2)	6.0 (1.8)	4.7 (0.3)	4.5 (0.4)	7.6 (2.7)
Stress at maximum load (MPa)	36.8 (0.8)	53.1 (1.3)	29.5 (0.7)	29.9 (1.3)	48.1 (1.3)
Strain at break (%)	195 (45)	21 (8)	588 (45)	559 (78)	30 (14)
Toughness (MPa)	32.3 (14.3)	8.9 (3.4)	114.1 (8.5)	121.3 (18.0)	11.2 (6.3)

Numbers in parentheses are the respective standard deviations.

cut from the middle point of the gauge length of each molding and sealed in aluminum pans. A heating rate of 20°C/min was applied.

RESULTS AND DISCUSSION

Mechanical properties

Table II summarizes the tensile testing results. The PB-1 and PP blends exhibited an increase in Young's modulus and the stress at maximum load ultimate tensile strength (UTS) after SCORIM processing. A 40% increase in Young's modulus and UTS was recorded for the SCORIM-processed 10/90 PB/PP blend. Similarly, a 60% increase in Young's modulus and UTS was recorded for the SCORIM-processed 30/70 PB/PP blend. It seems that the gain in stiffness due to the application of macroscopic shears during solidification was greater for the higher PB content blend.

Young's modulus and the 0.8% secant modulus decreased strongly with increased PB-1 content. This trend was observed in both SCORIM and conventional moldings. It appears that the increase in the PB-1 content was more influential on the properties than the application of SCORIM. The decrease in Young's modulus and the 0.8% secant modulus was in agreement with the observation of Lee and Chen.[7] The tensile strength and the displacement at maximum load did not exhibit any significant change with the change in the composition of the blends. From the study by Lee and Chen, it is known that the ultimate tensile strength and the ultimate elongation show a maximum at a 25% content of PB-1. The two compositions chosen for this study lie on either side of the maximum observed by Lee and Chen. Taking these findings into account, we found that the effect of an increase in the PB content on the tensile properties at the peak could not be assessed clearly. However, Table II clearly indicates that the application of SCORIM enhanced the tensile properties at the peak in both blends.

However, there was a substantial decrease in the strain at break and toughness when the blends were processed with SCORIM. Figures 1 and 2 show the

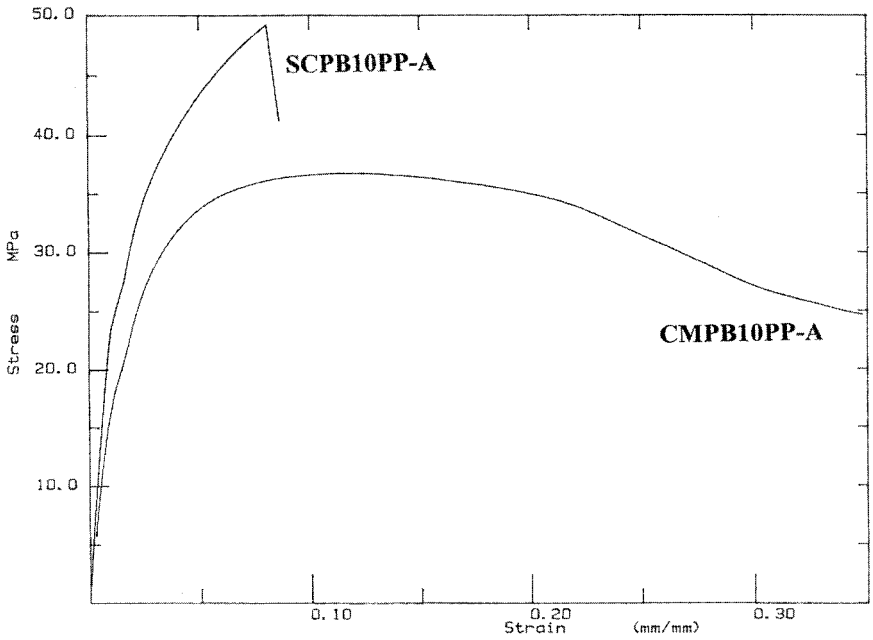

Figure 1 Stress–strain curves for CMPB10PP-A and SCPB10PP-A.

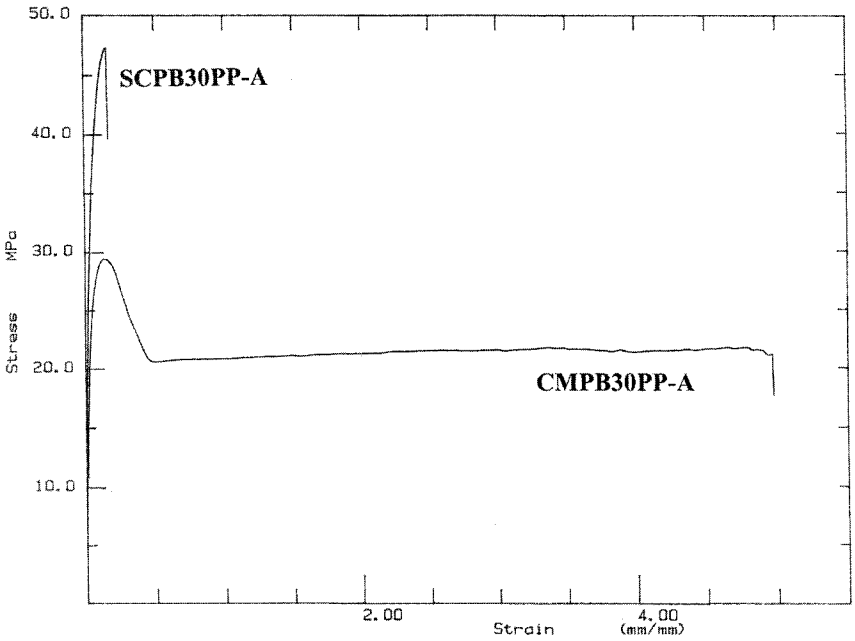

Figure 2 Stress–strain curves for CMPB30PP-A and SCPB30PP-A.

stress–strain curves for CM and SCPB10PP-A and CM and SCPB30PP-A, respectively. An increase in the content of PB-1 enhanced the strain at break considerably, as evident from the comparison of CMPB10PP-A and CMPB30PP-A, which exhibited a threefold increase in the strain at break in comparison with the former. This could be due to the plasticizing effect of PB-1 on PP. The drastic decrease in toughness in SCORIM-processed samples, as evident from the stress–strain curves and the data in Table II, would result in the conclusion that conventional injection molding is favorable for these blends when the impact resistance is important for the application. CMPB30PP-A exhibited strong necking, whereas the SCORIM molding of the same blend showed much less appreciable necking.

Morphological studies

Figures 3 and 4 show the whole longitudinal cross sections of CMPB10PP-A and SCPB10PP-A between crossed polars. CMPB10PP-A exhibited an oriented zone between the skin and transitory layers and the wide spherulitic core. The transitory layer appeared spherulitic. The spherulitic core exhibited a very fine morphology. Even at higher magnifications, it was not possible to distinguish different types of spherulites. SCPB10PP-A (Fig. 4) did not exhibit a spherulitic core. The morphology of SCPB10PP-A appeared layered, and some of the layers, especially those toward the edges, exhibited a weak lamellar texture at higher magnifications. It was shown elsewhere that such seemingly featureless parts of micrographs of PP[11] and PB-1[12] exhibit shish-kebab morphology. Interfacial features can be observed between the layers.

Figures 5 and 6 show the whole longitudinal cross sections of CMPB30PP-A and SCPB30PP-A between crossed polars. CMPB30PP-A exhibited skin layers, a transitory region with apparently distorted spherulites, and a wide spherulitic core. There was no oriented layer, and this corresponded to the lower mechanical properties observed in CMPB30PP-A in comparison with

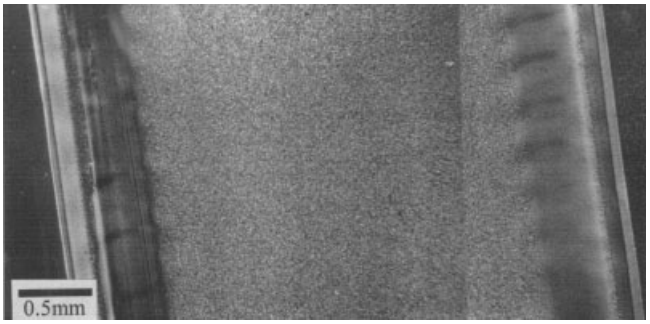

Figure 3 Whole longitudinal cross section of CMPB10PP-A.

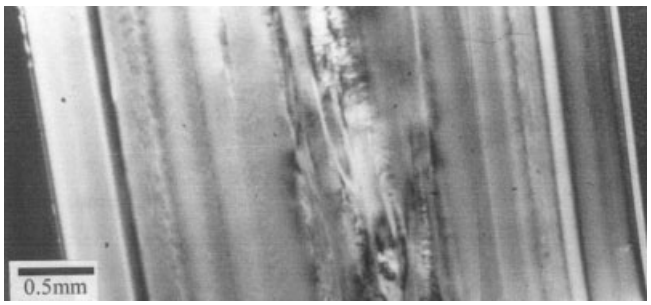

Figure 4 Whole longitudinal cross section of SCPB10PP-A.

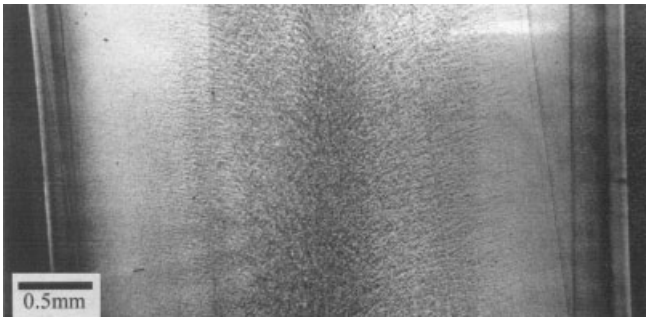

Figure 5 Whole longitudinal cross section of CMPB30PP-A.

CMPB10PP-A. The spherulitic core exhibited a fine texture. It was hardly possible to discern individual spherulites even at higher magnifications. The spherulite size appeared to increase toward the core, which manifested itself in a less fine texture. Because of the fine morphology of the spherulitic core, a comparison between the spherulite size in CMPB10PP-A and CMPB30PP-A was barely possible. Judging from photographs taken at a medium resolution, we found no significant difference (Fig. 7). SCPB30PP-A did not exhibit a spherulitic core and appeared highly oriented like SCPB10PP-A. At a higher magnification, a layered structure could be identified with a partly lamellar texture (Fig. 8). This type of morphology was very similar to the morphology observed in SCPB10PP-A. Interfacial features, as also observed for SCPB10PP-A, were even more conspicuous in SCPB30PP-A. These interfaces were postulated to be the result of segregation due to shearing.[13] The segregated areas then crystallized at different times because of the considerable difference in the crystallization speeds of PB-1 and PP.[4,5] These interfacial features were thought to be the main reason for the low ductility of the SCORIM moldings observed in tensile testing, as these interfaces diminished cohesion in the transverse direction. This defect would become more important at higher test loads. It manifested itself in low values for the strain at break and toughness.

DSC results

Figures 9 and 10 show the DSC thermograms for CMPB10PP-A and SCPB10PP-A (blends containing 10%

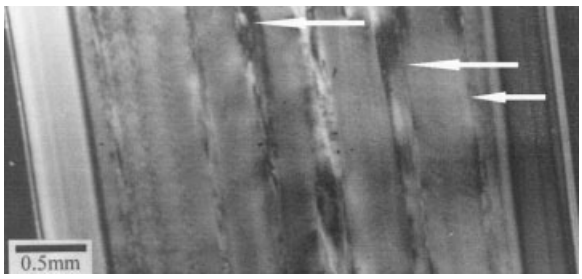

Figure 6 Whole longitudinal cross section of SCPB30PP-A. The white arrows point to interfacial features.

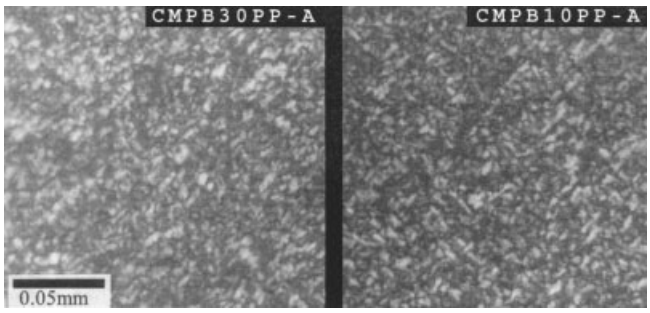

Figure 7 Comparison of the spherulitic core morphologies in CMPB10PP-A and CMPB30PP-A.

PB), respectively. The main melting endotherm was of α-phase PP for both CM10PP-A and SCPB10PP-A. However, there was a shoulder at 117°C for the conventionally molded sample that corresponded to the melting point of the metastable PB form II. There was also a very shallow peak at 96°C that corresponded to the melting of stable form I′, which formed at high cavity pressures, both for the conventional and SCORIM samples. It is known from the literature that form I′ recrystallizes into form II above 100°C. It is, therefore, more reasonable to assume that the melting endotherm of form II is related to the recrystallization of form I′.[14] The moldings were stored long enough before testing to ensure a complete transformation of form II into form I.[15–17] The DSC thermograms suggest that PB and PP were immiscible. This immiscibility refers to the crystalline phases. It is worth emphasizing that PB-1 and PP might be miscible in the melt and amorphous phase. There was no peak for PB-1 form I melting, neither in the DSC thermogram for CMPB10PP-A nor in that for SCPB10PP-A. The reason for this can be seen in the huge difference in the latent heats of fusion.[18,19] The peak of PB-1 form I was expected to be much smaller than the peak of α-phase PP and, therefore, likely to be covered by the latter. The main melting peak of the SCORIM molding was broader than that of the conventional molding, and this may be seen

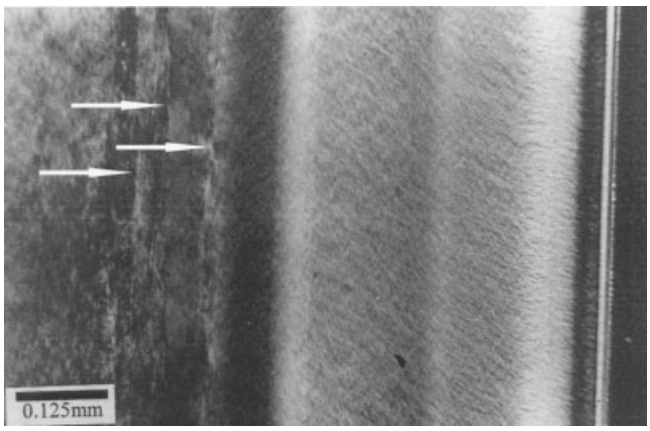

Figure 8 Morphology of SCPB30PP-A at the edges. The white arrows point to interfacial features.

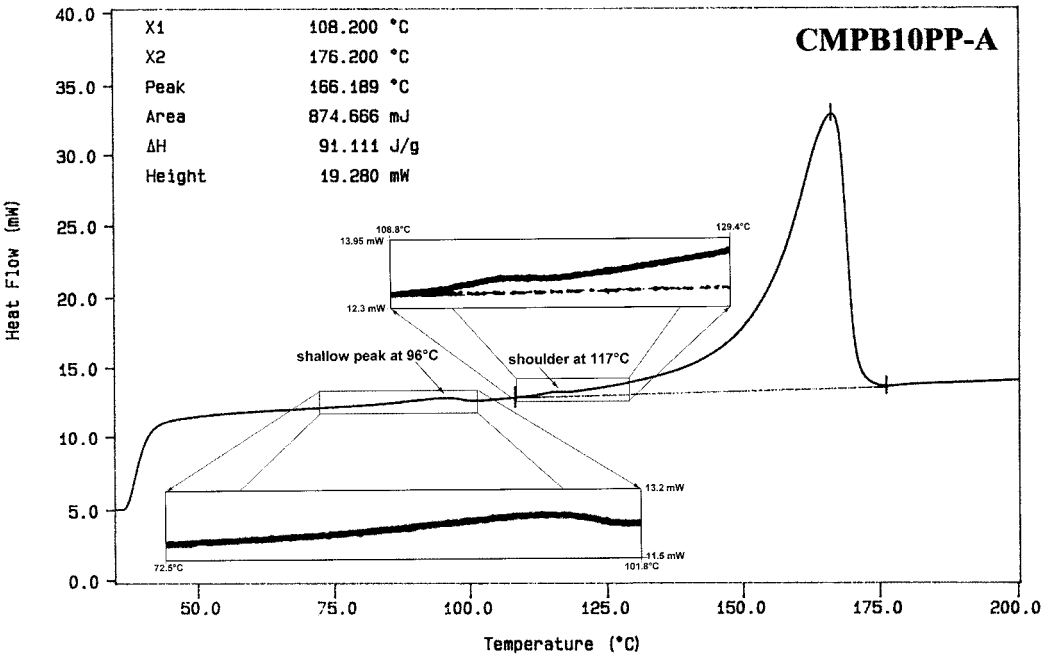

Figure 9 DSC thermogram of CMPB10PP-A.

as an indication for the merging of the PB-1 peak into the PP peak.

Figure 11 shows the DSC thermogram for CMPB-30PP-A. The main melting endotherm at 165.3°C was again of the α phase. CMPB30PP-A exhibited two more melting endotherms at 114 and 95°C for form II and form I′, respectively. Compared with CMPB10PP-A, the higher PB-1 content in CMPB30PP-A resulted in more pronounced peaks at 114 and 95°C. SCPB30PP-A (Fig. 12) exhibited a similar DSC thermogram with a shoulder at 113°C and a melting peak at 93°C. The form I′ melting peak at 93°C had an enthalpy of fusion (ΔH) value of 7.79 J/g, which was higher than the ΔH value of the corresponding peak in CMPB30PP-A. From this evidence, one can conclude that the application of SCORIM enhances the formation of form I′. It is interesting to compare these results to the findings of Lee and Chen.[7] In their study of conventional moldings, Lee and Chen

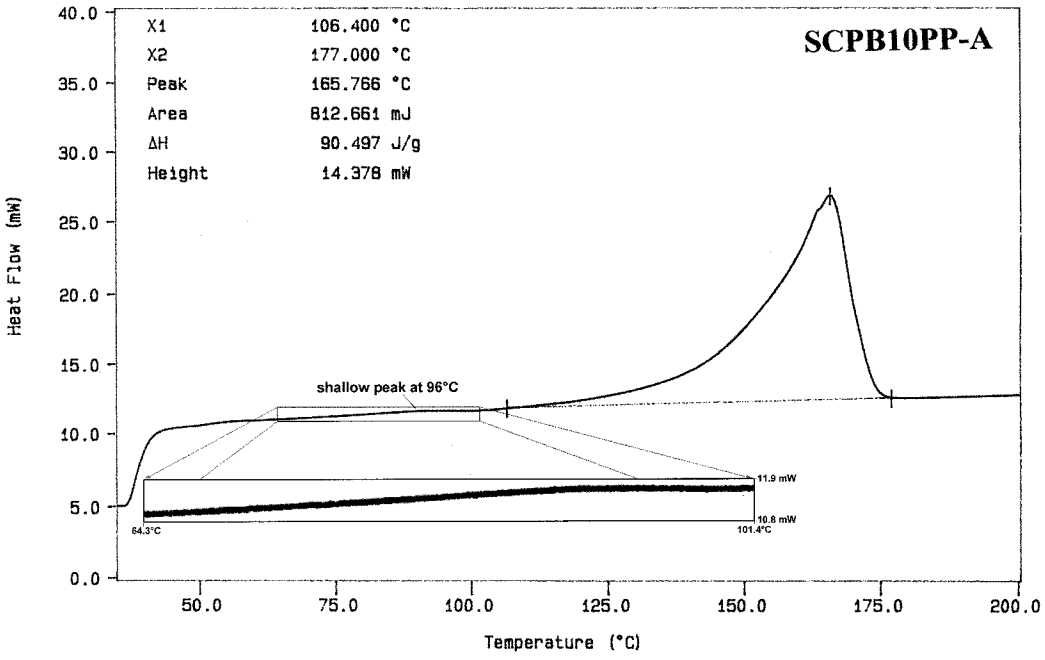

Figure 10 DSC thermogram of SCPB10PP-A.

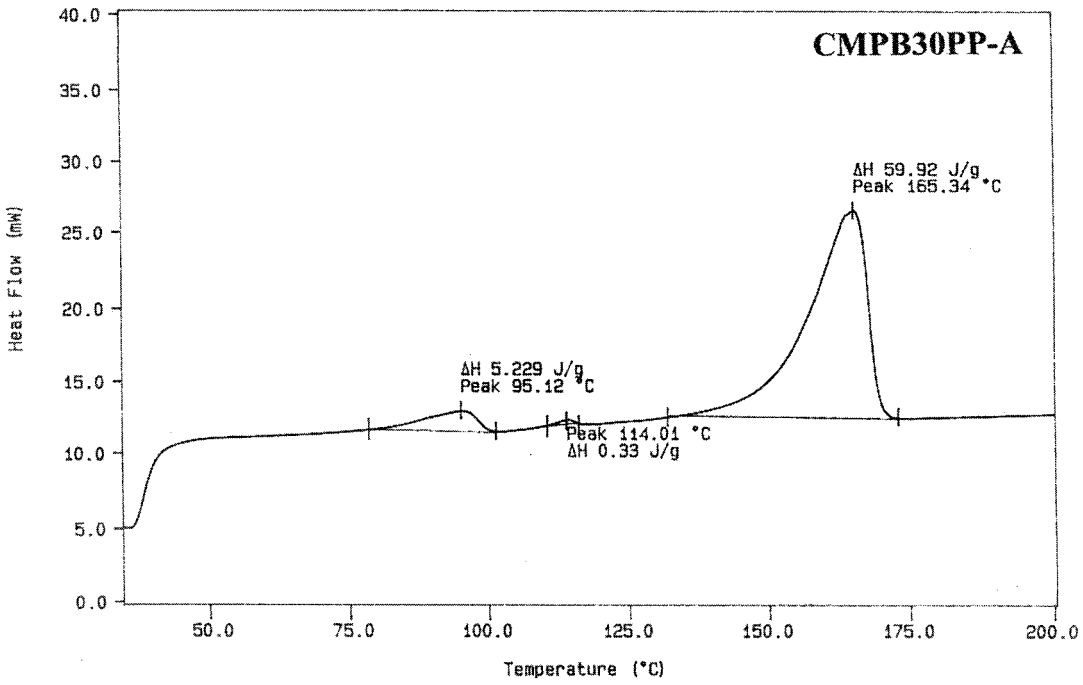

Figure 11 DSC thermogram of CMPB30PP-A.

found that the homopolymer PB-1 did not exhibit form I′. The blend with 25% PB-1 content showed the maximum amount of form I′, whereas the peak of form I′ melting diminished again with a higher PB-1 content.

Neither the DSC thermogram of CMPB30PP-A nor the that of SCPB30PP-A yielded any information about the melting of PB-1 form I as those of CMPB10PP-A and SCPB10PP-A did. It is, therefore, not possible to evaluate the thermograms for information on the total crystallinity.

CONCLUSIONS

The PB-1 and PP blends exhibited an increase in Young's modulus and UTS after SCORIM processing.

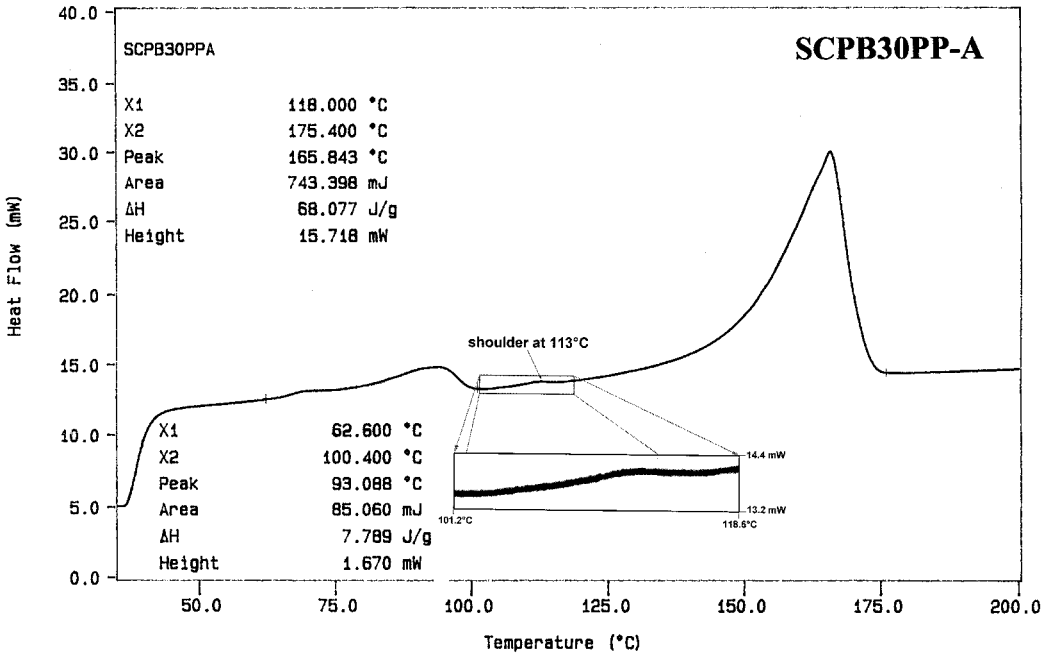

Figure 12 DSC thermogram of SCPB30PP-A.

It seems that the gain in stiffness was greater for higher PB content blends. A 40% increase in Young's modulus and UTS was recorded for the SCORIM-processed 10/90 PB/PP blend. Similarly, a 60% increase in Young's modulus and UTS was recorded for the SCORIM-processed 30/70 PB/PP blend. However, there was a substantial decrease in the toughness when the blends were processed with SCORIM. The drastic decrease in the toughness for the blends would result in the conclusion that conventional injection molding is favorable for these blends when the impact resistance is important for the application.

The morphological studies showed that the enhancement of Young's modulus and UTS was achieved by an increase in the oriented structure due to the application of SCORIM. The micrographs of the SCORIM moldings did not exhibit any spherulitic morphology. The presence of interfacial features in the SCORIM moldings may indicate the occurrence of segregation during the application of SCORIM. These interfacial features are seen as the main reason for the decrease in the toughness.

The DSC thermograms confirmed that the PB-1 and PP blends were not miscible in the crystal phase. SCORIM and conventional moldings exhibited form I′ formation in the PB-1 component. The application of SCORIM promoted the formation of form I′.

The results show that the application of macroscopic shears during solidification is effective in enhancing mechanical performance. However, this study of PB-1/PP blends also shows that shearing during solidification may cause segregation with adverse consequences.

The processing and characterization work were carried out in the Wolfson Centre for Materials Processing of Brunel University, where both authors were previously employed. The tensile testing was performed at the University of Minho in Portugal.

References

1. Polybutylene: Specialty Polymers; Shell Chemicals Data Sheets (Sc: 867-96); Shell Chemicals, Houston, TX, 1996; pp 1–3.
2. de Clippeleir, J.; Hwo, C. C.; Kasakevich, M. L. Presented at the SPE Polyolefin RETEC Conference, Houston, TX, 1997.
3. Scott, J. A. N., Shell Chemicals SA (Louvain-La-Neuve, Belgium), 1998, personal communication.
4. Ratajski, E.; Janeschitz-Kriegl, H. Colloid Polym Sci 1996, 274, 938.
5. Monasse, B.; Haudin, J. M. Makromol Chem Macromol Symp 1988, 20, 295.
6. Wasiak, A.; Wenig, W. Colloid Polym Sci 1984, 262, 435.
7. Lee, M.-S.; Chen, S.-A. Polym Eng Sci 1993, 33, 686.
8. Allan, P. S.; Bevis, M. J. Brit. Pat. 2170-140-B (1987).
9. Kalay, G.; Allan, P. S.; Bevis, M. J. Kunststoffe 1997, 87, 768.
10. Kalay, G.; Bevis, M. J. J Polym Sci Part B: Polym Phys 1997, 35, 241
11. Kalay, G.; Bevis, M. J. J Polym Sci Part B: Polym Phys 1997, 35, 265.
12. Kalay, G.; Kalay, C. R. J Polym Sci Part B: Polym Phys 2002, 40, 1828.
13. Liang, H. Ph.D. Thesis, Brunel University, 1995.
14. Armeniades, C. D.; Baer, E. J Macromol Sci Phys 1967, 1, 309.
15. Natta, G.; Corradini, P.; Bassi, I. W. Nuovo Cimento Suppl 1962, 1, 52.
16. Nakafuku, C.; Miyaki, T. Polymer 1983, 24, 141.
17. Hong, W.; Spruiell, J. E. J Appl Polym Sci 1985, 30, 3163.
18. Starkweather, H. W., Jr.; Jones, G. A. J Polym Sci Part B: Polym Phys 1986, 24, 1509.
19. Bu, H. S.; Cheng, S. Z. D.; Wunderlich, B. Makromol Chem Rapid Commun 1988, 9, 76.