Structure and Physical Property Relationships in Processed Polybutene-1

G. Kalay, C. R. Kalay

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

Received 4 February 2002; accepted 26 June 2002
Published online 12 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11800

ABSTRACT: The effect of SCORIM was investigated on three grades of polybutene-1 and one grade of ethylene–butene-1 copolymer. The methods and processing conditions used for injection molding and the properties of the moldings are reported. Phase transformations and their relationship with mechanical properties are discussed in detail. Both, conventional and shear-controlled orientation injection molding (SCORIM) were employed to produce 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 by performing mechanical tests, fractographic analysis, differential scanning calorimetry studies, wide-angle X-ray diffraction, polarized light microscopy, and atomic force microscopy. The application of SCORIM improves the mechanical performance. Molecular orientation results in the formation of shish-kebab morphology. One grade of polybutene-1 exhibited a greater than fivefold increase in Young's modulus. The application of high cavity pressures favored the formation of the stable Form I′ in polybutene-1. The formation of Form I′ led to a decrease in crystallinity and mechanical properties. However, this loss was by far smaller than the gain obtained via the formation of shish-kebab morphology. The relationship between mechanical properties and micromorphologies of the investigated materials is explained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 814–824, 2003

Key words: polyolefins; injection molding; structure–property relations; shear; crystallization

INTRODUCTION

Isotactic polybutene-1, or poly-1-butene, is a semicrystalline, thermoplastic polymer with high molecular weight. Natta and coworkers first synthesized polybutene-1 in 1954 using two-component catalyst systems containing organoaluminum compounds and transition metal salts and halides. Subsequent modifications to the original Ziegler–Natta catalytic systems by other researchers helped to improve the degree of isotacticity. Various catalytic systems have been developed to prepare 1-butene–ethylene and 1-butene–propylene copolymers.[1] Polybutene-1 has a high degree of flexibility and toughness. It is resistant to stress cracking, abrasion, and long-term creep. It retains its physical properties at elevated temperatures.[1]

Polybutene-1 exhibits polymorphic crystallization behavior. Five different crystalline modifications have been reported in the literature, which are referred to as I, II, III, I′, and II′.[2–12] The most important phenomenon is the transformation of Form I into Form II, which takes place in polybutene-1 at room temperature after crystallization from the melt. Natta et al.[2] were the first to discover that polybutene-1 assumes an 11/3 helical conformation with a tetragonal unit cell when crystallizing from the melt. This crystalline structure is known as Form II. It is unstable and transforms into a stable 3/1 helix conformation (Form I) with hexagonal (rhombohedral) unit cells at room temperature and atmospheric pressure. This transformation results in the desirable properties of the material. The melting point increases from 120 to 135°C. The transformation is accelerated by the application of pressure of only a few hundred bars.[2] Form III has been observed in films of polybutene-1 precipitated from certain solvents.[3] The appearance of Form I′ and Form II′ is related to crystallization under pressure. Nakafuku and Miyaki[4] studied the effect of pressure on the crystallization behavior of isotactic polybutene-l and reported that its melt crystallization under high pressure produces stable Form I′, which shows the same X-ray diffraction pattern as Form I but has a much lower melting temperature (96 versus l30°C) at atmospheric pressure. Above 2 kbar, Form I′ and Form II′ are crystallized from the melt.[4] Form II′ shows the same X-ray diffraction pattern as Form II, but a lower melting temperature than Form II. Form II′ is metastable at atmospheric pressure and transforms to Form I′ on standing at room temperature.[4]

The primary aim of the research reported in this article was to explore the relationships between processing conditions and physical properties of poly-

Correspondence to: G. Kalay (gkalay@sabanciuniv.edu).

TABLE I
Processing Conditions for the Conventional and SCORIM Moldings of PB0110

Condition	Molding				
	CMPB1-A	CMPB1-B	SCPB1-A	SCPB1-B	SCPB1-C
Injection pressure (bar)	76	76	100	76	76
Holding pressure (bar)	44	160	69	95	82
Injection time (s)	0.38	0.38	0.33	0.44	0.41
Holding pressure time (s)	30	30	53	53	67
Cycle time (s)	88	85	85	90	121
Mold temperature (°C)	40	40	40	40	40
Melt temperature (°C)	190	190	190	190	190
Cavity pressure (bar)	235	868	441	721	706

butene-1. Several grades of commercially available polybutene-1 were processed using conventional injection molding and shear-controlled orientation injection molding (SCORIM).[15–17] Different processing methods have a pronounced effect on the micromorphology of polymeric products. SCORIM processing results in a high level of molecular orientation, which forms the basis for the property enhancing effect reported previously for several semicrystalline polymers.[13–21] During processing, macroscopic shears are applied to a solidifying semicrystalline melt, which enhances the molecular alignment and leads to increases in stiffness without loss of impact strength.[13–21]

EXPERIMENTAL

Materials

Three grades of unfilled, isotactic polybutene-1 and one ethylene–butene-1 copolymer were investigated. All four materials were supplied by Shell Research SA (Louvain-la-Neuve, Belgium). PB0110, the first grade of isotactic polybutene-1, is a nucleated homopolymer. PB0110 exhibits a number average molecular weight (M_n) of 128 700, a weight average molecular weight (M_w) of 854 800, and hence a polydispersity (M_w/M_n) of 6.6. The melt flow index (MFI) and density of PB0110 are, respectively, 0.4 g/10 min and 0.915 g/cm^3. The second grade, PB0300, is a general-purpose medium melt flow homopolymer with an M_n of 98 6000, an M_w of 391 800, and hence an M_w/M_n of 4.0. The MFI and density of PB0300 are, respectively, 4.0 g/10 min and 0.915 g/cm^3. The third material investigated, DP4137, was developed especially for the use in hot water pipes. The material exhibits an MFI of 0.4 g/10 min and a density of 0.93 g/cm^3. The results for PB0110 and PB0300 are discussed in this article, and those for DP4137 are discussed in more detail in a separate article.[22]

The ethylene–butene-1 copolymer, DP8310, is a medium melt flow copolymer with 6 wt % ethylene content (high ethylene copolymer resin). It exhibits an M_n of 116 200, an M_w of 396 100, and, hence, an M_w/M_n of 3.4. The MFI and density of PB8310 are, respectively, 3.0 g/10 min and 0.895 g/cm^3.

Injection molding

Both conventional injection molding and SCORIM were employed in processing. Width-waisted tensile test bars were molded. A Demag 150 injection molding machine equipped with a double live-feed molding device was used for the production of bars. The thickness of the gauge section of the test bars is 5 mm in diameter.

PB0110 grade polybutene-1 was used to produce two sets of conventional (CMPB1-A and -B) and three sets of SCORIM (SCPB1-A, -B, -C) moldings. The general processing conditions for these moldings are shown in Table I. The effect of pressure in processing on the properties of conventional and SCORIM moldings should be identifiable by comparison of the structure and properties of A and B series conventional and SCORIM moldings. The maximum recorded cavity pressures for CMPB1-A and -B were, respectively, 235 and 870 bars (Figure 1). SCPB1-A and -B were produced under average cavity pressures of 440 and 720 bars, respectively (Figure 2). The SCPB1-C moldings were subjected to longer periods of repeated shear action than the SCPB1-A and -B moldings, and to the application of high packing pressure after the completion of the out-of-phase SCORIM piston movements.

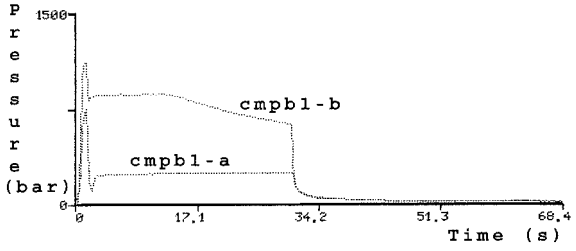

Figure 1 The cavity pressure profiles for CMPB1-A and CMPB1-B.

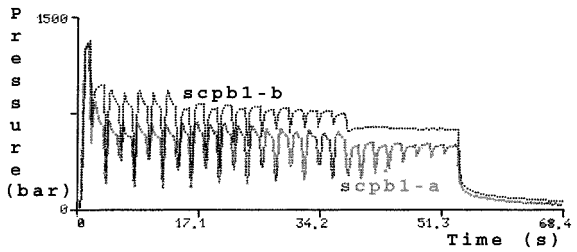

Figure 2 The cavity pressure profiles for SCPB1-A and SCPB1-B.

The average cavity pressure for SCPB1-C was 700 bars.

One set of conventional (CMPB2-A) and one set of SCORIM (SCPB2-A) moldings were produced with PB0300 grade polybutene. Similarly, one set of conventional (CMPB3-A) and one set of SCORIM (SCPB3-A) moldings were produced with DP8310 grade copolymer. The processing conditions for these four sets of moldings are summarized in Table II. DP4137 was used to produce one set of conventional moldings and one set of SCORIM molding. The general processing conditions were similar to those used in the production of CMPB1-A and SCPB1-A, with average cavity pressures of 288 bars for the conventional molding and 329 bars for the SCORIM process. All the moldings were kept under room conditions.

Mechanical testing

An Instron 4500 Series tensile testing machine at a crosshead speed of 25 mm/min and a test temperature of 23°C was used in tensile testing of PB0110. Strain was measured with a clip-on strain gauge. Young's modulus data were measured at a crosshead speed of 1 mm/min. The tensile testing of PB0300 and DP8310 moldings was carried out on an Instron 4505 Series tensile testing machine. The crosshead speed of 5 mm/min was applied up to the strain of 1.5% and then 50 mm/min until failure. An Instron 2630 resistive extensometer, with a gauge length of 10 mm, was used. The Young's modulus and the secant modulus at 0.8% strain were calculated. A toughness value, also quoted in the Results, is calculated as the energy at break point divided by the product of the cross-sectional area of the sample multiplied by the gauge length.

An un-notched flexural Charpy impact test was performed to determine the impact on a Ceast Charpy flexural impact testing machine. The initial span was 22 mm, and the tests were done after cooling the samples to −20°C. Tensile and impact testing results reported in this article were obtained after 1 month of injection molding the samples.

Scanning electron microscopy (SEM)

Scanning electron microscopy was employed to examine the impact and tensile failure surfaces of some of the moldings. For fractographic examination, the fracture surfaces of the failed specimens were mounted on stubs and coated with Au/Pd and subsequently examined by SEM.

Wide-angle X-ray diffraction

CuK_α radiation was used for the production of Debye patterns. The Debye patterns were used to record preferred orientation. For the conventional and the SCORIM moldings, the samples used were 1.5-mm thick and cut parallel to the injection direction. Debye patterns were recorded at positions 1.5 mm from the edge of the moldings. A 100-μm diameter aperture was used to define the position and cross-section of the incident X-ray beam. The Debye patterns were obtained from 3-month-old samples.

Microtomy and light microscopy

Thin sections of ~10-μm thickness were prepared with a Leitz rotary microtome. A tungsten carbide hardened steel knife of small included angle was used to cut thin sections. The knife and the specimen were maintained at room temperature. Sections were cut

TABLE II
Processing Conditions for the Conventional and SCORIM Moldings of PB0300 (CMPB2-A, SCPB2-A) and DP8310 (CMPB3-A, SCPB3-A)

Condition	Molding			
	CMPB2-A	CMPB3-A	SCPB2-A	SCPB3-A
Injection pressure (bar)	100.8	100.8	100.8	100.8
Holding pressure (bar)	63	63	63	48
Injection time (s)	0.08	0.08	0.07	0.08
Holding pressure time (s)	30	40	49	61
Cycle time (s)	90	106	98	128
Mold temperature (°C)	40	40	40	40
Melt temperature (°C)	180	140	180	140
Cavity pressure (bar)	400	360	320	260

TABLE III
Tensile Test Data for Both Conventional (CM) and SCORIM (SC) Moldings of PB0110 Polybutene-1[a]

Molding	% Strain at Peak (%)	Stress at Peak (MPa)	% Strain at Break (%)	Young's Modulus (MPa)
CMPB1-A	16.540 (2.392)	34.59 (6.84)	16.550 (2.4)	920.4 (149)
CMPB1-B	18.06 (3.35)	37.94 (4.24)	18.06 (3.35)	1059 (177.4)
SCPB1-A	24.45 (6.53)	58.06 (3.71)	—	2882 (361.3)
SCPB1-B	17.64 (2.54)	47.85 (1.87)	18.38 (2.57)	1963 (203)
SCPB1-C	14.59 (4.411)	48.19 (3.25)	15.22 (3.82)	2191 (135)

[a] Numbers in brackets are the standard deviations.

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.

Atomic force microscopy (AFM)

AFM studies were carried out at Shell Research and Technology Centre, Amsterdam, by Dr. Constant A. J. Putman. The samples were prepared by etching for 4 min with a permanganic etchant. The AFM was operated in tapping mode.

Differential scanning calorimetry (DSC)

A Perkin Elmer DSC-7 was used in the measurements of DSC thermograms. Approximately 10-mg samples were cut from the middle point of the gauge length of each molding and sealed in aluminium pans. A heating rate of 20°C/min was applied. DSC was performed 2 months after the molding.

RESULTS AND DISCUSSION

Mechanical properties

The tensile test data of all the PB0110 moldings are summarized in Table III. In conventional moldings, the Young's modulus increases noticeably, by ~15%, following the application of a higher cavity pressure. CMPB1-A and CMPB1-B exhibit Young's moduli of 920 and 1059 MPa, respectively. This tendency is not observed in SCORIM moldings. It seems that high cavity pressures result in some decrease in tensile properties. SCPB1-B and -C were processed at a higher cavity pressure than was SCPB1-A and both exhibit lower tensile properties than SCPB1-A. This result is attributed to a lower melting point phase formation as a result of high pressures and greater molecular alignment. However, DSC thermograms show that the low melting point phase does not occur substantially in CMPB1-B. Details are discussed later in the section on DSC results.

The PB0110 moldings exhibit substantial improvement following the application of SCORIM. CMPB1-B and SCPB1-A exhibit 1.1 and 2.9 GPa Young's moduli, respectively, which represents a >2.5-fold increase with SCORIM. A 55% increase in ultimate tensile strength (UTS) is also observed for PB0110 with SCORIM. Finally, comparison of CMPB1-B and SCPB1-A demonstrates that the application of macroscopic shearing during solidification leads to improved properties without increasing the cycle time.

The results of the impact testing of the PB0110 moldings (Table IV) exhibit the same tendencies as the tensile test results. The impact resistance increases with an increase in mold cavity pressure in conventional molding but not in SCORIM. This result is further evidence that the formation of low melting point phase is detrimental. The flexural Charpy impact test results show a substantial increase in impact resistance of PB0110 following SCORIM processing. The SCPB1-A moldings exhibit more than a twofold increase in impact resistance compared with the CMPB1-B moldings.

The tensile and impact test data of the PB0300 and DP8310 moldings are summarized in Table V. The PB0300-grade polybutene-1 exhibits substantial improvement following the application of SCORIM. The stress–strain curves for CMPB2-A and SCPB2-A are shown in Figure 3. CMPB2-A and SCPB2-A exhibit Young's moduli of 0.31 and 1.61 GPa, respectively. This result indicates a greater than five-fold increase with SCORIM. A 70% increase in the stress at maximum load with SCORIM is also observed for PB0300.

TABLE IV
Charpy Flexural Impact Testing Results for Both Conventional (CM) and SCORIM (SC) Moldings of PB0110 Polybutene-1

Molding	Impact Energy (J)[a]
CMPB2-A	1.09 (0.2134)
CMPB2-B	1.31 (0.195)
SCPB2-A	2.7 (0.1535)
SCPB2-B	2.05 (0.2477)
SCPB2-C	2.092 (0.1781)

[a] Numbers in brackets are standard deviations.

TABLE V
Tensile Test and Impact Test Data for the Conventional and the SCORIM Moldings of PB0300 (PB2-Series) and DP8310 (PB3-Series)[a]

Molding	Young's Modulus (MPa)	0.8% Secant Modulus (MPa)	Displacement at Max. Load (mm)	Stress at Max. Load (MPa)	Strain at Break (%)	Toughness (MPa)	Impact Energy (J)
CMPB2-A	308 (62)	316 (54)	31.4 (7.2)	20.8 (1.0)	67 (49)	10.9 (8.9)	1.335 (0.102)
SCPB2-A	1611 (268)	1490 (193)	39.8 (21.1)	35.8 (1.3)	39 (32)	11.3 (11.4)	1.438 (0.152)
CMPB3-A	134 (28)	144 (27)	19.3 (14.6)	15.7 (0.9)	110 (22)	13.0 (3.2)	—
SCPB3-A	251 (65)	251 (63)	9.6 (9.4)	20.1 (1.3)	155 (62)	26.3 (12.1)	—

[a] Numbers in brackets are standard deviations.

However, the ductility of the SCORIM moldings is sharply decreased compared with that of the conventional moldings. The strains at break for CMPB2-A and SCPB2-A are 67 and 39%, respectively. The toughness values do not show any significant difference. This result is consistent with the Charpy flexural impact test results that show almost the same impact resistance for CMPB2-A and SCPB2-A.

The ethylene–butene-l copolymer, DP8310, also exhibits improved mechanical properties with SCORIM. The stress–strain curves for CMPB3-A and SCPB3-A are shown in Figure 4. The CMPB3-A and SCPB3-A moldings exhibit Young's moduli of 134 and 251 MPa, respectively. This result represents about a twofold increase as a result of SCORIM processing. There is also a 30% increase in the stress at maximum load for DP8310 with SCORIM. The toughness has improved twofold as well. The results in Figure 4 also show that the SCORIM processing of the copolymer did not lead to a reduction in ductility, unlike in the case of the homopolymer PB0300.

Fractographic analysis

Because the improvement in mechanical performance of PB0110 confirmed that the polybutene-1 homopolymer responded well to the SCORIM process, the impact and tensile failure surfaces were analyzed to gain further information about the morphology. The fractographic analyses were performed on samples from the sets CMPB1-A and SCPB1-A. The impact failure surface of conventionally molded PB0110 exhibits a planar failure (Figure 5). There is a clear skin formation, which appears to rupture in a tensile manner in flexural impact testing. The other two zones are the transitory zone and the core. The core region appears more granular, whereas the narrow transitory region exhibits some short-range orientation. The tensile failure surface of the conventionally molded polybutene-1, PB0110, also exhibits three zones, which is consistent with the impact failure surface observations. The tensile failure is also planar. The impact failure surface of the SCORIM-processed SCPB1-A, which exhibited the best mechanical performance, is shown in Figure 6. The SCORIM-molded samples exhibit more severe failure compared with the conventionally molded samples. The tensile and compression regions of the flexural failure are clearly distinguishable. The tensile region, on the left in Figure 6, is considerably broader and more strongly deformed than the comparable region of the conventional molding shown in Figure 5. The compression region of the SCORIM molding appears to have a layered structure, and there is a comparably small granular core region.

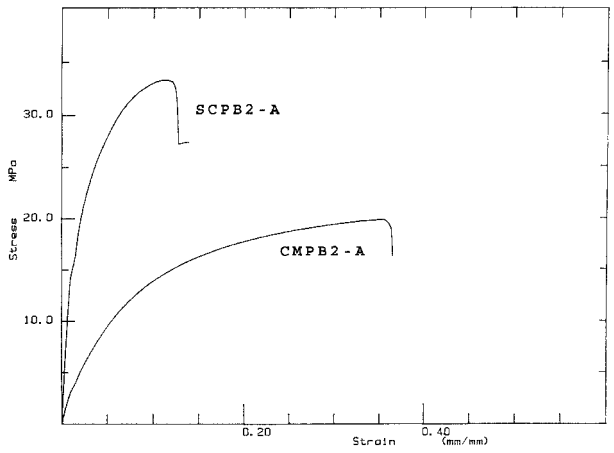

Figure 3 Stress–strain curves for CMPB2-A and SCPB2-A.

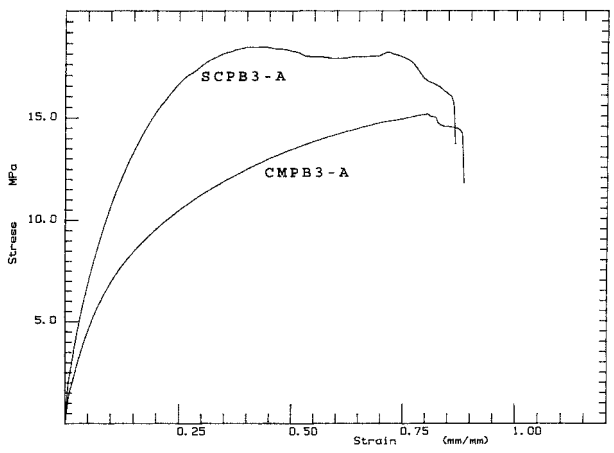

Figure 4 Stress–strain curves for CMPB3-A and SCPB3-A.

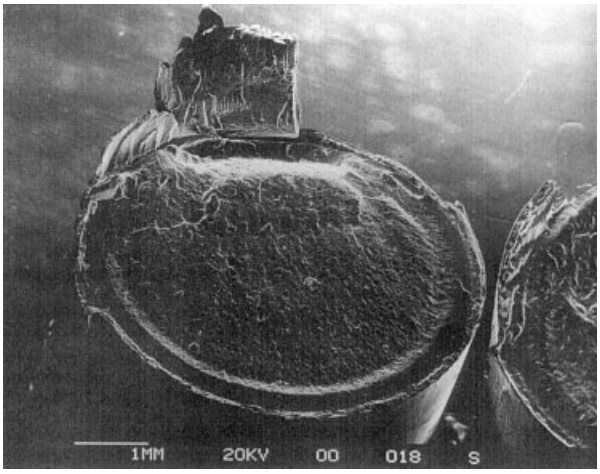

Figure 5 The impact failure surface of CMPB1-A.

Morphological observations

The morphology found in the micrographs obtained from the CMPB1-A set of samples corresponds to the results of the fractographic analysis. The micrograph of CMPB1-A, shown in Figure 7, exhibits four regions: the featureless skin, the transcrystalline subskin, a transitory zone, and the spherulitic core. The difference in the observed number of zones is due to the fact that skin and subskin are more clearly discernible in the optical micrograph. The transitory region, which contains short-range, oriented structures, leads over to the spherulitic core region. The spherulite size in the core region varies noticeably, which can be attributed to the added nucleating agent in PB0110. The morphology of CMPB1-B contains one additional zone. As a result of high cavity pressure, a fairly broad featureless oriented zone is formed between the transitory and the core region. The transitory region in CMPB1-B exhibits sporadic formation of spherulites. The spherulitic core region in CMPB1-B is considerably smaller than the core in CMPB1-A.

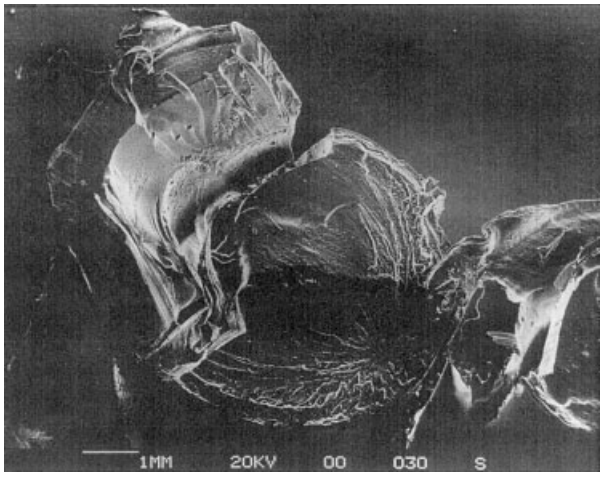

Figure 6 The impact failure surface of SCPB1-A.

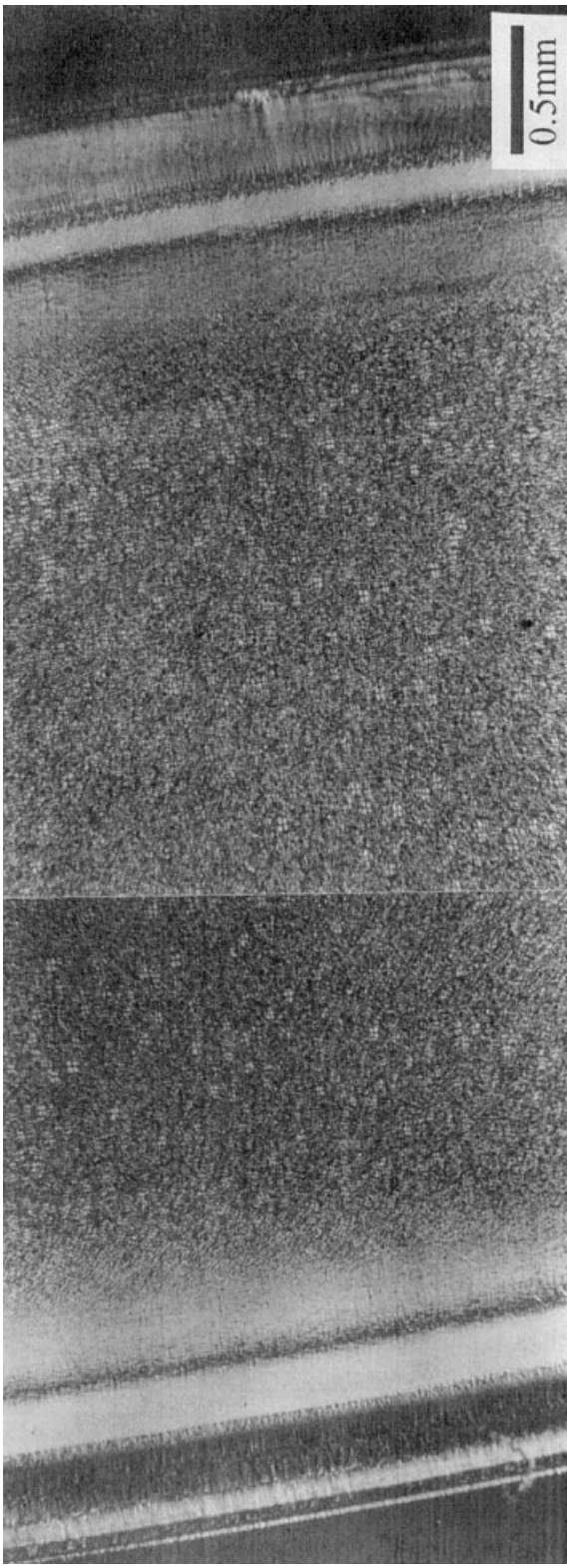

Figure 7 The whole longitudinal cross-section of CMPB1-A.

The morphology of SCPB1-A (Figure 8) is in some ways quite similar to the morphological structure of CMPB1-B. Skin and transcrystalline subskin of SCPB1-A are followed by a transitory region, which

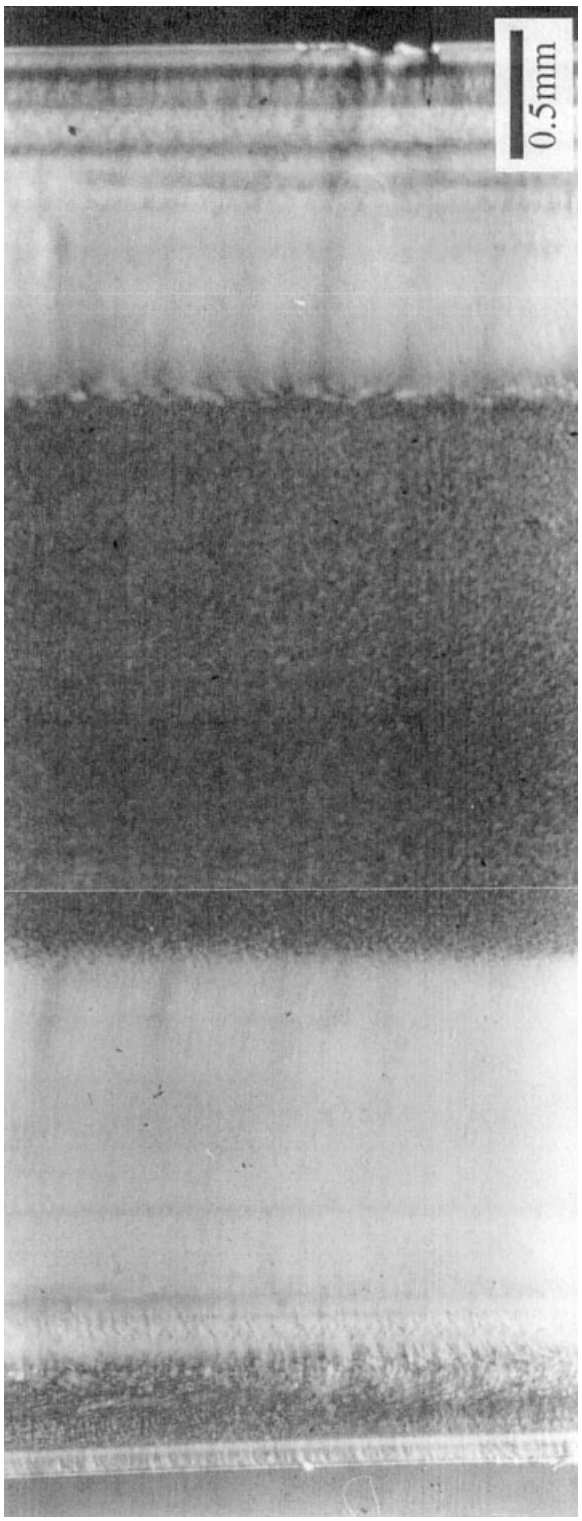

Figure 8 The whole longitudinal cross-section of SCPB1-A.

exhibits more orientation in the injection direction than the comparable region in CMPB1-B. The featureless shear region in SCPB1-A is extended, which reduces the spherulitic core. The spherulitic texture of the core region in SCPB1-A is much finer and more uniform than that in CMPB1-A. A comparison between the micrograph and the impact failure surface is more difficult in the case of SCPB1-A than in the case of the conventional molding because of the strong deformation found in the tensile and compression regions of SCPB1-A. However, it is evident that the severe failure mainly relates to the shear region.

The effect of SCORIM action combined with high cavity pressures results in morphologies that are predominantly featureless. The number of zones is difficult to discern. There is some weak indication of a granular texture in the core and of a transcrystalline-like formation between the skin and the shear region.

The SCORIM moldings of the second polybutene-1 homopolymer, PB0300, exhibit a predominantly featureless appearance. The layered structure in the edge region of SCPB2-A becomes more clearly observable at a higher magnification (Figure 9). There is a skin, a subskin exhibiting transcrystalline features, a transition zone showing distinct lamellar structure, and the oriented region extending all through the core. The lamellae appearing in the transition zone are perpendicular to the orientation of the injection direction, but they grow into the oriented zone extending towards the injection direction as if they are being pulled by the melt flow induced by the SCORIM pistons. SCPB2-A shows a predominantly featureless appearance, like SCPB1-B and SCPB1-C, although the molding of PB0300 was done at a much lower cavity pressure than that of PB0110. CMPB2-A exhibits a spherulitic morphology, with no distinct layer structure. The spherulites are smaller and vary less in size (Figure 10) than those observed for PB0110 moldings. This result is an indirect indication of the effect of the added nucleating agent in PB0110.

It was not possible to microtome the conventionally molded copolymer at room temperature because it was very soft. The greater stiffness of the SCORIM-molded copolymer subtly manifested itself during microtomy as clearly indicated by the easier ejection during injection molding of these moldings compared with conventional moldings. The SCORIM moldings exhibit two distinct regions under a polarized light

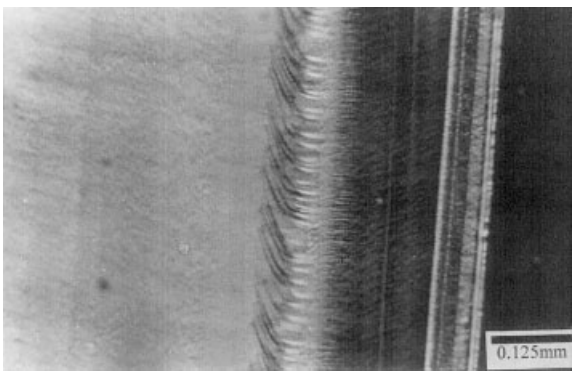

Figure 9 The morphology of SCPB2-A at the edges.

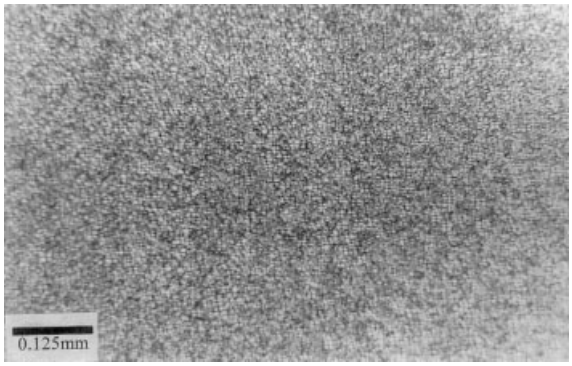

Figure 10 The spherulitic morphology of CMPB2-A.

microscope: the featureless oriented region and a small core region, which exhibits a very finely grained spherulitic morphology.

The often featureless appearance of large parts of the morphology in SCORIM moldings indicates that the resolution of polarized light microscopy is not sufficient for morphological studies. Therefore, AFM studies were performed on moldings of DP4137. AFM analysis of these samples proved that the SCORIM-molded polybutene-1 exhibits a shish-kebab morphology (Figure 11). The Debye patterns of the same samples confirmed the strong molecular orientation in the injection direction present in SCORIM samples. The Debye pattern of SCORIM moldings exhibits pronounced arching that is not evident in the Debye pattern of conventional moldings (Figure 12). The reflections visible in both Debye patterns are mainly related to Form I (or Form I′, respectively). The appearance of a weak {200}-reflection indicates that a small amount of Form II must still be present in the molding.

Figure 11 AFM image of the shear region of a SCORIM molding of polybutene-1 (DP4137). The depicted area is 5 × 5 μm, and the z-scale is 200 nm.

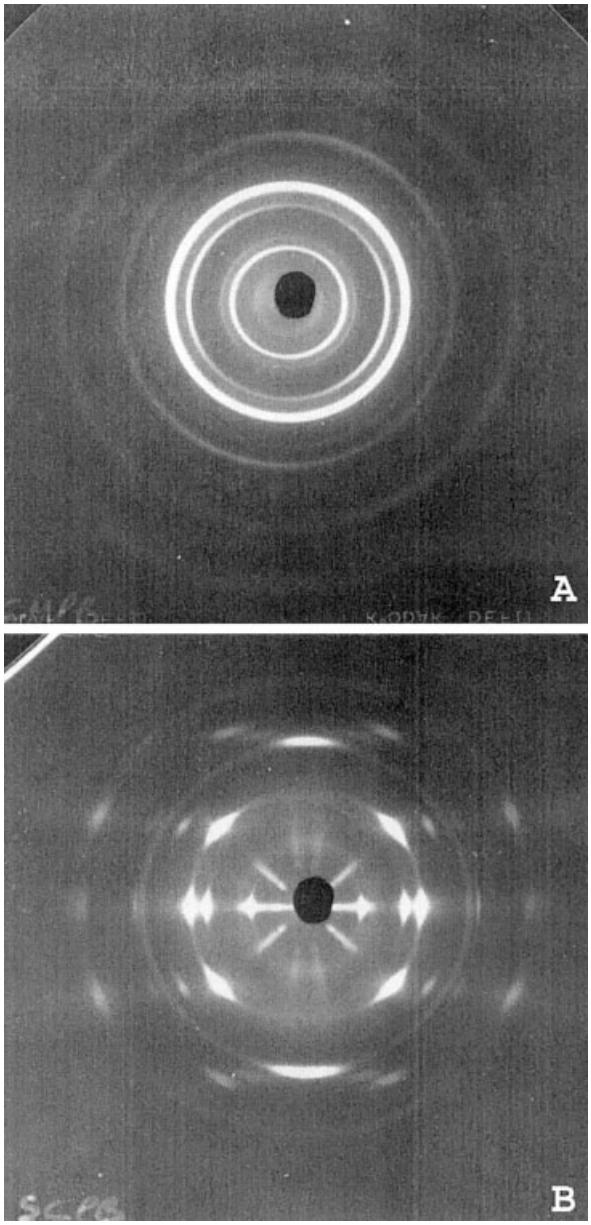

Figure 12 X-ray Debye patterns of two differently processed moldings of polybutene-1 (DP4137): (A) conventional molding; (B) SCORIM molding.

DSC results

The DSC studies were mainly aimed at identifying which modifications were present in the moldings. The thermograms were also used to calculate the crystallinity of the samples. The calculations were based on the literature data by Starkweather and Jones,[23] who reported the melting point and heat of fusion (ΔH_f) data for polybutene-1 Forms I and II. The melting temperature and the ΔH_f for Form I are, respectively, 133°C and 135 J/g. The melting temperature

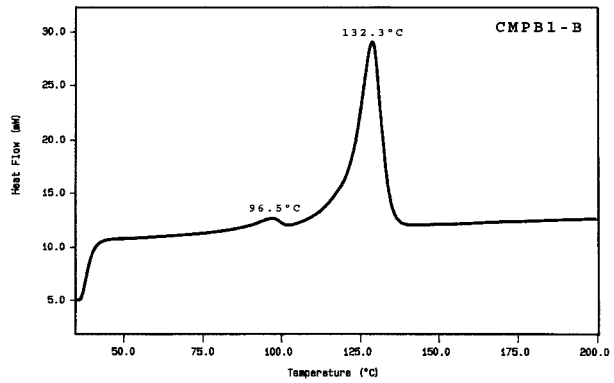

Figure 13 The DSC thermogram for CMPB1-B.

and the ΔH_f for Form II are, respectively, 119.7°C and 146 J/g. Given the fact that the data of Starkweather and Jones[23] were calculated from crystallographic measurements obtained by X-ray diffraction, it will be assumed that Form I′ has more or less the same heat of fusion as Form I, bearing in mind that both forms are reported to have the same X-ray pattern.[6, 7] The DSC results for the moldings of the two polybutene-1 homopolymers, PB0110 and PB0300, are summarized in Table VI. The overall crystallinity represents the amount of Forms I′ and I present. The presence of original Form II can be neglected given the long storage period between the molding and the testing. From the literature it is known that Form I′ will recrystallize into Form II during heating.[6] Therefore, the overall crystallinities were corrected, if necessary, by assuming that Form I′ would completely recrystallize into Form II, the melting of which would be seen as a low-temperature shoulder in the second, higher melting endotherm.

The application of shear at lower pressures to PB0110 moldings (CMPB1-A and -B, and SCPB1-A, -B, and -C) resulted in increased crystallinity. However, when the shear is applied at relatively high pressures, as in the case of SCPB1-B and -C, the overall crystallinity decreased. The application of high cavity pressures in conventional molding also resulted in decreased crystallinity. This decrease in crystallinity is accompanied with the emergence of a second, lower melting endotherm at 96°C. It is known that the melt crystallization of polybutene-1 under high pressures produces stable Form I′, which shows the same wide-angle X-ray diffraction pattern as Form I but has a much lower melting point (i.e., 96°C) at atmospheric pressure.[6] From the recorded thermograms it is clear that injection molding at high pressures results in the formation of the stable Form I′. This phase resulted in poorer mechanical properties for the SCORIM moldings. No deterioration of mechanical properties was observed for CMPB1-B despite the formation of Form I′ (Figure 13). CMPB1-B also exhibited less decrease in overall crystallinity for the high cavity pressure applied. This effect is certainly related to the fact that a smaller amount of Form I′ is formed during conventional molding at high pressure, as evident from the difference in the observed values for the enthalpy of fusion. SCPB1-B and -C exhibit higher intensity low melting endotherms. However, the formation of an oriented zone, which appears featureless in the micrograph of CMPB1-B, seems to have an overriding influence on the mechanical properties of this particular set of moldings. It is worth emphasizing that although SCPB1-B and -C exhibit poorer mechanical properties compared with SCPB1-A, they exhibit substantially greater mechanical properties compared with either set of the conventional injection moldings. None of the thermograms discussed so far exhibits any trace of Form II melting. Therefore, one can conclude from the DSC results that the transformation from Form II to Form I is complete. However, the Debye pattern shown in Figure 14 contradicts this assumption, as it exhibits a weak {200}-reflection, which can only be attributed to the presence of original Form II. The sample of DP4137 used for the production of the Debye pattern was even older than the PB0110 moldings investigated by DSC. This contradictory evidence demonstrates the differing sensitivities of DSC and X-ray diffraction with respect to the detection of small amounts of specific crystal modifications.

The application of high pressure seems to result in an increase in the melting temperature of Form I. This endotherm appears at 127.1°C for CMPB1-A, whereas it appears at 128.8°C for CMPB1-B. The same observation can be made for the SCORIM moldings. SCPB1-A exhibits the peak of the Form I melting endotherm at 129.6°C, whereas SCPB1-B and -C exhibit it at 132.3 and 130.7°C, respectively. Another interesting point is the occurrence of a shoulder at 118°C on the

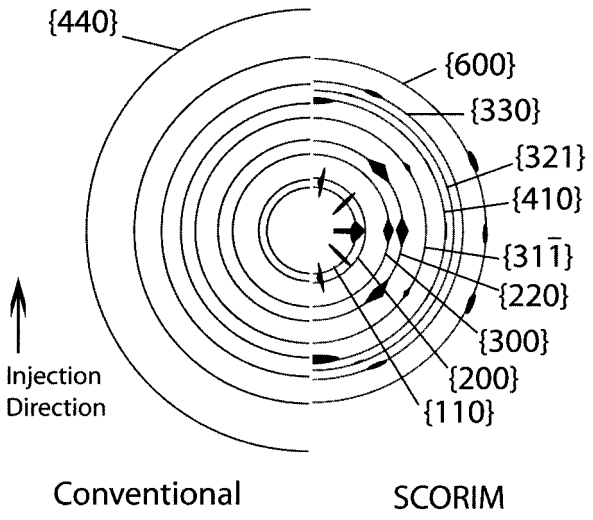

Figure 14 Schematic representation of the Debye patterns of conventionally molded and SCORIM processed polybutene-1. The DSC thermogram for CMPB1-B.

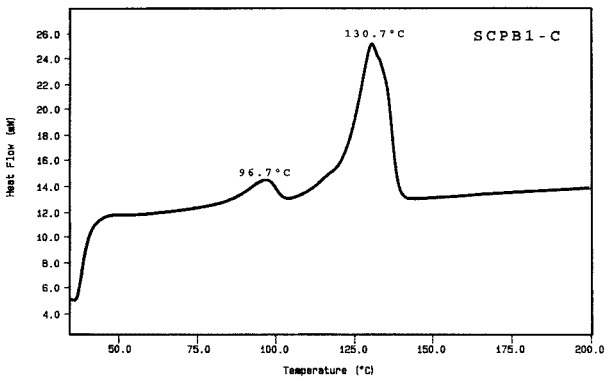

Figure 15 The DSC thermogram for SCPB1-C.

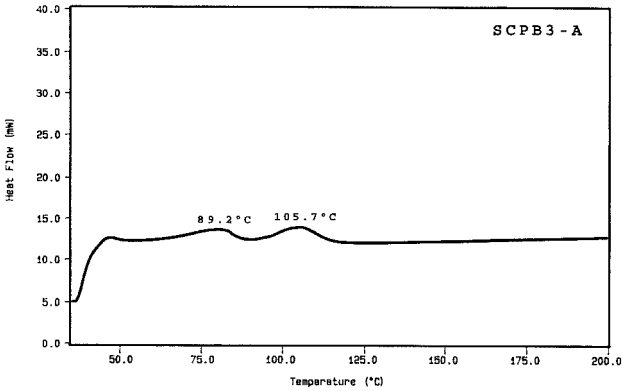

Figure 16 The DSC thermogram for SCPB3-A.

main melting endotherm for SCPB1-C (Figure 15). This temperature corresponds to the melting point of the metastable Form II. From the DSC results for CMPB1-A and SCPB1-A, it is known that the original transformation from Form II to Form I is complete. The appearance of the low-temperature shoulder is forced by the melting of Form II, which was formed during the DSC scan through recrystallization of Form I′. The melting of Form II cannot be observed very clearly in the thermograms of CMPB1-B and SCPB1-B.

The thermograms of CMPB2-A and SCPB2-A exhibit only a melting endotherm for Form I. This result indicates complete transformation of the metastable Form II into Form I. There appears to be no significant difference in the crystallinities of these moldings (Table VI). However, the SCORIM-molded sample exhibits a greater melting point than the conventionally molded one. This difference is consistent with the findings reported for PB0110. There is no Form I′ present in either of the moldings.

The interpretation of the thermograms of the ethylene–butene-l copolymer is more difficult, as we have no information on the crystal structure of the phases present in this copolymer. CMPB3-A exhibits one melting endotherm with a melting point of 99.7°C. SCPB3-A exhibits two melting endotherms at 89.2 and 105.7°C (Figure 16). SCORIM processing seems to result in an increase of the melting point of the higher melting point phase (i.e., from 99.7 to 105.7°C) as well as the occurrence of a lower melting point phase. The shift in melting point of the high melting point phase with SCORIM is consistent with the observations made for polybutene-1 homopolymer.

CONCLUSIONS

The investigated polybutene-1 homopolymers and the ethylene–butene-l copolymer responded to the application of SCORIM processing, resulting in improved mechanical properties. The morphological aspects of processed polybutene-1 were given special emphasis in the reported research. The main conclusions can be summarized as follows:

1. Shish-kebab morphology forms in polybutene-1 processed by SCORIM.
2. The improvement in mechanical properties is dependent on the polybutene-1 grade. The nonnucleated homopolymer PB0300 exhibits the best improvements in tensile properties, showing a fivefold increase in Young's modulus and a 70% increase in ultimate tensile strength following the application of SCORIM. The nucleated homopolymer PB0110 shows only a twofold increase in Young's modulus. However, this increase in stiffness is combined with a simultaneous increase in impact resistance. The ethylene–butene-1 copolymer also responds to

TABLE VI
DSC Results for the Moldings of PB0110 (CMPB1- and SCPB1-Series) and PB0300 (CMPB2-A and SCPB2-A)

Molding	T_{melt} for Form I′ (°C)	ΔH_f for Form I′ (J/g)	T_{melt} for Form I (°C)	ΔH_f/ for Form I (J/g)	Overall Crystallinity (%)
CMPB1-A	—	—	127.1	72.23	53.5
CMPB1-B	96.5	2.35	128.8	68.39	50.5
SCPB1-A	—	—	129.6	75.28	55.8
SCPB1-B	96.9	5.95	132.3	49.16	36.1
SCPB1-C	96.7	5.38	130.7	50.65	37.2
CMPB2-A	—	—	123.3	60.55	44.8
SCPB2-A	—	—	128.4	58.36	43.2

the application of SCORIM with a combined increase in stiffness and impact resistance.

3. SCORIM polybutene-1 moldings produced at relatively low pressure exhibit greater overall crystallinity than do moldings produced by conventional injection molding. When SCORIM is applied with high cavity pressures, a substantial decrease in crystallinity is observed. However, the mechanical properties of SCORIM moldings with lower crystallinities are substantially greater than those of the conventional moldings.
4. The application of high pressure in injection molding of polybutene-1 causes the formation of the stable Form I′, which exhibits a low melting endotherm (96°C). The presence of this phase may be detrimental for the mechanical properties.
5. The application of high pressure in injection molding of polybutene-1 causes an increase in the melting point of the Form I.
6. Because SCORIM processing results in stiffer polybutene-1 moldings, the ejection of the moldings is easier than that of conventional injection moldings. This difference is postulated to be due to the near completion of the transformation of Form I to Form II in SCORIM.

Overall, the reported results show that the application of specified shears can be used to induce changes in the micromorphology during solidification of polybutene-1 moldings. These changes impart substantial enhancement of mechanical properties, in particular a combined increase in stiffness and impact resistance.

The processing and characterization work were carried out in the Wolfson Centre for Materials Processing, Brunel University, where both authors were previously employed. The authors gratefully acknowledge the funding of the European Commission under the Brite-Euram Programme for the Decrypo Project (No. BE 95-2067).

References

1. Luciani, L.; Seppälä, J.; Löfgren, B. Progr Polym Sci 1988,13, 37.
2. Natta, G.; Corradini, P.; Bassi, I. W. Nuovo Cimento Suppl 1962, 1, 52.
3. Boor, J., Jr.; Youngman, E. A. J Polym Sci 1964, B2, 903.
4. Nakafuku, C.; Miyaki, T. Polymer 1983, 24, 141.
5. Holland, V. F.; Miller, R. L. J Appl Phys 1964, 35, 3241.
6. Armeniades, C. D.; Baer, E. J Macromol Sci — Phys Ed 1967, B1(2), 309.
7. Boor, J., Jr.; Youngman, E. A. Polym Lett 1964, 2, 903.
8. Gohil, R. M.; Miles, M. J.; Petermann, J. J. Macromol Sci — Phys Ed 1982, B21(2), 189.
9. Petermann, J.; Schultz, J. M. Colloid Polym Sci 1984, 262, 217.
10. Hsu, T. C.; Geil, P. H. J. Macromol Sci-Phys Ed 1989, B28(1), 69.
11. Hong, W.; Spruiell, J. E. J Appl Polym Sci 1985, 30, 3163.
12. Fujiwara, Y. Polym Bull 1985, 13, 253.
13. Allan, P. S.; Bevis, M. J. Plast, Rubber Compos Process Appl 1987, 7, 3.
14. Allan, P. S.; Bevis, M. J. Composites Manufacturing 1990, 1, 79.
15. Allan, P. S.; Bevis, M. J. Brit Pat 2170-140-B (1987).
16. Kalay, G.; Allan, P. S.; Bevis, M. J. Kunststoffe 1997, 87/6, 768
17. Kalay, G.; Bevis, M. J. J Polym Sci, Polym Phys Ed 1997, 35, 241.
18. Kalay, G.; Bevis, M. J. J Polym Sci, Polym Phys Ed 1997, 35, 265.
19. Kalay, G.; Bevis, M. J. J Polym Sci, Polym Phys Ed 1997, 35, 415.
20. Kalay, G.; Ogbonna, C. I.; Allan, P. S.; Bevis, M. J. Trans Inst Chem Eng, Part A: Chem Eng Res Design 1995, 73, 798.
21. Kalay, G.; Sousa, R. A.; Reis, R. L.; Cunha, A. M.; Bevis, M. J. J Appl Polym Sci 1999, 73, 2473.
22. Kalay, G; Kalay, C. R. J Polym Sci, Phys Ed 2002, 40, 1828.
23. Starkweather, H. W., Jr.; Jones, G. A. J Polym Sci, Polym Phys Ed 1986, 24, 1509.