Effects of Processing on the Microstructure, Melting Behavior, and Equilibrium Melting Temperature of Polypropylene

B. E. TIGANIS,* R. A. SHANKS, and YU LONG

Department of Applied Chemistry, Royal Melbourne Institute of Technology, 124 Latrobe St., Vic 3001, Australia

SYNOPSIS

Polypropylene (PP) was extruded and injection-molded several times to mimic the effect of recycling procedures on PP. Differential scanning calorimetry (DSC) was used to follow crystallization rates under isothermal conditions in a temperature range of 120–130°C. Melting behavior and equilibrium melting temperatures were studied using the Hoffman–Weeks method of extrapolation. Optical microscopy combined with a hot stage was also used to follow the spherulite microstructure and crystal phase upon recycling of PP. Wide-angle X-ray spectroscopy identified the crystal phase at different isothermal crystallization temperatures. Twin melting peaks obtained for PP melting following isothermal crystallization were associated with crystal rearrangement during fusion. PP spherulite size and equilibrium melting temperatures were seen to increase with processing events, whereas reprocessing decreased nuclei density. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recycling of polymers and their blends has been shown to have significant effects on mechanical properties and blend morphology.[1-4] Analysis of polymer crystallization kinetics allows for the elucidation of a polymer/blend equilibrium melting temperature (T_m^0). The equilibrium temperature is a true reflectance of a polymer's microstructure and the morphology of a blend, unlike an experimental melting temperature which is dependent on the thermal history of the polymer and the experimental conditions.[5]

In this article, the effects of recycling or reprocessing on toughened polypropylene (PP) by considering crystallization behavior and spherulite microstructure will be presented.[6-9] The phenomenon of twin melting peaks obtained upon melting of PP will be discussed and related to crystal rearrangement during fusion.[10-12] Equilibrium melting temperatures for PP and processed PP using the Hoff-

man–Weeks equation and extrapolation method will be determined.

EXPERIMENTAL

Toughened PP (5% ethylene incorporation) was kindly supplied by ICI Engineering Plastics Australia. PP was extruded using a Brabender twin-screw extruder and then injection-molded into tensile and impact test bars by use of a Johns CF 550 injection molder. Two batches were produced to obtain reproducible results.

These batches were then also reprocessed. To mimic recycling, reprocessed blends were granulated, extruded, and then reinjection-molded. This sequence was repeated up to three recycling events. Polymer which was injection-molded directly from the pellet form to the tensile and impact test pieces will be referred to as virgin polymer. Virgin and processed polymers were thermally analyzed using a Perkin-Elmer DSC-7. DSC samples were maintained as melts at 180°C for 5 min and then cooled at 200°C/min to an isothermal crystallization temperature in the range of 120–130°C and allowed to
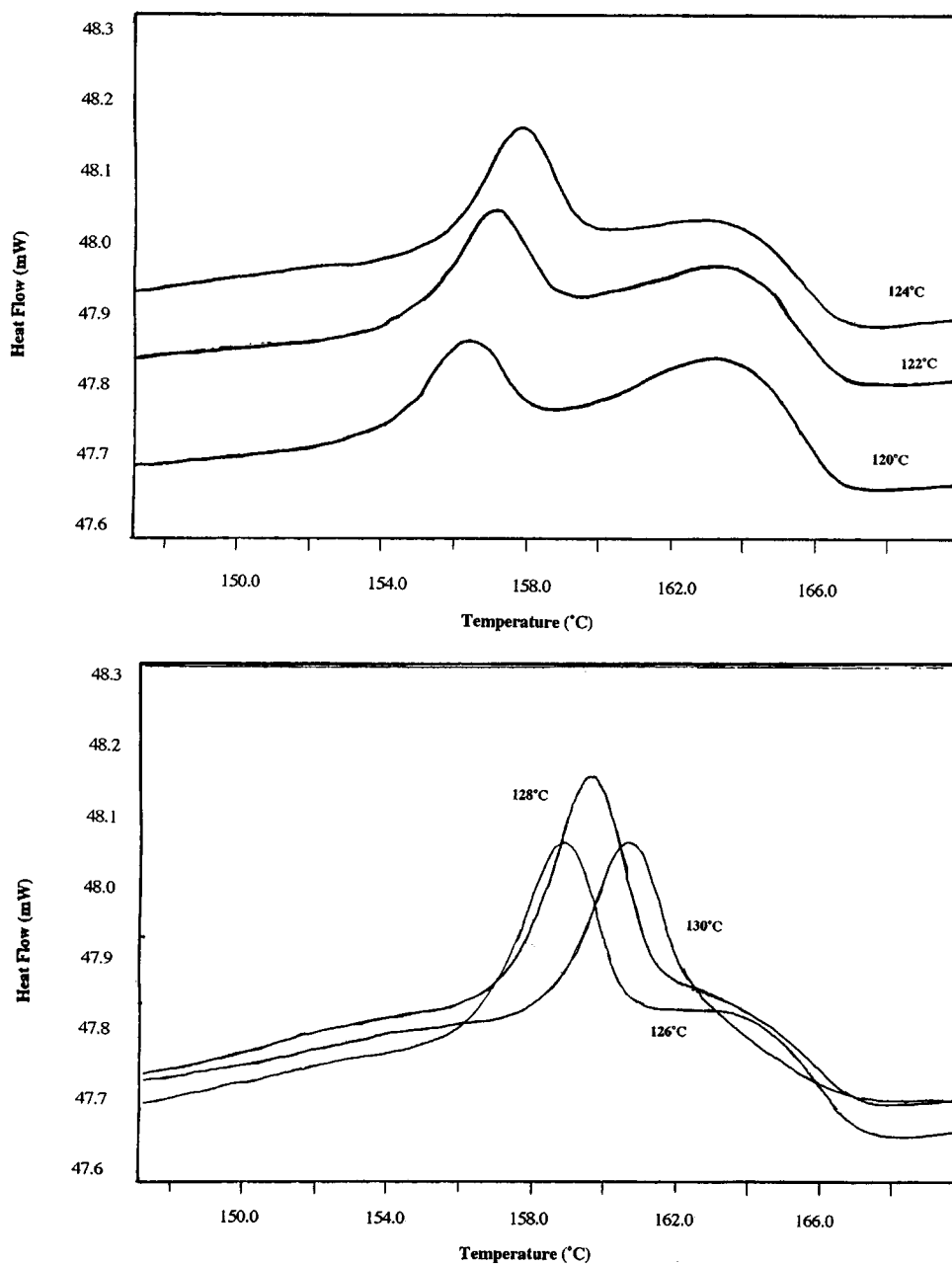

Figure 1 (a) Isothermal crystallization of toughened PP after quenching from the melt; temperatures of crystallization being 120, 122, and 124°C. (b) Isothermal crystallization of toughened PP after quenching from the melt; temperature of crystallization being 126, 128, and 130°C.

crystallize (crystallization was found to be complete within 10 min).

The Avrami analysis method for isothermal crystallization was used to calculate crystallization half-times which were used as a measure of crystallization time.[13] The Hoffman–Weeks equation was used to obtain equilibrium melting temperatures. Nonisothermal crystallization was also fol-

lowed by using heating and cooling rates of 10°C/min.

Wide-angle X-ray diffraction spectroscopy (WAXS) studies were performed on a Rigaku instrument with the following conditions: $2J \pm 0.028$ and scanning in a range of 5–35° at a speed of 5°/min. Samples for WAXS were formed by melt pressing toughened PP at 190°C for 5 min and then

immediately immersed into liquid nitrogen to prevent crystallization. Crystallization was then allowed to occur in controlled oven temperatures of 120 and 130°C ± 1°C. WAXS analyses were then performed on both samples three times on individual specimens for reproducibility.

The morphology of toughened PP at various isothermal crystallization temperatures was also examined using hot-stage optical microscopy (HSOM) and scanning electron microscopy (SEM). Optical microscopy involved the microtoming of 10 μm polymer samples, which were placed under coverslides on glass slides which had been previously washed using a chromic acid solution. Crystal structure was studied using polarized light on Nikon Labophot-2 microscope. Samples studied by microscopy were kept in the melt form at 180°C for 5 min and cooled at a rate of 20°C/min to isothermal crystallization temperatures of 135 and 140°C, to follow the number and size of spherulites appearing during crystallization. These isothermal crystallization temperatures were selected since the rapid crystallization at lower temperatures prevented an accurate visual study of crystallization. The microstructure of spherulites of virgin and recycled PP was studied at 145°C.

This temperature would play a role in determining the types of spherulites forming, and, thus, the significant observation would not be the type of spherulite, but the actual differences existing between virgin and recycled spherulites. SEM analyses were performed on a JSM-840A scanning electron microscope. Specimen fracture surfaces were prepared for SEM analysis by immersing impact test bars (molded as described previously) in liquid nitrogen for 10 min, followed by mechanical fracture. The final step in preparation for SEM observations was a vacuum coating of samples using a Dynavac sputter coater SC150 in argon using gold foil.

Mechanical properties of processed and virgin polymers were tested in terms of tensile and impact properties using a Davenport Izod impact tester for impact properties (according to ASTM D256) and

Table II   Melting Temperatures of Toughened PP After Isothermal Crystallization in the Range of 120–130°C

Crystallization Temperature (°C)	T_m Peak 1 (°C)	T_m Peak 2 (°C)
120	156.4	163.7
122	157.1	163.7
124	157.9	163.8
126	158.6	163.8
128	159.3	164.0
130	160.3	—

a Lloyd 200 apparatus for tensile properties (ASTM D638).

RESULTS AND DISCUSSION

Isothermal crystallization of virgin and reprocessed PP allowed crystallization kinetics to be measured and also a study of the equilibrium melting temperature (T_m^o) and melting behavior. Crystallization was studied in the temperature range of 120–130°C. The kinetic analysis by crystallization half-times showed a general decrease in the rate of crystallization as the isothermal temperature increased. As crystallization temperatures increased, the degree of supercooling was less; thus, the number of active heterogeneous nuclei decreased (causing rates to decrease), also causing an increase in the spherulite radii.[14]

Following each crystallization process, the solidified polymer was heated to the melt at a rate of 2°C/min. Experimental melting data provide a direct indication of melting and crystallization conditions, and any assumptions made from these must be done with experimental conditions being the main variable rather than the polymer or blend itself. Equilibrium melting temperatures are indicators of polymer microstructure and blend morphology.

Table I   Equilibrium Melting Temperatures and Nonisothermal Crystallization Parameters

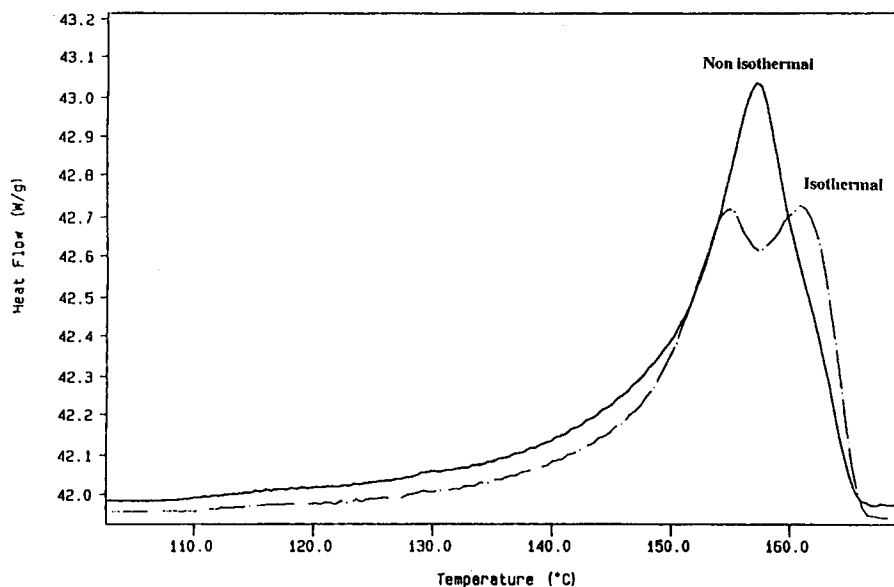| Polymer	Processing Events	T_m^o (°C)	Gamma γ	Nonisothermal Data T_m (°C)	T_c (°C)	ΔH (J/g)
PP	Virgin	178.1	2.8	157.8	—	83.2
PP	One recycle	180.8	—	—	—	—
PP	Three recycles	184.4	2.4	160.0	118.3	83.7

Figure 2 Melting peaks of injection-molded toughened PP, derived prior and after non-isothermal crystallization at a scan rate of 10°C/min.

Polymer melting temperatures increase linearly as crystallization temperatures are increased.[13] By plotting melting temperatures against isothermal crystallization temperatures, it is possible to obtain a linear plot, which, using the Hoffman–Weeks equation, allowed extrapolation to the point where $T_m = T_c$, i.e., to the equilibrium melting temperature[5]:

$$T_m = T_m^0(1 - 1/\gamma) + T_c/\gamma \qquad (1)$$

The melting process for both PP and reprocessed PP showed two endothermic peaks on the DSC scan, which have been discussed previously.[10–12] The twin-peak behavior varied with the isothermal crystallization temperature (in the range of 120–130°C) prior to melting. At 120°C, the twin-peak phenomenon was most prominent, with the peak at a lower temperature being more significant.

As T_c increased, the second of the two peaks gradually disappeared, to finally leave a single peak upon melting following crystallization at 130°C. Many sources in the literature, in attempts to obtain the T_m^0, have reported twin melting peaks in isothermal and nonisothermal crystallization. From previous studies, it has been proposed that the phenomenon of double melting peaks was due to either the melting of α, β, γ crystalline phases or the melting and reorganization of single crystalline phase.[10–12]

The DSC heating scans for toughened PP after isothermal crystallization in the range of 120–130°C show that the twin melting peaks disappear as the crystallization temperature approaches 130°C [Fig. 1(a) and (b)]. The first of the twin two melting peaks corresponds to the melting of the crystals formed upon isothermal crystallization. Table I shows the T_m^0 for virgin toughened PP. The first of the two melting peaks for toughened PP increases by approximately 4°C in the temperature range of 120–130°C (Table II). This increase in melting temperature is expected since crystallization at increasing isothermal crystallization temperatures would cause crystal spherulites with larger radii to form, thus elevating the melting temperature.

The second melting peak is believed to be indicative of the melt reorganization of crystals remaining constant at 163–164°C for PP. Table II illustrates the twin melting peaks for virgin PP at different isothermal crystallization temperatures. The explanation for these observed results in Table II is that the crystals that undergo reorganization would form similar degrees of order and therefore melt at similar temperatures.

It is also seen that the second peak diminishes as the temperature of crystallization increases and this is due to the fact that crystals formed at higher temperatures are more highly ordered and fewer crystals undergo recrystallization. The term "reorganization or recrystallization of crystals during the melt" will be defined in this article as the process of increasing order in crystal spherulites with a decrease in spherulite fibril deformities, interfibrilar growth, and crystal thickening. Paukkeri and Lehtinen[11] suggested that there is a transition of α_1 to α_2 where
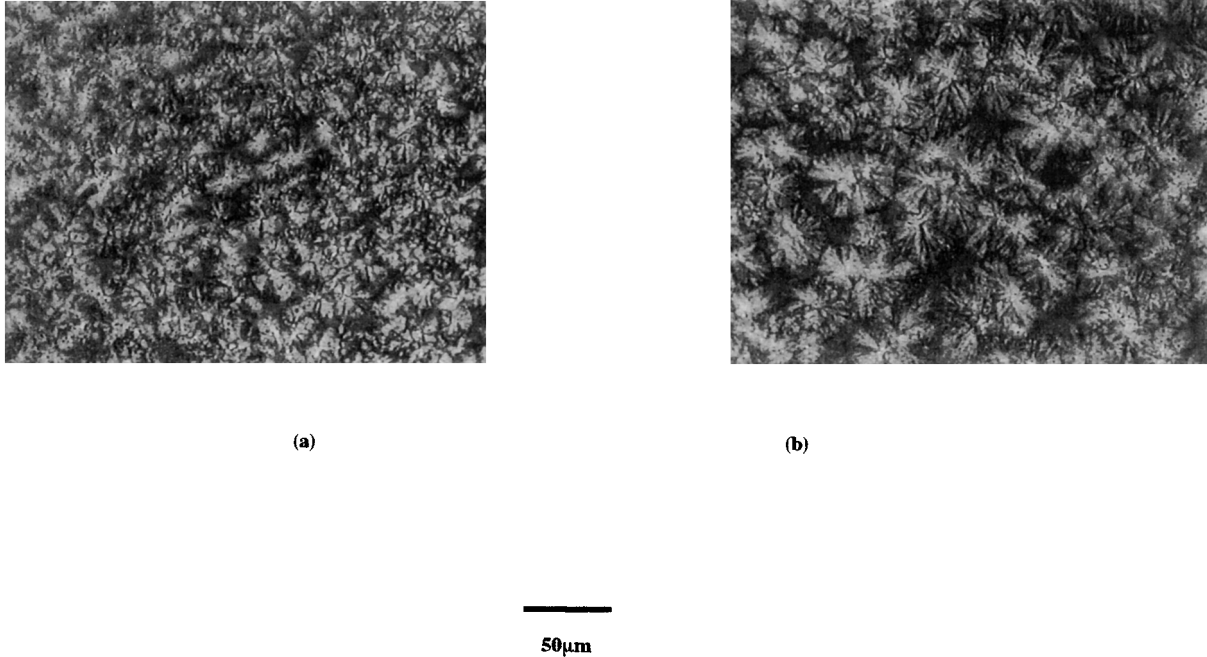
(a)

(b)

50μm

Figure 3 Isothermal crystallization of toughened PP at (a) 120°C and (b) 130°C, showing type I and II spherulites (α crystals). The difference in spherulite size between 120 and 130°C is significant.

amorphous regions in spherulites form regions of order. Nonisothermal DSC traces showed that twin melting peaks were obtained upon melting after quench cooling a sample. A single melting peak corresponding to the first peak of the twin peaks was obtained upon melting after nonisothermal crystal-

lization (from 180 to 40°C at 10°C/min) (Fig. 2). Microscopic observations suggest that at both isothermal temperatures (120 and 130°C) the spherulitic nature of the crystals is of α type, showing distinct Maltese cross patterns (Fig. 3). Figure 3 clearly shows that the size of the crystallites was
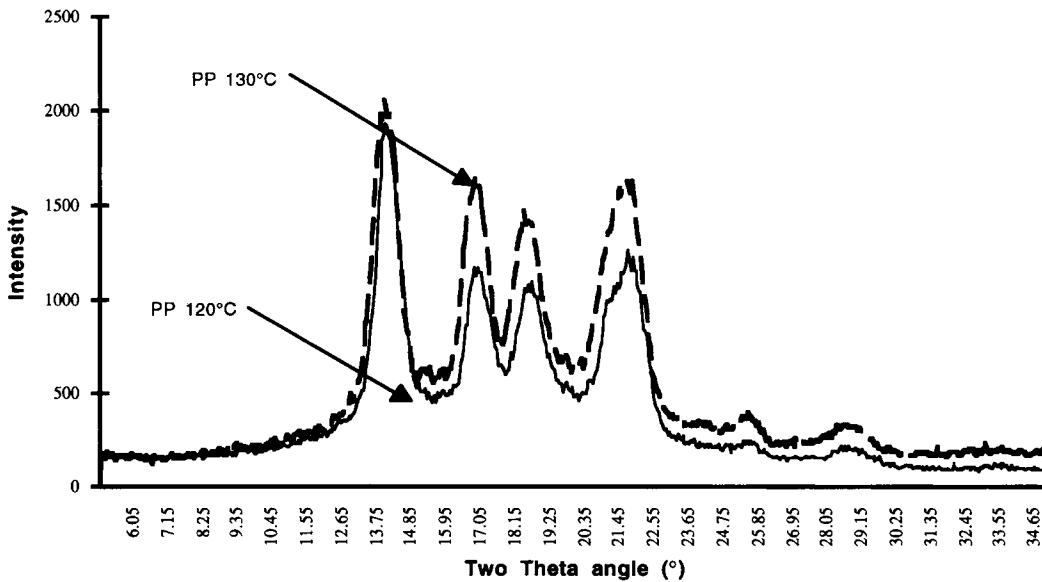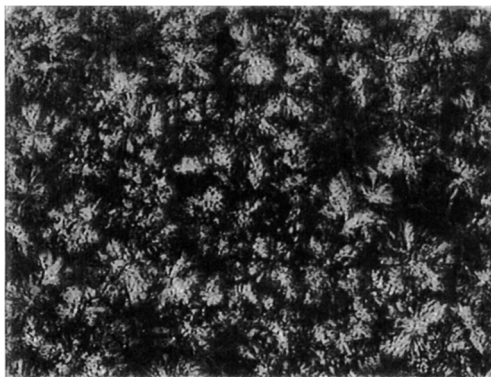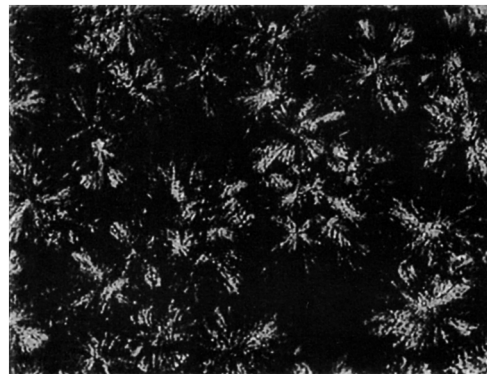

Figure 4 WAXS spectra of PP crystallized isothermally at 120°C and PP at 130°C after quenching from the melt. Both spectra show the presence of α-type crystalline phase only.
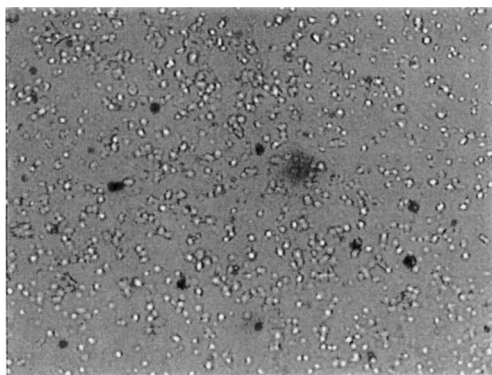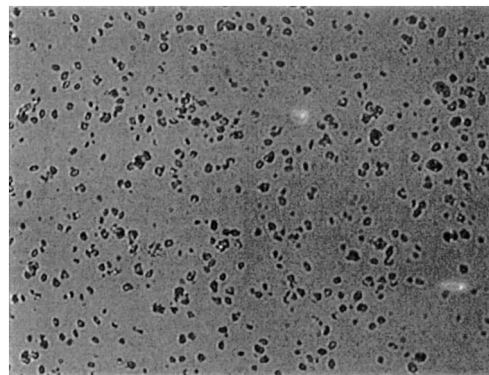
(a)   (b)

50µm

Figure 5   Isothermal crystallization at 140°C: (a) toughened PP; (b) toughened PP re-cycled three times. Spherulites are of the same nature but different in size, with recycled polymer spherulites being larger.

(a)   (b)

50µm

Figure 6   Initial stages of isothermal crystallization at 140°C: (a) toughened PP; (b) toughened PP recycled three times. Note that the nuclei density for virgin PP is greater than that for recycled PP.
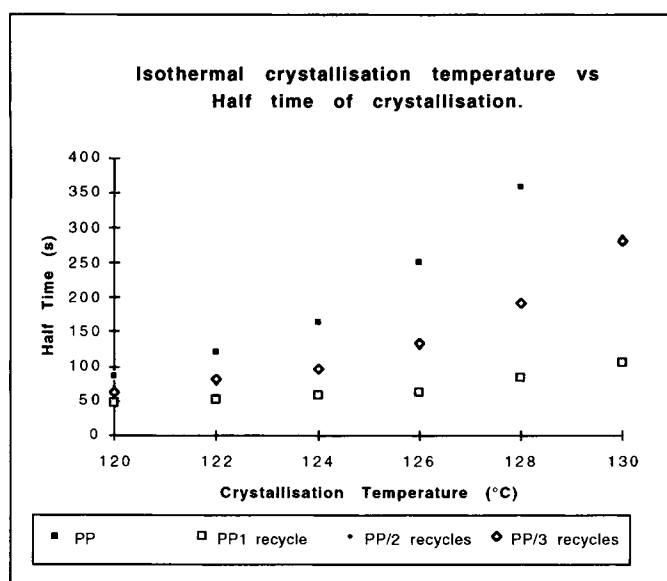
Isothermal crystallisation temperature vs Half time of crystallisation.

Figure 7 Crystallization half-times for PP and recycled PP.

smaller for crystallization at 120°C, and this was expected, as, comparatively speaking, the quenching rate from 180 to 120°C was greater than that for 180 to 130°C.

Yu and Tiganis[15] showed that the molar mass distribution of toughened PP itself was quite broad (even more so for recycled toughened PP). It has been suggested that inhomogeneities in molar mass could be responsible for the double melting peaks observed. Again, Paukkeri and Lehtinen[11] showed that PP samples obtained upon fractionation of molar mass show a decrease in the second melting peak with increasing heating rate (therefore, less reorganization of crystals is occurring).

WAXS results confirmed that both at 120 and 130°C only α phase crystals were present, and the possibility of a double melting peak arising from the melting of separate crystalline phases is, in this case, not viable. Figure 4 (a) shows WAXS studies of PP crystallized at 120 and 130°C. Both WAXS spectra in Figure 4 (a) show distinct peaks at 2ϑ angles 13.9°, 16.8°, 18.5°, and 21.7° (a combination of two peaks)

and two small shoulders at 25.5° and 28.7°. These patterns correspond to α phase crystals only.[16] Thus, crystallization at 120 and 130°C after quenching from the melt at 190°C revealed only α type crystals. It was expected that for an injection-molded quenched PP sample both α and β phase crystals would prevail. The WAX analysis of an injection-molded PP sample which has been quenched to 40°C corresponded to a mixture of crystal phases, most dominantly α and β phase crystals. Results showed an additional peak at 15.5° and an increase in width of the peak at 21.7° due to the combination α phase crystals at 21.7° and β phase crystals at 21°, the significant observation being that at both 120 and 130°C the phase of crystallinity is typical of α phase crystals only. Therefore, the possibility of a double melting peak arising from the melting of separate crystalline phases is in this case not possible.

Equilibrium melting temperatures and gamma parameters for PP (ethylene toughened 5%) and reprocessed PP are shown in Table I.[5] It is evident that reprocessing of the PP causes the equilibrium melting temperature to increase according to the Hoffman–Weeks extrapolation method. Nonisothermal crystallization data (Table I) also shows an increase in melt temperatures for reprocessed polymer. Alamo et al.[12] suggested that the Gibbs–Thompson equation, a variation of the Hoffman–Weeks equation, is suitable only for polymers with low levels of crystallinity and deviation occurs in linearity during extrapolation to high isothermal temperatures. Considering the possibility of errors involved in the determination of T^0_m, hot-stage optical microscopy (HSOM) shows an increase in equilibrium melting temperatures with reprocessing. Figure 5 shows that at isothermal crystallization temperatures of 135 and 140°C (for 2 h) reprocessed polymer forms larger spherulites than does virgin polymer and concomitantly less nuclei. This increase in spherulite size correlates with the increase in equilibrium temperature seen upon reprocessing using DSC. Table I shows that the proportionality factor (gamma) between initial and final lamellar thickness decreased for recycled polymer, indicating

Table III   Mechanical Properties of Virgin and Reprocessed Toughened PP

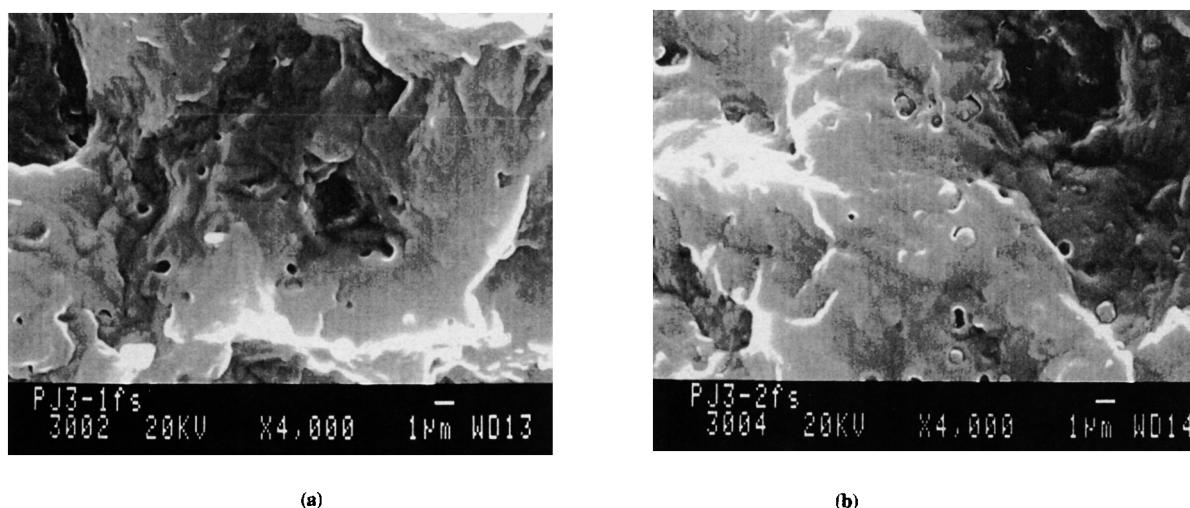| Polymer	Processing Events	Tensile Strength (MPa)	Modulus (MPa)	Elongation at Break	Impact (J/m²)
PP	Virgin	23.49 ± 0.23	660.9 ± 21.40	29.9 ± 5.70	54.13 ± 4.62
PP	One recycle	23.88 ± 0.20	660.1 ± 21.60	24.3 ± 3.00	53.18 ± 5.29
PP	Two recycles	23.91 ± 0.24	668.0 ± 23.20	33.4 ± 4.50	52.08 ± 4.27
PP	Three recycles	23.41 ± 0.32	589.9 ± 12.70	43.3 ± 21	76.43 ± 17.22

(a)   (b)

Figure 8 Scanning electron micrographs for (a) virgin and (b) recycled PP (×4000).

that crystal dimensions increased due to reprocessing. Table I shows that the extent of crystallization provided by nonisothermal crystallization using the DSC for PP and reprocessed polymer is similar.

Initial expectations were that reprocessed polymer would have more nuclei and therefore smaller crystals forming than virgin polymer due to impurities introduced during reprocessing, which act as heterogeneous nuclei. It seems that the effect of additional foreign nuclei is minimal as compared to the destruction of nuclei caused by processing events. Figure 6 shows that reprocessed polymer has fewer substrates in the melt than in virgin polymer. These substrates (combined with sites that are not visible) are responsible for nucleation.[17] Crystallization kinetics of PP and PP recycled one to three times are shown in Figure 7. Kinetics were measured using half-times of crystallization; the inverse of crystallization half-times is proportional to the rate of crystallization.[14,18] Since crystallization is an infinite process, measuring half-times of crystallization allows observation of the kinetics of a polymer (by consistently measuring kinetics up to the maximum point of the exothermic trace).

A computer program manipulates the Avrami exponent (m) and the growth rate of crystals (k) using the following equation to derive a half-time;

$$t\frac{1}{2} = (\ln 2/k)^{1/m} \qquad (2)$$

Figure 7 shows that one recycling event caused a dramatic increase in rate as compared with virgin PP. Consecutive recycles show a decrease in rate, yet the rates were still faster than those measured

for virgin PP. These rates seem anomalous, considering that fewer nuclei (or initial spherulites) were observed for reprocessed polymer. To closely look at crystallization, the nucleation behavior of PP, both virgin and processed, must be considered as well as subsequent crystallization. It would be expected that a propylene polymer toughened with 5% ethylene would undergo homogeneous nucleation, considering that self-seeded nuclei would not be destroyed at a maximum melt temperature of 200°C. The fact that propylene is polymerized with the use of a catalyst means that, undoubtedly, there will be contaminants present which will cause heterogeneous nucleation to be the dominant form of nucleation. Reprocessing a polymer several times introduces considerable impurities and this is optically evident by comparing virgin and processed polymer samples. Yet, reprocessing has also been known to reduce the number of heterogeneous nuclei. Bartczak et al. showed that reprocessing at high temperatures causes degradation which causes a decrease in nuclei.[19] Yu et al. showed that mixing causes heterogeneous nuclei to migrate from iPP to the ethylene phase in iPP/LDPE and iPP/EP copolymer blends.[20] Galeski et al. also showed this and believed it to be due to the difference in interfacial energy between the nuclei and the molten components of the blend.[21] Thus, reprocessing may cause heterogeneous nuclei to be reduced in two ways: (i) reduction of nuclei by degradation and (ii) migration of iPP nuclei from the iPP phase to the ethylene-propylene copolymer phase.

Crystallization of PP at 145°C for 2 h shows little degradation, whereas for reprocessed PP crystallized at these conditions, degradation was most substan-

tial.[22] The fact that the processed polymer degraded upon these conditions (145°C) points out that the previous processing events exhausted the stabilizer required to prevent degradation. This also reflects that recycling without an additional stabilizer may cause degradation of nuclei.

The effect of processing (shear and heat) was expected to have an effect on the polymer at the molecular level, reducing molar mass and altering its distribution.[1] Rheological data reported by Yu and Tiganis[15] supports the argument that the effects of shear and heat during reprocessing decrease the molar mass of the polymer by scission and increase the molar mass distribution. Thus, even though reprocessing causes a reduction in nuclei, it also causes chain scission and the presence of shorter polymer chains in the melt may have an positive effect on their mobility.[23,24] Thus, upon cooling, these smaller chains may be responsible for the increased rates of crystallization observed for the recycled polymer.

Finally, it was observed that the rate of crystallization for polymer reprocessed two or three times was slower than polymer only undergoing one processing event. In this case, all recycled polymers have smaller chains and foreign nuclei, yet polymer recycled more than once may have formed crosslinks, causing crystallization rates to decrease.

Mechanical testing of properties for virgin and recycled material revealed no significant differences for tensile and impact properties (Table III). Figure 8 shows electron micrographs for virgin and processed PP. Both micrographs are typical of ethylene-toughened PP showing a slightly ductile character, with ethylene inclusions distinguishable as round spots (some being pulled out during fracture).

CONCLUSIONS

Evidence provided by DSC, WAXS, and HSOM indicate that dual melting peaks observed in toughened PP are due to melt crystallization or rearrangement of crystal structure rather than a variety of crystal phases. Reprocessing of PP introduces foreign substrates that may act as heterogeneous nuclei, yet this increase is overshadowed by a negative effect of reprocessing on nuclei density believed to be due to the migration of iPP nuclei to the ethylene–propylene phase.

Recycled polymer exhibited larger and fewer spherulites than did virgin polymer, yet crystallization rates measured by half-times were greater. Reprocessing is suggested to cause polymer chain scission, therefore forming smaller molecules with greater mobility and accelerating the crystallization process on nuclei substrates. In consistency with spherulite size, reprocessing increased the equilibrium melting temperature (T_m^0) of PP.

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