

Crystalline Morphology of Polypropylene and Rubber-Modified Polypropylene

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Synopsis

The crystalline morphology of injection-molded polypropylene (PP), its relationship with crazing, and the effects of various impact modifiers on the morphology, crystallization, and fusion of PP have been studied. The highly oriented skin layer of an injection-molded tensile bar after deformation was found to be free from crazing in contrast to the heavy craze density in the randomly oriented spherulitic core zone. Reasons for the difficulty in craze nucleation in a preoriented zone are given in light of Argon's theory of craze initiation. Addition of a rubbery phase results in an irregular texture of spherulite, smaller spherulitic diameter, and decrease in the degree of undercooling, but no appreciable change in heats of fusion and crystallization other than a trivial volume effect. The rubbery phase is not pushed by the melt-solid interface to relocate to the interspherulitic boundaries. Rather, it is engulfed by the growing melt-solid interface, leaving behind a random spatial distribution of rubber particles in the PP matrix.

INTRODUCTION

Polypropylene (PP), while having a number of valuable properties, has inadequate low-temperature fracture resistance. Experience on toughening of glassy plastics has indicated that a great deal of mechanical energy can be absorbed by the development of crazes and/or shear bands, which may be promoted by the second-phase rubber particles dispersed in the matrix plastics.^{1,2} A proper particle size distribution of the dispersed phase may lead to an optimum impact resistance.

Emerging is an increasing number of reports indicating that the impact strength of PP can be favorably influenced by its physical blending with various elastomers such as ethylene-propylene copolymer (EPR), ethylene-propylene-diene terpolymer (EPDM), styrene-butadiene (SBR), or styrene-isoprene (SIS) copolymers, butyl rubbers, polyisobutylene (PIB), and polybutadiene (PB). Macroscopic physical properties of PP blends with various elastomers have been investigated to some degree.^{3-8,12} Morphological studies on these blends have also been reported sporadically.⁸⁻¹²

As part of the effort to study the rubber-toughening mechanisms of semicrystalline polymers we have carried out a detailed investigation into the injection-molding morphology of polypropylene, its relationship with crazing, and the effects of various impact modifiers upon the crystallization, fusion, and morphology of PP. Results of this investigation are reported here. Detailed discussion on crazing, shear banding, and impact fracture behavior of rubber-toughened PP will appear elsewhere.

EXPERIMENTAL

Materials and Sample Preparation

Materials used in this study included general-purpose polypropylene homopolymer (PP), ethylene/propylene/diene monomer (EPDM) rubber, ethylene/propylene copolymer (EPR), and styrene/butadiene copolymer (SBR). Most of the materials were commercial polymers except for S-7, which was an experimental polymer supplied by Dr. Henry Hsieh of Phillips Petroleum (Table I).

Compositions (e.g., M-3 for PP-4-N3-30 contains 70% of PP-4 and 30% of N-3 EPDM, etc.) in forms of pellet or chip were mixed by a Brabender extruder with $L/D = 15$ at a speed of 80 rpm, barrel temperature of 200°C, and die temperature of 200°C. The materials were extruded and granulated twice to ensure good dispersion. Samples for crazing study were further injection-molded into dog-bone-shaped tensile bars under conditions of zone temperatures 190°C, back pressure 3000–6000 psi, injection pressure 4000 psi, and mold temperature 40°C. An Ingersoll-Rand Model V2-18FA lab-scale injection-molding machine was used throughout the whole study.

Electron and Light Microscopy

The two-phase morphology of rubber-modified PP, the morphology of injection-molded PP homopolymer, and its relationship with crazing were characterized by the use of a scanning electron microscope (AMR SEM Model 1000A), transmission electron microscopes (Philips EM-300 and EM-200), and a polarized light microscope (Reichert).

Light microscopy samples were prepared by microtoming thin sections (3–5 μm thick) at low temperatures (-50°C) and pressing these sections between two glass slips. The surface of the remaining block, which has been polished by a microtome diamond knife, was vacuum-coated a thin layer of gold (20 nm) to avoid charging problem during SEM examination. Microtome-trimmed sample was, in some cases, etched by chromic acid to reveal crazing and crystalline morphology.

TABLE I
Raw Materials

Designation	Type of polymer	Commercial name	Supplier	Comments ^a
PP-4	Polypropylene	Profax 6523	Hercules	MFR=4, high ρ
N-3	Ethylene-propylene diene Terpolymer (EPDM)	Nordel 2522	DuPont	Little or no crystallinity
N-4	EPDM	Nordel 2722	DuPont	Semicrystalline, low ρ
E-2	Ethylene-propylene rubber (EPR)	Epcar 307	B. F. Goodrich	Low ρ
S-7	Styrene-butadiene rubber (SBR)	Solprene 425P	Phillips	$M_w/M_n = 240/180 \times 10^3$, MFR ≈ 0 (180°C/5 kg)

^a Based on supplier's characterization, ρ = melt viscosity.

Ultrathin sections, 50–100 nm in thickness, were cut at -90°C with an LKB Ultramicrotome equipped with a cryogenic unit and a DuPont diamond knife. Samples were exposed to OsO_4 staining solution to harden the rubbery phase, thus reducing the possible microtoming damage, and to enhance the electron contrast between the rubbery phase and PP matrix.

Differential Scanning Calorimetry (DSC)

Differential calorimetry (Perkin Elmer DSC-2) was carried out at a scanning rate of $20^{\circ}\text{C}/\text{min}$ (between 320 K and 480 K) to study the influence of the rubber on the kinetics and thermodynamics of PP crystallization and fusion. Samples scanned included PP, PP + EPDM (N3), PP + EPDM (N4), PP + EPR, and PP + SBR, each at 5, 15, 30, and 50% (by weight) of elastomers. All samples were prepared by extrusion except those with 15% rubber having been injection-molded after extrusion. The information obtained from DSC consisted of the melting temperature (T_m), the heats of fusion (H_m), the crystallization peaks (T_c), the heats of crystallization (H_c), the degrees of undercooling ($T_m - T_c$), and the ratios of $H_m(\text{blend})/H_m(\text{PP})$. The last was used to determine if, other than trivial volume effects, the impact modifiers induce any change in fusion.

RESULTS

Crystalline Morphology of PP

The morphology illustrated in Figure 1 is typical of the morphology of a thin section (cut parallel to the flow direction) in the gauge length of polypropylene tensile bars. These optical micrographs reveal that there exists three discrete phases or morphological layers in the gauge section of the molding: they are, in order, the skin, shear, and core zones, respectively.

Microscopic observation of the skin between crossed polarizers at magnification of 500 shows no perceptible crystalline development. The molecules in the skin are highly oriented with flow direction, as evidenced by relatively high birefringence and uniform extinction of the white polarization color as the specimen is rotated in plane on the light microscope stage.

The skin layer is followed by an intermediate zone of oriented spherulites. The oriented spherulites or "sheaves" in this shear zone are packed tightly together along thin, negatively birefringent rows. The spherulites that were nucleated from each row are nearly identical in size and shape with their size increasing with increasing distance from the skin-shear zone boundary. It can be observed that the majority of the oriented spherulites in this zone are the negatively birefringent type III variety, characteristic of the metastable hexagonal crystal form (β -form).^{12,13}

The core zone is composed of larger but randomly sized spherulites, which are primarily the positively birefringent type I variety representing the stable, monoclinic polymorph (α -form). The type III spherulites, however, appear sporadically and stand out clearly (bright white) in great contrast to the darker type I matrix. The morphology in the core differs from that

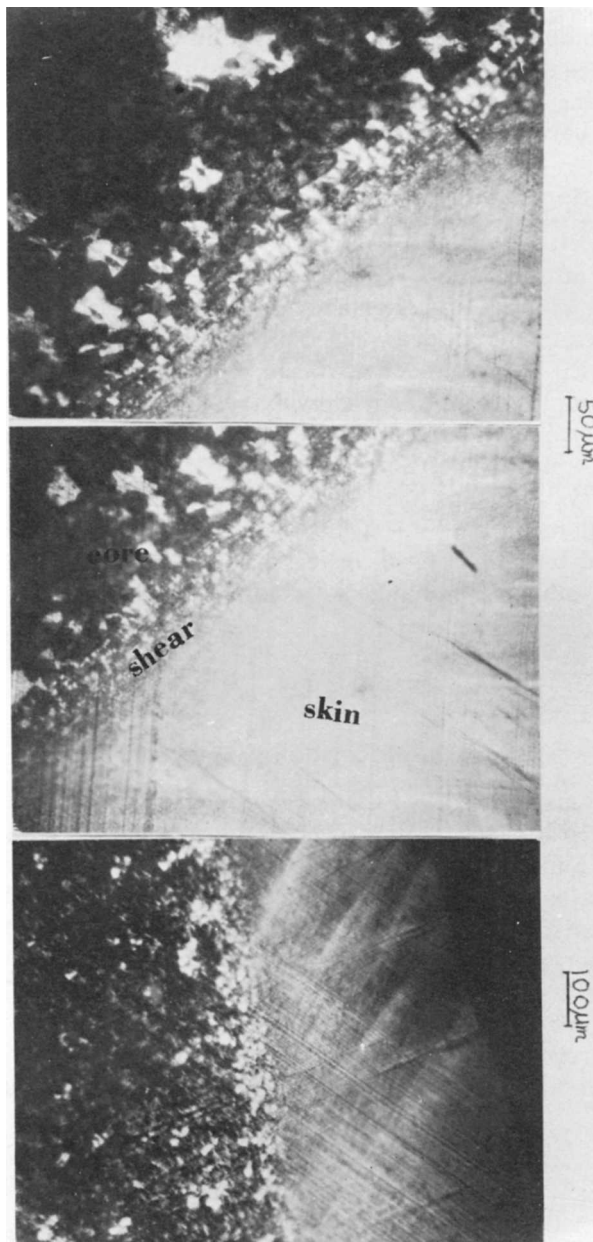


Fig. 1. The crystalline morphology in injection-molded polypropylene tensile testing bar. Polarizing light micrographs showing three morphological layers: skin, shear, and core zones.

in the shear zone in that the spherulites in the shear region are oriented while those in the core are randomly nucleated.

In Figure 2 is shown a tensile fracture surface ($\dot{\epsilon} = 1/18 \text{ s}^{-1}$ and $T = 0^\circ\text{C}$) in the gauge section of PP. When observed in cross section, the boundary between the nonspherulitic skin and spherulitic core appears quite sharp; no obvious shear zone can be identified. The shear zone is not easily recognized in the cross sections of fracture surfaces because, when using optical

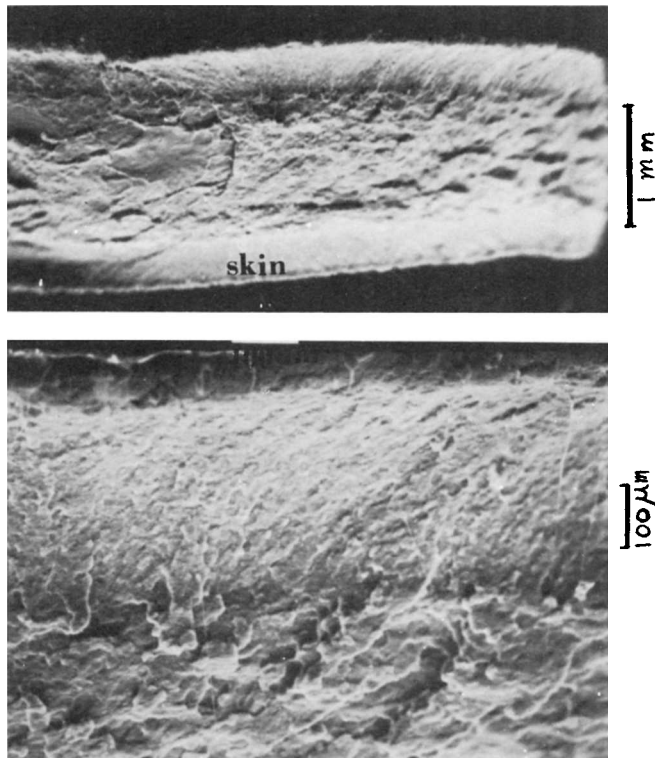


Fig. 2. Scanning electron micrographs showing the fracture surface of an injection-molded polypropylene tensile testing bar.

microscopy, the birefringence of the oriented spherulites viewed parallel to the cylindrical axes of the fibrils differs little from that of the core spherulites. Besides, the fracture surface without subsequent etching is obscured since the interspherulitic boundaries are not clearly delineated.

Craze Structure and Morphology

It was observed that in the injection-molded PP tensile bars there invariably exist layers of skin which are highly oriented. It would be of interest to see if these skin layers play any role in the crazing behavior of PP.

Figure 3(a) illustrates a typical razor blade-cut surface parallel to the tensile stress direction. The surface has been etched in chromic acid for 72 h followed by rinsing with acetone and distilled water. It is clear from this SEM micrograph that a large concentration of crazes has been created, essentially all of which are restricted to the core zone of the specimen. Indeed, after a careful sampling we found that the above observation is true of most of the crazed samples of PP, with the exception that a few heavily crazed, highly deformed samples did show crazes developing into the skin layers. Nevertheless, even in the latter cases, the majority of crazes were found to occur in the core zone [Fig. 3(b)]. The implication of this finding will be discussed in a later section. Additional examples of crazes/core zone association are given in Figure 4 where the skin layers appear relatively bright under cross nicols and show the absence of any crazes.

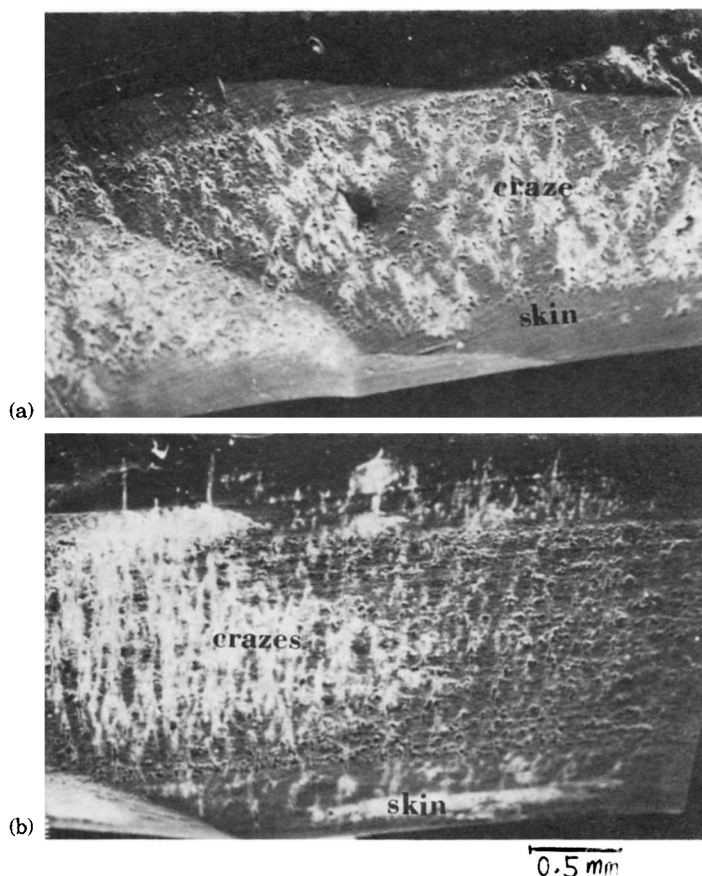


Fig. 3. Razor blade-cut surfaces (a) etched in chromic acid showing that crazes developed preferentially in the core zone (b) of polypropylene injection molding.

The Effects of Rubber upon the Spherulitic Structure of PP

Figure 5 illustrates the core zone morphology of the injection-molded tensile bar of EPDM-modified PP. Ultrathin sections (50 nm) obtained from microtoming at low temperatures (-50°C) followed by osmium tetroxide staining were investigated in the transmission electron microscope (TEM). The dark, more or less spherical, particles represent the rubbery phase, preferentially stained with osmium and dispersed in the PP matrix. A third feature, relatively less dark in contrast, appears to radiate outwards from a common center, seemingly delineating the outline of a spherulite. From polarizing light microscopy we observed that the same core zone was spherulitic with average spherulite diameter being in the neighborhood of 40 μm . It thus leaves us no doubt that the radiating features seen in Figure 5 reflects a spherulite of PP.

It is of interest to find that the spatial distribution of the rubber particles is quite random in the PP matrix. The rubber phase is not preferentially pushed to stay in the interspherulite boundaries. The dispersed phase appears to have been engulfed by the growing fibrils comprising a spherulite.

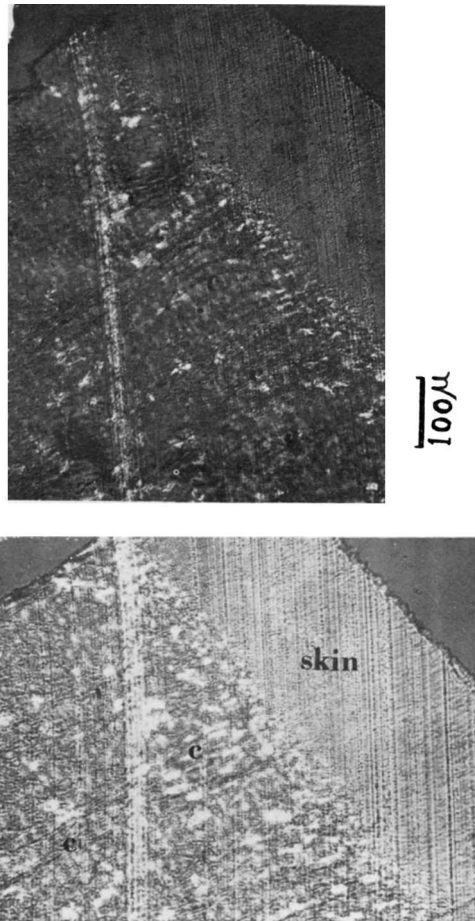


Fig. 4. Polarizing light micrographs showing that crazes (indicated by letter c) are not generally formed in the highly oriented skin zone of PP injection molding.

Some of the spherulitic centers were occupied by rubber particles. Others, however, appeared to be uncorrelated with the rubber particles.

Unmodified PP has a regular structure with a relatively ordered spherulitic texture. Addition of impact modifier, such as SBR, EPR, or EPDM results in a less regular spherulite texture with less sharp spherulite boundaries. Not only the spherulite structure but also the size of the spherulite is changed markedly by the incorporation of the rubbery phase. The average spherulite diameter of a sample containing 15% rubber is about half of that of the unmodified PP, as indicated by polarizing light microscopic study. In general, the spherulite size was only further reduced to a small extent with the incorporation of additional impact modifier. The above statements are true of samples either compression-molded or injection-molded (core zone). They are also independent of the type of modifier involved. The skin in the injection-molded bar of the rubber-modified PP appears to be similar in morphology to that of the unmodified PP.

After an extensive polarizing light microscopic study on thin sections cut

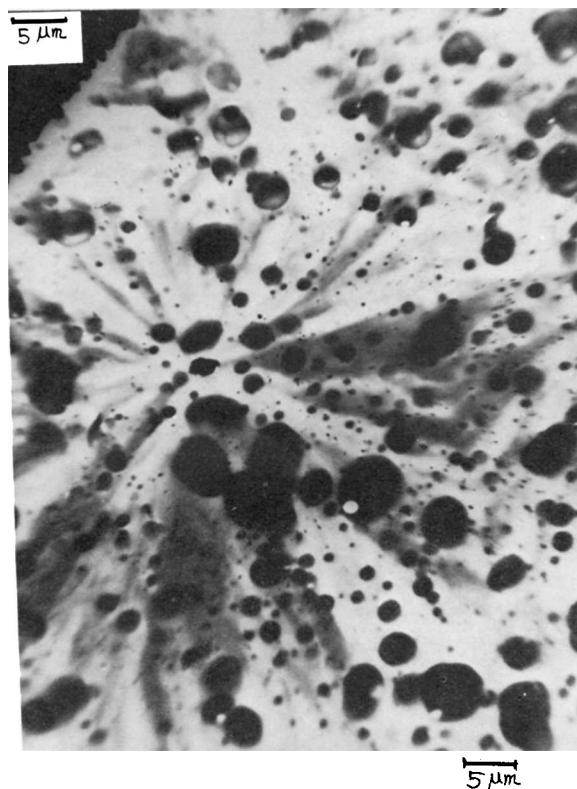


Fig. 5. The core zone morphology of the injection-molded tensile bar of EPDM-modified PP. TEM specimens were prepared by microtoming at -50°C followed by osmium tetroxide staining.

from a variety of rubber-modified PPs we found that, in general, the impact modifier tends to promote α -type (monoclinic) as opposed to β -type (hexagonal) spherulites.

Fusion and Crystallization of PP Systems (DSC Results)

The data presented in this section were obtained from DSC traces recorded by a Perkin-Elmer DSC-2 at a heating rate of $20^{\circ}\text{C}/\text{min}$ and cooling rate of $20^{\circ}\text{C}/\text{min}$. The samples involved are PP homopolymer and its blends with EPDM, EPR, and SBR with the weight percentage of elastomer in each blend varying from 0, 5, 15, 30 to 50%.

As shown in Table II, with the addition of the elastomers, the melting peak of the polymer blend shifted to lower temperatures while the crystallization peak of the blends shifted to higher temperatures. As a consequence of both effects, the degree of undercooling, defined as the difference between the fusion peak and cooling peak temperature, decreases. It was noted from the polarizing light microscopic studies that the superstructure was changed by the incorporation of an elastomer phase resulting in the formation of smaller spherulites. Both DSC and microscopy techniques seem consistently to point out the possibility for the impact modifier to act as a fair nucleating agent in reducing the degree of supercooling.

TABLE II
DSC Melting and Crystallization Results of Polypropylene and Rubber-Modified Polypropylene

Sample code	Composition	Melting peak, T_m (°C)	Heat of fusion, H_f (cal/g)	H_f (blend) H_f (PP) (%)	Crystallization peak, T_c (°C)	Heat of cryst., H_c (cal/g)	Degree of undercooling, T (°C)
M-1	PP-4-N3-5	162.5	12.78	98.3	108.5	11.50	54
M-2	PP-4-N3-15	166	10.58	81.4	105	10.58	61
M-3	PP-4-N3-30	165	9.19	70.7	109	8.65	56
P-3	PP-4-N3-50	166	8.65	67.7	106	8.21	60
M-4	PP-4-N4-5	165	12.15	93.5	108	11.48	57
M-5	PP-4-N4-15	164	11.05	85.0	105	11.05	59
M-6	PP-4-N4-30	164.5	8.75	67.3	110	8.75	54.5
P-6	PP-4-N4-50	166	8.81	67.7	109.5	7.93	56.5
M-7	PP-4-E2-5	164	12.55	96.5	106	11.5	58
M-8	PP-4-E2-15	164	12.55	96.5	106	10.93	58
M-9	PP-4-E2-30	164.5	8.69	66.8	106.5	8.47	58
M-10	PP-4-S7-5	165	12.46	95.8	107	11.34	58
M-11	PP-4-S7-15	166	10.37	79.8	107	9.87	59
M-12	PP-4-S7-30	166	8.39	64.5	107	8.29	59
P-9	PP-4-S7-30	166	6.77	52.1	106	5.97	60
PP-4	PP4	168	13.00	100	106	11.86	62

Both the heats of fusion and crystallization were calculated from the areas enclosed by the base line and the endotherm or exotherm. The thermal energies involved in these transitions decrease as the concentration of the impact modifier is increased. Nevertheless, data on the ratio of fusion heats for the blends to the fusion heat for the unmodified polypropylene, taking into account the concentration effect, indicate that the effect of the rubber upon the extent of PP crystallization is not significant.

We have noted before that the introduction of a rubbery phase not only reduced the average size of spherulites but also inhibited the formation of the less stable β -type spherulites. DSC results actually confirmed this observation. The lowest-temperature endothermic melting peak represents the β -type spherulite while the highest-temperature peak the α -type spherulites of PP.¹⁴ All the DSC curves show that the peak corresponding to the β -type spherulites becomes less pronounced with the addition of the impact modifier.

DISCUSSION

Crystalline Morphology

It was observed in our study and others^{16,17} that the injection-molded test bars of PP homopolymer were a laminate composite structure of different morphologies. Three distinct types of layers were identified: (1) a nonspherulitic skin having a high degree of chain orientation parallel to the injection flow direction; (2) a shear zone with spherulites grown preferentially normal to the flow direction; and (3) a randomly grown spherulitic core. The respective origins of these layers are discussed qualitatively as follows:

Kamal and Kenig¹⁶ in a study of the melt flow behavior during injection molding proposed a model for the process based on three stages: (1) filling, (2) packing, and (3) cooling. The filling stage was treated in terms of the flow of a non-Newtonian melt into a cavity held at a temperature much below the freezing point of the polymer. Additional flow of polymer into the cavity was required in the packing stage to compensate for the shrinkage of polymer caused by partial solidification. Then follows the cooling stage when the rest of the polymer solidifies.

During the filling stage, some portion of polymer is brought to contact with the cold mold wall first and thus is cooled rapidly. These molecules should experience higher shear than those farther away from the wall of mold. The shear stress near the wall orients the molecules in the flow direction; the orientation thus created may be preserved because the viscosity of this oriented layer increases rapidly as the temperature declines dramatically and crystallization takes place.

Clark¹⁷ explained that the shear zone developed during the packing stage of injection-molding when additional polymer flowed into the cavity to offset the shrinkage of the polymer from partial crystallization and cooling. The possibility exists that the stress experienced by molecules in the shear zone, although lower than that in the skin, is still high enough to ensure the formation of oriented crystallites. It should be noted, however, that the existence of a shear stress is not essential to the formation of the tran-

scrySTALLINE morphology observed in the shear zone. A high temperature gradient such as that between the cold mold wall and the hot melt may be sufficient to produce oriented spherulites. We have observed that PP unidirectionally solidified through a temperature gradient exhibited similar transcrySTALLINE morphology (Fig. 6). In this zone, molecular chain is aligned essentially parallel to the wall while the fibrils of the oriented spherulites are perpendicular to the wall. The nucleation density along the plane of the skin-shear interface was so high that the crystallites are constrained to grow predominantly in the direction of the temperature gradient. The temperature gradient itself promotes the oriented growth of spherulites as well.

The growth of the hexagonal polymorph (β -type spherulites) is known to be stimulated by pressure.¹⁸ The high pressure inside a mold cavity may explain why the crystallites in the shear layer are predominantly the hexagonal crystal structure in contrast to the monoclinic structure that comprises the spherulites in the core which developed at the final stage of injection-molding when much smaller pressure was involved. It may be noted that the pressure inside the mold increases relatively gradually during the filling stage and then rapidly during the packing stage, reaching a maximum before the cooling stage sets in when the pressure begins to drop monotonically.¹⁶ In the core zone both the shear stress and extensional stress are small so that nucleation occurs in an essentially quiescent state allowing the random growth of spherulites (no orientation).

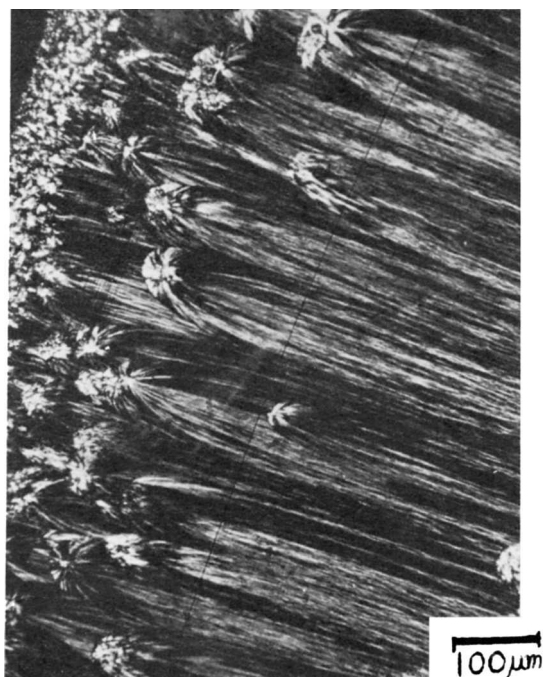


Fig. 6. The transcrySTALLINE morphology of PP directionally solidified through a temperature gradient.

Dependence of Crazeing upon Orientation

It has been observed (Figs. 3 and 4) that in most of the injection-molded PP samples no crazes are observed in the skin zones. Even in samples which exhibit heavy crazing only a small number of crazes can be identified in the skin layers.

The plausible explanation of these observations is that molecular orientation increases the resistance of the material to crazing. This point may be understood on the basis of the well-known mechanism of craze nucleation proposed by Argon,^{19,20} in which precursor micropores are nucleated by the stress concentrations of inhomogeneous plastic deformation on a scale of the order of 50–100 Å. This is followed by the plastic expansion of these holes to form a craze nucleus under the action of the negative pressure existing in the stress field. Recognizing that formation of pores requires inhomogeneous plastic flow (at a molecular level) and relatively stable retention of porosity requires inhomogeneous distribution of stress, Argon²⁰ specifically proposed a model for the formation of the porosity, the precursor, or nucleus of a craze. The formation of porosity (microcracks) will follow the arrest of microshear bands by the molecular heterogeneity. The activation free energy ΔG^* for the formation of such a slip nucleus under a shear σ was obtained to be

$$\Delta G^* = (0.15)^2 \pi (\mu / \sigma) (\mu \phi^3)$$

where μ is the shear modulus of the polymer at the given temperature and ϕ is the relative displacement across the sheared region. Forming a stable microcrack, however, requires expenditure of surface energy which was calculated¹⁸ to be

$$\frac{\sigma l^2}{4\phi E} \geq \alpha$$

With a greater values for μ in the preoriented zone higher stress (σ) with be needed to ensure that $(\sigma l^2 / 4\phi E) \geq \alpha$. Further, ΔG^* will also be higher with larger μ . These considerations explain the observation that it was more difficult for crazes to nucleate in preoriented polymer.

The effects of molecular orientation on craze formation have long been recognized. One example came from the study of the relationships between crazing stress and orientation in tensile tests on hot-drawn PMMA.²¹ It has been found that predrawn PMMA exhibits a higher resistance to crazing than the isotropic polymer when the stress is applied parallel to the orientation direction, and a lower resistance to crazing when stressed at 90° to this direction. In the former case, the stress required for craze initiation was found to increase linearly with the degree of anisotropy, as measured by the birefringence of the polymer.²¹ PS injection-molded bars.²² Crazes were found to form readily in the interior of the tensile bar, where little or no orientation existed, and propagate

outwards toward the surface, where the high orientation along the injection flow direction brought them to a stop.

The Effects of Impact Modifier upon PP

Similar skin-shear-core morphology can also be identified from the rubber-blended PP. Although the demarcation between two zones usually becomes more obscure with the addition of a rubbery phase, one still can differentiate one region from the other without much difficulty. Increasing the rubber content results in an irregular spherulitic texture and smaller average diameter of the spherulites.

It is of interest to observe that the rubber particles are randomly distributed within PP matrix. Some of them are located at the interspherulite boundaries, but the majority are inside the spherulites. The significance of this observation may become clearer if one recognizes that the crazes and cracks in PP do not in general propagate along the interspherulite boundaries.²³ Morphology of randomly dispersed rubber particles would be more efficient in controlling craze and crack formation than that of rubber particles preferentially located along spherulitic boundaries.

The reduction of average spherulite size, as observed from polarizing light microscopy, may imply that the impact modifier is an effective nucleating agent for PP crystallization. We further checked this point by running DSC over samples with a variety of modifiers and, given a modifier, various concentrations. The results have been summarized in Table II. Similar data extracted from the literature are presented in Table III for comparison. As indicated in Figure 7, the incorporation of a rubbery phase not only decreases the temperature of the fusion peak but increases that of the crystallization peak at fixed heating and cooling rates, resulting in a smaller degree of undercooling. These results, covering a range of elastomers commonly used in impact modification, in conjunction with the data of light scattering and x-ray diffraction,¹¹ should leave no doubt that the impact modifier can act as a nucleating agent for PP crystallization, decreasing the degree of undercooling. This is a positive factor in terms of reducing the cycle time for processing. It may be noted that the mechanical properties of spherulitic polymers have been found to be a function of average spherulite diameter \bar{D} ²⁴ and other morphological features.²⁵⁻²⁷ Way et al.²⁴ observed that the tensile yield strength of PP first increased with increased \bar{D} , reached a maximum at about $\bar{D} = 60 \mu\text{m}$ and then decreased. Friedrich²⁷ reported that the fracture resistance of PPs critically depend on \bar{D} as well. Reduction in spherulite size by rubbery phase therefore represents one of the mechanisms responsible for property modification. A discussion on various rubber-toughening mechanisms of PP will be published in a forthcoming paper.

The melting peak in DSC traces corresponding to β -type spherulites (lowest temperature peak)¹⁴ was found to disappear gradually as the concentration of the second phase increased. The same result was borne out by polarizing optical methods, indicating that the modifier tends to nucleate α -type and inhibit the formation of β -type spherulites.

TABLE III
DSC Data of Polypropylene and Rubber-Modified PP from Previous Studies

Composition	Raw materials	Melting peak, T_m (°C)	Heat of fusion, ΔH_f (cal/g)	ΔH_c (blend)/ ΔH_f (PP) (%)	Cryst. peak, T_c (cal/g)	Degree of undercooling, T (°C)	Reference
80% EPDM	Moplen PP (Montedison)	163	3.8	18.5			10
60% EPDM	Dutral EPDM (Montedison)	163	7.8	38.0			
40% EPDM		162	11.7	57			
20% EPDM		162	15.4	75.1			
PP		164	20.5	100			
PP	Daplen DM55	164.5			104	60.5	11
5% EPR	PP(Chemie LinZ A.G.)	162			105	57	
10% EPR	Dutral	161.5			107	54.5	
20% EPR	Co 054 (Montedison)	160.5			107	53.5	
40% EPR		160			117.5	42.5	
5% ISO	DM55 PP Cari	163.5			103.5	60.5	
10% ISO	flex polyisoprene IR305 (Shell)	161.5			105	56.5	
PP	Prefax 6523 (Hercules)	161.5			104	57.5	
5% SBR	TR 1102 SBR (Shell)	160.5			105	55.5	
10% SBR		160.5			106	54.5	

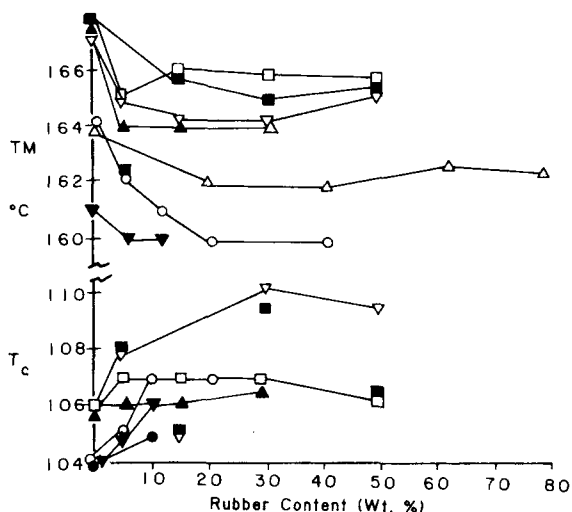


Fig. 7. The DSC fusion and crystallization peak temperatures of various modified PP systems as a function of rubbery phase content: (Δ) PP + EPDM¹⁰; (\circ) PP + EPR¹¹; (\bullet) PP + polyisoprene¹¹; (\blacktriangledown) PP + SBR; (\square) PP + SBR; (\blacksquare) PP + EPDM; (∇) PP + EPDM; (\blacktriangle) PP + EPR.

Data on the heats of fusion are summarized in Figure 8 where the normalized quantity $[1 - H_f(\text{blend})/H_f(\text{PP})]$, taking into account the trivial volume concentration effect, is plotted against rubber content. The diagonal line represents the situation where the rubbery phase has no effect on the heat of fusion. It can be inferred from this figure that, within experimental error, the rubbery phase has no significant effect on the extent of crystallization.

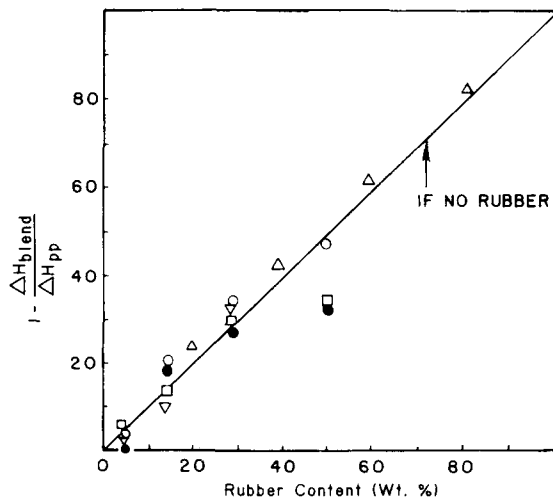


Fig. 8. The heats of fusion of PP in several polyblends of PP and rubber. $H_f(\text{blend})$ = heat of fusion per unit polyblend, $H_f(\text{PP})$ = heat of fusion per unit PP, and $H_f(\text{blend})/H_f(\text{PP})$ characterizes the effect of rubbery phase: (Δ) EPDM/PP (Danesi and Porter¹⁰); (\circ) SBR/PP (Solprene 425P); (\bullet) EPDM/PP (Nordel 2522); (\square) EPDM/PP (Nordel 2722); (∇) EPR/PP (Epcar 807).

CONCLUSION

The crystalline morphology of injection-molded polypropylene, its relationship with crazing, and the effects of various impact modifiers upon the morphology, crystallization, and fusion of polypropylene have been investigated.

The three morphological layers commonly found in injection-molded crystalline polymers have been interpreted as due to the different levels of shear stress, elongational stress, and pressure and the temperature gradient induced between the mould wall and the crystallizing melt. The highly oriented skin layer is found to be usually free from crazing. The higher shear plastic resistance and the higher activation free energy to form a craze nucleus in the preoriented zone, based on Argon's theory of craze nucleation, have been proposed to explain the difficulty for a craze to occur in the highly oriented skin of an injection moulding.

Addition of a rubbery phase results in an irregular spherulitic texture, smaller spherulites, loss of sharpness of the spherulite boundaries, and decrease in the degree of undercooling, but no appreciable change in heats of fusion and crystallization other than a trivial volume effect. During crystallization of PP, the rubbery phase is not pushed along by the melt-solid interface leaving behind a random spatial distribution of rubber particles in the PP matrix.

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