

Rubber-Toughening in Polypropylene

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Synopsis

To deformation and fracture behavior of several polypropylene (PP) and rubber-modified PP materials have been investigated. Plastic deformation mechanisms of these systems depend upon the test rate and temperature with high rates and low temperatures being in favor of crazing. The ductility and toughness of these materials are explained in light of the competition between crack formation and the degree of plastic deformation through crazing and shear yielding. The second phase morphology with smaller average rubber particle diameter D appears to be more efficient than that with larger D in toughening PP. Theoretical calculations indicate that the stresses imposed upon the rubber particles due to volume shrinkage of PP during crystallization are sufficient to compensate for the stresses due to differential thermal contraction in cooling from solidification temperature to end-use temperature. The difference between these two is small, and therefore they provide very little contribution to interfacial adhesion between rubber particle and PP matrix, the adhesion being insufficient for the rubber particles to be effective in controlling craze propagation. The rubber particles, in addition to promoting crazing and shear yielding, can also improve the fracture resistance of PP by varying the crystalline structure of PP (e.g., reducing the spherulite dimensions).

INTRODUCTION

Rubber-toughening of plastics has been a subject of active research in the past two decades.¹⁻⁴ Various theories have been proposed to explain the toughening of polymers with a dispersed rubbery phase, including energy absorption of rubber,^{5,6} stress relief by cavitation around rubber particles,^{7,8} crack branching caused by rubber particles,⁹ crack termination at rubber particles,² crazing promoted by the rubbery phase,^{1-4, 10-14} shear yielding,^{3,15-19} and combined crazing and shear yielding.^{2,4,13,20} These theories have been formulated mainly based on the studies on amorphous plastics. Rubber-toughening mechanisms in semicrystalline polymers have been studied only to a limited extent.²¹⁻²⁵ Because of the complex polycrystalline nature additional possible mechanisms may be anticipated for toughening crystalline polymers. For instance, it has been suggested that by acting as a nucleus for the crystallization of matrix polymer, the rubber particles may serve to reduce the average spherulite size, thereby increasing the impact resistance of polymer.²¹ Other morphological changes induced by the rubbery phase may also occur. Further, deformation mechanisms unique to crystalline polymers may prove important in determining the toughening mechanisms. However, such speculations remain to be verified, and there exists a need to examine various mechanisms of toughness improvement for crystalline polymers.

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Polypropylene (PP) has poor low-temperature fracture resistance, although it has a number of valuable properties. Emerging is an increasing number of reports indicating that the impact strength of PP can be improved by its physical blending with various elastomers. Macroscopic physical properties of PP blends with elastomers have been investigated to some extent.^{21,24,26-28,35-38} Morphological studies on these blends have also been reported sporadically.^{24,28-36} Summarized here are the results of a detailed investigation into the rubber-toughening mechanisms of PP. Particular attention has been directed to studying the change in deformation mechanism in response to a variation in test temperature and strain rate, the possible effects of the rubbery phase upon the polycrystalline morphology, the interfacial adhesion, and the rubber particle size dependence of ductility and toughness. The implication of this study may be applicable to the toughening of other crystalline polymers as well.

EXPERIMENTAL

Material and Sample Composition

The materials used in this study encompass polypropylene homopolymer (PP), ethylene/propylene/diene monomer (EPDM rubber), ethylene/propylene copolymer (EPR), and styrene/butadiene copolymer rubber (SBR). The materials (Table I) were commercial samples except the SBR samples, which were experimental polymers provided by Dr. Henry Hsieh of Philips Petroleum. The sample composition (15 wt % rubber) and the resulted average rubber particle size are listed in Table II. The mixer employed was a Brabender Plasticord single-screw ($L/D = 15$) extruder; the injection molding unit was an Ingersoll-Rand Model V2-18FA. Both are laboratory-scale machines.

TABLE I
Raw Materials

Type of material	Material designation	Commercial name	Supplier	Comments ^a
PP	PP-4	Profax 6523	Hercules	MRF=4, high ρ
	PP-12	Profax 6323	Hercules	MRF=12, low ρ
EPDM	N-1	Nordel 1070	DuPont	high ρ
	N-2	Nordel 1320	DuPont	low ρ
	N-3	Nordel 2522	DuPont	low ρ
	N-4	Nordel 2722	DuPont	low ρ
	N-5	Epcar 545	B. F. Goodrich	low ρ
EPR	E-1	Epcar 306	B. F. Goodrich	low ρ
	E-2	Epcar 807	B. F. Goodrich	low ρ
				$(M_w/M_n) \times 10^{-3}$
SBR	S-1	Solprene P244S	Phillips	200/155
	S-2	Solprene P243S	Phillips	61/57
	S-3	Solprene 422P	Phillips	190/150
	S-4	Solprene 416P	Phillips	140/110
	S-5	Solprene 411S	Phillips	300/220
	S-6	Solprene 414P	Phillips	130/100
	S-7	Solprene 425P	Phillips	240/180
	S-8	Solprene 410	Phillips	82/68

^a ρ = viscosity.

TABLE II
Sample Composition and the Average Rubber Particle Size

Sample I.D.	Composition	Average rubber particle diameter (μm)
A-1	PP-4 + N1	0.64
A-2	PP-4 + N3	0.40
A-3	PP-12 + N1	1.05
A-4	PP-12 + N3	0.50
B-1	PP-4 + E1	—
B-2	PP-4 + E2	—
B-3	PP14 + N5	—
C-1	PP-12 + N4	0.78
C-2	PP-12 + N2	0.28
H-1	PP-4 + S1	0.63
H-2	PP-4 + S2	0.13
H-3	PP-4 + S3	1.80
H-4	PP-4 + S4	0.38
H-5	PP-4 + S5	1.28
H-6	PP-4 + S6	0.40
H-7	PP-4 + S7	0.50
H-8	PP-4 + S8	0.51

The extrusion was conducted at a speed of 40 rpm and at barrel temperature of 200°C and die temperature of approximately 180°C. The materials were extruded and granulated twice to ensure good dispersion. Samples for crazing study were further injection-molded into dogbone-shaped tensile bars under conditions of zone temperatures 190°C, back pressure 3000–6000 psi, injection pressure 4000 psi, and mold temperature 40°C.

In order to assess the effects of rubbery phase upon the crystalline morphology and degree of crystallinity a series of compositions with rubber content ranging from 0% to 50% for each type of rubber were also prepared. The same extrusion conditions were used throughout the study. Various grades of elastomer and PP with varying relative viscosity were combined in the hope that various rubber particle size distributions may be obtained for crazing and fracture study.

Tensile and Charpy Impact Tests

Standard ASTM D638-76 tensile tests were performed on samples A-1, A-3, B-1, H-2, and H-4. In light of the high sensitivity of polymers to temperature and strain rate, tests were carried out over a wide spectrum of rates and temperatures. A temperature chamber adapted to an Instron universal testing machine was used to provide constant temperatures. The chamber was provided with resistance coils (heat), a coolant source (liquid N₂), and two internal fans, and a bilevel Delta temperature controller. A separate thermocouple was placed in contact with the surface of the specimen being tested to measure the actual test temperature. The objective of this phase of study was to understand the possible variations in deformation mode or in fracture mode due to a change in deformation rate and/or temperature. Emphasis was placed on identifying inhomogeneous plastic deformation features such as crazing and shear banding.

Temperature dependence of high-rate fracture behavior was investigated

by performing notched Charpy impact tests over a wide range of temperatures from -196 to $+100^{\circ}\text{C}$. An attempt was also made to correlate the rubber particle size dependence of tensile fracture strain and of impact fracture resistance of PP-EPDM blends.

Electron and Light Microscopy

The two-phase morphology of rubber-modified PP, the morphology of injection-molded PP homopolymer and their 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 polarized light microscope (Reichert). Whether the average spherulite diameter \bar{D}_s is dependent upon the rubber type or concentration was studied as well since \bar{D}_s has been found^{37,38} to affect the mechanical properties of spherulitic polymers.

Light microscopy samples were prepared by microtoming thin sections ($3\text{--}5\ \mu\text{m}$ 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 ($20\ \text{nm}$) to avoid charging problem during SEM examination. Microtometrimmed sample was, in some cases, etched by chromic acid to reveal crazing and crystalline morphology.

Ultrathin sections, $50\text{--}100\ \text{nm}$ 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.

The stained thin sections were then examined in a transmission electron microscope. The rubbery phase appears as dark particles embedded in the white PP matrix (e.g., Fig. 5). The particle size distribution was assessed by an image analyzer (Joyce-Lobel Magiscan) assisted with a Data General minicomputer. The average rubber particle size was accurately calculated through the use of this instrument.

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 and $480\ \text{K}$) to study the influence of the rubber in the crystallization and fusion of PP. Samples scanned included PP, PP + EPDM (N-3), PP + EPDM (N-4), PP + EPR, and PP + SBR; each of 5% , 15% , 30% , and 50% by weight elastomers. The information obtained from DSC consisted of the melting temperatures (T_m), the heats of fusion (H_m), the crystallization peaks (T_m), 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 quantity was used to determine if, other than trivial volume effects, the impact modifiers induce any change in the heat of fusion. This study was carried out to help understand if the rubber particles are nucleating agents for PP crystallization (undercooling reduced?) or if PP and elastomer have natural affinity (heat of fusion altered or degree of crystallinity changed?) to each other.

THEORETICAL CALCULATIONS OF SOLIDIFICATION STRESSES

The stresses that develop in the rubber-modified polymers due to differential thermal contraction of the two phases during cooling from the molding temperature have been a subject of some research effort.^{39,40} In general, the thermal expansion coefficient of the rubber inclusion is significantly higher than that of the matrix. According to Beck et al.,³⁹ the thermal stress distribution for the simple model of a single spherical particle surrounded by an indefinite matrix may be calculated through a straightforward application of the theory of elasticity. The results⁴¹ of such a calculation indicated that the thermal contraction imposes a triaxial tension on the rubber particle and tensile radial and compressive tangential stresses on the surrounding matrix if the interphase adhesion is sufficient to prevent separation at the interface.

Qualitatively similar results have been reported⁴⁰ for the distribution of thermal stresses within and around the rubber particles with varied amounts of glassy occlusion; the magnitude of the thermal stresses, however, was reduced by a factor which was inversely related to the volume fraction of the occlusion. Both of the above two reports were based on the assumption that a sufficient interphase adhesion has been secured. This may be true of the cases such as high impact polystyrene (HIPS) where grafting is often adequate to warrant the interfacial bonding. Majority of polymer-polymer blends are nevertheless immiscible and thus may possess poor or little adhesion. It is the objective of this section to identify the possible sources of interfacial adhesion of a polyblend and determine if the differential thermal contraction with or without applied external stresses will induce interfacial separation (dewetting) between the rubber particles and the matrix. Two representative cases will be discussed: (1) both phases are amorphous (e.g., polystyrene + polybutadiene), and (2) one phase is semicrystalline (e.g., polypropylene + EPDM). In the second case, additional stresses will develop because of differential volume shrinkage during crystallization.

Case I

Let us first consider the case of PS-PB blend where no crystallization volume shrinkage exists since both phases are amorphous. We will begin the calculation by assuming the interphase adhesion to be sufficient to prevent the separation at the interface. Then the magnitude of the radial stress will be the minimum attraction between the two phases to prevent dewetting. An application of the elasticity theory leads to the following results for the thermal stresses³⁹:

$$\sigma_r = \frac{4(\alpha_i - \alpha_m)(1 + \nu_i)G_m G_i \Delta T}{2(1 - 2\nu_i)G_m + (1 + \nu_i)G_i} \quad (1)$$

$$\sigma_\phi = \sigma_\theta = -\frac{1}{2}\sigma_r \quad (2)$$

where σ_r , σ_ϕ , and σ_θ are the stresses in the radial and in two orthogonal tangential directions, respectively; α is the linear coefficient of thermal expansion, G is the shear modulus, ν is the Poisson ratio, ΔT is the temperature decrease giving rise to the stresses, and the subscript i and m denote the rubbery inclusion and the matrix, respectively.

Since PB and PS are thermodynamically incompatible, there exists little or no intimate mixing near the interface. The possible source of attraction would be the dispersion or van der Waals force. To illustrate the order of magnitude of the dispersion force, we may take⁴²

$$f(x) \approx Ha/6x^2 \quad (3)$$

as an approximation, where H is the Hamaker constant, which is of the order of 10^{-13} erg, a is the radius of a rubber particle, and x is the separation between the rubbery phase and the matrix which may be considered as the "thickness of interface". Assuming $a \approx 1 \mu\text{m}$ and $x \approx 10 \text{ \AA}$, then we have

$$f(x) \approx \frac{10^{-13} \text{ erg} \cdot 10^{-4} \text{ cm}}{6 \cdot (10^{-8} \text{ cm})^2 \cdot 10^2} = \frac{1}{6000} \text{ dyn} \quad (4)$$

The stress (attractive) exerted over the whole surface of a rubber particle would be

$$\sigma = \frac{F}{A} = \frac{1}{6000} \times 10^{-5} \text{ (newton)} \frac{1}{4\pi(10^{-6})^2} \text{ (m}^{-2}\text{)} = 1.32 \times 10^2 \text{ N/m}^2 \quad (5)$$

which is orders of magnitude smaller than the necessary interfacial adhesion, as will be discussed later. Other sources of attraction may be electrostatic forces and, possibly, mechanical interlocking; both are believed to be insignificant.

Case II

It is a well-known phenomenon that a polymer can exhibit a pronounced volume shrinkage during crystallization. It is therefore necessary to consider the stresses imposed upon the rubbery phase due to both the volume shrinkage during PP crystallization and the differential thermal contraction during cooling stage of fabrication.

It may take a long time for a polypropylene to complete the crystallization process, which includes the primary crystallization and the subsequent secondary crystallization. To simplify the calculation, we may assume that the density of amorphous phase equals that of the melt ($d_a = 0.854$) and the overall crystallinity ($d_c = 0.946$) of PP matrix equals 77%. Then the total volume shrinkage of PP phase (excluding rubber particles) would be

$$\frac{d_c - d_a}{d_c} \times 70\% = 7\% \quad (6)$$

Shrinkage (Δi) of PP phase produces a uniform hydrostatic pressure of the amount P on the spherical inclusion:

$$\Delta_i = -K_i P = -\frac{3(1 - 2\nu_i)}{E_i} P$$

In the meantime, the matrix material just outside the rubbery inclusion exhibits a uniform negative pressure (triaxial dilation) $-P$,

$$\Delta_m = -K_m(-P) = \frac{3(1 - 2\nu_m)}{E_m} P$$

The volume shrinkage of the amount 7% is shared by both inclusion and matrix. Therefore, we have

$$\Delta_i - \Delta_m = -\frac{3(1 - 2\nu_i)P}{E_i} - \frac{3(1 - 2\nu_m)}{E_m} P = -7\%$$

or

$$P = \frac{7\%}{3[(1 - 2\nu_i)/E_i + (1 - 2\nu_m)/E_m]} \quad (7)$$

The magnitude of P represents the radial stress imposed upon the rubber particle due to the crystallization of PP matrix.

RESULTS AND DISCUSSION

Crazing in Polypropylene

The results of an extensive tensile test conducted over a wide spectrum of strain rates and temperatures may be summarized in the following paragraphs:

The deformation of semicrystalline PP depends strongly on the strain rate and temperature. For a given test temperature, there appears to exist a critical strain rate above which crazing dominates and below which shear yielding is dominant. Similarly, for a given strain rate, there exists a critical test temperature which demarcates crazing from shear yielding.

The origin of the shear yielding-crazing transition resides in the different temperature and rate dependencies of shear yield strength and of craze initiation stress. Experimental results (e.g., Refs. 41 and 43) indicate that the shear yield strength of a polymer increases appreciably with decreasing test temperature or/and increasing strain rate. However, the triaxial or crazing yield strength seems to be relatively unaffected by these variables. It is believed⁴⁴ that the specimen either yields in shear, if the shear component of stress field exceeds the shear yield strength, or crazes in response to the triaxial tension, if the triaxial stress exceeds the stress required for craze formation. As the temperature is decreased and/or strain rate is increased, the shear yield strength will increase more dramatically than the craze initiation stress. It therefore becomes more difficult for shear yielding to operate.⁴¹ The morphology of a typical craze in PP is shown in Figure 1.

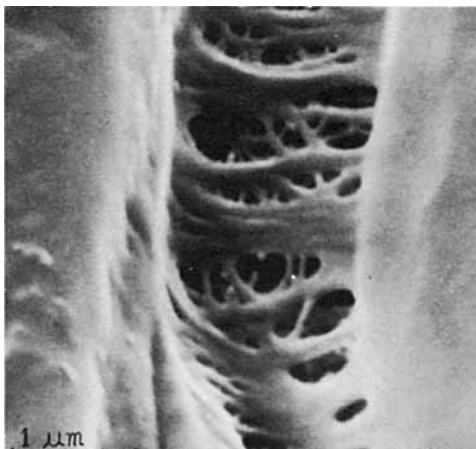


Fig. 1. Scanning electron micrograph showing the typical craze morphology in a polypropylene homopolymer.

Crazes in crystalline PP were found to be morphologically similar to those in glassy polymers, and to exhibit high reflectivity, large area-to-thickness ratio, and planarity. They usually run perpendicular to the principal stress direction, although local deviation up to 15° is not uncommon (likely due to the presence of structural order). Crazes in PP have a higher tendency to bifurcate than those in glassy polymers. They do not in general follow an interspherulitic path, but propagate through spherulites. The length of a craze in PP is not restricted to one spherulite diameter, nor does it preferentially grow radially. However, it may be noted that, by imposing different heat treatments on melt-grown PP of different molecular weight and tacticity, Friedrich⁴⁵ obtained five morphologically different PPs. Depending upon the morphology, crazes could develop preferentially at the interfaces between coarse spherulites, within larger spherulites, or at the boundaries of small ones, each corresponding to a distinct fracture resistance value. This observation suggests a possible toughening mechanism if a rubber phase could change the crystalline morphology of PP.

Rubber Particle Size Dependence of Crazing

After extensive SEM and TEM investigation over many rubber-modified PP samples subjected to plastic deformation or fracture, we discovered that no crazes appear to nucleate from any rubber particle with diameter (D) smaller than approximately $0.5 \mu\text{m}$. The higher the D , the higher the propensity to form crazes. It has been suggested³⁶ that the loss of craze nucleation efficiency of small particles were due to the small size of the stress-concentrated region being insufficient to accommodate the formation of a craze with its characteristic structure.

This is an important observation since it could serve as one of the guidelines for designing rubber particle sizes if crazing plays a role in toughening. It is conceivable that every plastic-rubber system should possess its own critical rubber particle size for craze nucleation since the associated stress concentration is dictated by the modulus ratio^{2,24,39,40} between rubber and

matrix. Donald and Kramer⁴⁶ have observed that in thin films of HIPS no crazes were nucleated from rubber particles smaller than $2\ \mu\text{m}$ in diameter. These workers⁴⁶ further suggested that a reasonable spatial criterion for the initial nucleating stress distribution would be that the stress enhancement must not drop to half its value at the particle surface in less than three craze fibril spacings. Evidence has yet to appear in other rubber-modified systems. A typical craze pattern in EPDM-modified PP is shown in Figure 2.

The Impact Behavior

As shown in Figure 3, the Charpy impact energy of sample B-3 (PP + EPDM) may be divided into four temperature regimes. In both the extremely low temperature regime (-196 – -100°C) and the low temperature regime (-100 – -60°C) impact resistance of PP was not improved by adding in rubber particles. In the intermediate temperature regime (-60 – 0°C) the impact energy began to rise with increasing temperature, and dramatic impact strength improvement was also observed implying that the rubbery phase started to function as an impact modifier (T_g of EPDM $\approx -60^\circ\text{C}$). In the high temperature regime (0 – 100°C) the impact strength of both PP and modified PP shoot up dramatically although modified systems were much tougher than unmodified PP. For EPR-modified PP samples (Fig. 3) and SBR-modified systems [Figs. 4(a)–4(c)], the low temperature and intermediate temperature regimes appear to merge together, suggesting that both SBR and EPR rubbers are still effective in imparting fracture resistance to PP. The glass transition range of both elastomers appears to extend to as low as -100°C .

The toughness of a material in general reflects the degree of plastic deformation before final failure. The objective of toughening a plastic is to achieve a maximum amount of crazed and/or shear banded volume if these two are important mechanisms of plasticity. Therefore, we may understand

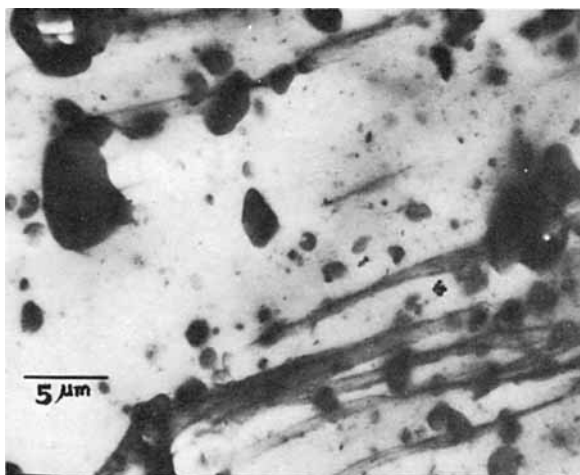


Fig. 2. Crazes formed in an EPDM-modified polypropylene. TEM specimens stained with O_2O_4 and microtomed at -90°C .

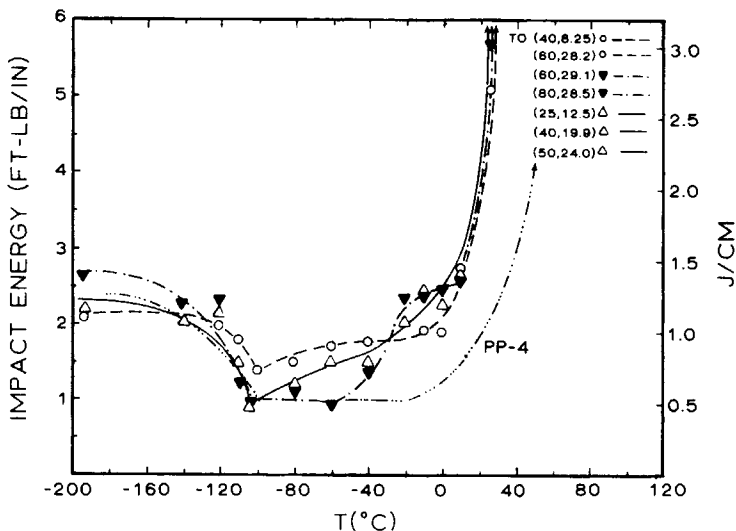


Fig. 3. The notched Charpy impact energies of pp-rubber blends tested at various temperatures. Rubbers used are EPDM: [sample B-3 (PP-4 + EPDM) (\blacktriangledown)] and EPR [samples B-1 (PP-4 + EPR) (\triangle) and B-2 (PP-4 + EPR) (\circ)].

the temperature dependence of impact improvement as reflecting the competition between the crack initiation/propagation and crazing/shear yielding, the latter being responsible for the extent of plastic deformation before material failure.

In the low temperature regime (regime II), taking sample B-3 as an example, where the rubber particles are in the glassy state they are unable to create a great extent of crazing at any stage of crack formation. The fast-propagating crack would thus overtake crazing, resulting in low impact

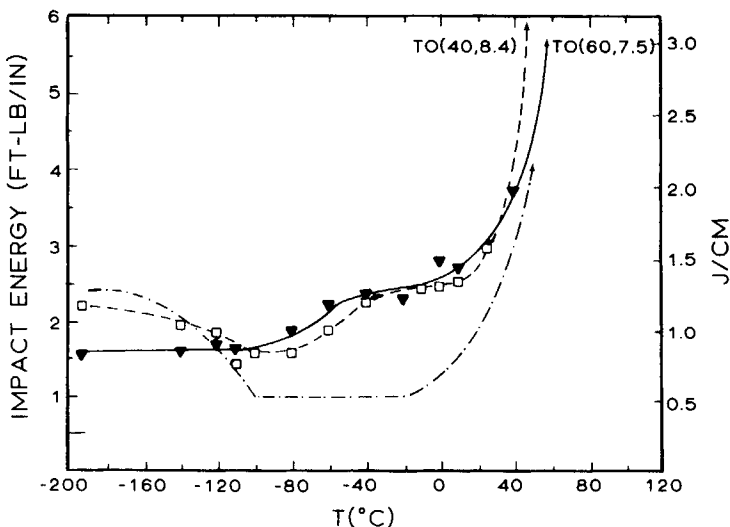


Fig. 4. The notched Charpy impact energies of SBR-modified PP systems in relation to test temperatures: (---) PP-4; (\blacktriangledown , —) H3; (\square , ---) H-4; (\triangle , —) H-5; (\bullet , ---) H-6; (\square , —) H-7; (\blacktriangledown , ---) H-8.

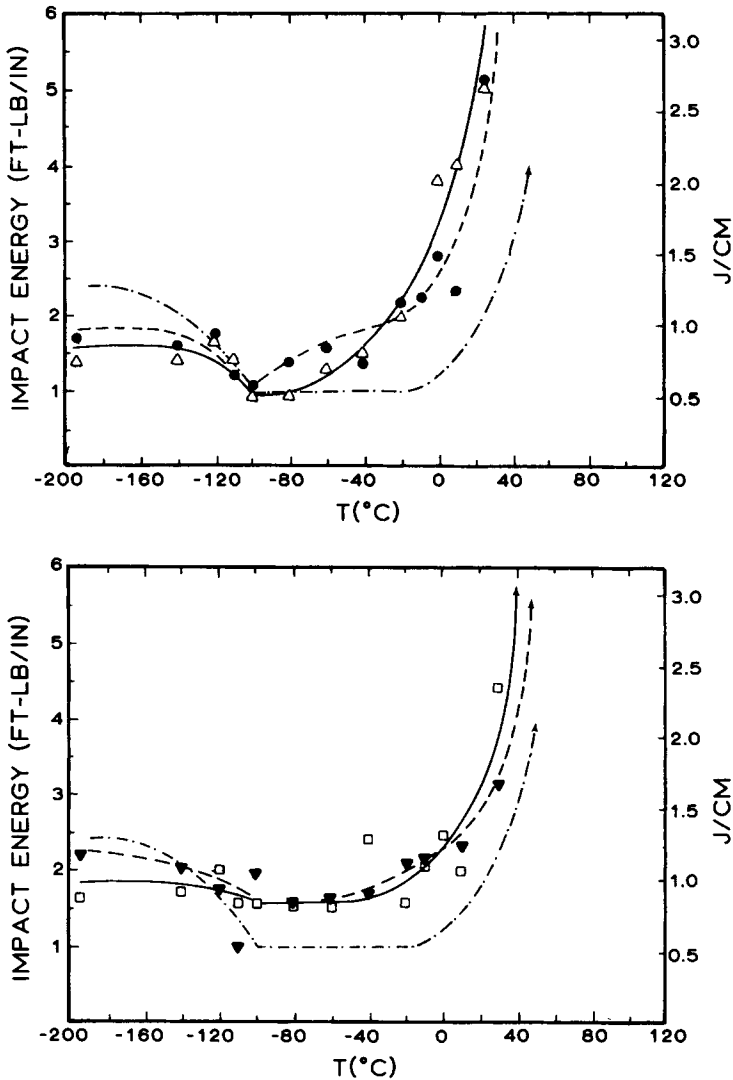


Fig. 4. (continued from previous page)

value as evidenced by the clean fracture surface. Shear yielding in this low temperature and extremely high test rate regime is negligible.

The rubbery phase in its glassy state behaves essentially like a glassy polymer, losing its advantage over other fillers (glass beads, e.g.) as a toughening agent. The reason may be given as follows: The craze-nucleating ability of a rubber particle is dependent upon the stress concentration which in turn is a function of the modulus difference between dispersed and matrix phases.^{2,24,39,40} As the temperature is decreased, the modulus of rubbery phase becomes closer to that of the matrix and the stress concentration will thus be drastically reduced.

At intermediate temperatures (-60 – 0°C ; or regime III) the rubber particles are above their glass transition temperature and become increasingly

rubbery as the temperature rises. The rubber particles are thus capable of nucleating crazes to various extents. Small degree of stress-whitening begins to appear on the fracture surface. The propagating crack encounters a stringent competition from crazing, and therefore improvement in toughness results.

Examination of the fracture surfaces of the samples tested at regime IV ($T > 0^\circ\text{C}$) shows a pronounced stress-whitening at the base of the notch, the extent of which expanding with increasing temperature. During the relatively slow buildup of stress at the base of the notch, a great amount of plastic deformation occurs through the formation of crazes and possibly shear yielding. Once the crack nucleation occurs, the degree of crazing will be drastically reduced during the process of crack propagation. The extent of stress-whitening in the subcritical stage of fracture widens as the temperature rises possibly because ductility of the matrix itself increases. It may be noted that the transition temperature (0°C) between regime III and IV coincides with the T_g of PP above which a greater degree of plastic deformation becomes more probable. That the transition temperature is independent of the rubber type involved and the impact energies of the unmodified PPs also start to rise up at about the same temperature seem to suggest that this transition temperature is intrinsic to the matrix polymer.

At relatively high temperatures ($\geq 60^\circ\text{C}$), some of the samples did not break completely. Both crazing and shear yielding are believed to be responsible for the high impact resistance values.

At the extremely low-temperature region (-190 – -100°C) the impact energies of most samples were abnormally high, increasing as the temperature was decreasing. Although the fracture surface is characteristic of brittle failure, similar to those tested at -100 – -60°C , crack bifurcation has almost always occurred near the fracture surface. The reason for easy crack branching at such low temperatures is not clear. It was suggested by Olf and Peterlin⁴⁷ that nitrogen gas at very low temperatures (e.g., $\leq 120^\circ\text{C}$), where the thermodynamic activity becomes sufficiently high, is an effective crazing agent. The greater number of crazes in the presence of such an active agent, promoting a higher propensity of crack bifurcation, could be responsible for the unusually high impact values at such low temperatures (as $T \rightarrow -196^\circ\text{C}$, the activity $\rightarrow 1$).

It may also be noted from the work of Mai and Williams⁴⁸ that the K_{c1} (plane strain fracture toughness) was temperature dependent. In PP, the linear relationship between K_{c2} (plane stress fracture toughness) and T was associated with the β and γ relaxation processes over the temperature range -180 – -10°C . (In nylon, there was a one-to-one correspondence between the K_{c2} changes and the $\tan \delta$ peaks due to the β and γ relaxation processes). The (plane stress) fracture toughness, K_{c2} , increases linearly as the temperature decreases from -100 to -180°C .

Rubber Particle Size Dependence of Ductility and Toughness

It has been shown that $D \cong 0.5 \mu\text{m}$ is the critical rubber particle size below which the particle could not nucleate crazes in PP.³⁶ As long as the majority of particles are greater than such a critical size for craze initiation,

a smaller average rubber particle size would imply a larger number of potential craze initiation sites, given the same volume fraction of rubbery phase. If the rubber particles do not play the role of controlling craze growth or if control of craze propagation is unimportant, then a larger density of crazes would lead to a greater extent of plastic deformation prior to fracture.

In the case of rubber-modified PP, the rubber particles may not be capable of either terminating the propagating crazes or serving as the reinforcing ligaments for such crazes since very little interfacial adhesion exists between rubbery phase and matrix (see next section). These rubber particles are probably not much better than cavities in controlling craze growth. What appears to be important is the number of particles effective in nucleating crazes and/or shear bands. For instance, the tensile fracture strain for a series of EPDM-modified PP samples increases in the order A-3 < A-1 < A-4 < A-2 as the corresponding average rubber particle size decreases in the same order (Table III).

It was also found³⁶ that, over the useful temperature range (-60 – $+100^{\circ}\text{C}$), the EPDM-modified PP systems with smaller rubber particles were more impact-resistant than the systems with larger ones. For instance, sample A-2 exhibits a higher impact energy than sample A-1 while A-4 is more fracture resistant than A-3. Critical evaluation of the normalized impact energy (impact energy of a PP-rubber blend/impact energy of the corresponding PP) in relation to test temperature indicated that the phase morphology with small \bar{D} is more effective than that with large \bar{D} in toughening PP. For example, A-1 is tougher than A-3 (same EPDM) while A-2 is tougher than A-4 (same EPDM). Both tensile and impact tests consistently show that, within the rubber particle size range investigated, a larger number of small particles is more effective than a small number of large particles in enhancing the fracture resistance of PP.

In all the modified samples studied, stress-whitening was observed before general yielding point, and such whitening phenomenon continued to intensify in the unnecked zone (if necking occurred) even after cold drawing started. Such a preyielding phenomenon was not observed in PP homopolymer under comparable test conditions (room temperature and medium strain rates), suggesting that it was due to the formation of crazes and/or shear bands promoted by the rubbery phase in the modified systems. The stress whitening occurred more uniformly along the gauge length in samples A-2 and A-4 where the average particle sizes are small.

In a study concerning toughness evaluation of PP-EPDM blends using instrumented puncture test, Dao⁴⁹ observed that, at a fixed rubber content (15%), a rubber dispersion with particle size lying between 0.1 and 1.0 μm and centered around 0.4 μm appeared to be the favorable conditions for

TABLE III
Tensile Fracture Strain in Relation to Average Rubber Particle Size

Sample	\bar{D} (μm)	ϵ_b (%)
A-3	1.05	26
A-1	0.64	95
A-4	0.50	163
A-2	0.40	610

maximum puncture toughness. Speri and Patrick²¹ similarly observed that impact strength of PP-EPDM blends was increased as the rubber particle size was reduced; $\bar{D} \approx 0.3 \mu\text{m}$ appeared to be adequate. Both studies^{21,49} seem to be consistent with our observations.

It may be noted that crazing is not the only deformation mechanism in modified PP and probably not the dominating one at room temperature and normal deformation rates⁴³ (e.g., conventional Instron crosshead rates). Since PP is a semicrystalline polymer with moderate ductility shear deformation may be the prevailing deformation mechanism under normal conditions. Under impact conditions (high rates), however, crazing should become important. Although it is not clear if there exists a critical rubber particle size in nucleating shear bands, small particles, being ineffective in promoting craze formation, still appear to be capable of toughening PP. For instance, a sizable number of particles dispersed in samples A-2 and A-4 are presumably too small for craze initiation. However, these samples are still much ductile than samples A-1 and A-3. The morphology with smaller \bar{D} seems to offer a more efficient use of rubber particles in promoting shear yielding and/or crazing and thereby imparting greater fracture resistance to PP. If interaction between shear bands and crazes play any role in toughening PP remains to be elucidated.

Differential Thermal and Crystallization Stresses

In order to illustrate the orders of magnitude of stresses induced by the differential thermal contraction in amorphous systems, a physical blend of PS and PB will be used as an example. Substitution of the physical constants (Table IV) into eqs. (1) and (2) leads to the following result:

$$\sigma_r = 1.67 \times 10^3 \text{ psi} \quad (1.15 \times 10^6 \text{ N/m}^2)$$

$$\sigma_\phi = \sigma_\theta = -8.3 \times 10^2 \text{ psi} \quad (-0.57 \times 10^6 \text{ N/m}^2)$$

It is clear that a radial tensile stress exists, which tends to separate the matrix from the PB rubber particles [recall that we assumed an adequate interfacial bonding in deriving eqs. (1) and (2)]. Therefore, the minimum attraction between the two phases required to avoid the interfacial debonding would be $\sigma_r = 1.67 \times 10^3 \text{ psi}$. Comparison of this value with the van der Waals force obtained in eq. (5) indicates that, in the blends of PS

TABLE IV
Physical Property Data Used in Calculating Thermal and Crystallization Stresses

Material	Tensile modulus (psi)	Shear modulus (psi)	Poisson ratio	Linear thermal expansion coeff. (in./in./°C)
Polystyrene	4.0×10^5	1.5×10^5	0.33	6×10^{-5}
Polybutadiene	5.0×10^2	1.7×10^5	0.499	25×10^{-5}
Polypropylene	2.0×10^5	7.5×10^4	0.33	10×10^{-5}
EPR	1.2×10^3	5.3×10^2	0.49	50×10^{-5}
EPDM	1.4×10^3	4.7×10^2	0.49	50×10^{-5}
SBR	2.5×10^2	8.3×10^1	0.49	50×10^{-5}

and PB, the dispersive force is not sufficient to compensate for the thermal stress and the rubber particles are physically separated from the matrix.

However, in the case of PP-rubber blends, the crystallization of PP (but not rubber) would produce additional stress that opposes the thermal stress. The stress imposed upon the EPR rubber particle due to crystallization of PP is, from eq. (7) and Table IV,

$$\begin{aligned} P_c &= 5.0 \times 10^3 \text{ psi} \\ \sigma_{rc} &= -P_c = -5.0 \times 10^3 \text{ psi} \\ \sigma_{\phi c} = \sigma_{\theta c} &= -\frac{1}{2}\sigma_{rc} = 2.5 \times 10^3 \text{ psi} \end{aligned} \quad (8)$$

The necessary interfacial adhesion to prevent separation during cooling from molding temperature to end-use temperature (temperature difference being $\approx 75^\circ\text{C}$) is

$$\sigma_{rt} = 1.88 \times 10^3 \text{ psi} \quad (9)$$

Comparison of eqs. (8) and (9) indicates that compressive (radial) stress exerted on the rubber particle due to volume shrinkage of PP crystallization more than makes up for the required interfacial adhesion to avoid dewetting caused by differential thermal contraction. Similar results could be obtained for the blends of PP and EPDM. For both cases, small amount of residual stress exists thanks to volume shrinkage of PP. Although the propylene chain of EPDM or of EPR may have some natural affinity with the PP matrix, the induced interfacial adhesion is believed to be insignificant.

In the case of PP-SBR blends, the crystallization stress may be calculated to be

$$\begin{aligned} P_c &= 2.86 \times 10^2 \text{ psi} \\ \sigma_{rc} &= -P_c = -2.86 \times 10^2 \text{ psi} \\ \sigma_{\phi c} = \sigma_{\theta c} &= -\frac{1}{2}\sigma_{rc} = 1.43 \times 10^2 \text{ psi} \end{aligned}$$

The corresponding differential thermal stress is

$$\sigma_{rt} = 1.34 \times 10^2 \text{ psi}$$

if the difference between molding and end-use temperatures is again taken to be 75°C . The results show that the volume shrinkage of PP during crystallization produces radial compressive stress on the rubber particle, which is probably sufficient to hold up the subsequent differential thermal contraction. Nevertheless, the difference, which represents the minimum externally applied stress required to separate one phase from the other, is insignificant. Both dispersion force and the possible force induced by physical entanglements between two phases are negligible.

The interfacial adhesion between rubbery phase and PP is so little that the microtoming force during TEM sample preparation is often enough to remove the rubber particles, leaving behind cavities in the PP matrix [Figs. 5(a) and (b)]. Well-bonded rubber particles in HIPS, subjected to the same microtoming conditions, were only slightly distorted; no particles were displaced from their original sites [Fig. 5(c)].

It is well-known that both glass beads and voids are effective in nucleating crazes. Yet such materials are not much tougher (and sometimes even poorer) than the unmodified polymer itself because the crazes nucleated break down rapidly to form cracks before plastic deformation due to crazing occurs to a great extent. In some way the rubber particles act to delay craze breakdown to allow for greater plastic strain to develop.

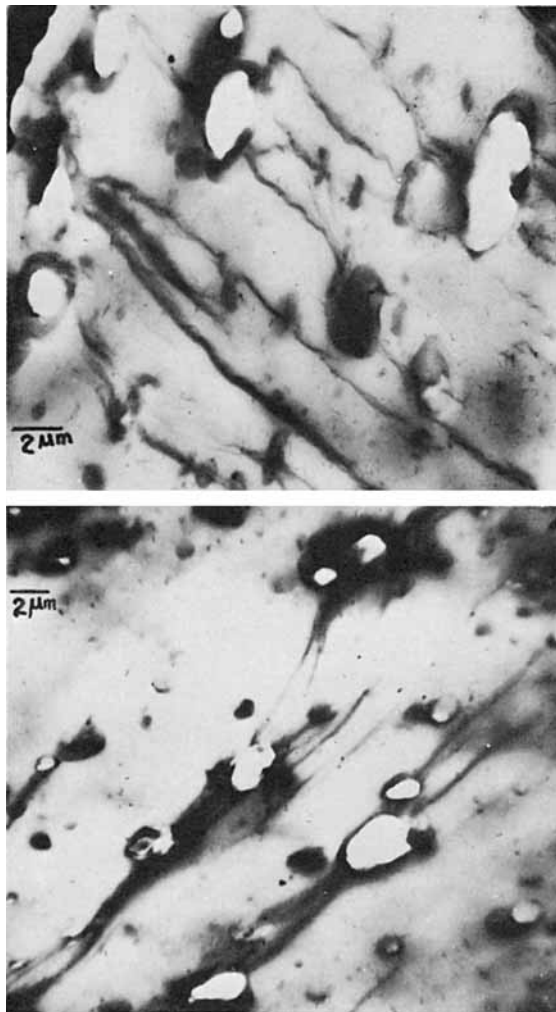


Fig. 5. TEM pictures showing that: (a) in PP-rubber blends with poor interfacial adhesion, the microtoming force may be sufficient to remove the rubber particles; (b) rubber particles in high impact polystyrene with adequate interfacial bonding were only slightly distorted, and no cavities were created by microtome knife.

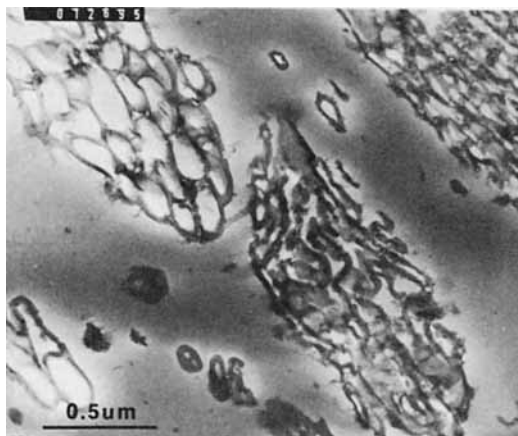


Fig. 5. (continued from previous page)

It was conventionally believed that the rubber particles may serve as "craze stoppers" and avoid the crazes from growing too large.^{2,4} This hypothesis assumes that the fibrils in long, thick crazes break down more rapidly to form cracks than to those in short, thin crazes. However, as pointed out by Kramer,²⁰ the craze thickening mechanism, which involves drawing fibrils from the craze surfaces, does not lead to craze fibril weakening. Further, the overall plastic strain, and thus ductility or toughness, produced by crazing, is shown²⁰ to be markedly decreased by decreasing the final lengths to which crazes can grow once they are nucleated. Kramer²⁰ therefore proposed that the well-bonded rubber particles are necessary as reinforcing ligaments across the craze, thus retarding the subcritical growth of voids in the craze to cracks of critical size.

Based on either hypothesis, an adequate interfacial adhesion would be of extreme importance in order to achieve optimum toughness through generation of crazes. As shown in this section, the interfacial bonding between matrix polymers such as polystyrene (amorphous) and polypropylene (crystalline) and the rubber particles such as polybutadiene, EPDM, EPR, and SBR is, in general, not adequate. Imposition of an external force, e.g., during tensile or impact test, will often be sufficient to cause interfacial dewetting between the rubber particle and the matrix. In certain cases, e.g., physical blends of PS and PB, merely the differential thermal contraction may be sufficient to produce interfacial debonding. Such a blend is therefore very brittle. Achieving valid interfacial adhesion through techniques such as grafting or copolymerization would be essential if the toughness of a rubber-modified system relies solely upon the profuse generation of crazes.

That a moderately ductile matrix, such as PP, can be toughened by physically blending in a rubbery phase without appreciable interfacial bonding suggests that crazing may not be the only toughening mechanism. Shear bands may play a synergistic role with crazing in providing toughness to PP. Whether improving interfacial adhesion between rubber and such a ductile matrix could further improve its toughness remains unclear. Further experimentation is required to clarify these speculations.

The Effects of Rubber Upon The Crystalline Nature of PP

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.^{32,35} 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 modified PP, as indicated in our 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 reduction of average spherulite size 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.³⁵ The results showed that adding a rubbery phase not only decreased the temperature of fusion peak but increased that of the crystallization peak at fixed heating and cooling rates, resulting in a smaller degree of undercooling. Both DSC and light microscopic studies suggest that the impact modifier can act as a nucleating agent for PP crystallization. Dao⁴⁹ observed that the average spherulite diameter \bar{D} decreased from 50 μm for unmodified PP to 20 μm for PP blends containing 20% EPDM. We have obtained similar data despite that these two studies^{35,49} involved slightly different materials and molding conditions. Another possible explanation for the decrease in spherulite size is that the rubbery phase decreases the spherulite growth rate. In a nonisothermal cooling experiment the average spherulite size may be smaller if the spherulite growth rate is reduced. Decreased spherulite growth rate could also account for the lower crystallization temperature observed when rubber is added to PP.

It may be noted that the mechanical properties of spherulite polymers have been found to be a function of \bar{D} ³⁷ and of other morphological features.⁴⁵ Way et al.³⁷ 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. Friedrich⁴⁵ reported that the fracture resistance of PPs critically depend on \bar{D} as well. Reduction in spherulite size by rubbery phase and other attendant morphological changes are therefore expected to be partially responsible for property modification.

Analysis of the DSC data showed that the heats of fusion and of crystallization per unit content of PP in PP-rubber blends (taking into account the trivial volume effect) was independent of the rubber content of the blend.³⁷ In other words, the degree of crystallinity of the PP matrix in the PP-rubber blends did not vary as the rubbery phase was added. It may be inferred that no or very little mixing at the molecular level existed in the solid state and very little interfacial adhesion is anticipated between the rubbery phase and PP matrix.

Also to be noted was the observation³⁷ that the rubber particles are randomly dispersed in the PP matrix. They were engulfed by the growing melt-solid interface during crystallization and did not preferentially reside along the spherulite boundaries. Such a random dispersion is believed to be more effective in inhibiting or retarding the subcritical growth of crack since

crazes were generally observed to propagate through the spherulites, not preferentially along spherulite boundaries.

CONCLUSION

The rubber-toughening mechanisms of semicrystalline polymers have been studied using polypropylene as an example. Several different grades of EPDM, EPR, and SBR elastomers have been blended with two homopolymers and their structure-property relationships examined. The results of this investigation may be summarized as followed:

1. Depending upon the test temperature and deformation rate, PP and rubber-modified PPs may exhibit crazing and/or shear-type yielding. High rates and low temperatures favor crazing while low rates and high temperatures promote shear yielding. The ductility and toughness of a given system lie in the competition between catastrophic crack propagation and the degree of plastic deformation through crazing and shear yielding.

2. The toughened PP systems with smaller average rubber particle size are more ductile and impact resistant. For EPDM-modified PPs the optimum average diameter appears to be approximately 0.4 μm . This phase morphology seems to represent a more efficient use of rubber particles in promoting crazes and/or shear bands.

3. It was demonstrated that the interfacial adhesion between polybutadiene and polystyrene phases in the PB-PS physical blends is essentially zero. Although the volume shrinkage due to PP crystallization produces a radial compressive stress on the rubber particles which is greater than the stress due to differential thermal contraction in cooling from solidification temperature to end-use temperature, the difference is very small. The interfacial adhesion between the rubber particles and PP matrix is believed to be insignificant being insufficient to "control" craze propagation or to retard crack initiation. With a better interfacial bonding, the fracture resistance of PP may be further improved.

4. Also demonstrated is the fact that the spherulite sizes are effectively reduced by the dispersed rubbery phase. This phenomenon may be partially responsible for the improvement of PP crack resistance.

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