

Mechanical Properties of Polypropylene/Crosslinked Rubber Blends

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Synopsis

Mechanical properties of rubber-modified polymers are not single-valued functions of rubber/matrix type and rubber content, but also vary with processing conditions. The variations in mechanical properties with processing conditions arise mainly from changes in rubber-phase dispersion. In our past work, by lightly crosslinking the rubbers to increase their melt tenacity and strength, we have succeeded in producing fine and consistent dispersions despite diverse processing conditions. In this study, mechanical properties of polypropylene/lightly crosslinked rubber blends are compared with those of polypropylene/uncrosslinked rubber blends. The results indicate that, like dispersion, mechanical properties of polypropylene/crosslinked rubber blends also appear to be consistent and independent of process variables. The influences on mechanical behavior of degree of crosslinking, rubber content, and rubber/matrix type are also discussed.

INTRODUCTION

Toughness of polymers can be enhanced by, among other means, blending with rubbers. Improvement in impact resistance as well as retention of blend stiffness, strength, and processability are essential if the blends are to receive wide acceptance. Crazing associated with stress whitening and microvoid development and shear banding associated with localized bands of intense shear deformations are main yielding mechanisms that raise the crack resistance of these rubber-modified polymers.¹⁻⁸ Blend stiffness is generally related to matrix and rubber stiffnesses and is therefore influenced by component elastic properties and rubber content. Low strength in blends arises from yielding at reduced loads as a result of strain softening due to craze and shear band formation around the rubber particles.⁷⁻⁹ Reduced processability results from increased blend viscosity with the addition of rubber. High matrix molecular weight and high rubber content are main causes for poor processability.^{10,11}

Mechanical properties of rubber-modified polymers are not single-valued functions of rubber and matrix type and rubber content but also may vary with processing conditions.¹²⁻¹⁸ Different shear fields developed during compounding and molding can result in strong variations in rubber particle size and size distribution,¹⁴⁻¹⁹ and past work showed strong dependence of blend properties on these particle parameters.^{14,20,21} For example, recent investigations in our laboratory¹⁶⁻¹⁸ revealed that Izod impact resistance and melt flow rate varied by a factor of 2 when processing conditions changed from low to high mixing and molding. The strong shear fields developed in intense mixing and molding caused matrix degradation and rubber particle recombination resulting in significant variations in rubber particle size and size distribution (dispersion) and property variability as observed. Low-molecular-weight, uncrosslinked rubbers

TABLE I
Polypropylenes Used in Blends

Polypropylene	Structure	Molecular weight	Melt flow, (g/10 min)	Notched Izod impact @ 23°C, J/cm	Gardner impact J		Tensile properties @ 23°C	
					23°C	-34°C	Yield strength MPa,	Modulus MPa
H65	Homopolymer	High	4	0.4	2.5	0.17	30	1580
H63	Homopolymer	Low	13	0.4	1.5	0.15	31	1800
C75	Copolymer ^a	High	3	1.3	36	4.1	23	1030

^a Propylene-ethylene terminal block copolymer.

that in laboratory conditions disperse fairly effectively^{15,19} can, in factory processing conditions, result in poor dispersion and property variations.¹⁶⁻¹⁸

Lightly crosslinking the rubbers to increase their melt tenacity and strength appears to minimize particle recombination and produce fine and consistent dispersions. Our study of the use of crosslinked rubbers in controlling rubber-phase dispersion has been described.²² Blend morphology, such as microstructure of the rubber and polypropylene phases, has also been detailed.²³ In this report, mechanical properties of these blends are presented. The results will show that, like dispersion, mechanical properties of polypropylene/crosslinked rubber blends also appear to be consistent and independent of processing conditions. The effects on mechanical behavior of crosslinks, rubber content, and polypropylene/rubber type are also discussed.

EXPERIMENTAL

Three commercial grades of polypropylene from Hercules Inc. were used as matrix materials. Their properties are listed in Table I. Four lightly crosslinked EPDM (ethylene-propylene diene terpolymer) rubbers were supplied by Uniroyal Inc. Table II lists the various properties of the EPDM rubbers. A corotating, twin-screw 53-mm Werner-Pfleiderer compounding machine was used for blending. Two screw designs were employed to provide "low" and "high" mixing shear. Molding of blends into test samples was carried out under three rates: "high," "low," and "zero" molding shear. The high molding shear was provided by a reciprocating-screw injection molder; the low molding shear, by a ram injection molder; and the zero shear, by casting samples in small shallow trays in a vacuum oven. More details on materials and processing technique

TABLE II
Crosslinked Rubbers Used in Blends

Designation	Type	Crosslinking ^a	Crystallinity
A	EPDM-1	Low	High
B	EPDM-2	High	Low
C	EPDM-2	High	Low
D	EPDM-1	High	High

^a Crosslinking ranges from 15% (low) to 40% (high) of total available crosslink sites.

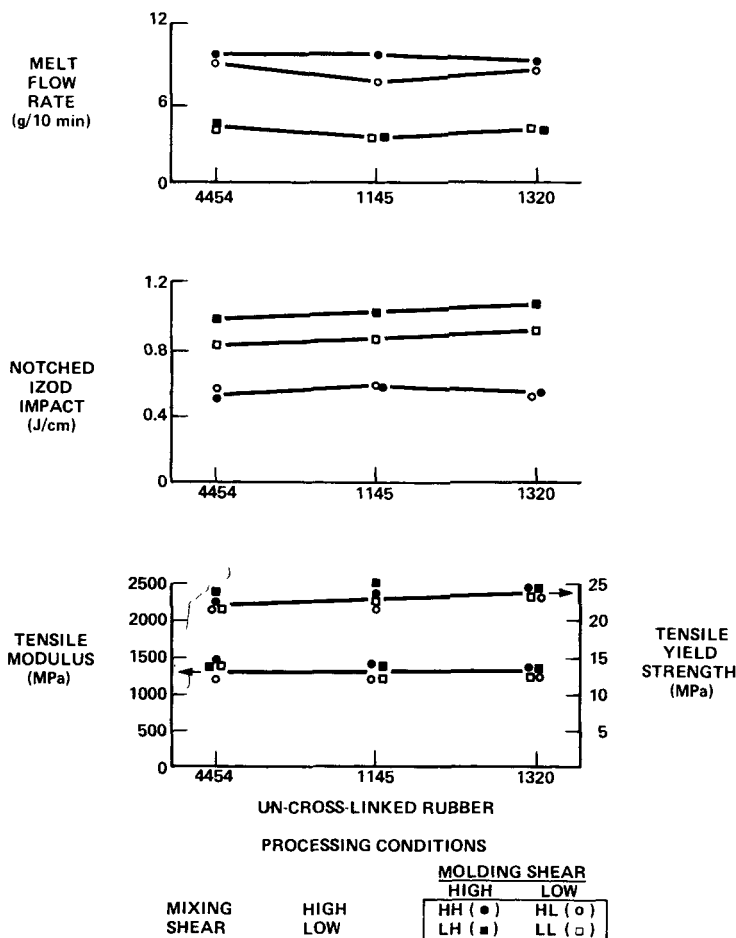


Fig. 1. Properties of polypropylene/uncrosslinked rubber blends (88% polypropylene H65/12% rubber).

were given in a previous report.²³

ASTM test methods were used for melt-flow, Izod-impact, and tensile property measurements. Our Gardner impact test fixture consisted of a 1.59-cm-diameter falling dart with a spherical nose and a 2.54-cm-internal-diameter retaining ring. Unless specifically stated otherwise, all mechanical properties were determined at 23°C and 50% relative humidity.

RESULTS AND DISCUSSION

Representative mechanical properties of blends with uncrosslinked rubbers determined earlier¹⁶⁻¹⁸ are plotted in Figure 1. High mixing shear (HH and HL) raises melt flow rate and lowers notched Izod impact resistance almost by a factor of 2. Higher melt flow rates for blends prepared with high mixing shear reflect chain degradation in the matrix. The reduction in impact resistance arises mainly from rubber particle recombination and resultant poor dispersions (large particles) in these blends. The effects of processing variables on blend modulus and yield strength are less significant. Modulus and strength are macroscopic

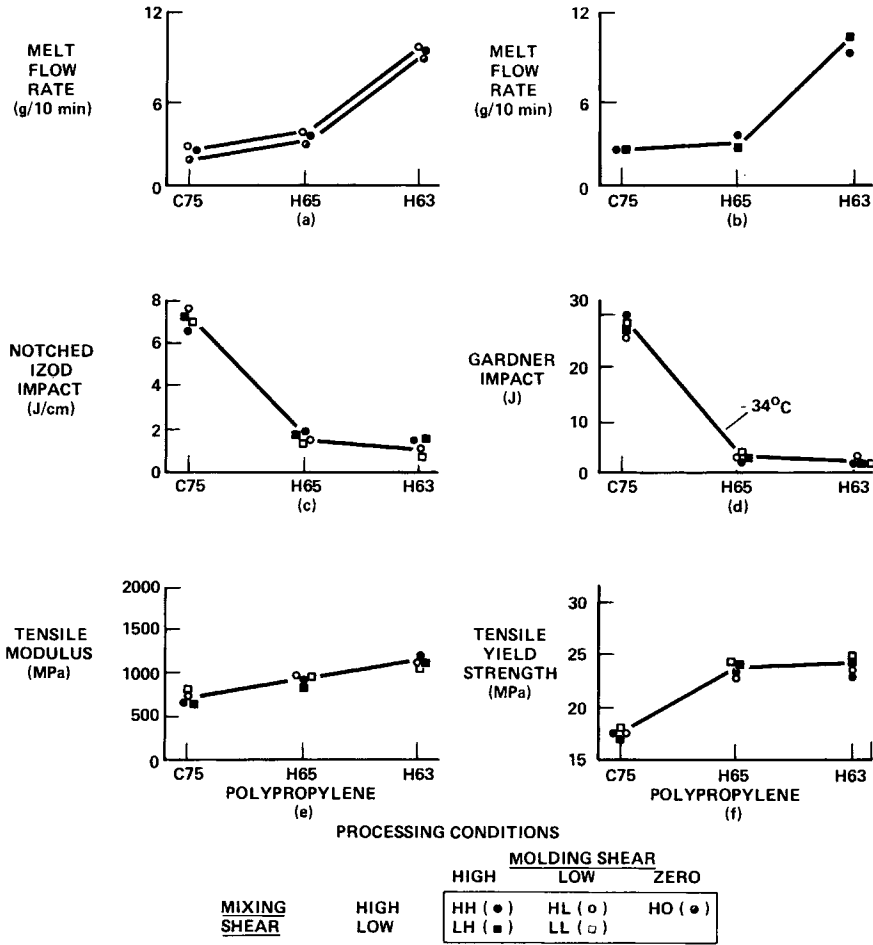


Fig. 2. Properties of polypropylene/crosslinked rubber blends (90% polypropylene/10% rubber D).

properties that are probably related more to composite bulk behavior and are less affected by microscopic changes due to processing.

Current results for blends with lightly crosslinked rubbers are shown in Figure 2. The five processing conditions vary widely and are essentially similar to those used to obtain results in Figure 1. With the exception of melt flow rate, other properties show negligible processing effects. Izod impact, Gardner impact, and tensile properties all exhibit no clear trends and change within the experimental errors. Melt flow rate varies very slightly with molding conditions [Fig. 2(a)] and remains unchanged with mixing shear [Fig. 2(b)]. Our experiments with other crosslinked rubbers (Table II) showed similar property independence of processing conditions.

Figure 3 shows mechanical properties of blends processed similarly (LH) and at the same rubber content (10%) to study the effects of matrix and rubber type. The influence of the matrix on the blend is significant. All blends exhibit properties that reflect their base matrix. For example, C75, an impact-grade ethylene-propylene terminal-block copolymer, compared with homopolymers

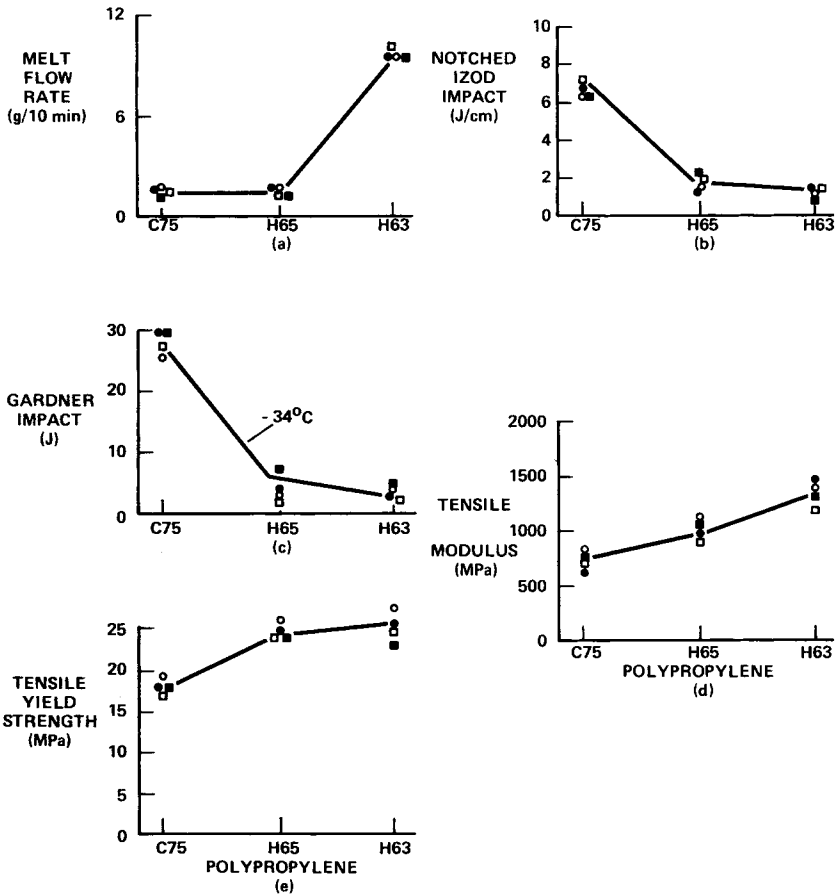


Fig. 3. Properties of polypropylene/crosslinked rubber blends (90% polypropylene/10% rubber; processing condition LH): (●) rubber A; (○) rubber B; (■) rubber C; (□) rubber D.

H65 and H63, when blended with rubbers, shows high Izod and Gardner impact resistance and low tensile modulus and strength. Similar correlation between mechanical properties and rubber type is not so clear. Although the rubbers differ in the degree of crosslinking, molecular weight, crystallinity, and viscosity, most mechanical properties vary only slightly within the standard deviation values.

Figure 4 shows typical mechanical properties of blends as functions of rubber content. The melt flow rate [Fig. 4(a)], being strongly dependent on polypropylene type, exhibits a gradual reduction with increasing rubber concentration. Easy-flow H63 polypropylene homopolymer, when blended with increasing amounts of rubber, shows largest reduction in melt flow rate, whereas equivalent melt flow changes in blends with H65 homopolymer and C75 copolymer are smaller. Improvements in notched Izod-impact resistance with rubber content are significant [Fig. 4(b)], while unnotched Izod-impact strength shows no notable increases. In fact, a slight reduction in unnotched Izod-impact strength with increasing modifier level is observed for all three polypropylenes. This reverse effect probably arises from the dependence of unnotched Izod-impact resistance on inherent flaws, and increasing rubber content raises the number and probably

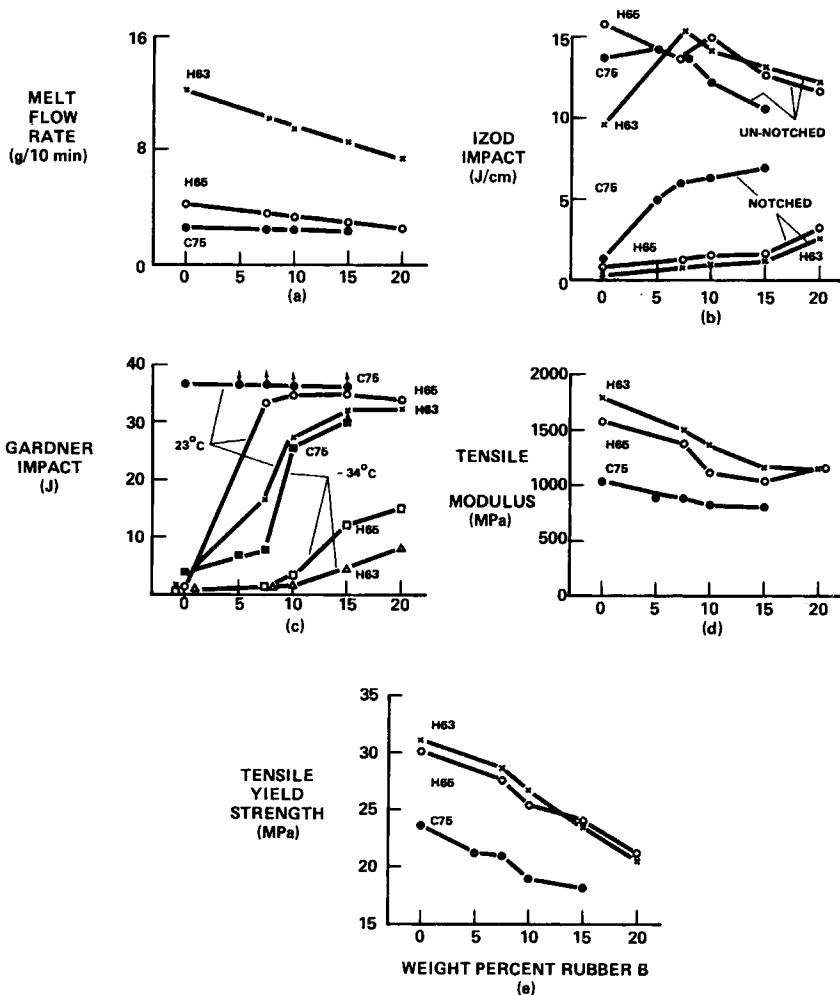


Fig. 4. Properties of polypropylene/crosslinked rubber blends.

the size of the rubber particles that invariably act as small defects. Toughness represented by Gardner impact energies also increases dramatically with rubber content [Fig. 4(c)]. The improvements (from brittleness to ductility) at -34°C are most notable, and the results indicate the important role of rubbers in toughening thermoplastics in this low temperature regime. Increasing modifier level causes loss of yield strength and a more serious loss of stiffness [Figs. 4(d) and 4(e)]. Lower-molecular-weight H63 polypropylene homopolymer gives higher strength and modulus because of its higher degree of crystallinity. The terminal-block polypropylene copolymer C75, itself a multiphase system, causes lower stiffness and strength in its blends.

Comparison with previous work shows the effects of rubber crosslinking (Fig. 5). For example, adding crosslinks to the modifier does not significantly change blend processability, modulus, and strength [Figs. 5(a), 5(b), and 5(c)] but typically produces a slight improvement in toughness [Fig. 5(d)].

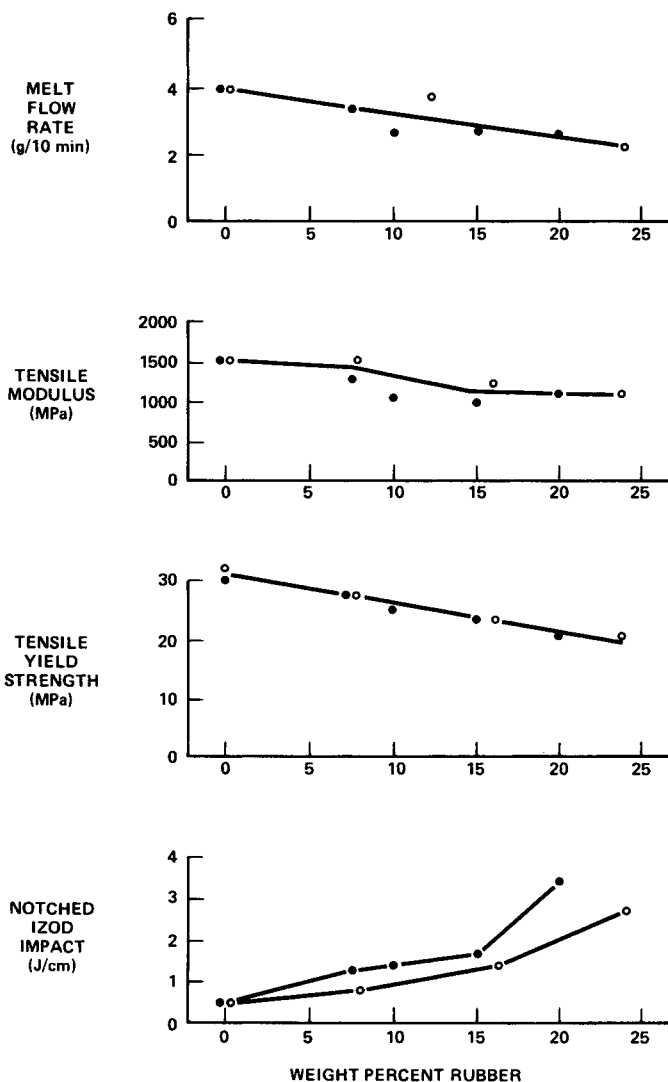


Fig. 5. Properties of blends of polypropylene H65 with uncrosslinked (O) and crosslinked rubber (●) prepared under low mixing and high molding shear (LH).

CONCLUSIONS

Mechanical properties of rubber-modified polymers can vary significantly with compounding and molding conditions. It is neither practical nor economical to place stringent controls on process variability in a manufacturing plant. Instead, by lightly crosslinking the rubbers, we have produced blends with consistent mechanical behavior independent of process variations.

Our polypropylene/crosslinked rubber blends exhibit the usual mechanical behavior dependence on rubber/matrix type and rubber content expected of polypropylene/uncrosslinked rubber systems. Moreover, lightly crosslinking the modifier seems to improve blend impact resistance without an accompanying severe change in stiffness, strength, and processability.

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