Selective Crosslinking in Polymer Blends. II. Its Effect on Impact Strength and Other Mechanical Properties of Polypropylene/Unsaturated Elastomer Blends

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SYNOPSIS

The effect of selective crosslinking of the unsaturated elastomer particles in polypropylene (PP) matrix was investigated. The crosslink system comprised N,N'-m-phenylene-bis maleimide and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroqinoline or polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline). The system, which produces only carbon radicals, crosslinks the elastomer particles selectively without causing excessive degradation of the PP matrix. The reaction was carried out under a dynamic crosslinking process using a twin extruder on PP/EPDM, PP/SBS, and PP/SIS blends, all of which comprised 80 wt % of PP and 20 wt % of the elastomer. After the crosslinking, the impact strength of the blends increased. Especially remarkable increase is obtained at 23°C where PP is above its T_g. The increase of interfacial adhesion caused by production of PP/elastomer graft copolymer at the interface is considered to be the most important factor in the improvement. It permits the interactions of the stress concentrate zone developed at the elastomer particles and causes shear yielding of the PP matrix. Impact fracture energy absorption can be thus changed by adjusting the degree of the interfacial adhesion even at essentially the same morphology. The crosslinked elastomer particles also play the role of a nucleation agent. The selective cross-linking of the elastomer particles in PP/elastomer blends is demonstrated to be an excellent technique to produce a high-impact, high-modulus PP. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

To improve impact strength of polypropylene (PP), various elastomers are incorporated under melt-blending conditions. It is the simplest technique to offer custom-tailored materials for varied requirements at comparatively low cost.

According to various interpretations presented for the mechanism of the impact strength improvement of multiphase plastic materials,[1-3] it may be concluded that it is necessary to satisfy the following conditions for the optimum impact strength improvement in PP/elastomer blends:

1. The elastomer particles are finely and uniformly dispersed in the PP matrix

2. The modulus of the elastomer is much less than that of the PP
3. The crystallinity of the elastomer is low
4. A certain degree of interfacial adhesion is attained between the elastomer particle and the PP matrix
5. The cohesive strength of the elastomer is large
6. A certain degree of entanglement of high-molecular weight polymer chain is attained in the PP matrix

These conditions could be classified into three categories according to the function in the improvement of impact strength.

The first condition is concerned with the number of elastomer particles functioning as stress concentrators[4-6] in blends. It is recognized that elastomer particles in the PP matrix play an important role in improving impact strength by func-

tioning as stress concentrators under deformation. They promote crazing or shear yielding in the matrix and suppress brittle fracture as a result. In semicrystalline polymers the shear yielding is important because it is considered to be the main energy absorption mechanism.[7] Thus, the first condition calls for an increase in the numbers of elastomer particles which function as stress concentrators at constant volumetric fraction of the elastomer. Since the elastomer particles can be considered as flaws in the matrix, the first condition also decreases the dimension of the flaws.

The second and third conditions are concerned with the effectiveness of elastomer particles functioning as stress concentrator[4-6] in blends. The second condition calls for increasing the difference of the Young's modulus between the elastomer and the matrix to promote the development of stress concentrate zones in the matrix. The third condition has the same effect as the second by increasing the difference of their Poisson's ratios.

The fourth condition makes it easy to develop stress concentrate zone in matrix and increase the amounts of energy dissipated when cleavage of interface between the particles and the matrix occurs.[9,10]

The fifth condition is concerned with the amounts of energy dissipated by cohesive fracture of the particles when it occurs under deformation.[11]

The sixth condition is concerned with the ability to develop the stress concentration zone in the PP matrix.

However, it is practically impossible for the melt-blending process to produce a PP/elastomer blend in which all of the conditions are realized. For example, in the case of PP/ethylene–propylene–diene terpolymer (EPDM) blends or PP/ethylene–propylene copolymer (EPR), which are the most common combination for impact strength improvement of PP and well investigated,[12-26] the first condition is favorable when the average molecular weight of EPDM is low but the fourth and fifth conditions are favorable when that it is higher. The second and third conditions are favorable when the propylene content in EPDM is lower but the fifth condition is favorable when it is higher. These indicate also that under common melt-blending process only a part of the improvement ability given by the incorporation of EPDM is realized in PP/EPDM or PP/EPR blend.

In order to optimize conditions, it would appear to be an attractive technique to change finely and uniformly dispersed particles of EPDM in the PP matrix, which can be obtained by a common melt-blending process when higher molecular weight PP and lower molecular weight EPDM are blended, to crosslinked EPDM particles. This could be accomplished by certain crosslinking systems under melt-blending conditions, so-called dynamic crosslinking.[27]

However, peroxide/coagent system, presently the most commonly used for the crosslinking reaction in PP/EPDM blend, is unfavorable for this purpose. This is because it also degrades the PP matrix and negatively affects the sixth condition and also unfavorably changes the mechanical and rheological properties.

On the other hand, the novel N,N'-m-phenylene-bis-maleimide (PM)/accelerator crosslink systems developed recently by the author, which does not involve organic peroxide, seems to be favorable for the purpose. Because they can crosslink EPDM or unsaturated elastomer particles in a PP matrix selectively without materially causing the degradation of the PP matrix.

The purpose of the research described is to investigate the effect of the crosslinking of unsaturated elastomer particles, mainly EPDM, in a PP matrix caused by the novel PM crosslink system and thereby to interpret the mechanism of impact strength improvement of PP/elastomer blends.

The character and the mechanism of the novel PM crosslink systems were discussed in Part 1 of this research.

EXPERIMENTAL

Materials

The PP used in this research is polypropylene homopolymer (h-PP) and polypropylene block-copolymer (b-PP). The unsaturated elastomers are EPDM, styrene–butadiene–styrene triblock copolymer (SBS), and styrene–isoprene–styrene triblock copolymer (SIS). All of them are commercial products and their commercial names, their basic properties are shown in Table I.

The crosslink systems comprises PM as a crosslink agent, and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ) or polymerized (2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ) as accelerator. They are also commercial products and used without further purification. Their chemical structures are shown in Figure 1.

Sample Preparation

Samples comprise 80 wt % of h-PP or b-PP and 20 wt % of elastomer. The extruder employed was a 30

Table I   Properties of Raw Materials Investigated

Type of Material	Material Designation	Commerical Name	Supplier	Comments
PP	PP-1	J120G	Nippon Petrochemicals	MFR = 1.5, (230°C/2.16 kg load), Homopolymer
	PP-2	J620G	Nippon Petrochemicals	MFR = 1.5, (230°C/2.16 kg load), Block-copolymer
	PP-3	J650G	Nippon Petrochemicals	MFR = 8.0, (230°C/2.16 kg load), Block-copolymer
	PP-4	J871M	Nippon Petrochemicals	MFR = 23.0, (230°C/2.16 kg load), Block-copolymer
EPDM	EPDM-1	EP57P	Japan Synthetic Rubber	ML_{1+4} (100°C) = 88, Iodine value = 15
SBS	SBS-1	KX-65	Shell Chemical	Styrene/Butadiene ratio = 38/62, triblock-type
SIS	SIS-1	TR1107	Shell Chemical	Styrene/Isoprene ratio = 14/86, triblock-type

mm diameter twin screw extruder with an L/D of 31.5. The combination of screw segments was designed to give high-intensive mixing to the molten blends. The samples were extruded and pelletized twice. In the first extrusion, only the thermoplastic and the elastomer were melt-blended to disperse the EPDM particle in the PP matrix. In the second extrusion, a mixture of the resultant blends from the first extrusion with the crosslink system were dynamically crosslinked.

The extrusion was conducted at a speed of 200 rpm and at a barrel temperature of 180–210°C. The residence time of the blends in the extruder was kept at about 60 seconds by adjusting the extrusion rate.

Figure 1 Structures of PM and its accelerators. (a) N,N'-m-Phenylene-bis-maleimide (PM); (b) 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ); (c) polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ).

The same extrusion conditions were used throughout the research.

The extruded samples were injection-molded into specimens for testing under a condition of barrel temperature of 210–230°C, injection pressure of 1,000 kgf/cm^2, and mold temperature of 50°C.

Tensile strength (TS) and ultimate elongation (UEL) were measured following ASTM D638. Flexural strength (FS) and flexural modulus (FM) were measured following ASTM D790. Izod impact strength (IIS) was determined using ASTM D256. Vicat softening temperature (ASTM D1525) was determined on 2 mm thick injection-molded samples.

In order to identify the character of the crosslink reaction hot-pressed 20 × 50 × 0.2 mm sheet of the samples in wire netting were immersed in refluxing xylene for 5 h. Two parameters are defined by eqs. (1) and (2). They are used to describe the character of the crosslinking reactions.

Xylene-insoluble fraction (%)

$$= \frac{\text{sheet weight after the immersion}}{\text{sheet weight before the immersion}} \times 100 \quad (1)$$

Degree of crosslinking (%)

$$= \frac{\text{xylene-insoluble fraction}}{\text{wt \% of elastomer in the blend}} \times 100 \quad (2)$$
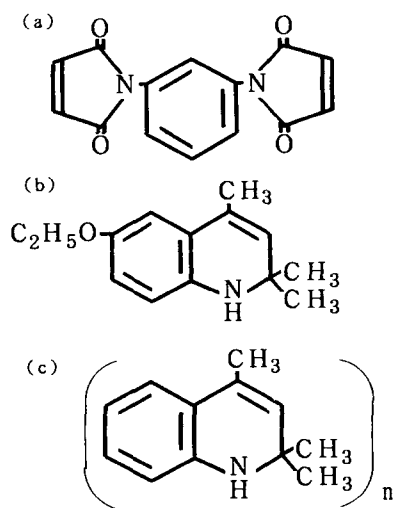
RESULTS AND DISCUSSION

Selectivity of the Crosslink Reaction

Following the xylene-insoluble fraction tests, the samples of high degree of crosslinking gave enough

residue to be analyzed by differecial scanning calorimetry (DSC). Each DSC thermogram of the residue exhibits only a trace or a small peak assigned to PP and reveals that the crosslink reaction proceeded selectively at the unsaturated elastomer particles.

Improvement of Impact Strength and Its Mechanism

Table II shows the effects of the novel PM crosslink reaction on mechanical properties of various PP/unsaturated elastomer blends.

After the crosslinking, notched Izod impact strength (IIS) increased in all of PP/EPDM blends independent of the specimen thickness. Especially at 23°C, a remarkable increase was obtained and the specimens made of PP/crosslinked EPDM blends were not broken under the given conditions. The degree of improvement of IIS is dependent on the ductility of PP with the same MFR, being greater for b-PP than h-PP. It is also dependent on the MFR of PP, being greater for lower MFR grades than higher MFR grades. This points up the effect of the size of the EPDM particles which become smaller as the viscosity of PP matrix increases at constant viscosity of EPDM or to polymer chain entanglement in PP matrix.

Scanning electron micrograph (SEM) observation of fracture surfaces of impact test samples A-01 and A-02 at −30°C show that the interfacial adhesion between the EPDM particles and the PP matrix increased after the crosslink reaction. Namely the surfaces of the EPDM particle in A-01 is smooth but in A-02 is covered with the PP (Figs. 2 and 3).

It is believed that the increase in interfacial adhesion is caused by the graft copolymer of PP and EPDM at the interface. It is quite possible that the graft copolymer is produced by coupling of EPDM radicals and PP radicals, or with participation of PM radicals (PP-PM-EPDM type), under dynamic crosslinking. It is recognized that the interfacial adhesion in a multiphase structure blend is increased by the presence of graft or block polymer of the blend components.[9] (The traces or the small peaks of PP involved in the DSC thermogram of xylene-insoluble fraction mentioned above may be assigned to those of the PP segment of the graft copolymer.)

At 23°C, PP is a ductile polymeric material, being above its T_g, and shear yielding is the primary mode of energy absorption under deformation. In order to promote shear yielding in the PP matrix, it is important that the stress concentrate fields developed from the EPDM particles interact effectively with each other in the PP matrix. If the interface between the particle and the matrix debond during the deformation before the interaction is attained, not only is the stress relieved reducing the possibility of the interaction, but also voids or flaws are produced. On the other hand, if the sufficient interaction is attained, a kind of continuous stress concentration zone is realized in the matrix and the blend. This enables shear yielding to occur easily and as the result, the energy absorption in the blends will increase dramatically.

Although it is observed that the dimensions of the EPDM particles decreased slightly, it is interesting that A-01 and A-02 have substantially the same morphology. Transmission electron micrograph (TEM) observation demonstrated that there is no difference in the occlusion of PP by the EPDM particles before and after the reaction, indicating that there was no change of the volumetric fraction of the dispersed particle also.

If the graft copolymer of PP and noncrosslinked EPDM is produced at an early stage in the dynamic crosslinked process predominantly, it will play a role of compatibilizer to reduce the dimension or diameter of the particles dramatically.[28] On the other hand, it is also clear that there is no cause to reduce the EPDM particles except the production of PP-EPDM graft copolymer, because during the crosslinking reaction the viscosity of PP matrix is apt to decrease and that of EPDM particle increase. Although a detailed close distribution analysis on the dispersed particles was not carried out in this research, the decrease of the dimension could be explained by the production of some graft copolymer at an early stage. Thus, the result from the SEM observations indicates that the crosslink reaction of the particles proceeds predominantly and the production of the graft copolymer proceeds as a side reaction.

This leads to a conclusion that the structure of most of the graft copolymer is not PP-(noncrosslinked EPDM) type but PP-(crosslinked EPDM particle) type, which is similar to the graft copolymer of polystyrene/crosslinked butadiene particle in high-impact polystyrene (HIPS) or the acrylonitrile–styrene copolymer/crosslinked butadiene particle in acrylonitrile–styrene–butadiene copolymer (ABS). It is recognized that graft copolymers of this type are easy to disperse uniformly in the matrix and act as effective stress concentrators because of the good interfacial adhesion to the matrix.[29,30] It is also notable that the crosslinking can prevent the elastomer domain from reaggregation

Table II Effects of the PM Crosslinking Reaction of Mechanical Properties of Various PP/Elastomer Blends

| Sample Designation | Composition Polypropylene/ Unsaturated-elastomer (wt %)/(wt %) | Cross-link System (wphr) | Mechanical Properties | | | | | Vicat Softening Temperature (°C) | Xylene-insoluble Fraction (wt %) | T_c (°C) |
| | | | MFR (230°C/ 2.16kg Load) | YTS (kgf/cm³) | UEL (%) | Notched-IIS (kg·cm/cm) | | | | |
						6mm Thickness 23°C/-10°C/-30°C	3mm Thickness 23°C/-10°C/-30°C			
A-00	PP-1(100)	None	1.5	355	210	7.2/2.8/3.7	8.2/3.6/3.6	154	<1.0	114.7
A-01	PP-1(80)/EPDM-1(20)	None	1.6	246	220	20.8/6.1/6.0	25.3/6.5/6.3	143	<1.0	112.6
A-02	PP-1(80)/EPDM-1(20)	PM(0.3)/ETMQ(0.2)	2.4	230	400	>66/14.4/10.2	63.8/15.8/10.7	148	18.0	113.0
A-03	PP-1(80)/EPDM-1(20)	PM(0.3)/PTMQ(0.2)	—	217	170	>66/13.3/9.0	—/—/—	149	17.0	124.5
B-00	PP-2(100)	None	1.5	270	300	18.3/6.0/5.3	—/6.6/6.0	147	<1.0	112.8
B-01	PP-2(80)/EPDM-1(20)	None	1.4	197	280	>66/18.6/11.0	—/16.0/13.0	134	<1.0	113.0
B-02	PP-2(80)/EPDM-1(20)	PM(0.3)/ETMQ(0.2)	2.2	181	400	>66/>66/13.2	—/76.1/59.7	140	20.8	122.8
C-00	PP-3(100)	None	8.0	280	220	11.1/4.8/4.7	12.2/5.5/5.3	149	2.6	111.5
C-01	PP-3(80)/EPDM-1(20)	None	4.5	210	250	>66/10.0/8.3	66.4/11.2/10.3	135	2.5	113.0
C-02	PP-3(80)/EPDM-1(20)	PM(0.3)/ETMQ(0.2)	5.9	190	400	>66/17.2/10.2	66.6/36.8/12.0	142	22.1	120.2
D-00	PP-4(100)	None	23.0	280	150	10.1/5.6/5.2	8.7/5.5/5.3	149	1.3	126.4
D-01	PP-4(80)/EPDM-1(20)	None	11.0	180	170	15.1/7.3/6.4	18.0/9.0/8.2	135	1.8	123.8
D-02	PP-3(80)/EPDM-1(20)	PM(0.3)/ETMQ(0.2)	5.0	190	290	40.7/13.2/8.8	61.6/13.2/10.3	140	20.8	123.1
B-11	PP-2(80)/SBS-1(20)	None	1.5	220	200	>66/45.7/8.0	—/47.3/10.5	135	<1.0	112.9
B-12	PP-2(80)/SBS-1(20)	DVB(0.4)/ETMQ(0.2)	0.7	199	400	>66/32.1/17.0	—/74.1/23.2	137	16.6	116.8
B-21	PP-2(80)/SIS-1(20)	None	2.6	201	400	>66/37.3/10.0	—/59.3/11.6	134	<1.0	117.5
B-22	PP-2(80)/SIS-1(20)	PM(0.3)/ETMQ(0.2)	1.3	195	400	>66/>66/15.6	—/75.8/21.9	140	8.4	117.8

Abbreviations: PM = N,N'-m-phenylene-bis-maleimide; ETMQ = 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; PTMQ = polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline).
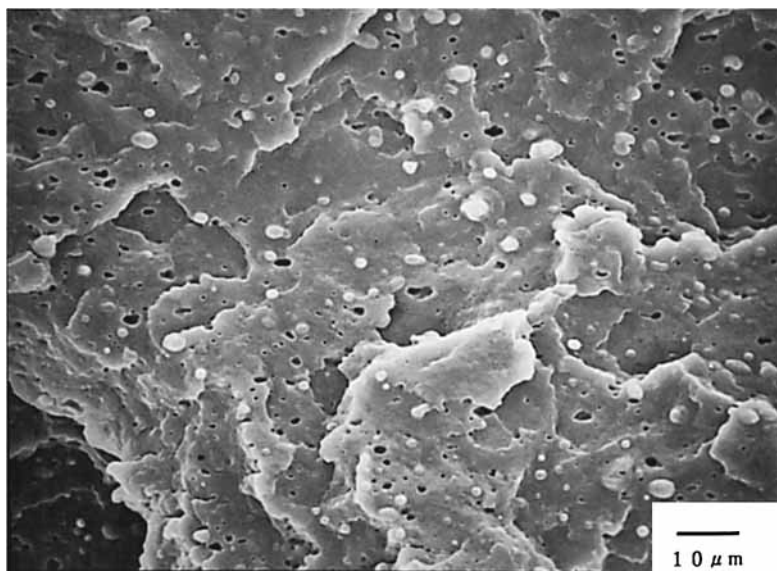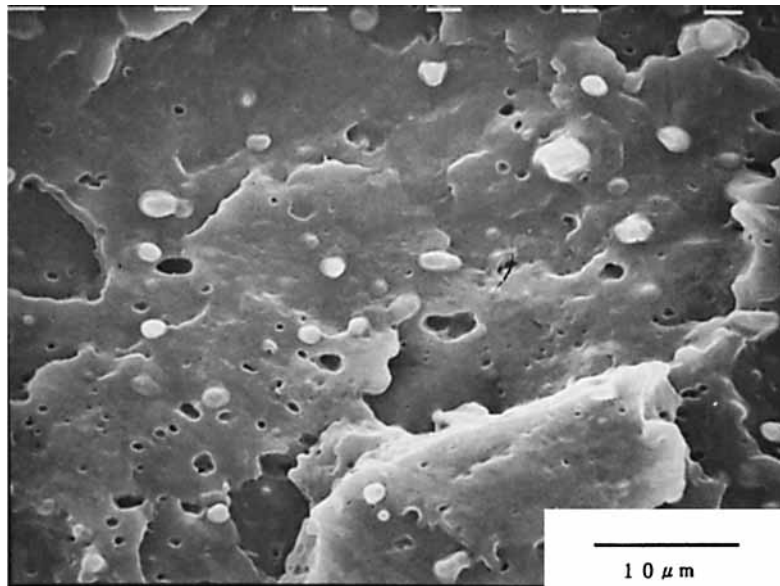
(a)
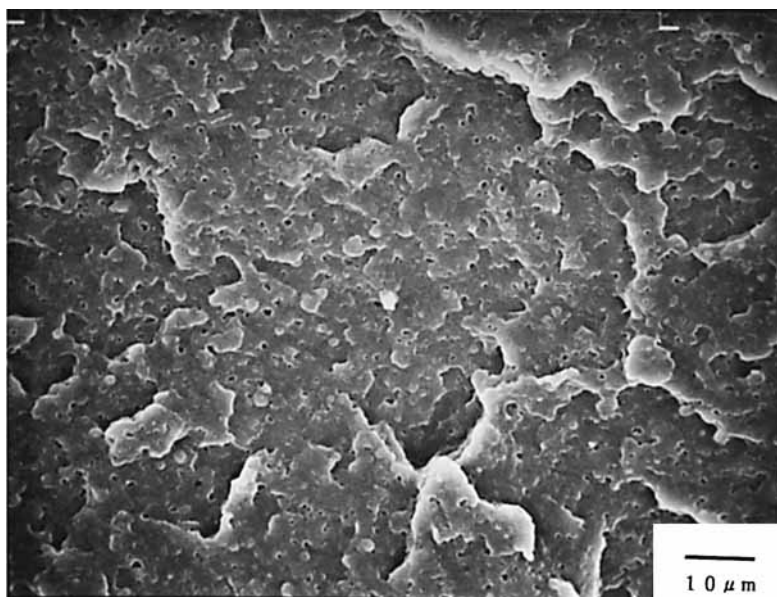
(b)

Figure 2 Scanning electron micrographs of fracture surfaces of PP/EPDM (80/20) blends specimen after Izod impact test at $-30°C$: (a) before the PM crosslinking (sample A-01) ($\times1000$); (b) after the PM crosslinking (sample A-02) ($\times1000$).

and breakdown at shear stress prevailing during the molding process and maintains mechanical properties effectively.

Since the dynamic crosslinking does not change the morphology of the blends nor the basic properties of EPDM particle as stress concentrator substantially, it is concluded that the remarkable im-

provement of IIS at $23°C$ is caused mainly by the increase of the interfacial adhesion. The effect of increase of the cohesive strength of the EPDM particles can be ignored because at $23°C$ the PP matrix is ductile and the greatest part of the impact energy is dissipated in the PP matrix. In other words, since among the conditions discussed in the Introduction

(a)
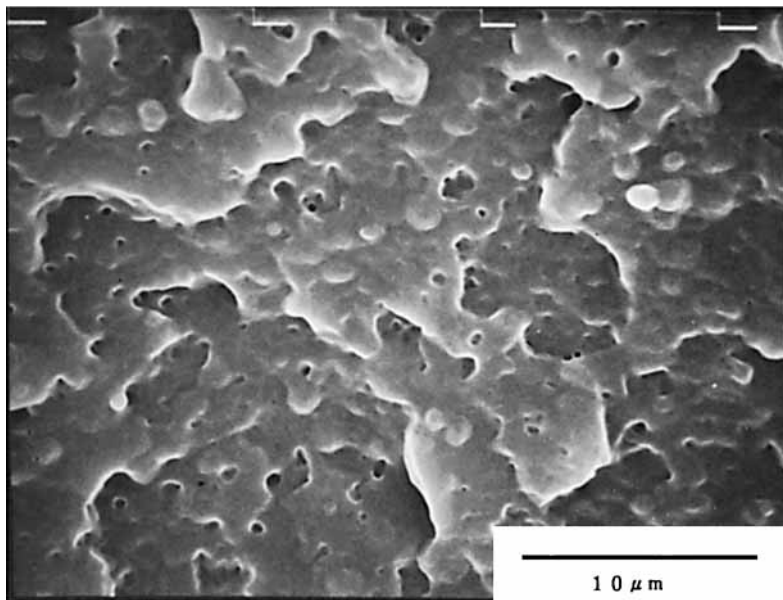
(b)

Figure 3   Scanning electron micrographs of fracture surfaces of PP/EPDM (80/20) blends specimen after Izod impact test at $-30°C$: (a) before the PM crosslinking (sample A-01) ($×3500$); (b) after the PM crosslinking (sample A-02) ($×3500$).

the conditions 1, 2, 3, and 6 are substantially constant and condition 5 is negligible, it should be concluded that condition 4 mainly causes the improvement of IIS.

Although D. J. Elliot also indicates the possibility of the formation of graft copolymer of PP and natural rubber (NR) in PP/NR blends under dy-

namic crosslinking conditions to improve impact strength,[31] it is rather surprising that even in PP/EPDM blends, in which one of the highest in compatibility among PP/elastomer blends, the increase of the interfacial adhesion resulting from the production of graft copolymer can improve the impact strength so remarkably.

Table III Effect of Various Amounts of the Crosslink Systems on Mechanical Properties of the PP/EPDM (80/20) Blends

Material Designation	Composition Thermopolastic/Rubber (wt %)	Additive for Vulcanization (p.p.h.p.)	YTS (kgf/cm²)	UEL (%)	FM (kgf/cm²)	Mechanical properties	Vicat Softening Temperature (°C)	Xylene-Insoluble Fraction (wt%)	Tc (°C)
						Notched-IIS (kg·cm/cm) 6 mm Thickness 23°C/-10°C/-30°C			
A-00	PP-1(100)	None	355	210	16,800	7.2/2.8/3.7	154	< 1.0	114.7
A-01	PP-1(80)/EPDM-1(20)	None	246	220	12,300	20.8/6.1/6.0	143	< 1.0	112.6
A-04	PP-1(80)/EPDM-1(20)	PM(0.3)	256	100	11,700	> 66/7.9/7.8	144	10.7	118.1
A-05	PP-1(80)/EPDM-1(20)	ETMQ (0.2)	247	120	11,200	30.5/7.8/7.0	144	1.4	114.9
A-06	PP-1(80)/EPDM-1(20)	PM(0.075)/PTMQ(0.02)	244	180	11,100	> 66/12.9/8.6	147	12.0	119.5
A-07	PP-1(80)/EPDM-1(20)	PM(0.15)/PTMQ(0.10)	238	400	11,200	> 66/13.7/8.8	146	16.0	122.2
A-08	PP-1(80)/EPDM-1(20)	PM(0.15)/PTMQ(0.2)	238	330	11,200	> 66/13.4/8.7	147	15.6	122.9
A-09	PP-1(80)/EPDM-1(20)	PM(0.3)/PTMQ(0.2)	217	170	11,700	> 66/13.3/9.0	149	17.0	124.5
A-03	PP-1(80)/EPDM-1(20)	PM(0.6)/PTMQ(0.3)	246	160	12,200	> 66/13.9/10.1	147	19.0	127.0
A-02	PP-1(80)/EPDM-1(20)	PM(0.3)/ETMQ(0.2)	230	400	—	> 66/14.4/10.2	148	18.0	124.4

Abbreviations: PTMQ = polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline); ETMQ = 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; PM = N,N'-m-phenylen-bis-maleimide.

Wu revealed that by reducing the average surface-to-surface interparticle distance to less than a so-called critical value, the mechanism of impact fracture of the blends will change from plane-stress to plane-strain with the impact strength of the resulting blend increasing dramatically.[32,33] The condition can be attained either by reducing the diameter of the elastomer particles at a constant elastomer volumetric fraction or by increasing the volumetric elastomer fraction at constant elastomer particle size.

However, the results from this research reveal that the change of the mechanism of impact fracture will occur also by increase of the interfacial adhesion at virtually the same morphology.

Although there is less compatibility between PP and SBS or PP and SIS, the IIS increased also after the reaction. The mechanism of improvement of impact strength of PP/SBS blend (Table II, B-12) and that of PP/SIS blend (Table II, B-22) can be explained similarly by the production of graft copolymer and an increase of the interfacial adhesion.

Table III shows the effect of various amounts of degree of crosslinking, which are obtained by varying the amounts of the crosslinking system, on the mechanical properties on PP/EPDM blends. Figure 4 shows the relation between the degree of crosslinking and the IIS at various temperature (23°C, -10°C, and -30°C).

The curve for the IIS at 23°C has a noticeable transition point. It indicates that the IIS will remarkably increase when a certain value of the degree of crosslinking is attained in the EPDM particle.

Since the graft copolymer produced under the crosslinking of the EPDM particles increases the interfacial adhesion, the result indicates that the transition occurs when relatively small concentration of the graft copolymer are produced. In other words, the critical interfacial adhesion, which is strong enough to increase the possibility of the interaction of stress concentrate zones facilitating the shear yielding of PP matrix, can be attained by relatively small amounts of the graft copolymer and they are produced by the early stages of the crosslinking reaction. It is also indicated that when the interaction or the overlapping is attained by a certain point in the increase of the interfacial adhesion, further increase cannot improve the impact strength. (However, another possible interpretation is that the further improvement in impact strength cannot be obtained because all of the surface of the elastomer particles are covered with graft copolymer at an early stage.) Although the curve shows that the critical value is attained at an early stage of the
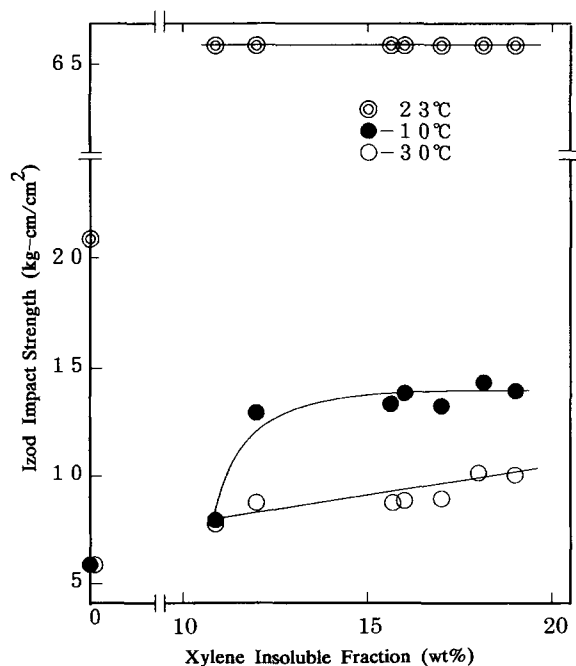
Figure 4 Correlation between the xylene-insoluble fraction and Izod impact strength on PP/EPDM (80/20) blend (data after Table III).

crosslinking reaction, it is not clear how strong the interfacial adhesion is needed to cause the transition.

At −10°C PP is a semiductile polymeric material, being around its T_g. The curve for the IIS at −10°C also has a sharp transition point to indicate that the change of the mechanism of impact fracture has occurred the same as at 23°C. The lesser degree of improvement may be caused by the lower ductility of PP matrix as compared to that of 23°C.

The curve for the IIS at −30°C shows a positive slope and no transition point. At −30°C PP is a brittle polymeric material, being below its T_g, and crazing in the PP matrix is considered to be the primary mode of fracture energy absorption. Under deformation and fracture, two energy dissipations will occur around and in the EPDM particles. One is the debonding of EPDM particles from the PP matrix and the other is the cohesive fracture of the EPDM particles. When the interfacial adhesion strength becomes greater than the cohesive strength of the crosslinked EPDM particle, fracture would occur not at the interfaces but rather in the EPDM particles. The linear relation indicates that the amount of fracture energy is governed by the cohesive strength of the particles, which increases with the degree of crosslinking rather than the promotion of crazing in the PP matrix, which increases as the interfacial adhesion increases.

It should be noted that in a semicrystalline polymer, a dramatic increase in impact strength, caused by a change of energy absorption mechanism, occurs when the polymer is capable of shear yielding under a given deformation rate. Although the whitening zone of both of fracture surface of impact test sample of 23 and −30°C increases after the crosslinking reaction, the degree of the increase is quite different.

Tensile Strength at Yield and Ultimate Elongation

Tensile strength at yield (YTS) and ultimate elongation (UEL) are given in Table II. After the crosslinking reaction the tensile strength at yield (YTS) of the blends decreased slightly but the ultimate elongation (UEL) markedly increased. The area under the stress–strain curve increased after the reaction demonstrating that energy absorbed by the specimen before fracture also increased. It was also observed that in the cross-section of tensile specimens of PP/crosslinked EPDM blends, neck formation is facilitated over a wider region as the deformation increases.

This change of behavior may be explained by the increase of interfacial adhesion and the increase of the interaction between the stress concentrate zones in the PP matrix, both of which caused by the formation of the graft copolymer similar to the case of impact strength improvement.

First, an increase of interfacial adhesion suppresses production of voids or flaws in the PP matrix, which might grow into cracks. Second, shear yielding can be promoted by the interaction between the stress concentrate zones. Following the onset of yielding the increased interfacial adhesion enables the deformation to occur easily in the cross-section and facilitates shear yielding.

Figure 5 shows the relation between the degree of crosslinking and tensile properties, YTS and UEL, based on the data in Table III.

Differing from the results on the IIS at 23°C, the UEL of the blends increases without a transition point. This may be explained by the difference of deformation rate between the impact test and the tensile test. The fracture mechanism of the polymeric material is sensitive to deformation rate. Although there is scatter in the relationship it suggests an interesting behavior. YTS seems to have a minimum value at 80% of the degree of crosslinking and conversely the UEL demonstrates a maximum value at the same point. This may be due partly to the excess degree of the crosslinking, which caused too strong a cohesive strength, reducing the UEL of the EPDM particles.
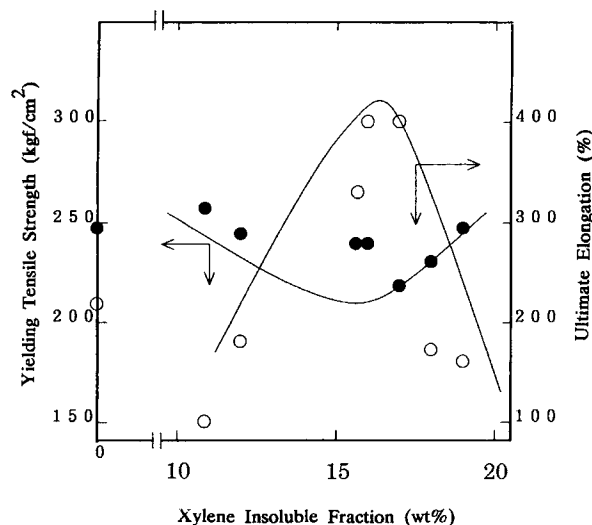
Figure 5 Correlation between the xylene-insoluble fraction, yielding tensile strength and ultimate elongation on PP/EPDM (80/20) blend (data after Table III).

Crystallization Temperature

Another noticeable change caused by the crosslink reaction in the blends is a rise of the crystallization temperature (T_c) of the PP matrix, determined by DSC at a scanning rate of 20°C/min from 230 to 40°C. Figure 6 based on the data in Table III shows clearly that the T_c depends on the degree of cross-linking. Since PP-4 involved commercial nucleating agents prior to the sample preparation, this nucleation effect by crosslinking is not observed in sample D-02.

Although the nucleation effect may change the dimension and the structure of PP spherulites in blends to effect the IIS, the IIS improvement obtained in sample D-02 indicates that the effect of nucleation on IIS is smaller compared with that of interfacial adhesion.

Considering that most nucleating agents decrease impact strength when they increase T_c, it is interesting that the produced crosslinked particles increased both of them at the same time.

CONCLUSION

The crosslinking of unsaturated elastomer particles in polypropylene (PP) matrix increases impact strength of the parent blends. The crosslinking is carried out by the system comprising N,N'-m-phenylene-*bis*-maleimide (PM) and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ) or N,N'-m-phenylene-*bis*-maleimide/polymerized-(2,2,4-tri-

methyl-1,2-dihydroquinoline) (PTMQ) under dynamic crosslinking conditions. On the basis of this study the effects of the crosslinking reaction is believed to be the following:

1. Under the intensive mixing of dynamic crosslinking, free radicals are produced on carbon at the allylic position in the unsaturated elastomer, which reacts with PM to initiate the cross-link reaction.
2. The PM/ETMQ system or the PM/PTMQ system forms a charge-transfer complex to produce a PM radical, which accelerates the crosslink reaction.
3. A small amount of PP/EPDM graft copolymer is produced by coupling of radicals causing slight reduction in the size of the EPDM particle.
4. At the interface between PP and crosslinked unsaturated elastomer particle the graft copolymer is produced which increases the interfacial adhesion.
5. The crosslinking of the unsaturated elastomer particles stabilize the morphology of the blends.
6. The increased interfacial adhesion permits the interaction of stress concentration zone developed from the elastomer particles under deformation and promote shear yielding in the PP matrix.
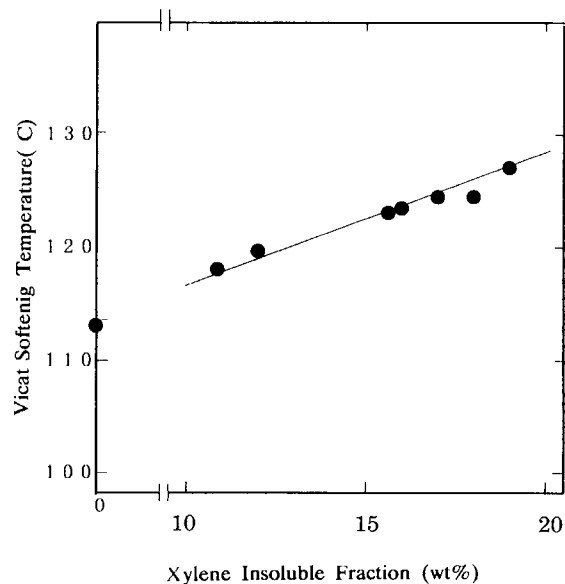

Figure 6 Correlation between the xylene-insoluble fraction and vicat softening temperature on PP/EPDM (80/20) blend (data after Table III).

7. During the crosslinking reaction, any radicals active enough to abstract hydrogen radical from PP, which degrade PP, are not produced and the impact strength of PP matrix is retained in the resultant blend.

8. The crosslinked particles also act as nucleating agents.

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