

# Selective Crosslinking Reaction in Polymer Blends.

## III. The Effects of the Crosslinking of Dispersed EPDM Particles on the Impact Behavior of PP/EPDM Blends

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### SYNOPSIS

The selective dynamic crosslinking reaction by means of the *N,N'*-*m*-phenylene-bismaleimide/poly-(2,2,4-trimethyl-1,2-dihydroquinoline) system was carried out on PP/EPDM blends and its effect on the Izod impact strength (IIS) was investigated. Three series of PP/EPDM combinations were adopted to establish different morphologies. In each series, the EPDM wt % varied from 5 to 30 at 5 wt % intervals. The system crosslinked the EPDM particles selectively without PP degradation and change of morphology. Following the crosslinking, the IIS at 23, -10, and -30°C increased in all blends, and the critical EPDM wt % at 23°C necessary to cause the dramatic IIS increase was lowered. The increase in interfacial adhesion is considered to be the most important factor necessary for the improvement. The nucleation effect of the crosslinked particles and the decrease of crystallinity of the EPDM were also considered to contribute to the improvement in the IIS. Impact fracture energy absorption can thus be changed by adjusting the magnitude of the interfacial adhesion by the dynamic crosslinking even at essentially the same morphology. © 1995 John Wiley & Sons, Inc.

### INTRODUCTION

Polypropylene (PP) is often blended with elastomers to improve its impact strength. Ethylene-propylene-diene terpolymer (EPDM) is one of the most effective elastomers for this purpose. The mechanism of impact strength improvement in PP/EPDM blends and other thermoplastics/elastomer blends is not completely understood and is the subject of much current research.<sup>1-24</sup>

In our previous articles,<sup>25,26</sup> a novel crosslinking system was described and an attempt was made to investigate the influence of crosslinking of the EPDM particles on the Izod impact strength (IIS). The crosslinking system employed is composed of *N,N'*-*m*-phenylene-bismaleimide (PM) and a dihydroquinoline derivative. The former is a crosslinking agent and the latter is an accelerator. The crosslinking reaction is considered to proceed in the EPDM particles selectively without excessive degradation of the PP matrix

by the PM radicals, which are produced via the charge-transfer complex of PM and dihydroquinoline derivative.<sup>25</sup> In the PP/EPDM blends containing 20 wt % of EPDM, the IIS was improved dramatically following the crosslinking.<sup>26</sup>

The purpose of this article was to investigate more precisely the effects of the crosslinking of EPDM particles in the PP matrix on the impact energy absorption behavior. Three series of PP/EPDM blends were prepared to create different morphologies and the wt % of EPDM was varied from 5 to 30 at 5 wt % intervals. In addition to the studies of basic mechanical properties, the investigation of fracture surfaces by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) analysis, and dynamic mechanical analysis (DMA) were conducted.

### EXPERIMENTAL

#### Materials

Two kinds of PP homopolymer and two kinds of EPDM, the diene being 5-ethylidene-2-norbornene,

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**Table I Basic Properties of Raw Materials**

Material Code	Commercial Name	Supplier	Comment
<b>1. Polypropylene (PP)</b>			
PP-1	E120G5	Nippon Petrochemicals	MFR = 1.8 homopolymer
PP-2	J150G	Nippon Petrochemicals	MFR = 8.0 homopolymer
<b>2. Ethylene-propylene-diene terpolymer (EPDM)</b>			
EPDM-1	EP57P	Japan Synthetic Rubber	$ML_{1+4}$ (100°C) = 88, C3 = 28 wt %, IV = 15
EPDM-2	EP132	Japan Synthetic Rubber	$ML_{1+4}$ (100°C) = 33, C3 = 32 wt %, IV = 18

with virtually the same iodine value and ethylene/propylene ratio were adopted in this research. The PPs were chosen with different MFR values, and the EPDMs, with different Mooney viscosities. All of them are commercial products and their commercial names and their basic properties are listed in Table I.

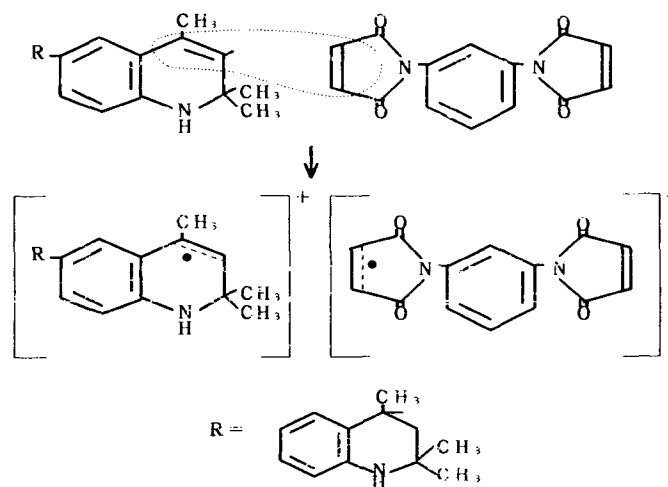
The crosslink system adopted in this research consisted of *N,N'*-*m*-phenylene-bismaleimide (PM), as a cross-linking agent, and poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ), as an accelerator. Both of them are also commercial products and were used without further purification. Their structures are shown in Figure 1. Possible crosslinking reaction mechanisms were discussed in a previous article.<sup>25</sup>

### Sample Preparation

Three series of PP/EPDM combinations were adopted to establish different morphologies. In the

Blend A series, PP-1 was blended with EPDM-1, i.e., standard molecular weight PP/standard molecular weight EPDM blends, to give the standard dispersion condition of EPDM particles. In the Blend B series, PP-2 was blended with EPDM-1, i.e., lower molecular weight PP/standard molecular weight EPDM blends, to give a relatively coarse dispersion condition. In the Blend C series, PP-1 was blended with EPDM-2, i.e., standard molecular weight PP/lower molecular weight EPDM blends, to give a relatively fine dispersion (Table II). In each series, six PP/EPDM blends were prepared by varying the wt % of EPDM from 5 to 30 at 5 wt % intervals. Before the preparation of the Blend C series, EPDM-2 obtained in bale-form was melt-blended with 30 wt % of PP-1 using a batch mixer and then pelletized. The effect of this preliminary operation on the mechanical properties is not considered in this research.

The extruder employed in the experiments was a



**Figure 1** Chemical structures of *N,N'*-*m*-phenylene-bismaleimide (PM) and poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ) and a proposed charge-transfer complex composed of them.

**Table II** Compositions of the Investigated Blends

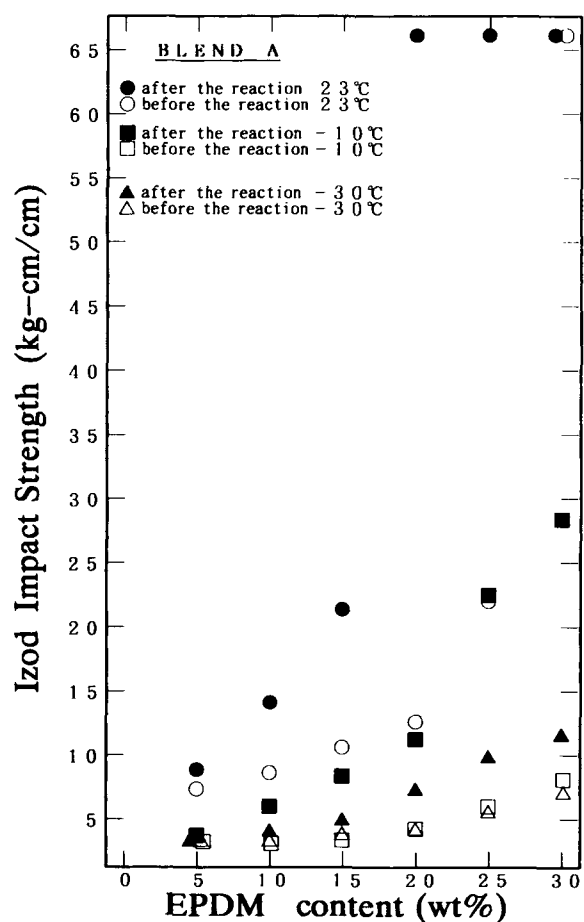
Blend Code	PP	EPDM	Comments
Blend A	PP-1	EPDM-1	Standard dispersion of EPDM particles
Blend B	PP-2	EPDM-1	Coarse dispersion of EPDM particles
Blend C	PP-1	EPDM-2	Fine dispersion of EPDM particles

30 mm-diameter twin-screw extruder with an  $L/D$  of 31.5. The combination of screw segments was designed to subject the molten blends to high-intensity mixing conditions. The samples were extruded and pelletized twice. In the first extrusion, only the PP and the EPDM were melt-blended. The purpose of the first extrusion was to disperse the EPDM particles in the PP matrix thoroughly before the crosslinking reaction. In the second extrusion, a mixture of the resultant blends of the first extrusion and the crosslink system were melt-blended, i.e., dynami-

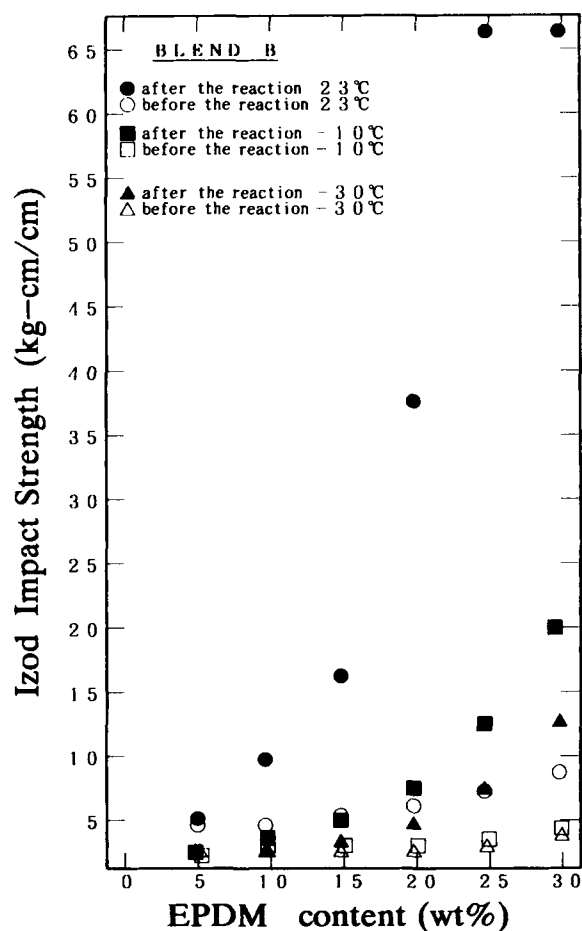
cally crosslinked. The concentrations of PM and PTMQ were maintained at kept 0.2 and 0.3 wphr with respect to the blend.

The extrusions were 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 s by adjusting the extrusion rate. The same extrusion conditions were used throughout the research.

All the first-extruded and second-extruded sam-



**Figure 2** Correlation between the EPDM content and Izod impact in PP/EPDM blends. (1) Blend A: PP : MFR = 1.8 (homopolymer); EPDM:ML<sub>1+4</sub> (100°C) = 88.



**Figure 3** Correlation between the EPDM content and Izod impact in PP/EPDM blends. (2) Blend B: PP : MFR = 8.0 (homopolymer), EPDM:ML<sub>1+4</sub> (100°C) = 88.

ples were injection-molded into specimens for testing under conditions of a barrel temperature of 210–230°C, injection pressure of 1,000 kgf/cm<sup>2</sup>, and mold temperature of 50°C.

To identify the character of the crosslinking reaction, the following tests were carried out. After the second extrusion, the samples of higher EPDM content were hot-pressed to 20 × 50 × 0.2 mm sheets. Each sheet was set in a wire net and immersed in refluxed xylene for 5 h. After the immersion, the xylene insolubles were weighted and analyzed by DSC. The thermograms of all of them exhibited only a trace or a small peak assigned to PP and revealed that the crosslinking reaction proceeded selectively in the EPDM particles. A measure the degree of crosslinking in Tables III–V was calculated using the following equation:

$$\text{Degree of crosslinking (\%)} = \frac{\text{the weight of the xylene insoluble}}{\text{the weight of the EPDM in the sheet}} \times 100$$

## RESULTS AND DISCUSSION

### The Impact Strength Increase at 23°C and Its Mechanism

The effects of the crosslinking on the basic mechanical properties are summarized in Tables III–V, and the relationships between the EPDM content and the IIS are shown in Figures 2–4.

Before crosslinking, the impact strength of Blend A (the standard EPDM dispersion) increased dramatically at 25+ wt % of EPDM (open circles in Fig. 2). This suggests that the IIS of PP/EPDM blends, or the impact energy absorption behavior of these, changes dramatically when the content of the EPDM reaches a certain critical value. This point will be called “a transition point for impact energy absorption behavior (TP)” in this article hereafter. The IIS of Blend C (the fine EPDM dispersion) behaves similarly (closed circles in in Fig. 4), but the TP appears at 20+ wt % of EPDM. On the other hand, there is no TP in the data of Blend B (the coarse EPDM dispersion) (open circles in Fig. 3). Fracture surfaces of these three blends via SEM revealed that the relative dimensions of dispersed EPDM particles among them are “Blend B” > “Blend A” > “Blend C” [Figs. 5(a), 6(a), and 7(a)]. If one ignores the difference of the IIS between PP-1 and PP-2 and one assumes a comparable degree of the interfacial adhesion between the PP and the EPDM in all of the blends, the results indicate that

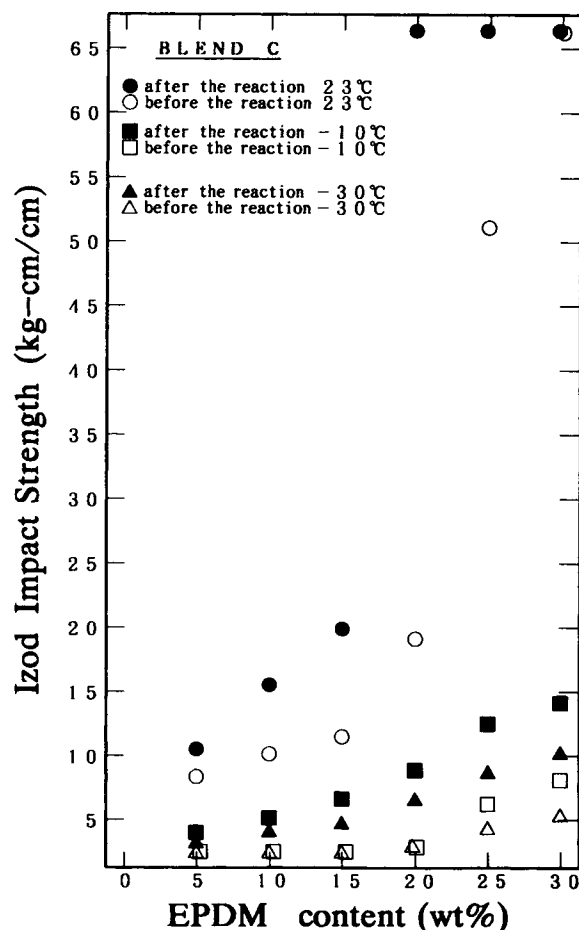
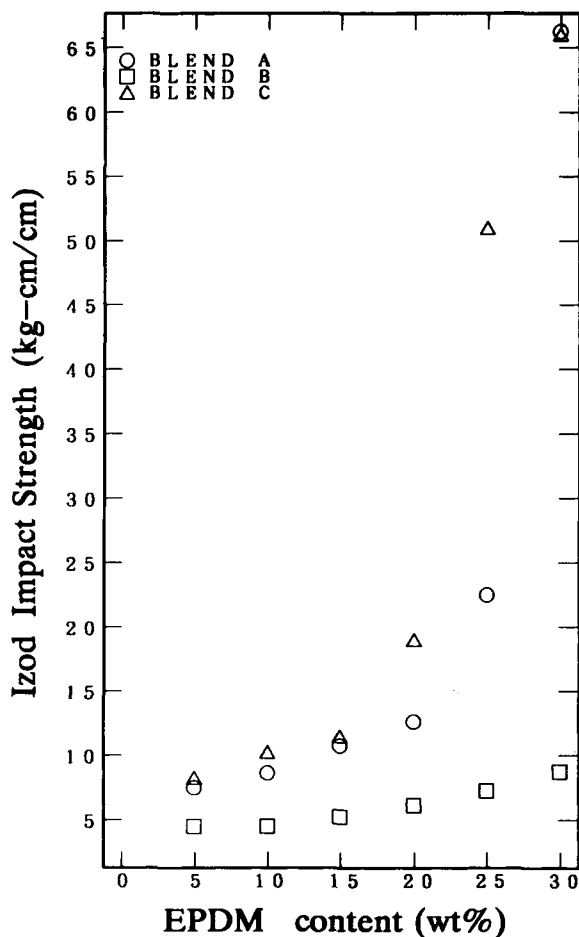


Figure 4 Correlation between the EPDM content and Izod impact in PP/EPDM blends (3) Blend C: PP : MFR = 1.8 (homopolymer), EPDM:ML<sub>1+4</sub> (100°C) = 33.

the TPs of PP/EPDM blends are dependent on “the critical ligament-thickness theory” proposed by Wu.<sup>9,10</sup> The impact strengths of the blends before the crosslinking are compiled in Figure 5.

After the crosslinking, the TPs of Blends A and C appeared to decrease by about 5 wt % (closed circles in Figs. 2 and 4). It is interesting that the TP appears in Blend B at about the same value as for Blend A (closed circles in Fig. 3). These data are compiled in Figure 6, which reveals that the difference of the IIS/EPDM content relation observed in Figure 5 becomes much smaller after the crosslinking reaction.

The fracture surface observations by SEM [Figs. 7(a) and (b), 8(a) and (b), and 9(a) and (b)] reveals that the crosslinking does not affect the morphologies to any extent and that the EPDM particles appeared to be covered with the PP after the crosslinking. The covered particles suggest that EPDM–PP graft copolymers are produced on the interface



**Figure 5** Correlation between the EPDM content and Izod impact in various PP/EPDM blends. (1) Before crosslinking.

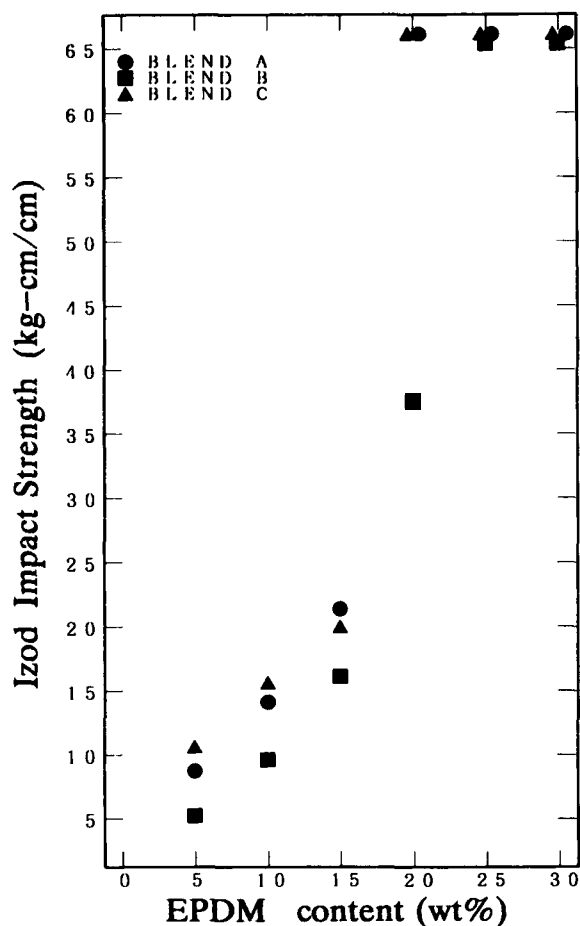
during the crosslinking and strengthen the interfacial adhesion. The same phenomena were also observed in the previous study.<sup>26</sup> In a previous article, it was indicated that the interfacial adhesion is one of the most important factors affecting the impact strength of multilayer polymer blends.<sup>26</sup>

Narisawa and Ishikawa indicated that the relation between the craze initiation stress and the shear yield initiation stress is important to determine whether polymeric materials are ductile or brittle.<sup>12</sup> Tables III-IV reveal that the yielding tensile strength (YTS) decreases after the crosslinking. The decrease is also considered to be caused by the interaction of the stress concentration zones. It is believed that the craze initiation stress in PP is not affected by the rate of deformation. Thus, it is necessary to suppress the propagation of catastrophic cracks to lower the YTS and promote shear yielding.

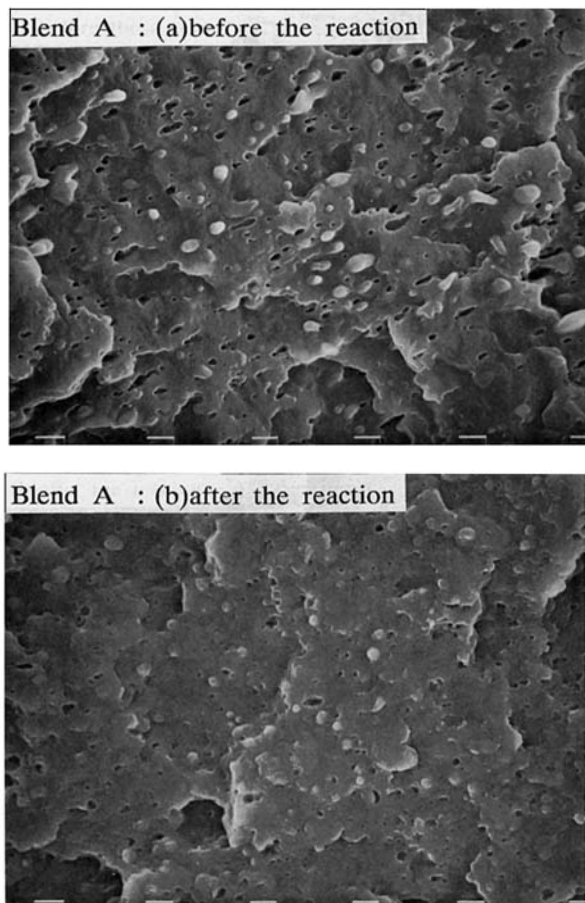
However, in this research, the relation between the YTSs and the TPs provides interesting infor-

mation (Tables III-V). In the Blend A series, before the crosslinking, the TPs before (A-06) and after crosslinking (A-14) appear at about the same YTSs. This result seems to be explained by the theory proposed by Narisawa and Ishikawa.<sup>12</sup> However, in the Blend B series, the TP does not appear even at 199 kgf/cm<sup>2</sup> (B-05) before the the crosslinking and it appears at above 200 kgf/cm<sup>2</sup> (B-15) after the the crosslinking. Also, in the Blend C series, they appear at above 188 kgf/cm<sup>2</sup> (C-05) and at 225 kgf/cm<sup>2</sup> (C-14), respectively. These relations suggest that the TP does not depend on YTS only and there is at least another important factor to affect the TP.

It is recognized that cracking and crazing are effective mechanisms to absorb impact energy. However, they would probably be accompanied by the propagation of catastrophic cracks and are considered less likely to cause the TP. If these mechanisms were controlling, the TP would be observed not only



**Figure 6** Correlation between the EPDM content and Izod impact in various PP/EPDM blends. (2) After crosslinking.



**Figure 7** SEM photomicrographs of the fracture surfaces of the specimen after Izod impact test at  $-30^{\circ}\text{C}$ . (1) Blend A: (a) Before crosslinking (sample A-05); (b) after crosslinking (sample A-15). The space from a head of white bar to the next head of a white bar equals  $10\ \mu\text{m}$ .

in the IIS above the  $T_g$  of PP but also in the IIS below the  $T_g$ . However, the TPs are not observed at  $-10$  and  $-30^{\circ}\text{C}$ .

The data reveal that the TP transitions occur in case PP is above its  $T_g$  and the good interfacial adhesion is attained. It may suggest that the dominating factor is concerned with the increase of the free volume of PP in the stress-concentration zone produced around the EPDM particle.

Bucknall and Smith indicated that the prevention of interfacial debonding is the essential factor required to result in high impact strength in the polystyrene (PS)/crosslinked elastomer particles blend, i.e., high impact polystyrene (HIPS).<sup>5,6</sup> However, in the case of HIPS, the introduction of the graft copolymer on the particle surfaces improves affinity between the phases and also improves the dispersion state of the particles. In addition to these effects, the particles incorporate PS in themselves during

the polymerization and increase their apparent volume. Thus, as three favorable factors for impact strength occur simultaneously under the one process, the pure effect of the debonding does not seem to be fully understood. The result obtained from our study makes it clear that the suppression of interfacial debonding is a very effective technique to improve the impact strength by itself.

The compiled impact strength data shown in Figure 6 reveals that the interfacial adhesion is one of the most important factors in the improvement of impact strength of PP/EPDM blends, not only overcoming the differences in the dimensions of the dispersed EPDM particle but also the IIS of the PP matrix itself.

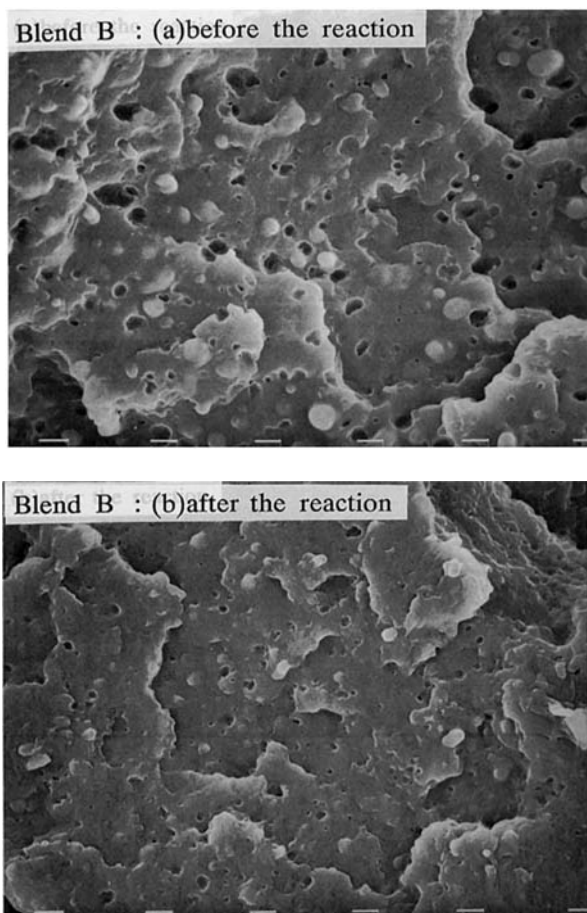
### The Impact Strength Increase Under $0^{\circ}\text{C}$ and Its Mechanism

At  $-10$  and  $-30^{\circ}\text{C}$ , the crosslinking reaction increased the impact strength also, but the TPs were not observed. In this temperature range, the PP matrix is brittle because it is at or below its  $T_g$  and has a greater YTS value and less free volume as compared with those at  $23^{\circ}\text{C}$ . These changed values are in directions which would tend to make the TP phenomenon disappear. The increase and decrease are less at  $-10^{\circ}\text{C}$  compared with those at  $-30^{\circ}\text{C}$ . Accordingly, the degree of the improvement of the IIS at  $-10^{\circ}\text{C}$  is greater than at  $-30^{\circ}\text{C}$ .

Figures 10–12 show the fracture surfaces of the Izod test specimen of  $-30^{\circ}\text{C}$ . It is clear that the whitening zones increase after the crosslinking when the samples belonging to the same blend series are compared. In the Blend A series [Fig. 10(a)], the dimensions of the whitening zone are roughly in proportion to the value of the impact strength. This relation is also observed in the Blend B series [Fig. 10(b)] and in the Blend C series [Fig. 10(c)].

The whitening zone is believed to be evidence of impact energy absorption by plastic deformation at the final stage. In other words, the whitening zone indicated how much the plastic deformation was extended just before the fracture. The results indicate that the crosslinking increased the impact strength by increasing not the absorption ability per volume of the plastic deformation zone, which is supposed to be calculated by dividing the IIS by the volume of whitening zone, but the extent of the plastic deformation zone just before the fracture. Thus, the TPs are not observed because a drastic change of impact energy absorption mechanism had not occurred.

Nonnotched Izod impact tests were also carried



**Figure 8** SEM photomicrographs of the fracture surfaces of the specimen after Izod impact test at  $-30^{\circ}\text{C}$ . (2) Blend B: (a) before crosslinking (sample B-05); (b) after the crosslinking (sample B-15). The space from a head of white bar to the next head of a white bar equals  $10\ \mu\text{m}$ .

out (all the specimens were not broken) and the dimension of the whitening zone produced around the blow point did not increase after the crosslinking. This indicates that the improvement mechanism caused by the crosslinking is more concerned with the stress concentration zone before the propagation of cracks and less with the initiation of cracks under the impact test condition.

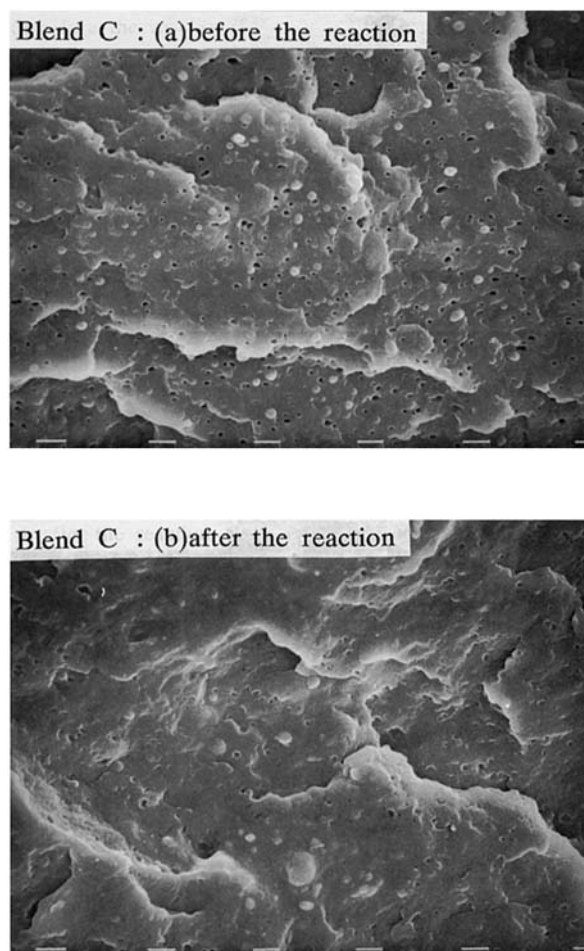
On the other hand, when the dimension of one whitening zone of a Blend A series specimen is compared with that of other blend series specimen, it is not clear which one has the greater IIS. This is true even when the whitening zone of Blend A is compared with those of Blend C, both of which have the same PP-1 as does the matrix. It suggests that the value of the impact energy absorption per volume unit in a given PP matrix, which is supposed to be calculated by dividing the IIS by the volume of

whitening zone, is not constant when the involved EPDM grade changes.

### Flexural Modulus (FM) and Crystallization Temperature ( $T_c$ )

The effect of the crosslinking reaction on the flexural modulus (FM) of the blends presents a rather different picture as compared with that on the YTS. In the Blend A series and Blend B series, it increased the FMs of the lower EPDM content blends and decreased the FMs of the higher EPDM content blends. However, the degree of the decrease is less in comparison with those in the YTS. The borderline seems to be between 15 and 20 wt %. In the Blend C series, it increases the FMs of all the blends.

It is to be expected that the strengthened interfacial adhesion would be accompanied by a decrease



**Figure 9** SEM photomicrographs of the fracture surfaces of the specimen after Izod impact test at  $-30^{\circ}\text{C}$ . (3) Blend C: (a) before crosslinking (sample C-04); (b) after crosslinking (sample C-14). The space from a head of white bar to the next head of a white bar equals  $10\ \mu\text{m}$ .

Table III Effects of the Crosslinking of the EPDM Particles on the Mechanical Properties of PP/EPDM Blends: (1) Blend A<sup>a</sup>

Sample Code	Composition PP/EPDM (Wt %)/(Wt %)	MFR (230°C/2.16 kg; g/10 min)	Mechanical Properties				Notched-IIS (kg-cm/cm) 6 mm Thickness 23°C/-10°C/-30°C	Degree of Crosslinking (%)	T <sub>c</sub> (°C)
			YTS (kgf/cm <sup>2</sup> )	UEL (%)	FM (kgf/cm <sup>2</sup> )	FM			
A-00	100/0	1.8	394		17,400	4.9/2.4/1.9	—	110.6	
Before the crosslink reaction									
A-01	95/5	2.4	342	40	14,900	7.6/2.9/3.1	—	114.5	
A-02	90/10	2.1	312	50	13,800	8.7/3.2/3.2	—	113.8	
A-03	85/15	1.9	289	60	12,800	10.8/3.3/4.2	—	113.8	
A-04	80/20	1.7	269	100	12,000	12.8/4.6/4.6	—	115.0	
A-05	75/25	1.4	240	100	10,500	22.1/6.3/5.9	—	113.6	
A-06	70/30	1.4	228	250	9,800	> 60/8.7/7.0	—	114.1	
After the crosslink reaction									
A-11	95/5	4.7	324	40	17,400	8.9/3.9/3.1	—	125.4	
A-12	90/10	3.9	285	60	15,200	14.2/6.0/4.1	—	124.5	
A-13	85/15	3.3	258	140	13,600	21.6/8.1/5.1	26	123.3	
A-14	80/20	2.2	225	200	11,500	> 60/11.8/7.3	54	122.2	
A-15	75/25	1.6	196	> 400	10,000	> 60/22.6/10.0	65	123.0	
A-16	70/30	1.4	190	> 400	9,500	> 60/28.5/11.6	56	121.7	

<sup>a</sup> PP: MFR = 1.8 (homopolymer), EPDM: ML<sub>1+4</sub> (100°C) = 88. Crosslinking system: N,N'-*m*-phenylene-bismaleimide (PM)/poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ) = 0.2/0.3 (wphr to the blend).



**Table IV** Effects of the Crosslinking of the EPDM Particles on the Mechanical Properties of PP/EPDM Blends: (2) Blend B<sup>a</sup>

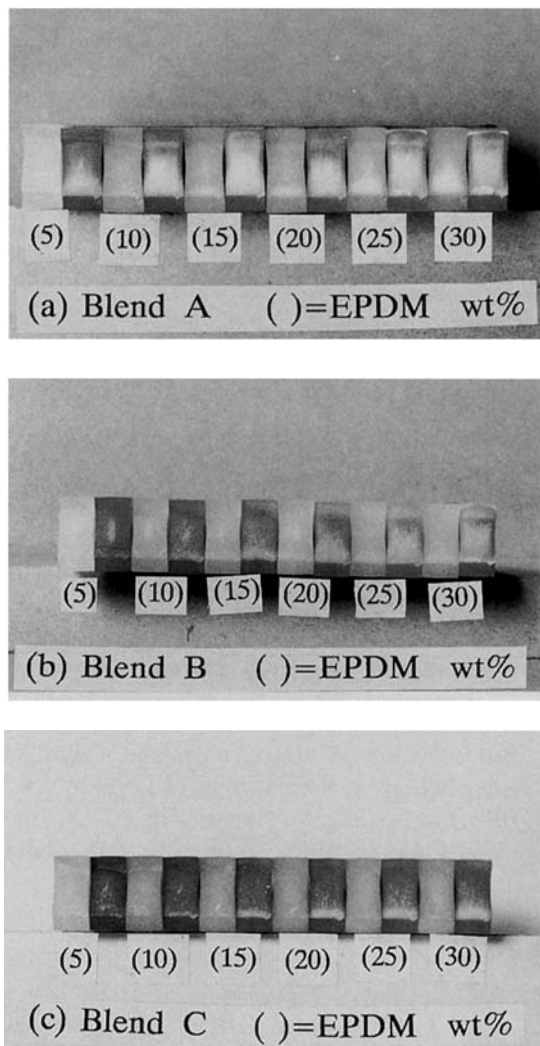
Sample Code	Composition PP/EPDM (Wt %)/(Wt %)	MFR (230°C/2.16 kg/10 min)	Mechanical Properties			Notched-IIS (kg-cm/cm) 6 mm Thickness 23°C/-10°C/-30°C	Degree of Crosslinking (%)	T <sub>c</sub> (°C)
			YTS (kgf/cm <sup>2</sup> )	UEL (%)	FM (kgf/cm <sup>2</sup> )			
B-00	100/0	8.0	372		18,700	3.0/1.9/1.9	—	113.0
Before the crosslink reaction								
B-01	95/5	10.5	332	60	17,100	4.6/2.7/2.8	—	115.4
B-02	90/10	8.9	303	90	15,200	4.7/3.1/2.8	—	114.8
B-03	85/15	7.6	276	110	13,700	5.4/3.3/2.8	—	114.9
B-04	80/20	6.6	255	130	12,800	6.2/3.3/2.9	—	113.4
B-05	75/25	5.3	222	260	10,900	7.3/3.7/3.1	—	113.3
B-06	70/30	4.4	199	> 400	9,800	8.8/4.2/4.0	—	113.2
After the crosslink reaction								
B-11	95/5	15.1	323	70	17,600	5.3/2.7/2.8	—	121.3
B-12	90/10	12.5	287	90	15,800	9.6/4.0/2.9	—	120.3
B-13	85/15	9.1	257	90	14,200	16.2/5.1/3.4	31	120.1
B-14	80/20	6.2	229	290	12,300	37.7/7.4/4.9	56	119.2
B-15	75/25	4.4	200	> 400	10,700	> 60/12.6/7.6	72	117.6
B-16	70/30	3.7	178	> 400	9,200	> 60/19.9/12.9	75	116.6

<sup>a</sup> PP : MFR = 8 (homopolymer), EPDM : ML<sub>1+4</sub> (100°C) = 88. Crosslinking system: N,N'-m-Phenylene-bismaleimide (PM)/poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ) = 0.2/0.3 (wphr to the blend).

Table V Effects of the Crosslinking of the EPDM Particles on the Mechanical Properties of PP/EPDM Blends: (3) Blend C<sup>a</sup>

Sample Code	Composition PP/EPDM (Wt %)/(Wt %)	MFR (230°C/2.16 kg; g/10 min)	Mechanical Properties			Notched-IIS (kg-cm/cm) 6 mm Thickness 23°C/-10°C/-30°C	Degree of Crosslinking (%)	T <sub>c</sub> (°C)
			YTS (kgf/cm <sup>2</sup> )	UEL (%)	FM (kgf/cm <sup>2</sup> )			
C-00 (A-00)	100/0	1.8	394		17,400	4.9/2.4/1.9	—	110.6
<u>Before the crosslink reaction</u>								
C-01	95/5	2.3	328	100	14,200	8.3/2.7/2.7	—	112.6
C-02	90/10	2.2	307	150	13,500	10.3/2.8/2.8	—	112.8
C-03	85/15	2.1	294	220	12,500	11.6/2.8/2.8	—	113.0
C-04	80/20	2.0	243	330	11,100	19.2/2.9/3.0	—	113.4
C-05	75/25	2.0	188	> 400	9,300	51.1/5.4/4.4	—	115.9
C-06	70/30	2.0	164	> 400	8,300	> 60/8.0/6.5	—	114.2
<u>After the crosslink reaction</u>								
C-11	95/5	4.7	314	130	16,200	10.6/4.2/3.2	—	123.6
C-12	90/10	4.3	285	190	14,800	15.6/5.2/4.1	—	122.6
C-13	85/15	3.5	259	280	13,500	20.0/6.7/4.7	22	120.6
C-14	80/20	2.2	225	> 400	11,500	> 60/8.9/6.3	62	119.3
C-15	75/25	1.7	187	> 400	9,700	> 60/12.4/8.8	80	120.2
C-16	70/30	1.3	167	> 400	8,500	> 60/14.2/10.3	76	119.1

<sup>a</sup> PP: MFR = 1.8 (homopolymer), EPDM: ML<sub>1+4</sub> (100°C) = 33. Crosslinking system: *N,N'*-*m*-phenylene-bismaleimide (PM)/poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTM<sub>Q</sub>) = 0.2/0.3 (wphr to the blend).



**Figure 10** Visual observation of the fracture surfaces of the Izod impact test specimen at  $-30^{\circ}\text{C}$ : (a) Blend A; (b) Blend B; (c) Blend C. Before the reaction: white surface. After the reaction: colored surface. From left to right, the content of EPDM increases from 5 to 30 wt % at 5 wt % intervals.

in the FM. However, in addition to the differences in the deformation process and the rate between the YTS tests and the FM tests, the nucleation ability of the crosslinked EPDM particles, which was reported in the previous study,<sup>26</sup> is believed not only to compensate for the expected decrease but also to overcome it, resulting in an increase in the FM.

The nucleation effect was evaluated by the crystallization temperature ( $T_c$ ) determined by differential scanning calorimetry (DSC) analysis. Equal weight samples ( $7 \pm 0.1$  mg) of the blends were analyzed under a cooling rate of  $20^{\circ}\text{C}/\text{min}$ . The crystallization temperatures ( $T_c$ 's) of the

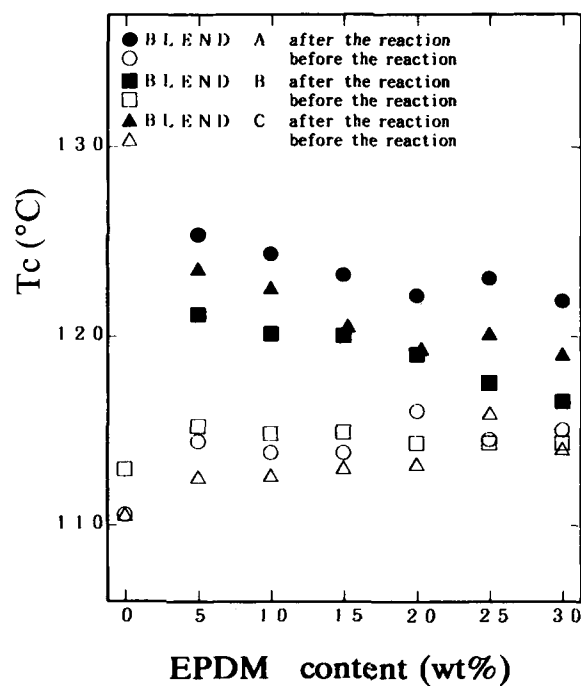
blends are shown in Tables II–IV and compiled also in Figure 11.

Although the incorporation of 5 wt % of EPDM increases the  $T_c$  of the parent blends, the  $T_c$ 's of the blend before the crosslinking reaction does not seem to be dependent on the content of EPDM above this concentration.<sup>15</sup> On the other hand, it is interesting that the  $T_c$ 's of the blends after crosslinking is inversely dependent on the content of EPDM, i.e., it is the highest at 5 wt % of EPDM and decreases as the content of EPDM increases. The degree of the  $T_c$  increase of Blend C is not the greatest among them but essentially the same as that of Blend A.

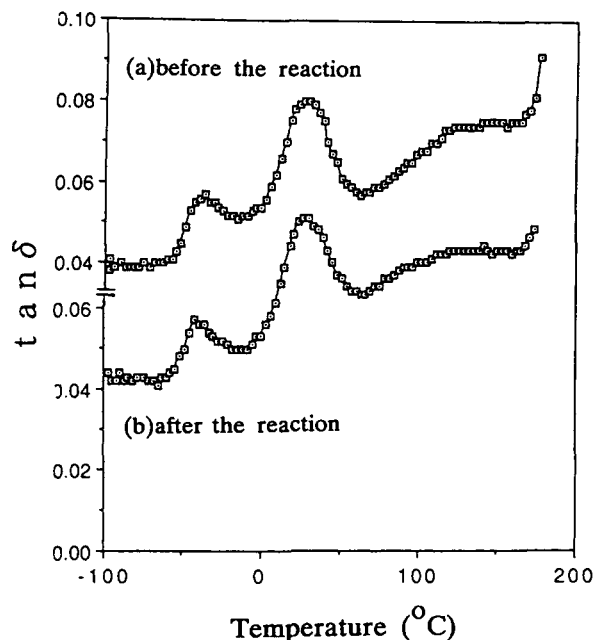
The nucleation effect probably changes the size of spherulites, the crystalline form in the PP matrix, and the impact properties of the PP matrix as a result.<sup>27</sup> The interpretation the total effect on the properties is not clear at present and further studies are needed.

### Dynamic Mechanical Properties

The effect of the crosslinking on the dynamic mechanical properties was investigated. Two kinds of 20 wt %-content EPDM blends of before and after crosslinking, namely, A-04 and A-14 and B-04 and B-14 were analyzed. The analysis was carried out from  $-100^{\circ}\text{C}$  to about  $170^{\circ}\text{C}$  at 110 Hz. To ensure



**Figure 11** The effects of the crosslinking reaction on the crystallization temperature ( $T_c$ ) of the PP/EPDM blends.



**Figure 12** The effects of the crosslinking reaction on the dynamic mechanical properties of the PP/EPDM (80/20) blends: (1) Blend A. Correlation between temperature and  $\tan \delta$ .

the uniformity of the samples, the test pieces (40 [L]  $\times$  6 [W]  $\times$  2 mm [T]) were taken from the same area of the injection-molded sheet (200 [L]  $\times$  100 [W]  $\times$  2 mm [T]).

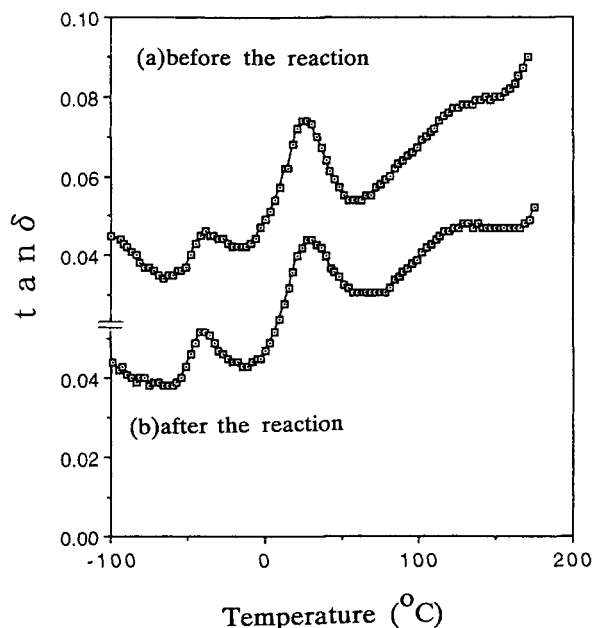
The  $\tan \delta$  vs. the temperature relation of A-04 and A-14 and B-04 and B-14 are shown in Figures 12 and 13, respectively. The  $\tan \delta_{\max}$  of EPDM at about  $-40^\circ\text{C}$  increased after the crosslinking, although the temperature of the  $\tan \delta_{\max}$  of EPDM is not shifted. Byrne and Hourston investigated the dynamic mechanical behavior of EPDM and reported that the  $\tan \delta_{\max}$  is increased by crosslinking, which is ascribed to the decrease of the degree of crystallinity.<sup>28,29</sup> The result is interpreted to mean that the crystallinity of EPDM in the PP matrix is decreased by the crosslinking. The decrease affects the IIS favorably. On the other hand, the  $\tan \delta_{\max}$  of PP, which appears at about  $25^\circ\text{C}$ , does not increase. These results are interpreted to mean that the crosslinking reaction proceeded in the EPDM selectively.

The temperature where  $\tan \delta$  rapidly increases ( $E'$  rapidly decreases) shifted upward after the crosslinking. It indicates that the EPDM is crosslinked and the interaction between the EPDM and the PP has increased. The same phenomenon was observed in the report by Coran and Patel in the case of the dynamic crosslinking in the PP/EPDM

blend by means of the phenolic resin/metal oxide compounds system.<sup>30</sup> The crosslinking system adopted by Coran and Patel is also believed to crosslink the EPDM particles selectively because the addition reaction of the phenolic resin occurs only at unsaturated bonds in the EPDM. The results indicate that the interaction between the PP and the EPDM are strengthened by the crosslinking reaction because of the production of the graft copolymer at the interface.

## CONCLUSION

1. Under the dynamic crosslinking in PP/EPDM blends by means of the *N,N'*-*m*-phenylene-bismaleimide/poly(2,2,4-trimethyl-1,2-dihydroquinoline) crosslink system, the magnitude of the PP/EPDM interfacial adhesion increase. The morphology of the blends is essentially the same before and after the reaction.
2. The increased interfacial adhesion can improve the impact strength without a change of morphology. It reveals that the magnitude of the interfacial adhesion is one of the most important factors concerning the impact strength.



**Figure 13** The effects of the crosslinking reaction on the dynamic mechanical properties of the PP/EPDM (80/20) blends: (1) Blend B. Correlation between temperature and  $\tan \delta$ .

3. When the PP is above its  $T_g$  and ductile, e.g., at 23°C, the impact strength increases dramatically when the EPDM wt % reach a critical value. The crosslinking of the EPDM and the increased interfacial adhesion reduce this critical value.
4. The crosslinked EPDM particles act as nucleating agents and can lead to a decrease in the dimension of the PP spherulites. The crosslinking of the EPDM decreases its crystallinity and can lead to an increase in the difference of the Poisson's ratios between the EPDM and the PP. Both effects can change the impact strength on the blend. These effects are not investigated in this research and need other studies.

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