

Selective Crosslinking Reaction in Polymer Blends. IV. The Effects on the Impact Behavior of PP/EPDM Blends (2)

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SYNOPSIS

Two PP/EPDM blends with 30 wt % of EPDM and different morphologies were selectively crosslinked under a dynamic crosslinking reaction using the *N,N'*-*m*-phenylene-bismal-imide/poly(2,2,4-trimethyl-1,2-dihydroquinoline) system. The resulting Izod impact strengths (IISs) were measured over a range of temperature. A transition point in the IIS curve, which is considered to dependent on the glass transition temperature (T_g) of the PP matrix, appeared to decrease by 5°C. Scanning electron microscopy (SEM) confirmed that the crosslink reaction did not affect the blends' morphology but did increase interfacial adhesion. Increased adhesion is considered to be a most important factor for shifting of the transition point, or apparent T_g , because it increases the free volume of the PP matrix under deformation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Among the many studies on polymer blends, the mechanism of impact strength improvement in thermoplastic/elastomer blends are of great interest. However, these mechanisms are not completely understood and continue to be the subject of current research.¹⁻⁴ In earlier work,⁵⁻⁷ the authors used a novel dynamic crosslinking method to crosslink the dispersed EPDM particles in PP/EPDM blends selectively and observed a change in the Izod impact strength (IIS).

For this work, a series of three PP/EPDM blends were made where the wt % of EPDM was varied from 5 to 30 in increments of 5 wt %. Following the dynamic crosslinking, it was observed that all the sample blends had an increase in IIS. Scanning electron microscopy (SEM) observations of the fracture surfaces revealed that the crosslink reaction had no virtual effect on the blends' morphology. Interfacial adhesion was increased as the result of crosslinking, which suggested the formation of a PP/

EPDM graft copolymer at the interfaces. It is concluded that the increased interfacial adhesion is largely responsible for the increase in IIS.⁷

In this present work, the effects of crosslinked EPDM particles were investigated as a function of temperature. Using two different grades of PP and one grade of EPDM, the procedures of earlier work was followed. Two blends were prepared, both with 70 wt % PP and 30 wt % EPDM, with each giving different morphologies. The IISs of these blends were measured at temperatures ranging from -25 to 20°C in 5°C increments. SEM observations of the fractured surfaces were made, and the crystallinities were observed with differential scanning calorimetry (DCS) and X-ray diffraction.

EXPERIMENTAL

Materials

Two blends were made from two grades of PP homopolymer, with different melt flow rates (MFRs), and one grade of EPDM, in which the diene was 5-ethylidene-2-norbornene. The blend containing a PP with a 1.8 MFR was designated Blend A, and the one with an 8.0 MFR, Blend B. The PPs and the EPDM were commercial products; their com-

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Table I Basic Properties of Raw Materials

Material Code	Commercial Name	Supplier	Comments
<u>(1) Polypropylene (PP)</u>			
PP-1	E120G5	Nippon Petrochemicals	MFR = 1.8 homopolymer
PP-2	J150G	Nippon Petrochemicals	MFR = 8.0 homopolymer
<u>(2) Ethylene-propylene-diene terpolymer (EPDM)</u>			
EPDM	EP57P	Japan Synthetic Rubber	ML ₁₊₄ (100°C) = 88, C3 = 28 wt %, IV = 15
<u>(3) Investigated blend system</u>			
Blend A			PP-1/EPDM = 70/30 (wt %/wt %)
Blend B			PP-2/EPDM = 70/30 (wt %/wt %)

mercial names and published specifications appear in Table I.

The crosslinker used in this work was *N,N'*-*m*-phenylene-bismaleimide (PM) and the accelerator was poly(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ), both of which were commercial products and were used without further purification following the procedures of earlier work.⁵⁻⁷

Sample Preparation

The extruder employed in the experiments was a 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 composed of 70 wt % of PP and 30 wt % of EPDM 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 step. In the second extrusion, a mixture of the resultant blends of the first extrusion and the crosslinking reactants were melt-blended, i.e., dynamically crosslinked. For each blended sample, the concentration of PM and PTMQ were 0.2 and 0.3 wphr, respectively.

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 samples were injection-molded into suitable specimens for testing under the following conditions: A barrel temperature of 210–230°C, an injection pressure of 1000 kgf/cm², and a mold tem-

perature of 50°C. This procedure for preparing samples is the same as that used in earlier work.⁵⁻⁷

RESULTS AND DISCUSSION

The IISs over a Range of Temperatures

Both Blends A and B were prepared with and without dynamic crosslinking. The IISs were measured on all four samples: Blend A before and after the crosslinking and Blend B before and after the crosslinking. These IISs were measured at temperatures ranging in 5°C increments between –25 and +20°C. The results of these IIS measurements are shown in Table II and Figures 1 and 2.

The fracture surfaces as seen by SEM [Fig. 3(a) and (b) and Fig. 4(a) and (b)] reveal that the morphology was basically not affected the crosslink reaction. The surface of the EPDM particles seemed to be covered with PP after the crosslinking [Figs. 3(b) and 4(b)]. These results were same as obtained in earlier work.⁵⁻⁷

Before the crosslinking, Blend A gave an IIS curve with increasing temperature to a transition point where a dramatic increase occurred between –5 and +5°C (open circles in Fig. 1). The IIS curve of Blend B increased similarly but with a smaller increase, due to the coarse dispersion of the EPDM particles and lower IIS of the PP matrix. However, a somewhat weak transition point appeared within the –5 and +5°C (open circles in Fig. 2).

Hereafter, this transition point, which is a function of temperature, will be termed TP-T. These results suggest that the TP-Ts are related to a glass transition temperature (*T_g*) of the PP matrices and not on the morphology and the IIS value of the blends.

Table II Effects of the Selective Crosslinking on the IIs of PP/EPDM (70/30 = wt %/wt %) Blends over a Range of Temperatures

Temperature (°C)	Blend A J120G5/EP57P 70/30		Blend B J150G/ EP57P 70/30	
	(1) ^a	(2) ^a	(1)	(2)
20	> 66.0	> 66.0	11.9	> 66.0
15	> 66.0	> 66.0	10.8	> 66.0
10	> 66.0	> 66.0	10.0	> 66.0
5	> 66.0	> 66.0	8.6	> 66.0
0	53.5	> 66.0	5.6	> 66.0
-5	31.4	> 66.0	5.8	> 66.0
-10	12.5	26.0	6.0	26.5
-15	10.8	21.0	6.6	17.3
-20	10.6	16.9	6.1	12.7
-25	9.6	11.3	5.9	10.0

PP-1: MFR = 1.8 (homopolymer); PP-2: MFR = 8.0 (homopolymer); EPDM: ML₁₊₄ (100°C) = 88; iodine value = 15. Crosslinking system: *N,N'*-*m*-phenylene-bismaleimide/poly(2,2,4-tri-methyl-1,2,-dihydroquinoline) = 0.2/0.3 (wphr to the blend).

^a Notched Izond strength (6 mm thickness, kg-cm/cm²). (1) Before crosslinking; (2) after crosslinking.

After crosslinking, the TP-Ts of Blends A and B appear to be more defined between -10 and -5°C (closed circles in Figs. 1 and 2). It is interesting that both of them appeared at virtually the same temperature zones. Figures 5 and 6 show that the temperature zone where the TP-Ts appear are virtually equal when the IIS curves are compared. If the temperature zones where the TP-T appears are mostly related to the T_g of the PP matrices, then the observed shift seems to indicate that the T_g of the PP matrices was lowered as the result of the crosslinking reaction.

However, in earlier work on the effect of crosslinking on the dynamic mechanical properties PP/EPDM blends (two different PPs with one EPDM at 80-20 wt %) where the relationship between the $\tan \delta$ and temperature was studied, it was shown that the crosslinking reaction does not affect the T_g of the PP matrix.⁷ Therefore, it seems reasonable to conclude that the shift of the TP-T is caused by an apparent lowering of the T_g of the PP due to an increase of the free volume of the amorphous phase of the PP under the deforming condition of the Izod impact test.

The same effect was found in high-impact polystyrene (HIPS) and the acrylonitrile-butadiene-styrene copolymer (ABS), when it was concluded

that the main function of the rubber particles in the amorphous polystyrene matrix was to increase the free volume in the stress concentration zone under deformation and also to enable shear yielding.⁸⁻¹⁰ Using this HiPS/ABS analogy, it seems reasonable to conclude that the greatest factor affecting the TP-T shift is the increase of the free volume of the PP matrix in the stress concentration zone caused by the difference between the Poisson's ratio of PP to EPDM. Such an effect is less likely to occur when the interfaces debond for lack of interfacial adhesion. Debond is minimized by increasing the interfacial adhesion under the dynamic crosslinking, which was confirmed by SEM observations, and it was concluded that some PP/EPDM grafting had occurred at the interfaces.

The PP used in this work was a semicrystalline polymer, i.e., it had both amorphous and crystalline phases. The amorphous phase deforms as a rubber above the T_g , but not below. Above the T_g , the PP molecules in the amorphous phase are able to move and rearrange themselves under deformation as the free volume increases. As a result, when there is a

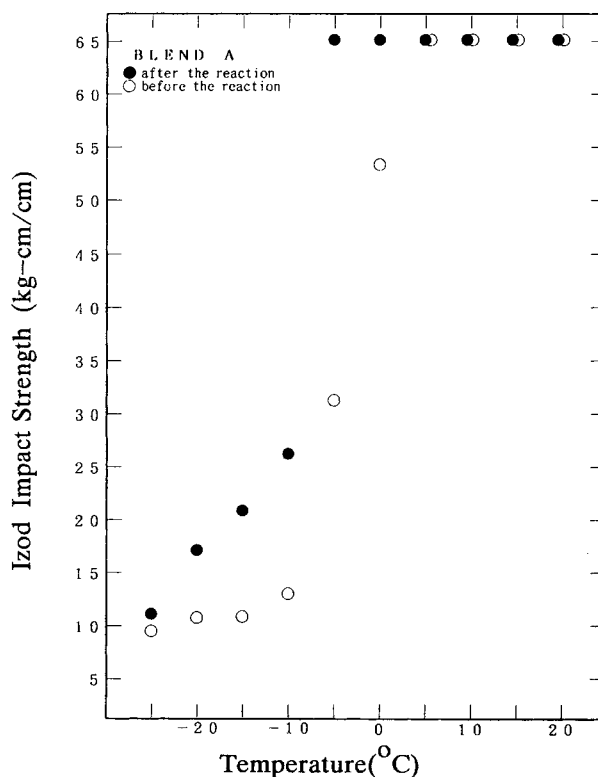


Figure 1 IISs over a range of temperatures for the PP/EPDM (70/30 = wt %/wt %) blend (1). Blend A: PP : MFR = 1.8 (homopolymer); EPDM : ML₁₊₄ (100°C) = 88.

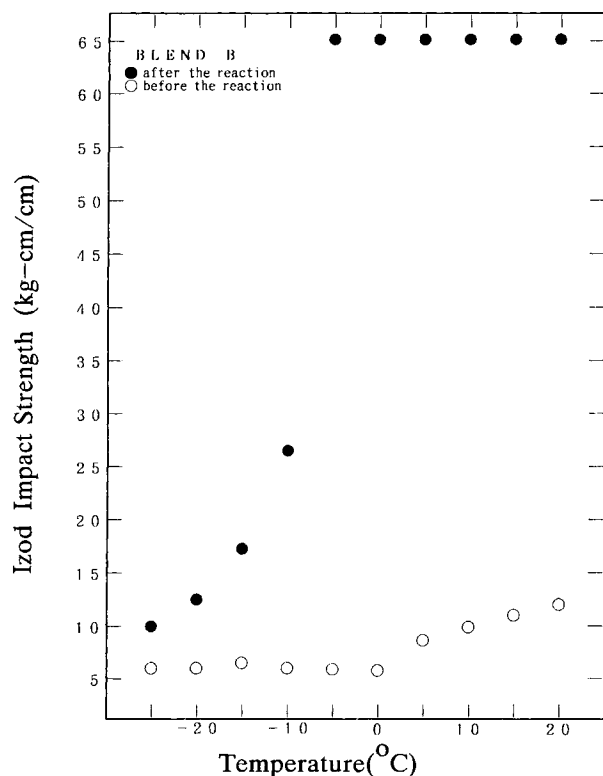


Figure 2 IISs over a range of temperatures for the PP/EPDM (70/30 = wt %/wt %) blend (2). Blend B: PP : MFR = 8.0 (homopolymer); EPDM : ML₁₊₄ (100°C) = 88.

significant increase in free volume, there will be a significant increase in IISs as well.

Similar transition points in the IIS curve of PP/EPDM blends when the EPDM content of the blends was varied were observed in an earlier work.⁷ With PP/EPDM blends having the same composition as that of Blend A, the IIS curve showed a dramatic increase at 25+ wt % before crosslinking and at 20+ wt % after crosslinking. With PP/EPDM blends that are the same as Blend B, the IIS curve did not show a dramatic increase before crosslinking but at 25+ wt % after crosslinking. For this present work, the transition point with varying contents of EPDM will be termed "TP-C."

TP-T and TP-C should be considered critical points since they are specific temperature and EPDM content where the absorption mechanism of the PP matrix against impact energy changes dramatically. However, there is a significant difference between them: TP-C seems to be related to the morphology or properties of the PP; for example, the TP-C of the PP-1/EPDM blend differs from that of the PP-2/EPDM blend, whereas their TP-Ts did not differ.

SEM observations, both from present and previous work, indicate that interfacial adhesion is a key property in determining the impact strength of PP/EPDM blends. The sifting of the TP-C caused by the crosslinking probably indicates that the critical distance,^{11,12} at which the stress-concentration zones developed from the EPDM particles can interact each other, could be decreased by increasing the interfacial adhesion. Thus, the TP-C would be affected by the morphology.

On the other hand, the TP-T, which relates to the free volume of the PP amorphous phase in the stress-concentration zone, should increase with interfacial adhesion. As a result, the TP-T should be less affected by the morphology and more by the volume fraction of the EPDM.

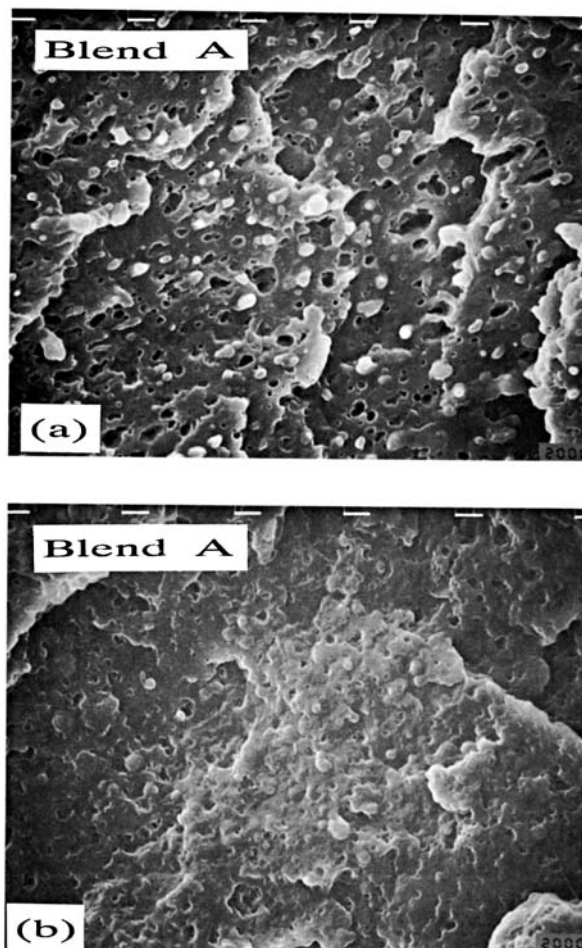


Figure 3 SEM photomicrographs of the fracture surfaces of the specimen after Izod impact test at -25°C (1). Blend A: (a) before crosslinking; (b) after crosslinking. The space from a head of a white bar to the next head of a white bar equals 10 μm .

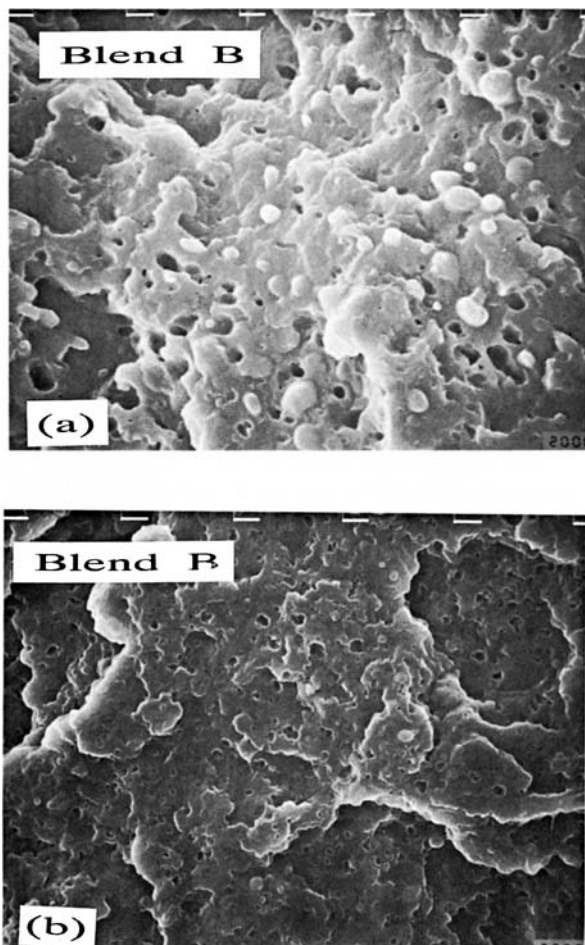


Figure 4 SEM photomicrographs of the fracture surfaces of the specimen after Izod impact test at -25°C (2). Blend B: (a) before crosslinking; (b) after crosslinking. The space from a head of white bar to the next head of a white bar equals to 10 μm .

To develop stress-concentration zones from EPDM particles, which are needed for their interaction, and to increase the free-volume PP matrices, the presence of molecular entanglement and a certain number of tie molecules between crystalline phases should be helpful. As Blend A involving higher molecular weight PP exhibited greater IIS and showed more defined TP-C, the higher molecular weight may have some effects on TP-T and TP-C.

It is generally believed that to increase the impact strength of polymeric materials it is necessary to ensure that the area or volume is large enough to dissipate the impact energy and avoid catastrophic cracks. More preferably, the area or volume should be continuous or interacting. Finite-element analyses have shown that when the rubber fraction is sufficiently high enough, interaction between the

stress-concentration zones occurs^{13,14} and the impact strength increases dramatically.^{14,15}

It is reasonable to conclude that both types of TPs can and do act synergistically to improve IIS. The increased interfacial adhesion caused by the crosslinking of EPDM results in greater interaction of the stress-concentration zone and free volume in the same zone. Together, both cause shear yielding and improve IIS. The TP is considered to be the point where this synergy effect reaches a critical value and enables extensive shear yielding.

Visual Observations of the Fracture Surfaces

Figure 7 shows the fracture surfaces of the Izod test specimen of Blend A. The after-crosslink reaction specimens are easier to observe because they are darkened with the crosslink agents to give a clear contrast between the whitening zone and the smooth surface. As can be seen, the whitening zones increased as the temperature increased. The fracture surface of the specimen of -5°C , which is the TP-T zone, exhibits a different appearance from those

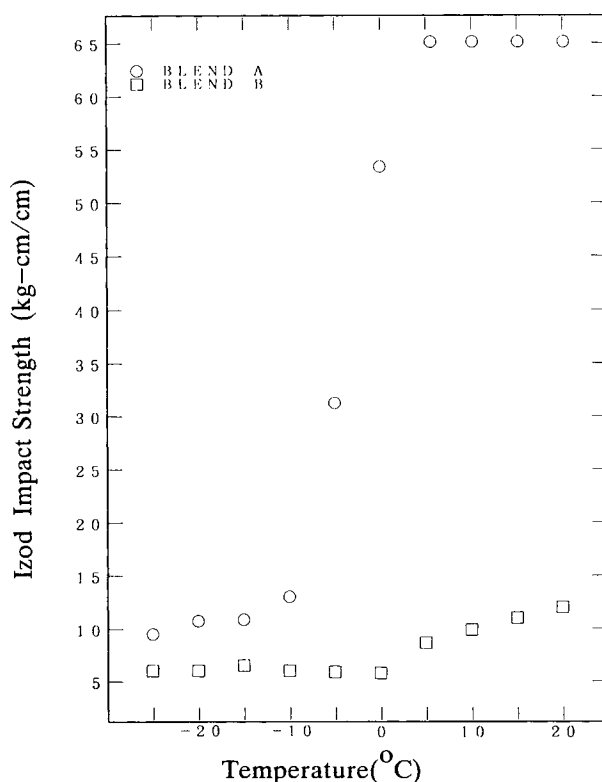


Figure 5 IISs over a range of temperatures for PP/noncrosslinked EPDM (70/30 = wt%/wt%) blends. Blend A: PP : MFR = 1.8 (homopolymer); EPDM : ML_{1+4} (100 $^{\circ}\text{C}$) = 88. Blend B: PP : MFR = 8.0 (homopolymer); EPDM : ML_{1+4} (100 $^{\circ}\text{C}$) = 88.

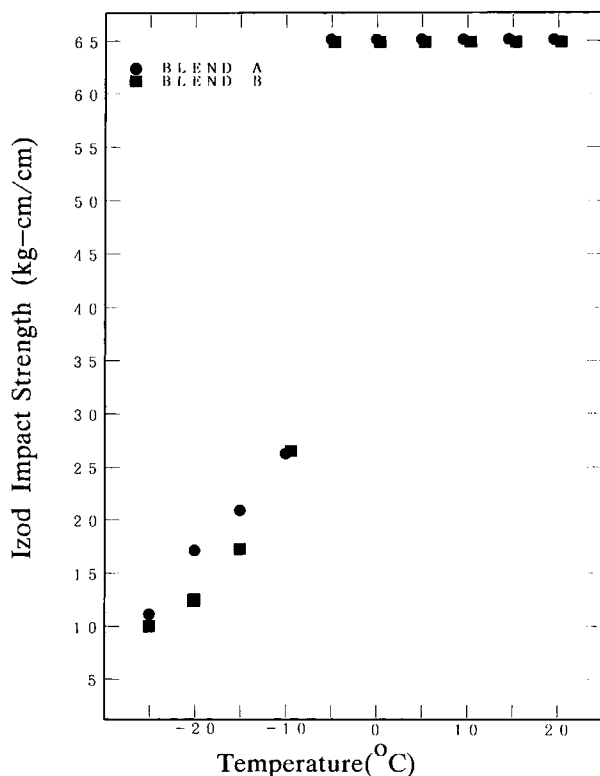


Figure 6 IISs over a range of temperatures for PP/crosslinked EPDM (70/30 = wt %/wt %) blends. Blend A: PP : MFR = 1.8 (homopolymer); EPDM : ML₁₊₄ (100°C) = 88. Blend B: PP : MFR = 8.0 (homopolymer); EPDM : ML₁₊₄ (100°C) = 88.

of other temperatures, which are under the TP-T zone or lower temperature. The whitening zone is not only greater but also denser. Also, the white small spots, which are found at the boundaries between the whitening zones and the smooth zones in the other specimen, are scarcely visible. This suggests that there is some difference in the absorption mechanism of the impact energy between the -5°C specimen and the lower-temperature specimen. In the -5°C specimen, most of the energy was dissipated by a massive plastic deformation, i.e., shear yielding, and in the other specimen, not by massive plastic deformation but by a smaller one because the stress concentration zones were not continuous.

These results suggest that the -5°C specimen has the ability to absorb the impact energy by shear yielding and more free volume in the PP amorphous phase while the other specimen is unable to do the same. These results also seem to indicate that the apparent T_g of the PP is located in the TP-T zone. Similar observations were made with the fracture surfaces from the Izod test specimen of Blend B after the crosslink reaction (Fig. 8).

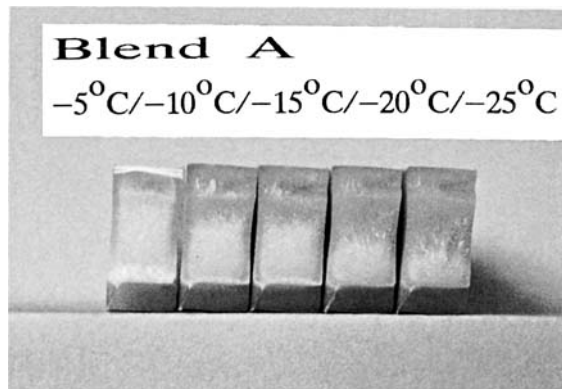


Figure 7 Visual observation of the fracture surfaces of the Izod impact test specimen (1). Specimen: Blend A after crosslinking. From left to right, the environmental temperature decreases from -5 to -25°C at 5°C intervals.

Crystallinity

Earlier work reported that crosslinked EPDM particles can function as nucleation agents.^{6,7} In this present work, crystallinity studies were made to determine whether any useful information on the properties of PP matrices could be obtained.

As a result, DSC measurements were made at cooling rate of $20^{\circ}\text{C}/\text{min}$ and heating rate of $10^{\circ}\text{C}/\text{min}$ on Blends A and B together with the references which had prepared in earlier work.⁷ The results are shown in Tables III and IV. With the Blend A series, it was found that under cooling the area of the endothermal peak was affected by the crosslink reaction, but under heating, the exothermal peak was not affected. Similar measurements with the Blend B series showed no changes during either heating or cooling.

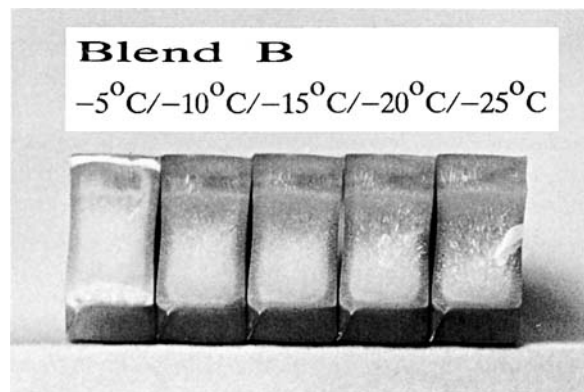


Figure 8 Visual observation of the fracture surfaces of the Izod impact test specimen (2). Specimen: Blend B after crosslinking. From left to right, the environmental temperature decreases from -5 to -25°C at 5°C intervals.

Table III Thermal Analysis by Differential Scanning Calorimetry on PP/EPDM (70/30 = wt %/wt %) Blends (1)

Sample Composition (PP-1/EPDM = Wt %/Wt %)	Sample Weight (mg)	T_c (°C)	ΔH_c (mJ/mg)	T_m (°C)	ΔH_m (mJ/mg)
<u>Before reaction</u>					
95/5	6.92	114.5	-86.6	161.3	85.9
90/10	7.00	113.8	-81.0	160.9	81.7
85/15	7.08	113.8	-77.1	161.3	77.7
80/20	7.02	115.0	-73.3	161.4	73.6
75/25	7.07	113.6	-65.6	161.1	66.0
70/30 = Blend A	6.95	114.1	-62.6	160.9	61.9
<u>After reaction</u>					
95/5	7.08	125.4	-87.5	163.8	91.4
90/10	7.00	124.5	-83.6	163.4	86.0
85/15	6.98	123.3	-78.5	163.1	80.9
80/20	7.09	122.2	-72.8	162.6	74.5
75/25	6.93	123.0	-68.0	163.1	69.3
70/30 = Blend A	6.97	121.7	-66.8	162.9	67.5

PP (= PP 1): MFR = 1.8 (homopolymer); EPDM: ML₁₊₄ (100°C) = 88. Crosslinking system: *N,N'*-*m*-phenylene-bismaleimide/poly(2,2,4-tri-methyl-1,2,-dihydroquinoline) = 0.2/0.3 (wphr to the blend).

The fact that the endothermal peak data of Blend A showed an increase after crosslinking indicates that crystallization proceeded more rapidly in the presence of crosslinked EPDM. However, the other peak data indicate that the crystallinity did not change virtually under the same condition.

X-ray diffraction did not give any clear information on the effect of the crosslink reaction on the crystallinity due to scattering. However, it was observed that all the samples (Blends A and B and the reference samples) had decreased β -form crystalline and increased α -form crystalline. These results sug-

Table IV Thermal Analysis by Differential Scanning Calorimetry on PP/EPDM (70/30 = wt %/wt %) Blends (2)

Sample Composition (PP-2/EPDM = Wt %/Wt %)	Sample Weight (mg)	T_c (°C)	ΔH_c (mJ/mg)	T_m (°C)	ΔH_m (mJ/mg)
<u>Before reaction</u>					
95/5	7.06	115.4	-88.3	161.3	88.3
90/10	7.04	114.8	-83.6	161.1	83.8
85/15	7.01	114.9	-77.4	161.6	78.1
80/20	7.00	113.4	-72.3	161.1	72.0
75/25	7.04	113.3	-66.8	160.6	65.4
70/30 = Blend B	6.91	113.2	-62.0	160.6	61.7
<u>After reaction</u>					
95/5	7.09	121.3	-88.4	163.3	88.4
90/10	7.09	120.2	-82.8	163.1	83.8
85/15	7.05	120.1	-80.7	162.9	80.2
80/20	6.99	119.2	-74.1	162.9	74.7
75/25	7.08	117.6	-68.2	162.3	67.8
70/30 = Blend B	6.97	116.6	-63.9	162.1	64.2

PP (= PP-2): MFR = 8.0 (homopolymer); EPDM: ML₁₊₄ (100°C) = 88. Crosslinking system: *N,N'*-*m*-phenylene-bismaleimide/poly(2,2,4-tri-methyl-1,2,-dihydroquinoline) = 0.2/0.3 (wphr to the blend).

gest that the dynamic crosslink reaction increases the crystallinity of the PP matrix and the α -form crystalline phase. These results confirm the ability of crosslinked EPDM particles to act as a nucleate agent. However, it is not clear that this change in crystalline forms could affect the IISs over a range of temperatures selected for this work.

CONCLUSION

1. The increased interfacial adhesion caused by the dynamic crosslinking in PP/EPDM blends permits more effective interaction of stress-concentration zones developed from the EPDM particles when measured by the impact test deformation rate.
2. The suppression of debonding permits increase in the free volume of the stress-concentration zone caused by the difference in the Poisson's ratios between PP and EPDM. As a result, the apparent T_g of the PP matrix is decreased and also the transition point of the impact strength, which is a function of the T_g . In a 30 wt % EPDM blend of PP/EPDM, the T_g decreased by 5°C.
3. Both of the above-mentioned effects are synergistically related and result in a significant increase in shear yielding, which causes a dramatic increase in impact strength.

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