

Properties of Dynamically Vulcanized Ethylene–Propylene–Diene Copolymer/Polypropylene Blends

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ABSTRACT: In this study, vulcanized thermoplastic elastomers were produced through the formation of crosslinks with peroxide for different ratios of ethylene–propylene–diene copolymer to polypropylene. Mixing was performed with a twin-screw extruder. Afterward, the yield, tensile strength, elastic modulus, elongation, Izod impact strength, hardness, melt flow index, Vicat softening point, heat deflection temperature, and density of the crosslinks were

determined. The thermal transition temperatures and microstructure were determined with differential scanning calorimetry and scanning electron microscopy, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3895–3902, 2007

Key words: blends; elastomers; poly(propylene) (PP); thermoplastics; vulcanization

INTRODUCTION

An elastomer, a polymeric material with a high molecular weight, can be elongated 2 times as much as its original length at room temperature, and it can return to its original length when the applied force is removed. Therefore, elastomers are materials with high molecular weights and long chains that are amorphous and semisolid when they are not vulcanized. In this state, they do not show any elongation or elastic properties. To impart these properties to elastomers, crosslinks are formed with elastomers and other polymers. This is called *vulcanization*.

Dynamic vulcanization, a vulcanization technique, was developed in 1962 by Fischer.¹ Dynamic vulcanization forms a bond under heat and pressure between unsaturated bonds, having low energy, with bond-making materials such as sulfur, metal oxide, and peroxide.¹ In the literature, there are many studies on ethylene–propylene–diene copolymer (EPDM)/polypropylene (PP) vulcanization mixtures. Among them, Xiao et al.² added some materials to form crosslinks in EPDM/PP mixtures of different ratios and investigated the changes in the mechanical properties, morphology, and rheology. Naskar and Noordmeer³ investigated the effects of different types of peroxides on dynamically vulcanized EPDM/PP mixtures. Jacob et al.⁴ investigated the effect of adding recycled EPDM to EPDM/PP thermoplastic compositions. Ghosh et al.⁵ searched for the effect of the vulcanization

technique on the morphology of polymers and on the mechanical properties. Similarly, Alagar and Kumor⁶ studied the morphology and mechanical properties of an EPDM-*g*-vinylxyaminosilane/linear low-density polyethylene (LLDPE) mixture, and Kim et al.⁷ investigated the properties of dynamically vulcanized EPDM/LLDPE mixtures. Ha et al.⁸ investigated the structure and properties of dynamically cured EPDM/PP blends. Furthermore, Kim et al.⁹ investigated dynamically vulcanized EPDM and LLDPE, and Zhang et al.¹⁰ investigated dynamically vulcanized nitrile rubber/PP thermoplastic elastomers. Datta et al.¹¹ searched for PP/EPDM blends dynamically vulcanized by multifunctional peroxides. Saroop and Mathur¹² also searched for dynamically vulcanized PP/styrene block copolymer blends.

As shown by these studies on EPDM/PP mixtures, the mechanical and thermal properties and morphology of vulcanized thermoplastic elastomers can be changed by changes in the vulcanization technique, the amounts of the crosslinkers, and the types of the crosslinkers.

In this study, crosslinks were formed between peroxide and EPDM/PP. On the basis of the PP/peroxide ratios in dynamically vulcanized thermoplastic elastomers, changes in the mechanical and thermal properties and morphology were identified. Through changes in the PP ratio, five groups of EPDM/PP thermoplastic elastomers were prepared. From these five groups, four minor groups were formed by changes in the peroxide ratio. The EPDM/PP ratios for the dynamically vulcanized thermoplastic elastomers that were formed are presented in Table I, and the properties of the materials used in this study are presented in Table II.

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TABLE I
Compositions of the Dynamically Vulcanized EPDM/PP Blends

		EPDM	PP	Peroxide (phr)
Group 1	1.1	75	25	0.0
	1.2			0.75
	1.3			1.00
	1.4			1.25
Group 2	2.1	70	30	0.0
	2.2			0.75
	2.3			1.00
	2.4			1.25
Group 3	3.1	60	40	0.0
	3.2			0.75
	3.3			1.00
	3.4			1.25
Group 4	4.1	50	50	0.0
	4.2			0.75
	4.3			1.00
	4.4			1.25
Group 5	5.1	40	60	0.0
	5.2			0.75
	5.3			1.00
	5.4			1.25

CaSt (0.2 phr) was added to all the groups.

EXPERIMENTAL

EPDM, also called Norden, was used in this study. EPDM (4770 R IP) was produced by DuPont (Akron, OH). Its density was 0.87 g/cm³. Its composition was 70 wt % ethylene, 25 wt % propylene, and 5 wt % ethylene norbornene (ENB). PP was produced by Repsol

Co. (Tarragona, Spain) under the trade name Isplen (PB 150 G2M). Its density was 0.91 g/cm³, and its melt flow index (MFI) was 11.3 g/10 min (at 230°C with 2.16 kg). The elongation at fracture was between 600 and 700%, and the yield strength was about 300–350 kg/cm². To form crosslinks, dicumyl peroxide was used. Dicumyl peroxide was produced by Pergan Co. (Bocholt, Germany) under the trade name Peroxan DC. The weight percentage of peroxide was about 98. The interaction temperature was about +75°C. As a slip agent, calcium stearate (CaSt), produced by Baerluer Co. (Germany), was used. EPDM, PP, and CaSt were mixed with a Saray mixer (Saray Machine Co., Istanbul, Turkey) with two vertical blades for 5 min at 1400 rpm. After that, the samples were mixed with a twin-screw extruder (Maris America Corp., Baltimore, MD). The extrusion conditions are given in Table III. To determine the mechanical properties of the dynamically vulcanized polymer mixtures, tensile samples were obtained by injection molding. The injection conditions are given in Table IV.

Test samples of the granulated polymeric blends were made in an Arburg injection machine (Arburg GmbH Co., Lossburg, Germany). To investigate the fracture behavior, Izod impact tests were performed at –30°C according to ASTM Standard D 256 with a Ceast impact test device (Ceast SpA, Pianezza, Italy). Flow testing of all the mixtures was performed according to ISO Standard 1133 with a Ceast MFI device (at 230°C with 2.16 kg). Thermal transition temperatures were determined with a Universal V2.6D

TABLE II
Physical and Mechanical Properties of EPDM, PP, Peroxide, and CaSt

Property	EPDM ^a	PP ^b	Peroxide ^c	CaSt ^d
Commercial name	Nordel	Isplen	Peroxan DC	
Type	IP 4770 R	PB 150 G2M	Dicumyl peroxide	Calcium stearate
Peroxide ratio (wt %)			98	
Density (g/cm ³)	0.87	0.91		
MFI (g/10 min) at 230°C with 2.16 kg		11.30		
Ash (%)				9.2–10.2
Bending strength (MPa)		735–784		
Yield strength (MPa)		29–34		
Shore A hardness	88			
Elongation at break (%)		600–700		
T_m (°C)	+42			
T_g (°C)	–45			
Ethylene ratio (wt %)	70			
Propylene ratio (wt %)	25			
ENB ratio (wt %)	5			
Appearance	Granule	Granule	Powder	Powder
Injection temperature (°C)			+75	
Crystallization (%)	13			

^a The data were taken from the 2005 DuPont product catalogue (Nordel-IP 4770 R).

^b The data were taken from the 2005 Repsol product catalogue (PB 150 G2M).

^c The data were taken from the 2005 Pergan product catalogue (Peroxan DC).

^d The data were taken from the 2005 Baerluer product catalogue (calcium stearate).

TABLE III
Extrusion Conditions Used in the Preparation of the Dynamically Vulcanized EPDM/PP Blends

Parameter	Group 1	Group 2	Group 3	Group 4	Group 5
Extrusion temperature (°C)	150–205	150–205	150–205	150–205	150–205
Torque (% A)	79–86	76–86	73–86	66–86	63–86
Screw speed (rpm)	300–350	300–350	350–300	300–350	300–350
Capacity (kg/h)	65–85	65–85	65–85	65–85	65–85

differential scanning calorimeter (TA Instruments, New Castle, DE; starting point = -90°C , ending point = 200°C , test rate = $20^{\circ}\text{C}/\text{min}$). Tensile testing was performed according to ASTM Standard D 412 with a Zwick Z010 testing machine (Zwick GmbH, Ulm, Germany). In the tensile tests, a 5 mm/min pulling speed was applied (sample dimensions: $150 \times 20 \times 4 \text{ mm}^3$). Hardness tests were performed according to ASTM Standard D 2240 with a Zwick hardness measurement device (sample dimensions: $100 \times 100 \times 10 \text{ mm}^3$). The tensile and hardness tests were performed at room temperature, and five measurements were taken to obtain an average value for each test.

The microstructure was determined with a JSM-T330 scanning electron microscope (JEOL, Peabody, MA) at 10 kV. Samples were coated with gold to a thickness of about 40 Å. To determine the degree of vulcanization, a permanent deformation test was conducted according to ASTM D 395 by the laboratory of

Design Group (Istanbul, Turkey) at 70°C for a 24-h dwell time (sample dimensions: $100 \times 100 \times 10 \text{ mm}^3$). The crosslink density was measured according to ASTM Standard D 6338-03. The measurement was performed at 160°C for 8 h in a sylohekan solution, and the weight difference was found by the blowing of the polymers and the subsequent vaporization of the solvent (Design Group).

TABLE IV
Injection Conditions Used in the Preparation of the Dynamically Vulcanized EPDM/PP Blends

Parameter	Value
Injection temperature (°C)	50–190
Injection pressure (bar)	70–80
Dwell time in the mold (s)	15
Injection speed (mm/s)	70
Mold temperature (°C)	50

TABLE V
Mechanical Properties of the Dynamically Vulcanized EPDM/PP Blends

Test	Standard	Peroxide				
		0.0 phr	0.75 phr	1.0 phr	1.25 phr	
Group 1	Strength at break (MPa)	ASTM D 412	12 ± 0.5	11 ± 2	12 ± 1	11 ± 1
	Elongation (%)	ASTM D 412	830 ± 7	550 ± 12	528 ± 8	480 ± 5
	Permanent deformation (%) at 70°C and 24 h	ASTM D 395	75 ± 2	49 ± 2	45 ± 0.5	41 ± 0.5
	Shore D hardness	ASTMD2240	38 ± 0.5	38 ± 1	35 ± 0	34 ± 0.5
	Izod impact strength (kJ/m^2) at -30°C	ASTM D 256	Not broken	Not broken	Not broken	Not broken
Group 2	Strength at break (MPa)	ASTM D 412	13 ± 1	10 ± 1	11 ± 2	11 ± 1.5
	Elongation (%)	ASTM D 412	620 ± 10	530 ± 7	450 ± 6	430 ± 11
	Permanent deformation (%) at 70°C and 24 h	ASTM D 395	79 ± 1	54 ± 0.5	45 ± 2	39 ± 1
	Shore D hardness	ASTMD2240	38 ± 1	39 ± 0.5	39 ± 0.5	39 ± 0
	Izod impact strength (kJ/m^2) at -30°C	ASTM D 256	Not broken	Not broken	Not broken	Not broken
Group 3	Strength at break (MPa)	ASTM D 412	13 ± 1	12 ± 0.5	12 ± 0.5	12 ± 0.5
	Elongation (%)	ASTM D 412	600 ± 9	550 ± 11	500 ± 12	500 ± 9
	Permanent deformation (%) at 70°C and 24 h	ASTM D 395	88 ± 1	57 ± 1	57 ± 0.5	55 ± 1
	Shore D hardness	ASTMD2240	44 ± 0	44 ± 0	43 ± 0.5	45 ± 0.5
	Izod impact strength (kJ/m^2) at -30°C	ASTM D 256	Not broken	Not broken	Not broken	Not broken
Group 4	Strength at break (MPa)	ASTM D 412	12 ± 2	13 ± 2	13 ± 1.5	13 ± 1
	Elongation (%)	ASTM D 412	420 ± 11	550 ± 3	300 ± 9	310 ± 9
	Permanent deformation (%) at 70°C and 24 h	ASTM D 395	85 ± 2	61 ± 1	54 ± 1	52 ± 1.5
	Shore D hardness	ASTMD2240	51 ± 1	48 ± 1	48 ± 1	48 ± 0
	Izod impact strength (kJ/m^2) at -30°C	ASTM D 256	Not broken	Not broken	Not broken	Not broken
Group 5	Strength at break (MPa)	ASTM D 412	13 ± 1	12 ± 0	11 ± 1.5	13 ± 1
	Elongation (%)	ASTM D 412	400 ± 12	500 ± 7	480 ± 9	530 ± 11
	Permanent deformation (%) at 70°C and 24 h	ASTM D 395	77 ± 0	74 ± 1	62 ± 1	81 ± 1
	Shore D hardness	ASTMD2240	51 ± 1	51 ± 1	48 ± 0	53 ± 1
	Izod impact strength (kJ/m^2) at -30°C	ASTM D 256	Not broken	Not broken	Not broken	Not broken

TABLE VI
Thermal Properties of the Dynamically Vulcanized EPDM/PP Blends

Group	Test	Peroxide			
		0.0 phr	0.75 phr	1.0 phr	1.25 phr
Group 1	MFI (g/10 min) at 230°C with 2.16 kg	Not flowing	Not flowing	Not flowing	Not flowing
	T_g for EPDM (°C)	-31.33	—	—	-29.11
	T_m for EPDM (°C)	54.82	—	—	47.80
	T_g for PP (°C)	—	—	—	—
Group 2	MFI (g/10 min) at 230°C with 2.16 kg	Not flowing	Not flowing	Not flowing	Not flowing
	T_g for EPDM (°C)	-32.51	—	—	-32.47
	T_m for EPDM (°C)	43.18	—	—	45.43
	T_g for PP (°C)	—	—	—	—
Group 3	MFI (g/10 min) at 230°C with 2.16 kg	0.4	Not flowing	Not flowing	Not flowing
	T_g for EPDM (°C)	-33.26	—	—	-49.13
	T_m for EPDM (°C)	50.71	—	—	45.26
	T_g for PP (°C)	—	—	—	—
Group 4	MFI (g/10 min) at 230°C with 2.16 kg	0.4	Not flowing	Not flowing	Not flowing
	T_g for EPDM (°C)	-35.29	—	—	-34.88
	T_m for EPDM (°C)	45.56	—	—	43.12
	T_g for PP (°C)	—	—	—	—
Group 5	MFI (g/10 min) at 230°C with 2.16 kg	1.3	0.8	2.8	2.2
	T_g for EPDM (°C)	-36.88	—	—	-56.74
	T_m for EPDM (°C)	44.92	—	—	43.48
	T_g for PP (°C)	—	—	—	—
	T_m for PP (°C)	168.22	—	—	166.68

RESULTS AND DISCUSSION

The fracture strength, elongation at fracture, amount of plastic deformation, hardness, and Izod impact strength of the dynamically vulcanized EPDM/PP polymer mixtures are presented in Table V. There was not much difference in the fracture strength with increases in the PP ratio in the EPDM/PP mixtures. In addition, an increase in the peroxide ratio did not cause an important change in the fracture strength. The elongation decreased with an increasing PP ratio in the mixture. Similar results were also observed for peroxide. It is thought that this was a result of an increase in the crosslink density. Xiao et al.¹³ reported that an increase in the curing agent in a EPDM/PP mixture reduced the elongation at break. They also determined that there was no important change in the strength at break.¹³

The permanent deformation increased with the PP ratio. However, increasing the peroxide ratio reduced the amount of permanent deformation. This is also thought to be a result of an increase in the crosslink density. The hardness of the mixtures increased with the PP ratio. This is due to the fact that PP is harder than EPDM. However, increasing the peroxide ratio did not have an important effect on the hardness. According to the study of Zhang et al.¹⁰ on vulcanized NBR/PP mixtures, the hardness increased with an increasing PP ratio. Because the structure was flex-

ible, Izod impact tests were performed at -30°C. Even at this temperature, the materials did not show any fracture behavior.

The thermal values obtained experimentally for dynamically vulcanized EPDM/PP polymer mixtures are given in Table VI. The density of the crosslinks is given in Table VII, and the differential scanning calorimetry (DSC) curves are given in Figure 1.

As shown in Table VI, increasing the PP ratio in the mixture resulted in a small increase in the MFI value. However, yielding was not observed. DSC tests were not performed for the samples with 0.75 or 1.0 phr peroxide. DSC tests for the groups with 0.0 or 1.25 phr peroxide showed that increasing PP in the mixture caused a small reduction in the glass-transition temperature (T_g) of EPDM. Similar results were also

TABLE VII
Crosslink Densities of the Dynamically Vulcanized EPDM/PP Blends

Group	Crosslink density (%)		
	0.75 phr peroxide	1.0 phr peroxide	1.25 phr peroxide
1	58 ± 1	60 ± 1	66 ± 1
2	47 ± 1	50 ± 0.5	55 ± 0.5
3	39 ± 1.5	44 ± 1	47 ± 1
4	30 ± 2	32 ± 2	35 ± 1
5	27 ± 1	29 ± 1.5	31 ± 1.5

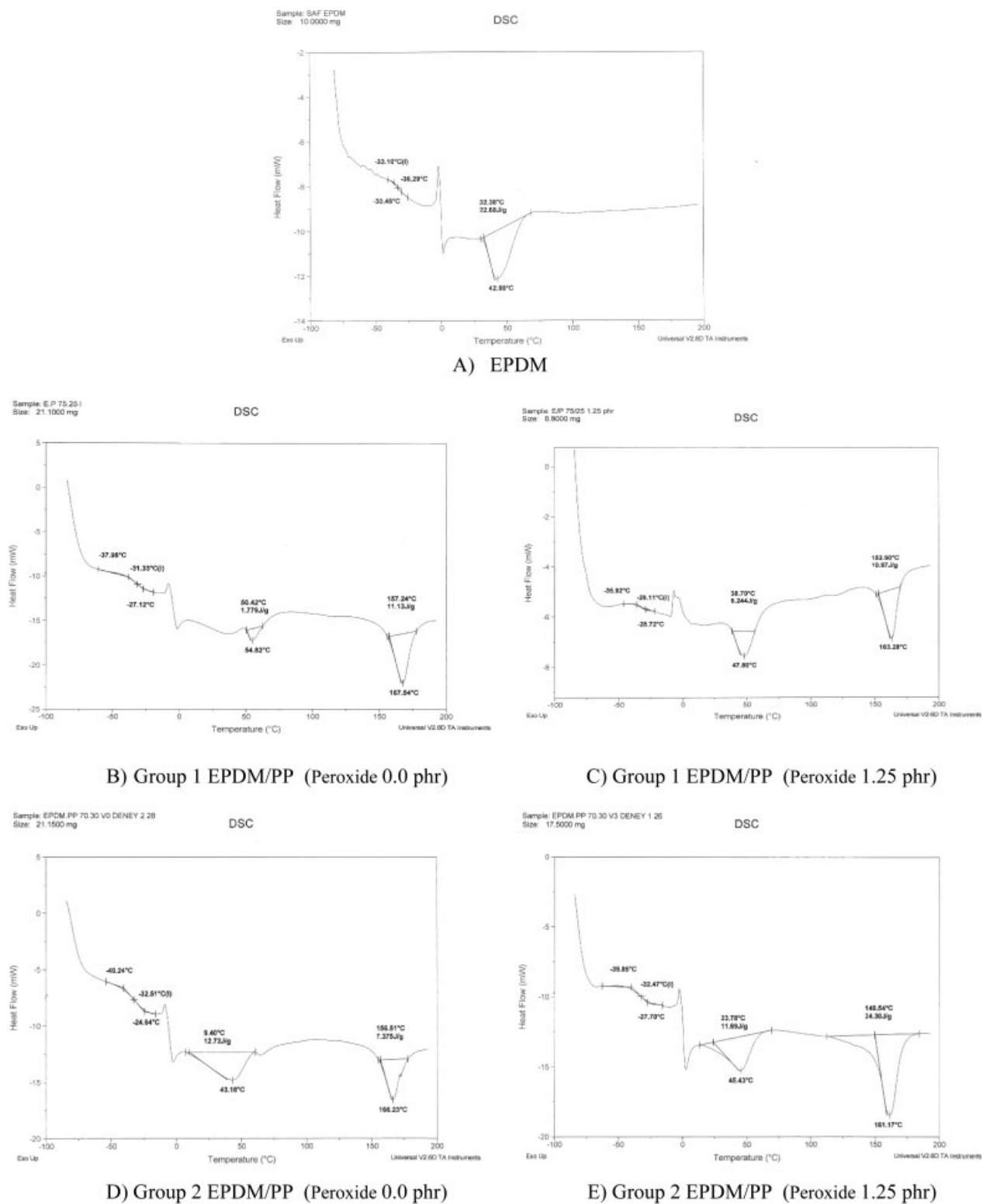


Figure 1 DSC curves for dynamically vulcanized EPDM/PP blends: (A) EPDM, (B) group 1 EPDM/PP (0.0 phr peroxide), (C) group 1 EPDM/PP (1.25 phr peroxide), (D) group 2 EPDM/PP (0.0 phr peroxide), (E) group 2 EPDM/PP (1.25 phr peroxide), (F) group 3 EPDM/PP (0.0 phr peroxide), (G) group 3 EPDM/PP (1.25 phr peroxide), (H) group 4 EPDM/PP (0.0 phr peroxide), (I) group 4 EPDM/PP (1.25 phr peroxide), (J) group 5 EPDM/PP (0.0 phr peroxide), and (K) group 5 EPDM/PP (1.25 phr peroxide).

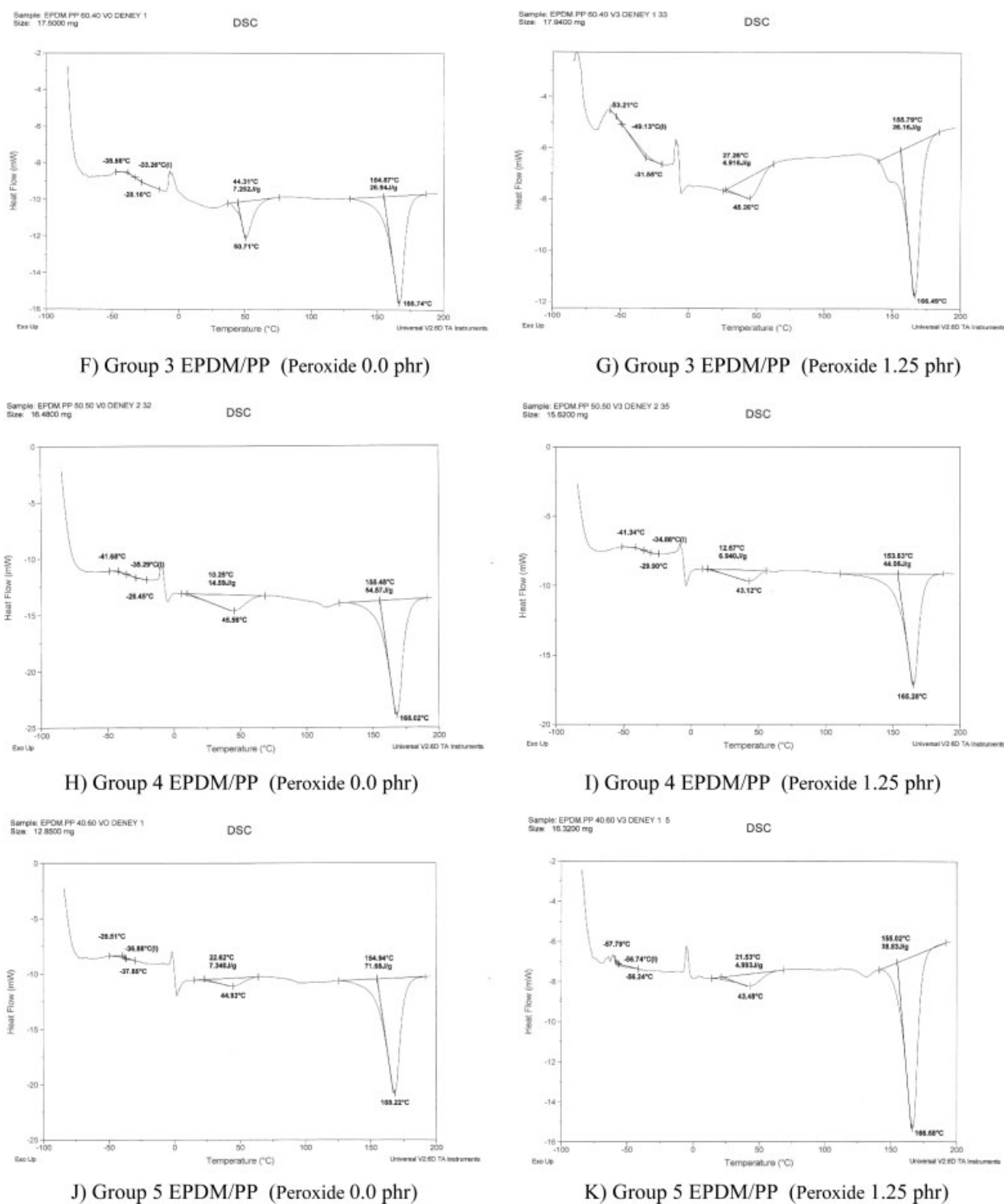


Figure 1 (Continued from the previous page)

seen in the groups modified with peroxide. A small decrease in the melting temperature (T_m) of EPDM was also seen in the groups with and without peroxide. Although there was no important change in the T_m value of PP, there was a small increase in the T_m value of PP for the group modified with 1.25 phr peroxide.

AN increase in the peroxide ratio resulted in an increase in the crosslink density for all the groups. However, these values decreased with the PP ratio.

Figure 2 shows scanning electron micrographs of the fractured surfaces of the EPDM/PP blends. The scanning electron micrographs of the fractured surfaces of the EPDM/PP blends show nearly the same tend-

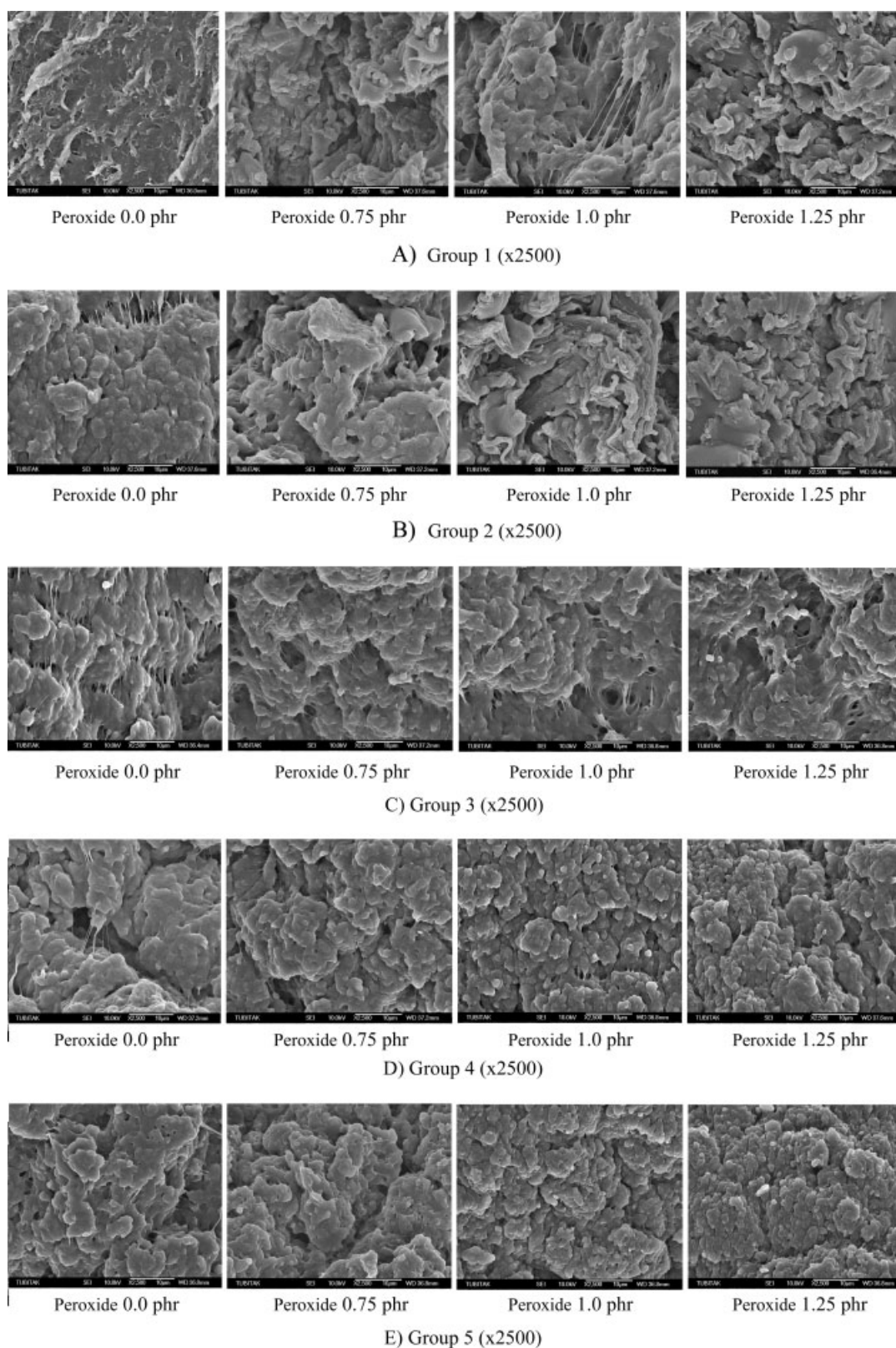


Figure 2 Scanning electron micrographs revealing the fracture surfaces of dynamically vulcanized EPDM/PP blends: (A) group 1, (B) group 2, (C) group 3, (D) group 4, and (E) group 5 (original magnification = 2500 \times).

ency as those of the dynamically vulcanized blends. However, a careful inspection of Figure 2 shows that the groups modified with peroxide had better adhe-

sion. The morphology implies that the compatibility of EPDM/PP was improved by the dynamic vulcanization process.

CONCLUSIONS

When the mechanical properties of the first, second, and third group of dynamically vulcanized EPDM/PP blends were investigated, we found that the fracture strength, elongation at fracture, and amount of permanent deformation decreased as the amount of peroxide increased. The samples tested for the Izod impact strength did not show fracture behavior at -30°C . In the case of the fourth group of dynamically vulcanized EPDM/PP blends, the fracture strength increased a little. For the fifth group of dynamically vulcanized EPDM/PP blends, the fracture strength and the amount of permanent deformation decreased, but for 1.25% peroxide, both properties increased. As the PP ratio increased in the dynamically vulcanized EPDM/PP blends, the fracture strength, hardness, and amount of permanent deformation increased. On the other hand, the elongation and density of the cross bonds decreased.

According to the MFI values obtained experimentally at 230°C with 2.16 kg, melt flow was only observed for the fifth group. Although there was a slight decrease in the MFI value of group 5.2, as the peroxide proportion increased, this value also increased. As the amount of peroxide increased in all the groups of dynamically vulcanized EPDM/PP blends, the density of cross bonds increased. On the basis of the DSC results, increasing the peroxide concentration reduced T_m of both EPDM and PP for the first, third, and fourth groups of dynamically vulcanized EPDM/PP blends. For the second group of dynamically vulcanized EPDM/PP blends, although increasing the peroxide concentration did not affect T_g , T_m of PP decreased. In the case of the fifth

group of dynamically vulcanized EPDM/PP blends, increasing the peroxide concentration resulted in reduced T_g and T_m values of EPDM and T_m values of PP. The scanning electron microscopy analysis showed that increasing the peroxide concentration resulted in increasing adhesion.

On the basis of these results, group 1.4 of the EPDM/PP dynamically vulcanized blends (75/25 with 1.25 phr peroxide) was the optimum group because of the lower fracture strength, lower elongation, and, most importantly, lower permanent deformation, which was characteristic of vulcanization, a lower density of crosslinks, and better adhesion.

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