The Effect of Dicumyl Peroxide Vulcanization on the Properties & Morphology of Polypropylene/Ethylene-Propylene Diene Terpolymer/Natural Rubber Blends

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This article discusses some properties such as tensile properties, chemical and oil resistance, gel content, crystallinity, and morphology of polypropylene (PP)/ethylene-propylene diene terpolymer (EPDM)/natural rubber (NR) blends. Dicumyl peroxide (DCP) was applied as a crosslinking agent. In terms of tensile properties, peroxide vulcanized blend shows higher tensile strength and tensile modulus (stress at 100% elongation, M_{100}) as compared with the unvulcanized blend. The elongation at break of the peroxide vulcanized blend is higher for the blend with NR rich content compared with the EPDM rich content. The improvements in chemical and oil resistance as well as gel content of peroxide vulcanized blends have also proved the formation of crosslinks in the rubber phase. Scanning electron microscopy (SEM) micrographs from the surface extraction of the blends support that the crosslinks have occurred during dynamic vulcanization. Dynamical vulcanization with DCP has decreased the percent crystallinity of blends that can be attributed to the formation of crosslinks in the rubber.

INTRODUCTION

PP/EPDM blends are some of the most studied thermoplatic elastomers. Several works on the dynamic vulcanization of PP/EPDM have been carried out using a variety of curing agents such as sulfur [1–3] and peroxide [4–6]. Replacement of EPDM with NR in PP/EPDM blends has been considered for cost reduction. It has also been observed that the partial replacement of EPDM by NR decreased the properties of PP/EPDM blends [7]. Therefore, dynamic vulcanization has been employed in the preparation of PP/EPDM/NR blends using dicumyl peroxide (DCP) to improve their properties.

The presence of DCP in the blends is to produce reactive radicals upon decomposition at elevated temperatures via exothermic reaction that is beneficial in a rubber compound. It is generally agreed that during the peroxide vulcanization of polyolefin and rubber, crosslinks or chain scission may occur simultaneously. According to Ho et al. [8] the polymer free radicals in PP induced by the peroxide decomposition lead predominantly to scission reaction, whereas in rubber, vulcanized properties of blends are determined by the crosslinked structures being formed [9–10].

This article examines the effect of dynamic vulcanization with DCP on the tensile properties, chemical and oil resistance, gel content of the PP/EPDM/NR blends, along with the accompanying characteristics of the crystallinity and morphology.

EXPERIMENTAL

Materials

Polypropylene (PP) homopolymer used in this study was an injection-molding grade, supplied by Titan PP Polymers (M) Sdn Bhd, Johor, Malaysia (TITANPRO 6331 grade) with a melt flow index (MFI) value of 14 gr/10 min at 230°C and 2.16 kg. Ethylene-propylene diene terpolymer (EPDM-EPT 3072E), with Mooney Viscosity, M_L (1 + 4) at 100°C of 74 was purchased from Luxchem Trading Sdn. Bhd. Natural rubber (SMR L), with Mooney viscosity M_L (1 + 4) at 100°C of 73 was obtained from Hokson Rubber Trading Sdn. Bhd, Seremban. Dicumyl peroxide (DCP) was purchased from Aldrich.

Preparation and Processing

Studies were conducted on PP/EPDM/NR blends consisting of two systems: unvulcanized blend and vulcanized blend with DCP. Each blend covered the following blend compositions: 50/50/0, 50/40/10,

50/30/20, 50/20/30, 50/10/40, and 50/0/50. Thermoplastic elastomer blends were prepared by melt mixing in an internal mixer, Haake Polydrive with Rheomix R600/610 at temperature and rotor speed of 180°C and 50 rpm, respectively.

During blending, the thermoplastic PP was first loaded into the internal mixer and premixed for two minutes, followed by the rubbers (EPDM and NR). For unvulcanized, the blends were taken out after 6 min of mixing. The corresponding blends with DCP were prepared in the same manner except that the DCP was added at 5 min of mixing and the mixing time was prolonged up to 8 min. The samples were then sheeted by passing through a 2-roll mill and allowed to cool at room temperature.

Specimens for testing were compression molded using an electrically heated hydraulic press machine. The machine was pre-heated at 180°C for 6 min and followed by another 4 min of compression at the same temperature. The specimen was allowed to cool under pressure for another 4 min. The same procedure was adopted for all blend systems.

Tensile Properties

Tensile tests were carried out according to ASTM D412 on an Instron machine. 2 mm thick dumbbell specimens were cut from the molded sheets with a Wallace die cutter. The specimen was tested using a constant rate (50 mm/min) at room temperature of 25°C. The results are quoted based on the average value of five specimens tested for each blend system.

Swelling Test

Determination of the swelling index was carried out according to ASTM D471. The specimens with dimensions of $30 \, mm \times 5 \, mm \times 2 \, mm$ were cut and weighed using an electrical balance. The test pieces were then immersed in toluene for 12 h and in oil (IRM 903) for 48 h at room temperature. The samples were then removed from toluene and oil, wiped with tissue paper to remove excess liquid from the surface, and weighed. The swelling index of the blends was then calculated as follows:

$$Swelling \ index = \frac{W_2}{W_1} \times 100\% \tag{1}$$

where: W_1 = weight of specimen before immersion; W_2 = weight of specimen after immersion.

Gel Content

The degree of crosslinking in the rubber was measured after extraction in boiling cyclohexane for 8 h. The samples were dried at 80°C for 30 min and subsequently weighed. The percentage of gel content of the blends was then calculated as follows:

$$\% \text{ gel content} = \frac{W_g}{W_o} \times 100\% \qquad (2)$$

where W_g and W_o are sample weights after and before extraction, respectively.

Morphology Studies

Morphological evaluations of PP/EPDM/NR surfaces were done using a scanning electron microscope (SEM), model Leica Cambridge S-360. The unvulcanized blend samples were solvent-extracted using n-hexane for 2 days at room temperature to extract the rubber phase from the blend. The samples were then dried to remove the solvent. The vulcanized samples were etched with nitric acid for two days, washed with water, and then dried. All the samples were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. The examinations were done within 24 h of preparation.

Differential Scanning Calorimetry (DSC) Study

Thermal analysis measurements of selected blends systems were performed using a DSC-7 Perkin Elmer Differential Scanning Calorimeter. The samples were program-heated at 20°C/min to about 200°C and maintained at this temperature for 10 min to ensure a complete melting of the crystals. The melting temperature (T_m) and the heat of fusion (ΔH_f) were measured during the heating cycle.

RESULTS AND DISCUSSION

Tensile Properties

Figure 1 shows a comparison of tensile strength between unvulcanized and vulcanized blend with DCP at various PP/EPDM/NR blend compositions. It shows that the tensile strength of the unvulcanized blends decreases with increasing NR content. This is because the EPDM interacts more effectively with the PP phase in the blend compared
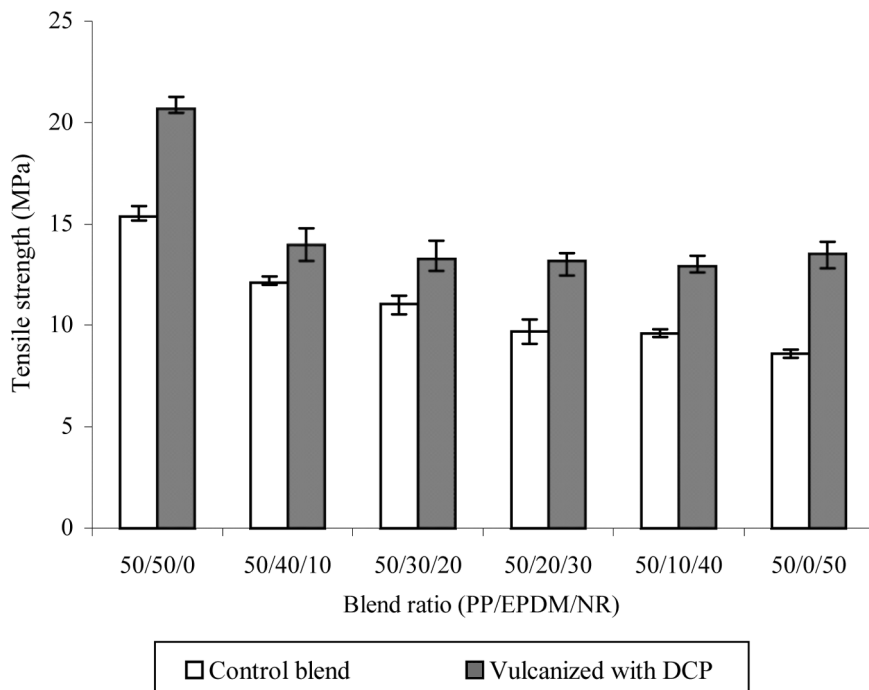
FIGURE 1 Comparison of tensile strength between unvulcanized and DCP vulcanized PP/EPDM/NR blends.

to NR with PP. Therefore, an increase in NR content will disturb the good interaction between PP and EPDM and thus cause a reduction in strength. For dynamic vulcanization with DCP, the tensile strength of each blend composition increases in comparison with the unvulcanized blends. As expected, this is due to the formation of crosslinks. According to Coran [9] and Dluzneski [10], the formation of crosslinks by DCP in unsaturated polymers such as rubber occurred through two mechanisms. One is through radical addition where the radical is transferred to another carbon atom that was part of a double bond in rubber (Figure 2).

The other mechanism is through abstraction, where two radicals come in contact, the two unpaired electrons coupling and forming a covalent bond or crosslink between the polymer chains (Figure 3).

The effect of peroxide vulcanization on the tensile modulus, M_{100} is shown in Figure 4. Tensile modulus of vulcanized blends with DCP is higher compare to the unvulcanized blends. This can again be related to the presence of crosslinks, which produce stiffer blends.
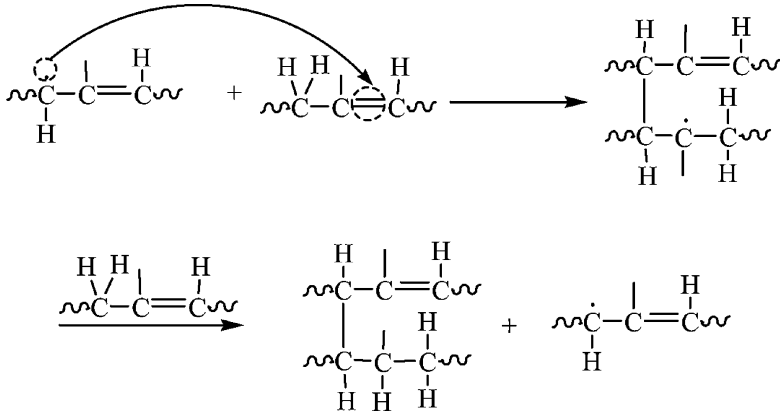
FIGURE 2 Radical addition to double bond in rubber.

Figure 5 shows the effect of crosslinked species on the elongation at break of PP/EPDM/NR blends. The elongation at break in the peroxide vulcanization of 50/50/0, 50/40/10, and 50/30/20 blends (EPDM rich blends) decrease, whereas in the blend rich NR content (50/20/30, 50/10/40, and 50/0/50) the properties increase. The reduction of elongation at break in EPDM rich blend is caused by the chain scission reaction, which is not only occurs in PP but also in EPDM.

Swelling Index

Table 1 depicts the swelling indices of unvulcanized and peroxide vulcanized PP/EPDM/NR blends in toluene and oil, which indicate the chemical and oil resistance, respectively. It can be seen that the swelling index of PP/EPDM/NR blends after immersion in toluene for 12 h increased with increasing NR content. Here, EPDM has a low level of polarity, consisting of carbon and hydrogen atoms with
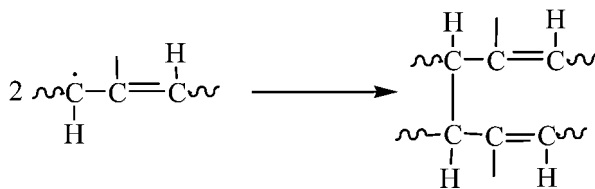

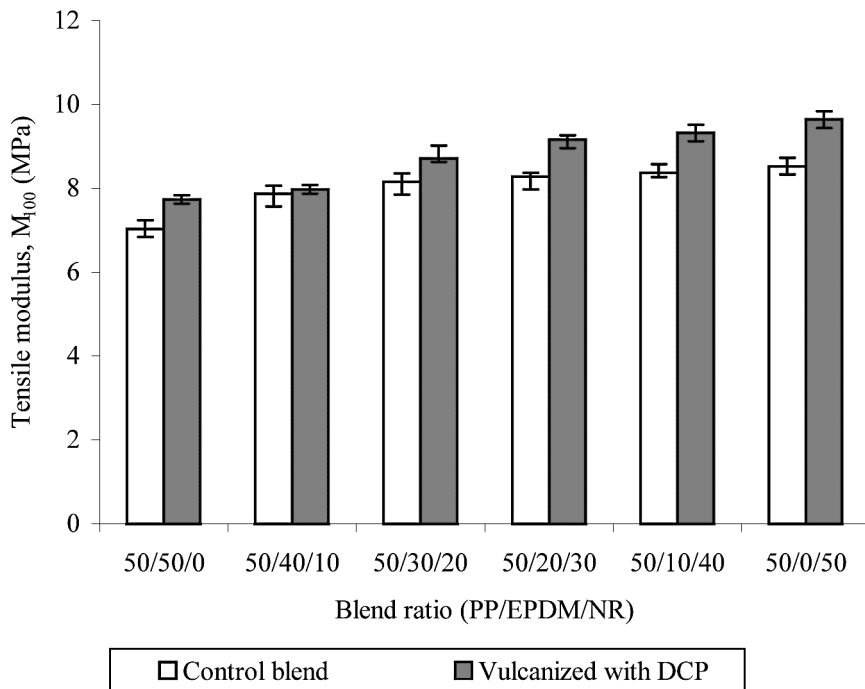**FIGURE 3** Crosslinks formation in rubber.

FIGURE 4 Comparison of tensile modulus (M_{100}) between unvulcanized and DCP vulcanized PP/EPDM/NR blends.

little unsaturation (the main chain has no double bonds) [11]. Compared with NR, which has double bonds in the main chain, EPDM is considered less polar. Therefore, EPDM swells less in toluene (polar liquid) compared with NR, and its blends consequently lead to high chemical resistance.

On the other hand, Table 1 also shows that the swelling index of PP/EPDM/NR blends after immersion in oil IRM 903 increase with increasing NR content. Even though EPDM has lower polarity than NR, it should swell easily in oil (non polar liquid) but due to the good interaction between PP and EPDM, the 50/50/0 PP/EPDM/NR blend possesses higher resistance to oil than those of other blend compositions.

However, the swelling indices of the vulcanized blends with DCP after immersion either in oil or toluene are lower than unvulcanized blends. This indicates that chemical resistance as well as oil resistance of the peroxide vulcanized blends increase in comparison with unvulcanized blend. Here, the crosslinking of the rubber phase has inhibited the penetration of the liquids (toluene and oil) into the blends.
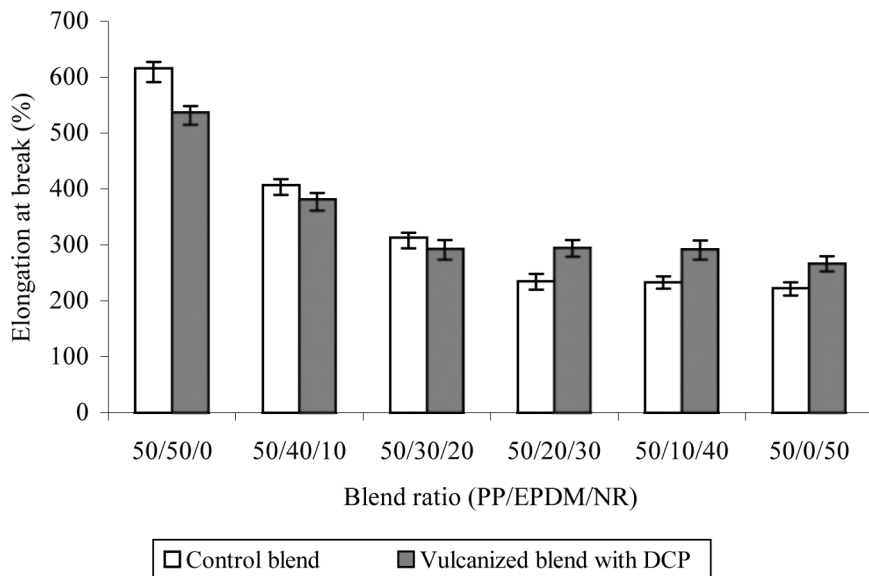
FIGURE 5 Comparison of elongation at break between control and DCP vulcanized of PP/EPDM/NR blends.

Gel Content

The degree of crosslinking of a vulcanized material is usually determined by percentage of gel content as depicted in Table 2. The results show that the introduction of NR into PP/EPDM blend decreases

TABLE 1 Comparison of the Swelling Index Between Unvulcanized and DCP Vulcanized PP/EPDM/NR Blend

Blend ratio (PP/EPDM/NR)	Swelling index			
	Unvulcanized blend		Vulcanized blend	
	Toluene (12 h)	Oil IRM 903 (48 h)	Toluene (12 h)	Oil IRM 903 (48 h)
50/50/0	1.57	1.40	1.34	1.27
50/40/10	1.60	1.45	1.41	1.3
50/30/20	1.69	1.47	1.50	1.35
50/20/30	1.73	1.52	1.55	1.41
50/10/40	1.79	1.52	1.53	1.41
50/0/50	1.86	1.59	1.54	1.40

TABLE 2 Comparison of Gel Content Between Unvulcanized and DCP Vulcanized PP/EPDM/NR Blends

	Gel content (%)	
Blend ratio (PP/EPDM/NR)	Unvulcanized blend	Vulcanized blend
50/50/0	61.2	90.3
50/30/20	57.2	91.1
50/0/50	52.3	92.6

the gel content of the blends. This effect is more pronounced for richer NR blend and indicates that NR is easier to extract by cyclohexane compared with EPDM because of lower interactions between PP and NR. On the other hand, the amount of gel content increases sharply in the peroxide vulcanized blends indicating that crosslinking of rubber has occurred. The crosslinks formation in the rubber phase has restricted the extraction of rubber. This is in agreement with Gaylord et al. [12] who has stated that when the blends were vulcanized with peroxide, the amount of insoluble polymer increased and the soluble polymer had decreased, indicative of crosslinks formation. Further, it is interesting to note that the gel content increases slightly with the NR content. This indicates that the formation of crosslinks in NR phase is more effective than in EPDM phase due to the chain scission in the EPDM rubber during processing.

Morphology Studies

Figure 6a–6c show the scanning electron microscopy (SEM) micrographs of the extracted surfaces of 50/50/0, 50/30/20 and 50/0/50 PP/EPDM/NR blends, respectively. The figures show a large number of voids, indicating the extraction of rubber domain after immersion in n-hexane. This is an indication of heterogeneous phase structure of PP/EPDM/NR blends. Here, the rubber domains are independently dispersed in the PP matrix, thus giving rise to a two-phase system [13–14]. The dispersed domains (holes) are large and inhomogeneous for the unvulcanized blends.

On the other hand, Figure 7a–7c show the PP/EPDM/NR blends that are dynamically vulcanized with peroxide, and reveal the finer morphology of a PP/EPDM/NR blend in which the peroxide was added into the blend. It is obvious that beside the size, the shape of the rubbery particles is also influenced by the peroxide addition. This difference in size influences the tensile properties, because the smaller

Halimatuddahliana et al.
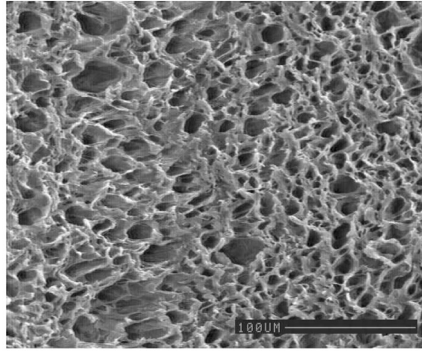
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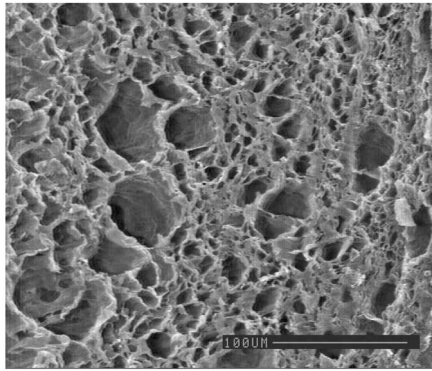
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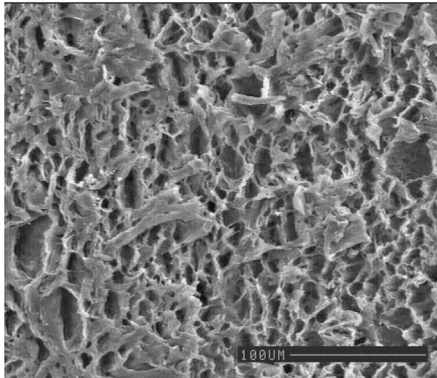
(c)

FIGURE 6 SEM micrographs of the extracted surfaces of unvulcanized PP/EPDM/NR blends a) 50/50/0; b) 50/30/20; c) 50/0/50.

(a)

(b)

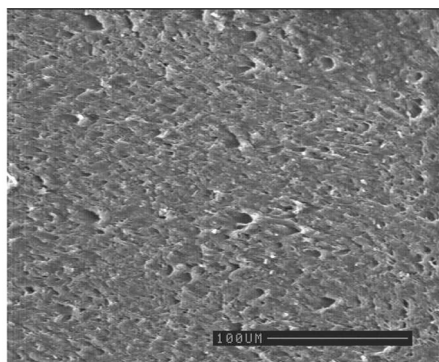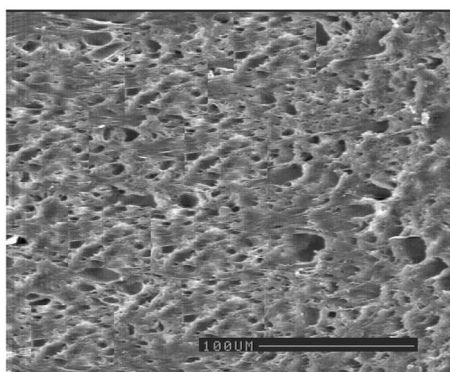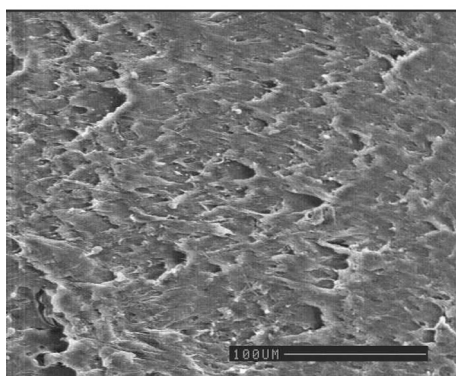(c)

FIGURE 7 SEM micrographs of the extracted surfaces of DCP vulcanized PP/EPDM/NR blends a) 50/50/0; b) 50/30/20; c) 50/0/50.

size tends to transfer stress more efficiently than large size. The presence of crosslinks in the rubber phase limits the flow and mobility of rubber particles. Hence, their coalescence was inhibited. It can also be seen that these domains are hardly extracted by solvent due to the crosslinks. Further, the SEM micrograph of the dynamically vulcanized 50/50/0 blend shows nearly the same morphology as that of the 50/30/20 blend. However, careful inspection in Figure 7a and b indicates that domain size is larger for the 50/30/20 blend than that of 50/50/0 blend. Figure 7c (50/0/50) also shows that the morphological observation are in agreement with the tensile strength of the blend. The system that has improved tensile strength, has a better phase distribution of rubber particles permitting good stress transfer during strain.

According to Sariatpanahi et al. [6], DCP, a well known crosslinking agent has also been used to compatibilize blends containing crosslinkable constituents, through dynamic vulcanization. When blend components have the ability to react with the peroxide in situ, they may form a copolymer interposed at the interface thus improving the interfacial interaction.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

In this work the focus of DSC analysis was limited to study the melting point and crystalline behavior of the blends. It was difficult to detect the T_g of PP, EPDM, or NR from DSC thermograms because the lowest temperature setting of the DSC was 50°C. The area of the melting endotherms was measured as the heat of fusion (ΔH_f). The parameter X_c, determines the percentage of crystallinity. The X_c in this study was calculated by dividing the measured ΔH_f by the ΔH_f of 100% crystalline material. The ΔH_f for polypropylene as a fully crystalline material is 209 J/g [15].

DSC results of the peroxide vulcanized blends as compared with control blends at selected blend compositions are shown in Figure 8. It can be seen that all blend compositions have almost the same pattern of the heating thermogram, where there was no change in the curves with inclusion of NR. Above 50°C the thermal properties of the blends are governed by the crystalline PP/EPDM blend alone because NR is a low T_g amorphous polymer. Therefore, only a marginal change in melting temperature (T_m) and onset temperature (T_o) of PP/EPDM blend was observed with the addition of NR, as can be seen in Table 3.

However, a slight increase of T_o in the 50/30/20 and 50/0/50 PP/EPDM/NR blends clearly indicates that the introduction of NR
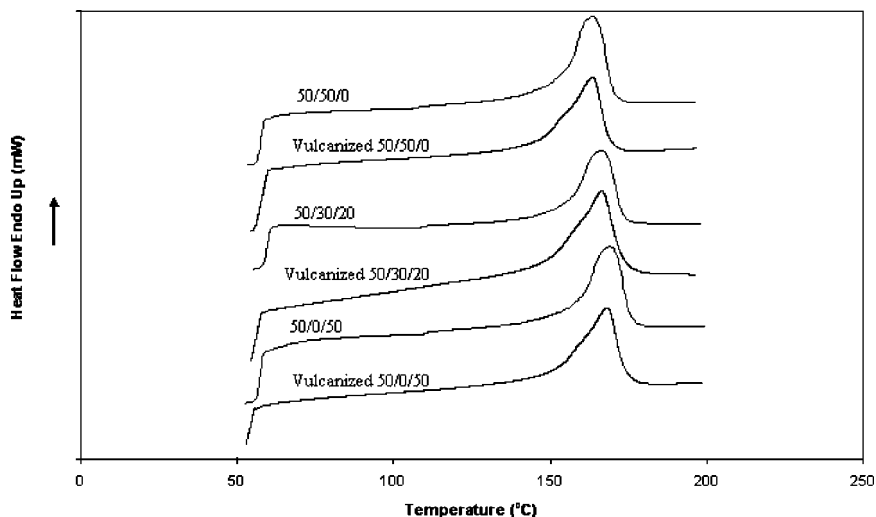
FIGURE 8 The effect of dynamic vulcanization (with DCP) on DSC scans of PP/EPDM/NR blends with different blend composition.

in PP/EPDM results in delayed nucleation and thus imply an increasing heterogeneity in spherulite size. The reduction rate of crystallization in the presence of NR is due to the restricted mobility of the PP/EPDM segments by NR addition.

The broad range of the half PP melting area (from the onset point to the melting point) of the peroxide vulcanized blends indicates that there are small crystals in the systems, some of which melt before the

TABLE 3 Thermal Properties of DCP Vulcanized PP/EPDM/NR Blends as Compared with Unvulcanized Blends Derived from DSC Scan Thermogram

Blend ratio (PP/EPDM/NR)	Onset temperature (T_o) °C	Melting temperature (T_m) °C	Fusion enthalphy (ΔH_f) J/g	% Crystallinity (X_c) %
Unvulcanized blend				
50/50/0	150.7	161.0	42.3	20.24
50/30/20	151.0	162.4	40.5	19.38
50/0/50	152.6	163.7	39.8	19.04
Vulcanized blend				
50/50/0	147.0	159.4	41.5	19.86
50/30/20	150.1	160.3	38.9	18.61
50/0/50	149.2	162.3	36.1	17.25

melting temperature (T_m). The lowered onset temperature (T_o) of PP with peroxide, as can be seen clearly from Table 3, seems to be due to decreased viscosity of PP by main chain scission, allowing the crystallization of PP at lower temperatures.

The melting temperature (T_m) of PP is decreased slightly by the presence of DCP. As can be seen from Table 3, compared with unvulcanized, the vulcanized blend shows slightly lower fusion enthalpy (ΔH_f) and hence percent crystallinity (X_c). It could be due to the degradation of PP by DCP that reduced the crystallinity of PP and the blends. In addition, the reduction in percent crystallinity of vulcanized blend with DCP may also be attributed to the formation of crosslinks in the rubber phase, disturbing the nucleation step. According to Abdel-Bary et al. [16], with the introduction of crosslinks, the C−C bonds that are formed between the molecular chains during crosslinking could further reduce the maximum layer thickness attainable so that no layer thickening is possible following the initial attachment of the polymer chain to the growing crystal because of decreased molecular mobility in the melt. Moreover, the incorporation of crosslinks into the system results in stress along the crystallizing chain, which opposes the incorporation of additional members of the same chain and thereby limits the initial length of the chain that can be incorporated into crystal and/or the extent of the thickening process.

CONCLUSION

Vulcanized PP/EPDM/NR blends with DCP exhibit higher tensile strength and tensile modulus (M_{100}) but lower elongation at break at EPDM-rich content than unvulcanized blends. Vulcanized blends have also shown better chemical and oil resistance. The development of finer vulcanized rubber particles improves the stability of the morphology, which increases the properties of the blends. The percent crystallinity of the PP/EPDM/NR blends has decreased by the DCP vulcanization.

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