

**PROPERTIES OF POLYPROPYLENE/ETHYLENE-PROPYLENE DIENE  
TERPOLYMER/NATURAL RUBBER (PP/EPDM/NR) TERNARY BLEND:  
THE EFFECT OF DYNAMIC VULCANIZATION**

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**ABSTRACT**

This paper discusses the effect of dynamic vulcanization on the process development and some properties such as tensile properties, gel content and morphology of the polypropylene (PP)/ethylene-propylene diene terpolymer (EPDM)/natural rubber (NR) blends. Blends were prepared in several blend compositions in Haake Polydrive with temperature and rotor speed of 180 °C and 50 rpm respectively. Dynamically vulcanized blends show higher stabilization torque than unvulcanized blends counterparts. In term of tensile properties, the tensile strength and tensile modulus (stress at 100% elongation,  $M_{100}$ ) of the vulcanized blends have been found to increase as compared with the unvulcanized blends. However, the elongation at break of the vulcanized blend is higher in the blend EPDM richer content compared with the NR richer content. These results can be attributed to the formation of cross-linking in rubber phase. The improvements in gel content of vulcanized blends have also proved the formation of cross-links in the rubber phase. Scanning electron microscopy (SEM) micrographs from the surface extraction of the blends support that the cross-links have occurred during dynamic vulcanization.

**INTRODUCTION**

Several works have been reported regarding the dynamic vulcanization of TPE especially on the PP/EPDM blends and most of the investigations focused on the processing and the improvements on mechanical and physical properties of the blends (Lopez Manchado & Arroyo, 2001; Sabet et al., 1996; Ellul, 2003; Xiao et al., 2002; Sariatpanahi, 2002). However, replacement of EPDM with NR in PP/EPDM blends has been considered due to the reduction of the cost. It has also been observed that the partial replacement of EPDM by NR decreased the properties of PP/EPDM blends (Halimatuddahlia et al, 2004). Therefore, dynamic vulcanization has been introduced in the PP/EPDM/NR blend to improve the properties such blends.

Dynamic vulcanization has been extensively applied to the vulcanization of the soft elastomer phase of a blend with rigid thermoplastic. The process is carried out under high shear and above the melting point of the thermoplastic at sufficiently high temperature to activate and complete the vulcanization. During dynamic vulcanization of rubbers, the polymeric chains of the base elastomer become interconnected,

converting the viscous gum into an elastic network. In dynamic vulcanization of thermoplastics elastomer, the structure is generated in small rubber particles dispersed in the thermoplastic polymer matrix. Various type of curatives can generally be used in dynamic vulcanized blends such as sulfur, phenolic resin and peroxide.

This paper examines the effect of dynamic vulcanization on the process development and some properties such as tensile properties, chemical and oil resistances and gel content of the PP/EPDM/NR blends along with the accompanying characteristics in the morphology.

## EXPERIMENTAL

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  $M_L(1+4)$  74 at 100 °C was purchased from Luxchem Trading Sdn. Bhd. Natural rubber (NR - HSL), with Mooney viscosity  $M_L(1+4)$  73 at 100 °C was obtained from Hokson Rubber Trading Sdn. Bhd, Seremban. Curatives i.e. 5 phr of zinc oxide (ZnO); 1.5 phr of stearic acid; 1 phr of N-cyclohexyl-2-benzothiazol sulfenamide (CBS), 0.4 phr of antioxidant and curing agent i.e. 2 phr of sulfur were industrial grade chemicals from Bayer (M) Sdn. Bhd.

Studies were conducted on PP/EPDM/NR blends consist of two systems viz. unvulcanized blend and vulcanized blend where each blend covering different blend compositions viz. 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, thermoplastic (PP) were first loaded into the internal mixer and pre-mixing for two minutes and followed by the rubbers (EPDM and NR). For unvulcanized, the blends were taken out after 6 minutes of mixing. The corresponding dynamic vulcanization blends were prepared in the same manner except that the curatives were added after 5 minutes of mixing and followed by sulfur at 7 minutes, the mixing time was prolonged until 10 minutes. The samples were then sheeted by passing through 2 roll-mill and allowed to cool at room temperature.

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

Tensile tests were carried out according to ASTM D412 on Instron Machine. 2 mm thick dumbbell specimens were cut from the moulded 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 were quoted based on the average value of five specimens tested for each blend system.

The degree of cross-linking in the rubber was measured after extraction in boiling cyclohexane for 8 hrs. The samples were dried at 80 °C for 30 minutes and subsequently weighed. The percentage of gel content of the blends was then calculated as follow:

$$\% \text{ gel content} = \frac{W_g}{W_o} \times 100\%$$

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

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 finally dried to remove excessive 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 hrs of preparation.

## RESULTS AND DISCUSSION

The plastograms of sulfur vulcanized blends as compared to unvulcanized blends of PP/EPDM/NR blend with 50/50/0, 50/30/20 and 50/0/50 blend compositions are shown in Figure 1. In sulfur vulcanization, curing ingredients minus sulfur were added at 5th minute while sulfur was added at 7th minute of mixing. The torque starts to rise after 7th minute at which sulfur is added and stabilize at higher values than corresponding unvulcanized blends.

The raised torque values of sulfur vulcanized blends over that of unvulcanized blends indirectly indicate the increasing melt viscosity at the processing temperature. This indicates that curing was occurred. As cross-links are formed in the rubber phase, intermolecular slippage is restricted and the deformability of the rubber particles is decreased (George et al., 2000). Consequently, melt viscosity of the blends increases requiring a higher energy requirement for the melt processing of sulfur vulcanized blends than the control counterparts.

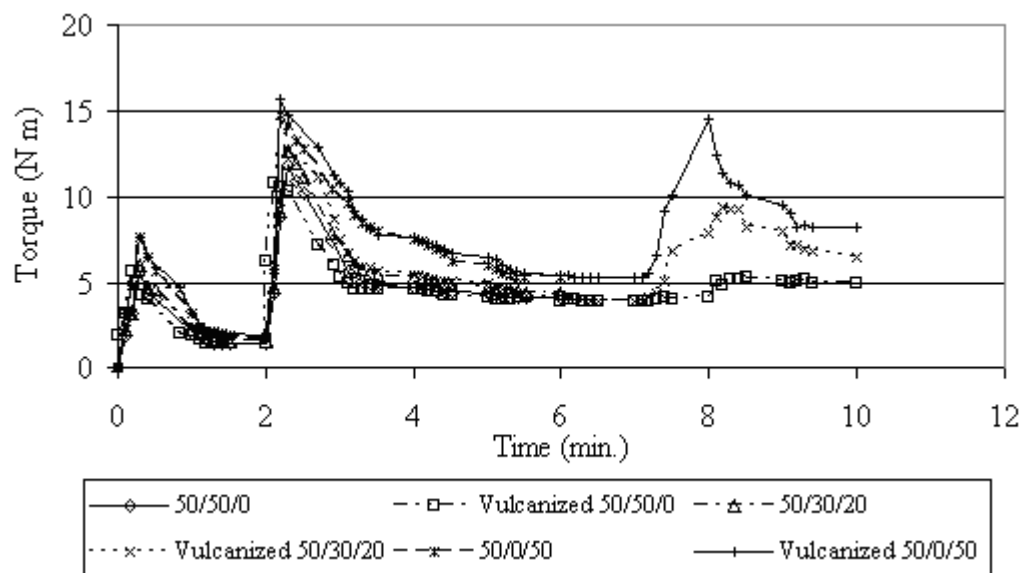


Figure 1: The effect of dynamic vulcanization on torque-time curve obtained during blending of PP/EPDM/NR

Further, they show an increasing a torque values as the NR content increase. As can be seen from the Figure 1, the increase in the torque with increasing NR content is an evident that the high cross-link formation was occurred more on the NR phase than on the EPDM phase. This behavior may be explained as follow; incorporation of NR involves with simultaneous replacement of a portion of cross-linkable EPDM in the blend. Consequently, the unsaturated bonds for formation of cross-link were increased, which are prepared by NR. EPDM, being copolymer of two olefin monomers (ethylene and propylene), is partially saturated elastomer; thus it is less cross-linked by the accelerated-sulfur cure systems, which is commonly employed in the vulcanization of NR. However, as mentioned above, interaction between NR and PP is weaker than PP and EPDM. Therefore, the increasing viscosity with increasing NR content and hence cross-link density may not be followed considerably with the tensile properties which will be discussed next.

It is also worth noting that on the vulcanized blend without NR content (50/50/0 PP/EPDM/NR) the torque did not increase significantly. This could be due to the type of the EPDM had been used, which contains oil extended. This allows the preparation of softer compositions with significant improvement in processability. In the melt, the oil partitions between the phases and greatly lowers the viscosity, resulting in improved processing. In addition, the oil expands the volume fraction of the solid cross-link rubber phase, resulting on improvement of processability (Sabet et al., 1996).

The comparison of stabilization torque values between sulfur vulcanized blends with unvulcanized blends are presented as a function of blend compositions in Figure 2.

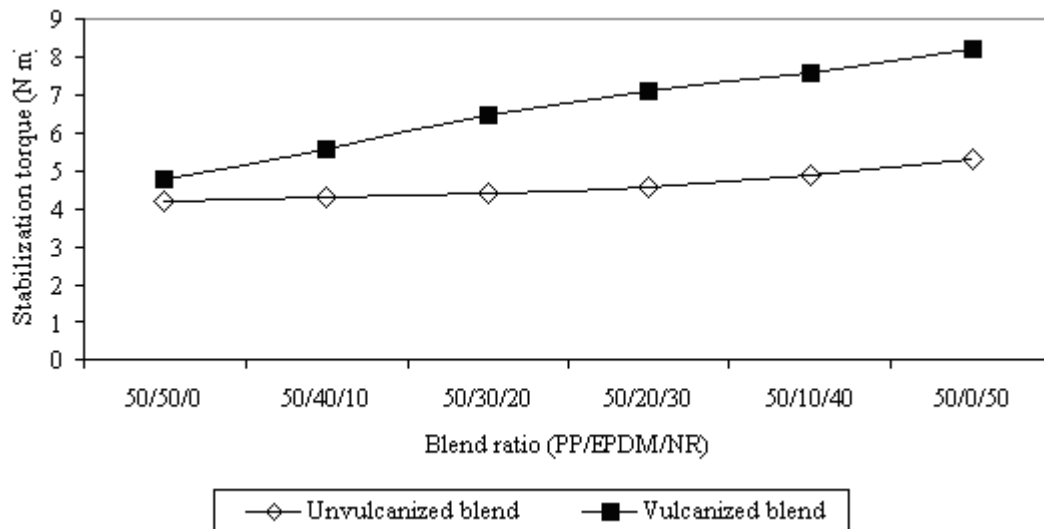


Figure 2: Comparison of stabilization torque between unvulcanized and vulcanized PP/EPDM/NR blends

It can be seen that the stabilization torque increased as NR content increase for both vulcanized and unvulcanized blends. When the NR present as an additional dispersed phase in PP phase, an unstable melt of blends could be expected as the PP become insufficient to provide a melt flow. As more NR particles are present in the PP continuous phase the amount of rubber particles, which can be exist as dispersed phase become more and consequently, the raised stabilization torque becomes higher.

Further, it shows that the stabilization torque of dynamically vulcanized blend lies above control blend for every blend composition. During mixing, the vulcanized molecules chains could not be easily deformed by shearing action of the rotor dealing with increasing on power requirement and enhances the frictional resistance of the blend again deformation (Coran & Patel, 1980). This increment in cross-link density increases the melt viscosity and hence the stabilization torques.

The effect of dynamic vulcanization on tensile strength, tensile modulus ( $M_{100}$ ) and elongation at break of PP/EPDM/NR blend as compared with the unvulcanized blends are presented in Figures 3, 4 and 5 respectively. It is clear from the results that the dynamic vulcanization process has significantly enhanced the tensile strength over unvulcanized blends as can be seen in Figure 3.

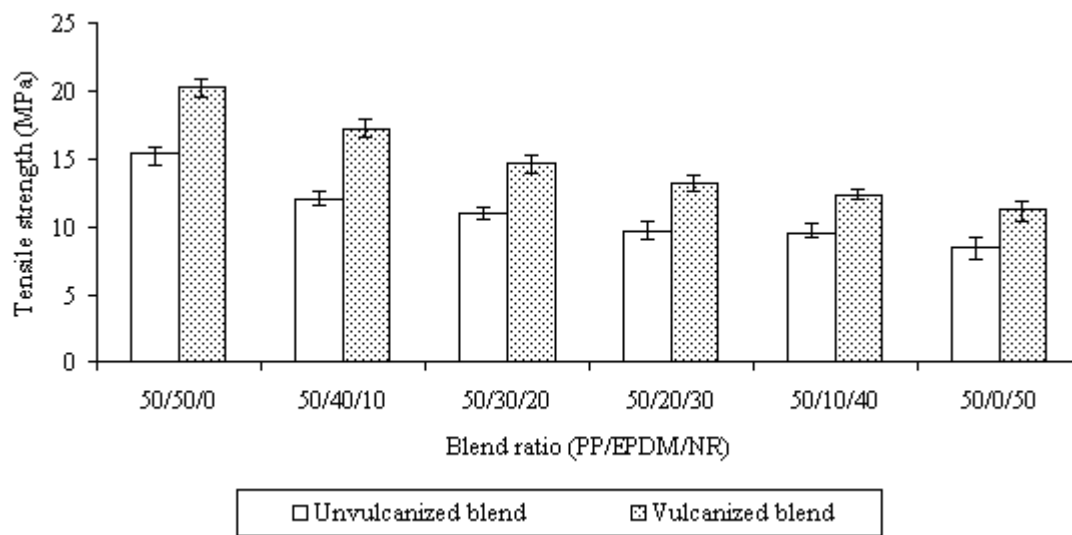


Figure 3: Comparison of tensile strength between unvulcanized and vulcanized PP/EPDM/NR blends

The enhancement of tensile strength by dynamic vulcanization is well explained in the literature of elastomer/plastic blends (Jain et al., 2000; Saroop & Mathur, 1997). Formation of cross-links in the elastomer phase facilitating stress transfer is the clear factor contributing to such enhancement. This enhancement is a result of many factors. Firstly, cross-linking increases the molecular entanglements and form a network structure resulting in an enhancement in stress transfer between phases. Secondly, under shear, the particle size of vulcanized rubber decreased, so the smaller the rubber particle size the higher the tensile properties are. Thirdly, the particles distribute more uniformly in the matrix and therefore, stress can be transferred to the material more effectively. Finally the dynamic vulcanization of rubber component restricts the rubber particles coalescence and improved the properties subsequently. Similar synergism in tensile strength of dynamically vulcanized PP/EPDM blends has been observed from studies reported by Coran & Patel (1980).

In tensile strength, the sulfur vulcanized blend has more pronounced effect in the EPDM richer blends over NR richer blends. This implies the formation of cross-links is not the only factor that governs this improvement. The dynamic vulcanization, which has resulted cross-link in the rubber phase and more pronounced on the NR rich blend is not indicated this possibility. The good interactions between PP-EPDM over PP-NR contribute to enhanced tensile properties. As the NR content was increased, the number of good interfaces regions available in the blends was decreased. This indicates that the interfacial adhesion between components plays an important role in achieving enhanced properties. The deterioration of tensile strength of the blend richer NR content indicates the less capability of vulcanized NR particles to support transfer of stress from the polymer matrix to the particles.

The effect of dynamic vulcanization on the tensile modulus ( $M_{100}$ ) of PP/EPDM/NR blend as compared to the unvulcanized blends is shown in Figure 4.

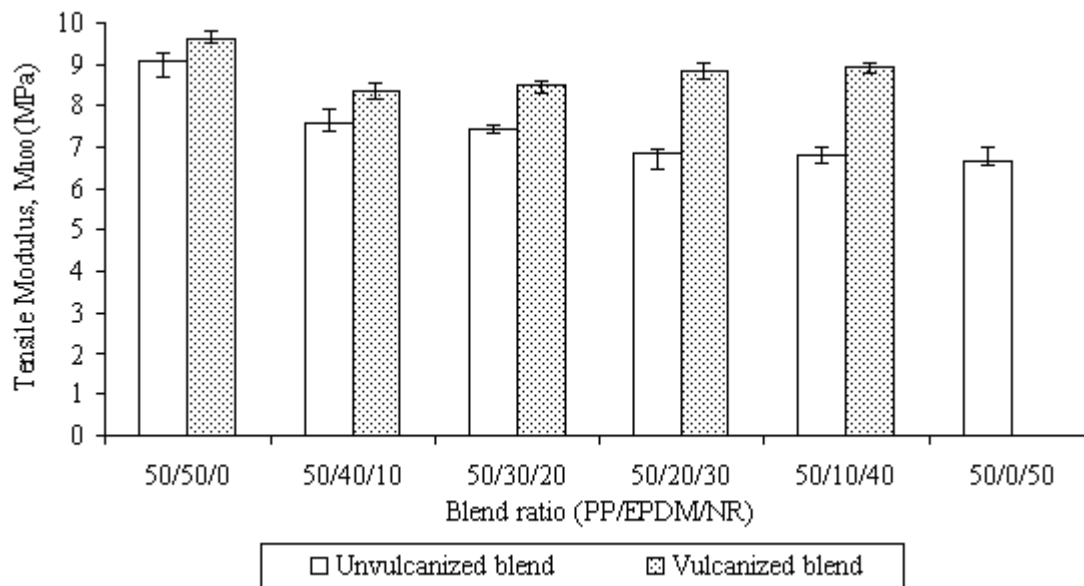


Figure 4: Comparison of tensile modulus ( $M_{100}$ ) between unvulcanized and vulcanized PP/EPDM/NR blends

The tensile modulus ( $M_{100}$ ) register a marked improvement with the dynamic vulcanization, which is proves the progressive development in cross-linking. This behavior is easily attributed to the increased strength in the rubber regions due to the cross-linking. This improvement is due to entanglements in the rubber phase owing to cross-linking and the implication is that increasing the stiffness of the blend. Here, vulcanized blends could not resist the deformability of the macromolecules hence increasing the  $M_{100}$ . However,  $M_{100}$  of 50/0/50 PP/EPDM/NR vulcanized blend is not reported as it rupture before 100% elongation at break is achieved.

Figure 6 shows the comparison of elongation at break between unvulcanized and sulfur vulcanized PP/EPDM/NR blends. It can be seen that vulcanized blends show higher elongation at break in EPDM richer blend. The elongation at break of the sulfur vulcanized blend containing richer NR show an inverse relation with the EPDM rich blend. It shows that dynamically vulcanized blend is lower than the unvulcanized one and decreases gradually as the NR has taken the dominant content over EPDM until minimum value is attained (at 50/0/50 blend). This indicates that the vulcanized rubber phase does not significantly increase the initial resistance to the deformation of the macromolecules in the NR richer blend. The reason should be as follows; although NR content increases, the chemical cross-linking of rubber restricts mobility of the polymer chain. In addition, when the NR content is high, vulcanized NR particles may exist mostly in the continuous phase resulting significant resistance to the deformation of macromolecules. This will narrow down the effect of rubber on the elongation at break. In addition, the number of poor interfaces regions available in the blends and lack in interfacial adhesion may be affect the elongation at break.

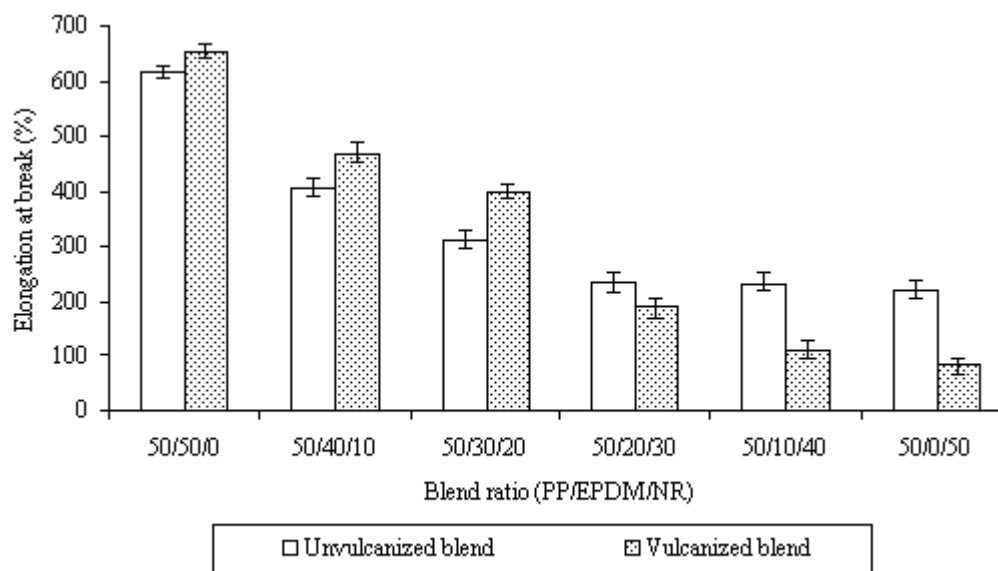


Figure 6: Comparison of elongation at break between unvulcanized and vulcanized PP/EPDM/NR blends

The effect of dynamic vulcanization on the percent gel contents of PP/EPDM/NR blend with respect to the unvulcanized blends is depicted in Table 1.

Table 1: Gel content of selected dynamically vulcanized PP/EPDM/NR blends as compared with unvulcanized blends.

Blend Ratio (PP/EPDM/NR)	Gel content (%)	
	Unvulcanized blend	Vulcanization with sulfur
50/50/0	61.2	89.2
50/30/20	57.2	86.6
50/0/50	52.3	83.0

The results show that dynamic vulcanization process gives rise to a sensible increase in gel content as well as a considerable reduction of the percent of extractable elastomer by cyclohexane with respect to the corresponding unvulcanized blends. A higher gel content means that there were less main chains have extracted, which can be attributed to the cross-links formation. During cross-linking reaction, the average molecular weight of the chain increases thus causing the sample to become gradually insoluble in solvent.



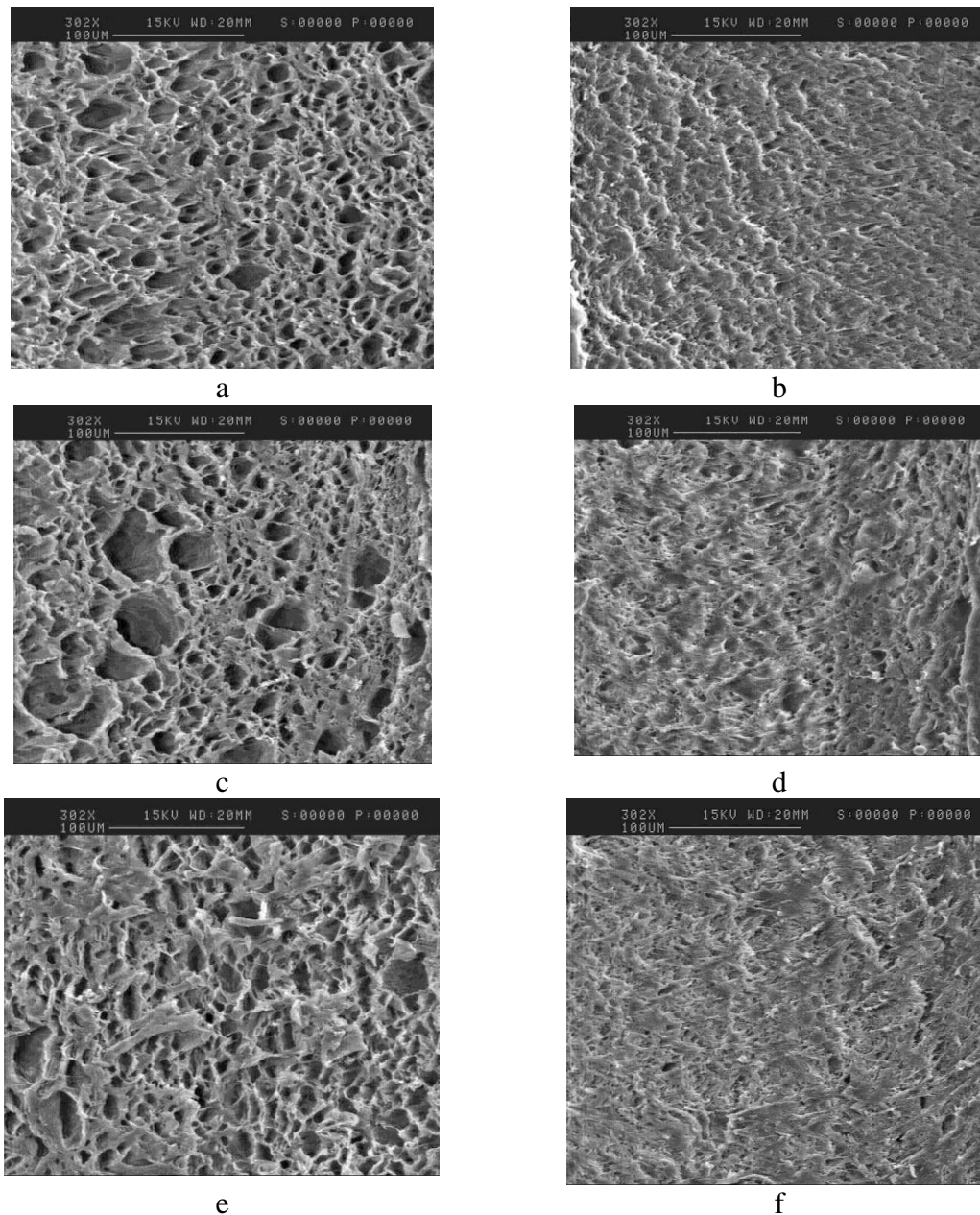


Figure 7: SEM micrographs of extracted PP/EPDM/NR blends; a. 50/50/0; b. 50/50/0 vulcanized blend; c. 50/30/20; d. 50/30/20 vulcanized blend; e. 50/0/50; f. 50/0/50 vulcanized blend

Figure 7 (a-f) presents the SEM micrographs of extracted selected PP/EPDM/NR blends for both dynamic vulcanized and unvulcanized blends. It can be seen that upon extraction, the rubber particles of vulcanized blends (Figs. 7b, d and f) were not easily extracted from the continuous phase. These nature micrographs reveal that the blends achieved vulcanized elastomeric properties due to the formation of crosslinks. Simultaneously, the holes in the vulcanized blends less obvious than those of

unvulcanized blends and the dispersibility of rubbers in PP matrix are markedly improved. Holes of smaller and more uniform in size can be obtained. Here, during dynamic vulcanization process, a stable domain morphology of vulcanized particles is obtained and consequently produce better blend properties.

The micrographs show the vulcanized rubber particles are dispersed in continuous phase of PP. This could be attributed to the immobilization of the rubber particles by cross-linking and therefore breaking down to small size under the applied shear field (Crevecoeur et al., 1995). According to Sabet et al., (1996), during dynamic vulcanization of TPE, the rubbers and the thermoplastic have undergo a phase inversion to maintain the thermoplasticity of the blend. In the initial stage of dynamic vulcanization, two co-continuous phase are generated and as the degree of cross-linking advances while mixing the continuous rubber phase become elongated further and further and then breaks up into polymer droplets. As these rubber particles are forming as droplets, the PP becomes continuous phase.

## CONCLUSION

Dynamically vulcanized PP/EPDM/NR blend exhibits higher stabilization torque, tensile strength and tensile modulus ( $M_{100}$ ), gel content but lower elongation at break at EPDM rich content than unvulcanized blends. The development of finer vulcanized rubber particles due to the cross-links formation improves stability of the morphology, which is increase the properties of the blends.

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