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Properties of NR/EPDM Blends with or without Methyl Methacrylate-Butadiene-Styrene (MBS) as a Compatibilizer

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Abstract

Ethylene propylene diene monomer rubber (EPDM) is an excellent rubber for outdoor use. Natural rubber (NR) containing EPDM may show improved weathering resistance. EPDM was blended with natural rubber with various blend ratios, after which the processing, cure characteristics, and mechanical properties of the NR/EPDM blends were determined. The results of the experiments show that the tensile strength of the blends progressively decreased with an increased amount of EPDM. The morphology of NR/EPDM blends was investigated by scanning electron microscopy. The heat and weathering resistance of the NR/EPDM blends were determined in terms of tensile properties of the blends with various blend ratios. The results showed that with the incorporation of EPDM, the blends possessed better stable tensile strength against thermal and weathering aging than NR rich blends. The effect of methyl methacrylate-butadiene-styrene (MBS) as a compatibilizer in a 50/50 NR/EPDM blend on the blend properties has been studied in detail. The addition of the compatibilizer improved the compatibility of the NR/EPDM blends.

Keywords: Ethylene propylene diene monomer rubber (EPDM), Natural rubber (NR), Blend, Graft copolymer

1. Introduction

In the manufacture of rubber products, the blending of rubbers produces new materials with a wide range of applications because they have the potential to combine the attractive properties of both the constituents in the blend, when compared with the economical and technical uncertainties associated with synthesizing new polymeric materials. EPDM is obtained by polymerizing ethylene and propylene with a small amount of a nonconjugated diene, which usually imparts good aging characteristics, good weathering oxidation, and chemical resistance. Usually, the outdoor properties of high diene rubbers such as polybutadiene (BR), nitrile rubber (NBR), styrene-butadiene rubber (SBR) or natural rubber (NR) can be very significantly improved by the) incorporation of low-unsaturated rubbers such as ethylene propylene diene monomer (EPDM rubber [1-11]. Among several high diene rubbers, natural rubber is a natural biosynthesis polymer having an attractive range of properties, which possesses excellent physical properties and good

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processing characteristics; however it is not so good with respect to heat and UV resistance. Therefore, blending of NR with EPDM is a useful approach for the preparation of new rubber materials with better aging resistance. This blend may provide a kind of rubber-rubber mixture, which may become technologically important as it combines the excellent outdoor properties of EPDM and the good elastic properties of NR [12-16]. Although blending looks very attractive; most of the rubber blends are immiscible and incompatible, thus resulting in poor mechanical properties. In the case of rubber blends, the incompatibility is not only due to the poor adhesion between the phases but also to the difference in cure rate. Many studies have dealt with the relationships between morphology, processing, and the physical, rheological and mechanical properties of incompatible blends. Suma et al. [2] reported that the effect of precuring the slower curing rubber (EPDM in NR/EPDM) as a possible route to attain a covulcanized state in NR/EPDM, thus resulting in an improvement of the mechanical properties. Botros and Sayed [4] investigated the effect of different blend compositions of NR/EPDM on the swelling behavior of the blend in motor oil under compression strain. A number of reports have appeared on improving the poor compatibility of EPDM with high diene content rubbers; such as the modification of EPDM with maleic anhydride (MA) as a compatibilizer for NR/EPDM, [5] the use of functionalization of EPDM with mercapto groups as a compatibilizing agent in NBR/EPDM blends [6], NR/EPDM blends [7] and brominated EPDM blends with NR [8]. All of these blends showed improved compatibility and rheological mechanical properties. Another method is to add a third component compatibilizer, which increases the interaction between immiscible phases; for example, the addition of *trans*-polyoctylene rubber (TOR), acting as a processing aid and also a compatibilizing agent which has improved the compatibility of NR/EPDM blends [9]. Go and Ha [10] reported that EPDM and BR were incompatible and the addition of a mixture of aliphatic and aromatic hydrocarbon resins (AAHR) was very effective in plasticizing an EPDM blend and in enhancing the compatibility between EPDM and BR. Also, the incorporation of bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) into EPDM before being mixed with NR improves the ultimate properties of the blends [11]. Singh et al. [17] have studied EDPM/PVC rubber blends, compatibilized by the addition of methyl methacrylate grafted EPDM rubber. It has been reported that graft copolymers widely used as compatibilizing agents, usually enhance interfacial interaction in polymer blends, thus improving their mechanical properties [18-19]. Based on this principle we have started to investigate graft copolymers as compatibilizing agents for natural rubber blends.

In the present research, the effect of NR/EPDM blend ratio on the Mooney viscosity, cure characteristics, and mechanical properties was investigated. The morphology of the NR/EPDM blends was also studied by Scanning Electron Microscopy (SEM). The heat and weathering resistance were determined in terms of the tensile properties, over a range of blend ratios. Rubber blends were mixed with graft copolymer to improve their processability and mechanical properties. Results on effects of a compatibilizer, methyl methacrylate-butadiene-styrene (MBS) graft copolymer, on the properties of 50/50 NR/EPDM blends were also included in this study.

2. Experimental

2.1 Materials

Rubber

NR: Natural rubber (STR 5 L) was supplied by Siamese Rubber Co., Ltd.

EPDM: The EPDM rubber used in the study was Royalene 521 (Uniroyal Chemical Company). It has an ethylene/propylene ratio of 52/48.

Compatibilizer

Graft copolymer (methacrylate-butadiene-styrene, MBS) supplied by Thai Plastic and Chemicals Co. Ltd. was characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectrum of this graft copolymer (Figure 1) shows several characteristic peaks attributed to C=C stretching of butadiene, C=O stretching of ester groups of methyl methacrylate, and the monosubstituted benzene ring of styrene at wavenumbers of 1640, 1732, and 698 cm^{-1}, respectively. This provides evidence that the graft copolymer was formed during the grafting of styrene and methyl methacrylate grafted onto the butadiene backbone.

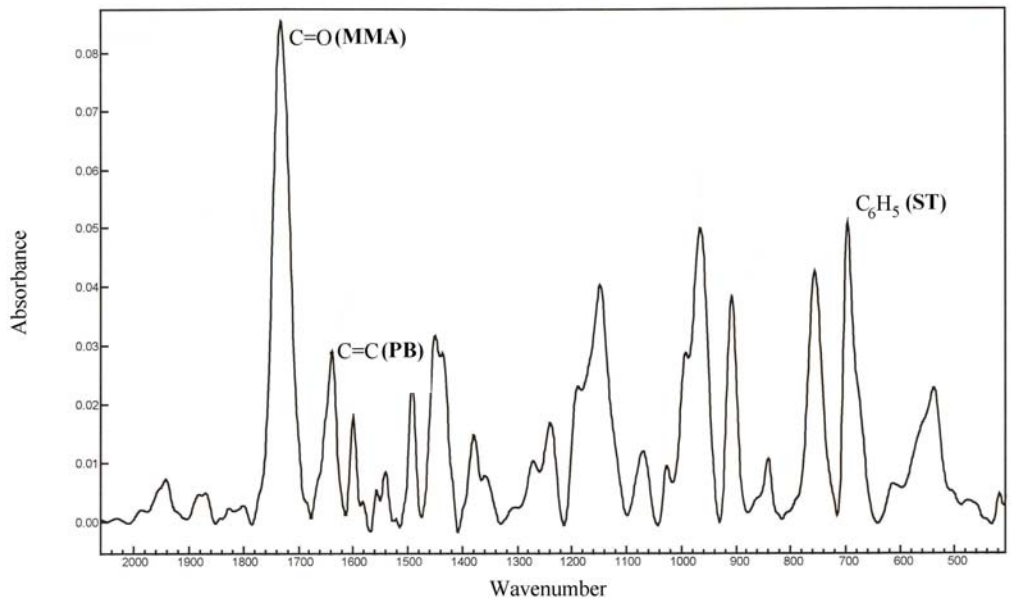


Fig. 1 FTIR spectrum of graft copolymer

Rubber Additives

The stearic acid, zinc oxide (ZnO), and sulfur (S), dibenzthiazyl disulfide (MBTS), mercaptobenzothiazole (MBT) and tetramethylthiuram disulphide (TMTD) were commercial grade as used in the rubber industry. All Chemicals were used as received

2.2 Preparation of NR/EPDM blends

The preparation of NR/EPDM blends was carried out in an internal mixer using conventional mixing procedures involving two stages: in the first stage, the mixing was carried out in a dispersion kneader machine with a fill factor of 0.7, at a chamber temperature of 75°C and a rotor speed of 40 rpm. NR was initially masticated in the mixer for 3 min. EPDM was mixed then followed by addition of the activators (zinc oxide and stearic acid) and accelerators. The blends were referred to as N_{100}, N_{75}, N_{50}, N_{25}, and N_0, where the subscripts denote the wt% of the rubber. Finally, the graft copolymer was added and blended. The 50/50 NR/EPDM blend with 5, 10, and 15 phr graft copolymer are denoted as $5N_{50}$, $10N_{50}$ and $15N_{50}$, respectively. In the second stage, completely vulcanized compounds were prepared by the addition of sulfur using a laboratory-sized two-roll mill at 70°C for 5 min. Table 1 shows the blend formulation used in this study.

Table 1 Formulation of Blend Compounds

Ingredient	phr[a]							
	N_{100}	N_{75}	N_{50}	N_{25}	N_0	$5N_{50}$	$10N_{50}$	$15N_{50}$
NR (STR 5L)	100	75	50	25	0	50	50	50
EPDM	0	25	50	75	100	50	50	50
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
MBT (mercaptobenzothiazole)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD (tetramethylthiuram disulfide)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBS (methyl methacrylate-butadiene-styrene)	0	0	0	0	0	5	10	15

[a] phr, parts per hundred of rubber

2.3 Cure Characteristic

Cure characteristics were studied using a rheometer (TECH-PRO) according to ISO 3414 method for 30 min at 150°C. The Mooney viscosity (ML1 + 4@100°C) was determined by using a Mooney viscometer (TECH-PRO). The testing procedure was conducted according to the method described in ISO 289-1.

2.4 Vulcanization Process

All compounds were compression molded at 150°C with a force of 17.5 MPa using a hydraulic hot press according to their respective cure time, $t_{90,}$ determined with a TECH-PRO viscometer. Blends were conditioned for 24 h before testing.

2.5 Mechanical Properties

Tensile Properties were determined using an Instron Testing Instrument (Model 1011) on C-type Dumbbell-specimens, according to ASTM D 412.

2.6 Accelerated Thermal Aging Test

Tensile specimens were aged at 100°C for 22 h in air-circulating aging oven and the tensile properties of the aged samples were determined using ASTM D573 (1994).

2.7 Accelerated Weathering Test

Tensile specimens were tested in the Q-U-V Accelerated Weathering Tester by exposing them to alternating cycles of light, using an UV lamp with 315 nm wavelength and 0.63 $W/m^2/nm$ intensity at 60°C/4 h, and moisture, condensation at 50°C/4 h, for 7 days according to ASTM G 154-00a.

2.8 Scanning Electron Microscopy

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples in a Joel Microscope (model JSM 5600 LV) at a magnification of 5000.

3. Results and Discussion

3.1 Processability and Cure Characteristics of NR/EPDM Blends

The Mooney Viscosity of the NR/EPDM uncured blends were determined and plotted vs. the NR/EDPM blending ratios as shown in Figure 2. It was observed that the Mooney viscosity decreased with 25/75 NR/EPDM blend ratio and then increased for a mix containing only the EDPM polymer (0/100 NR/EPDM). NR exhibits higher viscosity than EPDM. The incompatible blends were characterized by a sharp interface and poor interaction between the two phases, resulting in interlayer slip between phases. This gives rise to a reduction in the viscosity of the blend.

Figure 2 also represents the optimum cure time (t_{90}) of various blend ratios vulcanized for their optimum cure time. The increase in the optimum cure time (t_{c90}) with increasing EPDM is sharp beyond the 50/50 NR/EDPM blend ratio. Concerning the cure rate, NR rich blends showed lower cure rates than the EPDM rich blends. The increase in cure time can be attributed to the low efficiency of EPDM when vulcanized with the sulfur system, since EPDM has a comparatively low diene content. Blends of rubbers, having similar cure rate exhibit almost additive properties, but dissimilar rubbers result in blends with inferior properties.

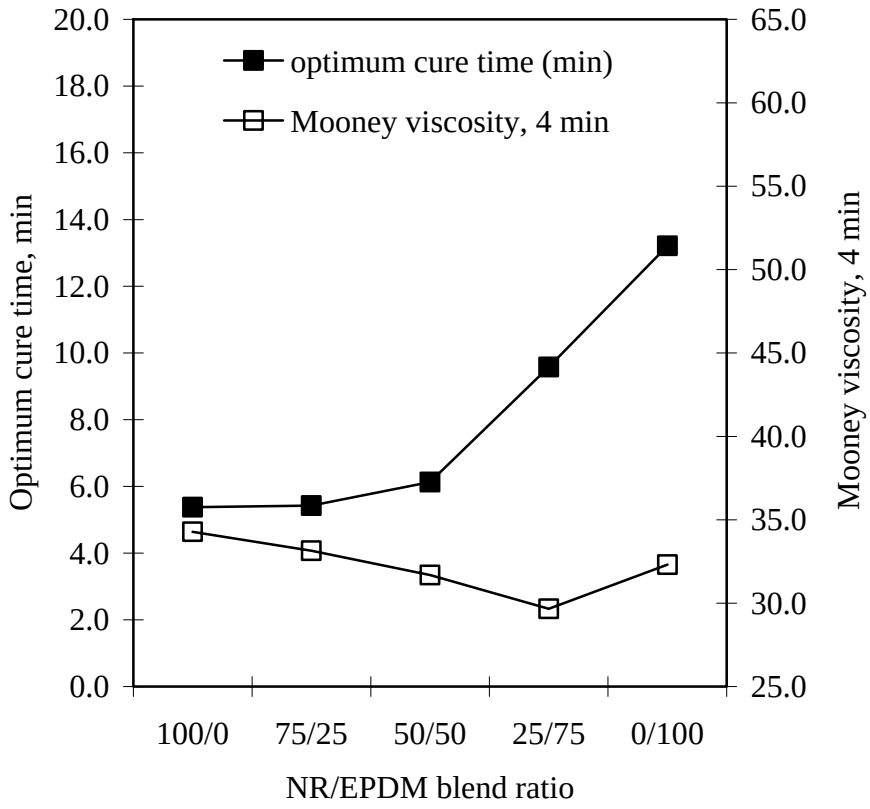


Fig. 2 Mooney Viscosity of the NR/EPDM uncured blend VS NR/EDPM blend ratio

3.2 Mechanical Properties of Natural Rubber Compounds

The tensile strength is an important characteristic of polymeric material because it indicates the

limit of final stress for most applications. Figure 3 shows tensile properties of such materials at various blending ratios. In general, the tensile strength and elongation at break are reduced as the EPDM contents increase. As expected, the tensile strength decreased sharply for a 75/25 NR/EDPM blending ratio, beyond which the tensile strength did not vary greatly. Tensile strength of these binary blends is primarily dependent on the EPDM content in the blend. Binary blends of NR and EPDM were incompatible and showed poor interfacial adhesion, thus resulting in poor strength properties. In addition, the trend of the results for elongation at break is similar to those for the tensile strength. The elongation at break decreased with increasing proportion of EPDM. It is clear that the NR rich blends possessed the highest tensile strength and elongation at break as expected, due to the NR crystallinity exhibited upon stretching. However, the lowest tensile strength and elongation at break was shown by EPDM rich blends. As discussed earlier for incompatible blends, the difference in unsaturation level between NR and EPDM results in a maldistribution in the blend system. This may indicate the poor interfacial adhesion among the constituent elastomers of the blend, thus leading to the formation of blends that exhibit lower tensile strength and elongation at break. These results agree with those found by Botros [5] in his studies concerning NR/EPDM blends.

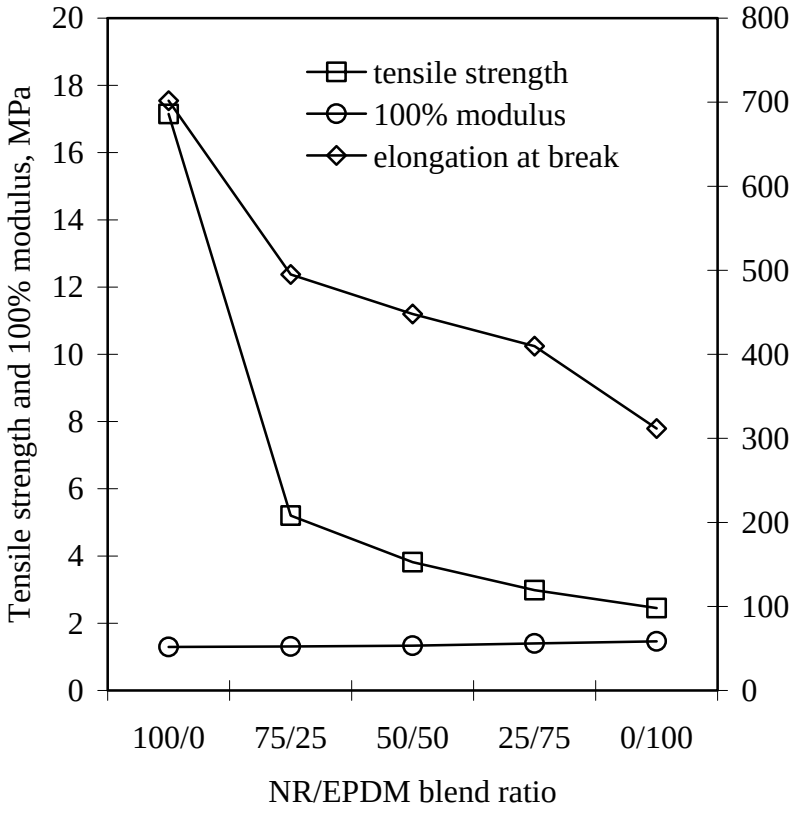
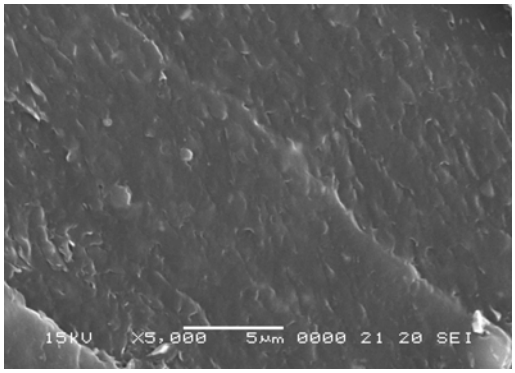


Fig. 3 Tensile strength and 100% modulus VS NR/EPDM blend ratio

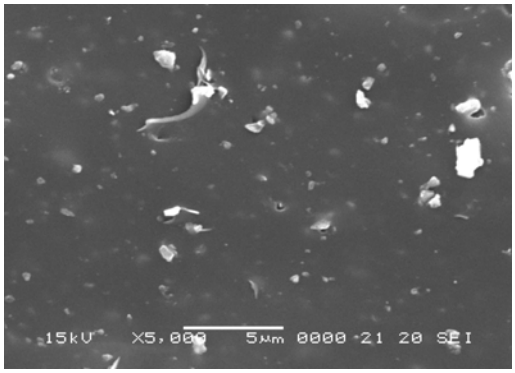
Modulus is an indication of the relative stiffness of the material. Figure 3 shows that 100% modulus of the blends increased marginally as the proportion of EPDM in the blend increases. It can be seen that the incorporation of the EPDM in the blends reduced the stiffness of the blends. As more EPDM is introduced into NR, the elasticity of the NR chains is reduced, resulting in higher rigid properties.

3.3 Morphology

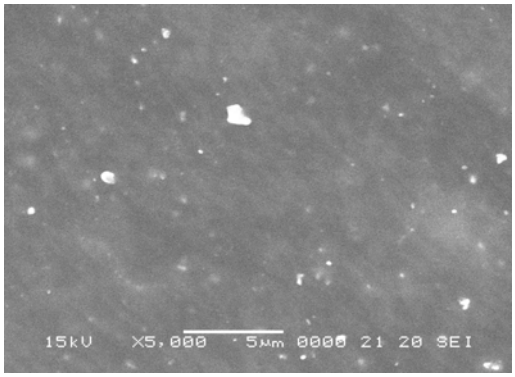
The morphology of the NR, EPDM, and 50/50 NR/EPDM rubber blend after tensile fracture is shown in Figure 4. The natural rubber present is identified as fibrils, and the introduction of long fibrils has been related to the ductility of the material which indicates the higher tensile strength of natural rubber materials (Figure 4a). A brittle fracture is observed in the case of EDPM with the surface showing microcharacteristics typical of a rigid and glassy surface. The EDPM matrix is relatively smooth, suggesting brittle failure (Figure 4b). As can be seen, the fractured surface of the 50/50 NR/EPDM rubber blend becomes relatively rough when an amount of EPDM is added into the blend (Figure 4c). The incorporation of EPDM in the NR changed the failure surface from a ductile to brittle type as evidenced by the absence of fibrils on the fracture surface. Consequently, the tensile strength is also low as shown by the experiments (compare to the NR rich blend).



(a)



(b)



(c)

Fig. 4 Morphology of the NR, EPDM, and 50/50 NR/EPDM rubber blend after tensile fracture

3.4 The Effect of Thermal and Weather Aging

Figure 5-7 show the influence of thermal and weather aging on the mechanical properties of NR/EPDM blends as a function of blending ratio. Regardless of their composition, all of the blends showed negative change in tensile strength, indicating a deterioration of this property with

thermal and weather aging. The reduction of tensile strength was due to degradation of NR matrixes in the blends. As shown in Figure 5, the NR rich blends were affected more by heat and artificial weathering than the EPDM rich blends, as expected. It can be seen that after thermal and weather aging, the tensile strength of NR rich blends decreased dramatically while EPDM rich blends showed no significant change of tensile strength compared to NR and the other blend ratios, after exposure to thermal and weather aging. The tensile strength of blends with the incorporation of EPDM, after aging, showed a small decrease compared to the NR rich blends. This indicates that the ability of EPDM to stabilize against aging. In addition, the trend of the results of elongation at break, after aging, is almost similar to those of tensile strength. The elongation (%) at break (Figure 6) of NR rich blends greatly decreased with aging. However, the EPDM blend showed the least elongation at break values with the best stability because of the low diene content of EPDM. However, all of the blends showed a different trend in 100% modulus tending to increase after aging. Natural rubber rich blends (Figure 7) showed the lowest 100% modulus. The EPDM rich blend showed the highest 100% modulus. Thus, the 100% modulus increased as the EPDM content increased in the blend. This clearly indicated the decreasing stiffness that occurred in matrixes because of thermal and weather aging. The results indicate that the presence of EPDM improved the aging behavior significantly such as resistance to heat, UV radiation, and moisture.

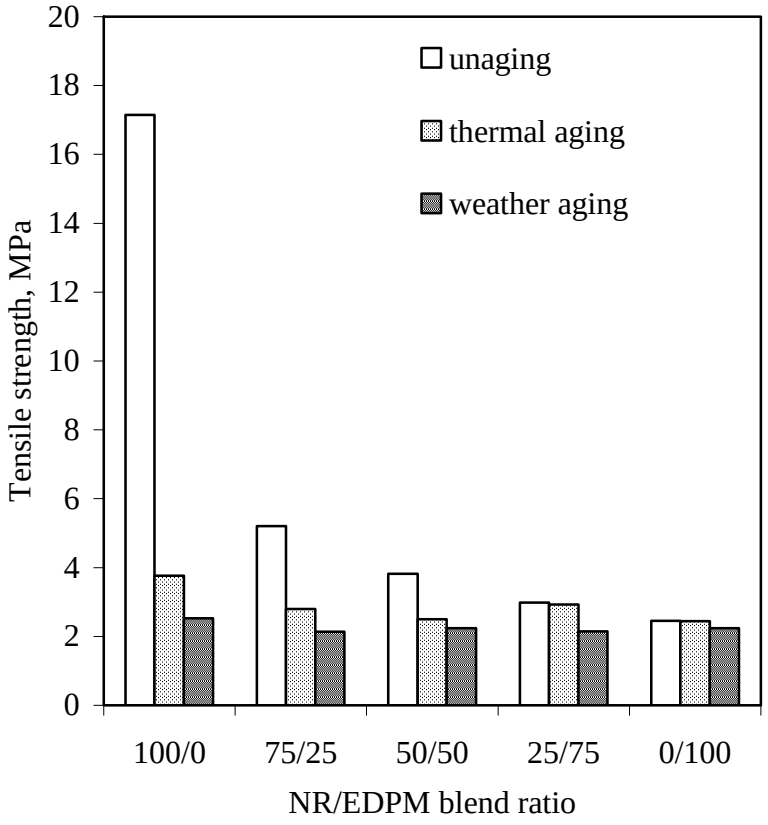


Fig. 5 Tensile strength of NR/EPDM blends

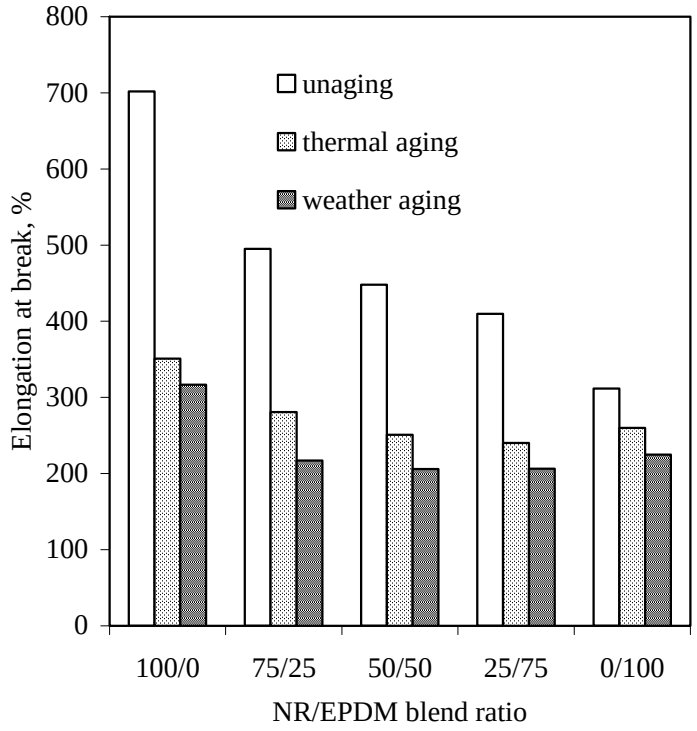


Fig. 6 Elogaation at break of NR/EPDM blends

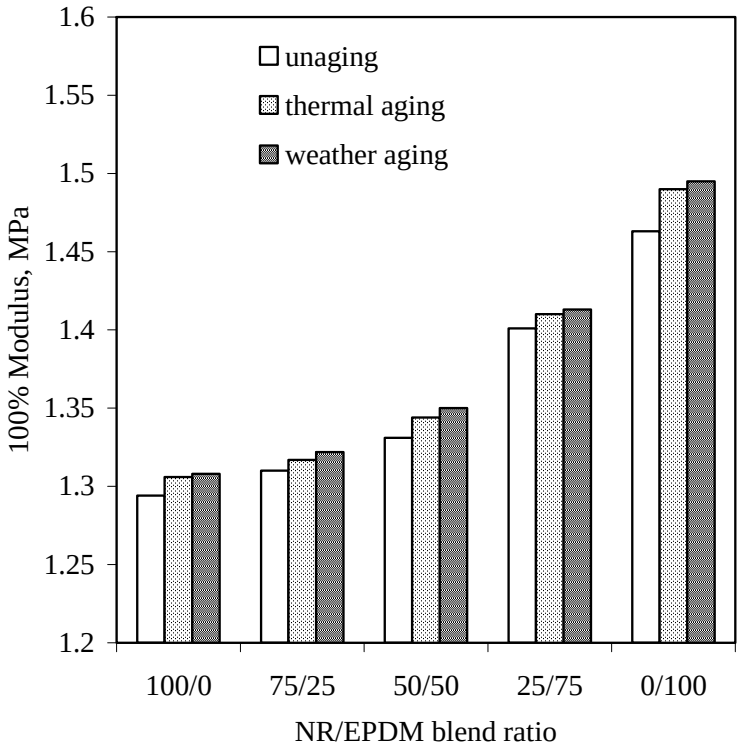


Fig. 7 100% modulus of NR/EPDM blends

3.5 The Effect of Compatibilizer on Processability and Cure Characteristics of 50/50 NR/EPDM blends

The Mooney viscosity and cure characteristics of 50/50 NR/EPDM with varying compatibilizer contents are shown in Figure 8 indicating that the blends become more viscous when the compatibilizer was added during compounding. The fact that the viscosities have increased indicated that there is less slippage at the interface as a result of the addition of compatibilizer. This is because the compatibilizer decreases the interfacial tension and hence the interaction between NR and EPDM becomes stronger. In MBS, polybutadiene constitutes the main polymeric chain to which two polymeric segments viz, polystyrene and poly(methyl methacrylate) are attached. The adhesion between the EPDM matrix and the styrene-methyl methacrylate grafted chain is possible as they make a compatible blend. This gives rise to an increase in the viscosity of the blends when MBS is added.

The effect of the compatibilizers on the curing time is more clearly seen in the blend having a 50/50 composition, as show in Figure 8. The addition of graft copolymer for the 50/50 blend decreased the cure time t_{90} with an increase in graft copolymer content. The result may be related to an increasing of the melt viscosity because of the presence of the functional group in the graft copolymer to induce the in situ formation of the compatibilizing interchain copolymer of EPDM and NR. This suggests that there are strong interactions at the interface between the rubber phases.

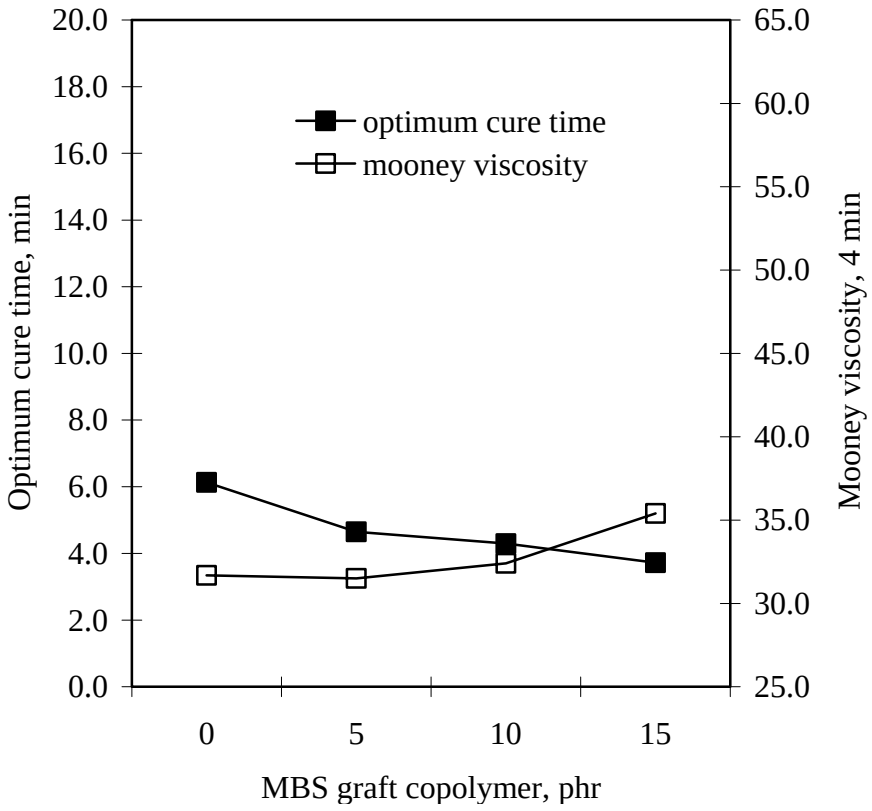


Fig. 8 Mooney viscosity and cure characteristics of 50/50 NR/EPDM

3.6 The Effect of Compatibilizer on Mechanical Properties of 50/50 NR/EPDM blends

The mechanical properties of the 50/50 NR/EPDM blends were plotted vs. the compatibilizer loading (Figure 9). A comparison between the 50/50 NR/EPDM blend with and without compatibilizer shows that the tensile strength and elongation at values of blend with MBS are higher than the blend without compatibilizer. The increase in tensile strength is rapid up to 10 phr of MBS in the 50/50 NR/EPDM blend, beyond which the increase is marginal up to 15 phr of MBS. The uncompatibilized blend exhibited low tensile strength. The change in tensile strength of the blends with graft copolymer concentration can be explained in terms of interfacial adhesion. The low tensile strength of the uncompatibilized system indicates lack of adhesion between components. The chain of polybutadiene in MBS is easy to mix and to adhere with NR. The poly(styrene-*co*-methyl methacrylate) of the compatibilizer can interact with the ethylene and propylene units present in EPDM. The compatibilizer may improve the tensile strength of the polymer blends because it plays a role as an adhesive between poly(styrene-*co*-methyl methacrylate) and polybutadiene. The elongation (%) at break followed a similar pattern as that shown in the case of tensile strength. Oommen and Thomas[20] observed a similar behavior for natural rubber/poly (methyl methacrylate)/natural rubber-g- poly (methyl methacrylate) blends.

As for the stiffness properties, the trend observed is that which was already expected. The 100% modulus decreased with increasing graft copolymer concentration, as shown in Figure 9. This result was expected because, as more graft copolymer is introduced into the 50/50 NR/EPDM blend, the adhesion between the components is improved, resulting in greater stiffness in the blends.

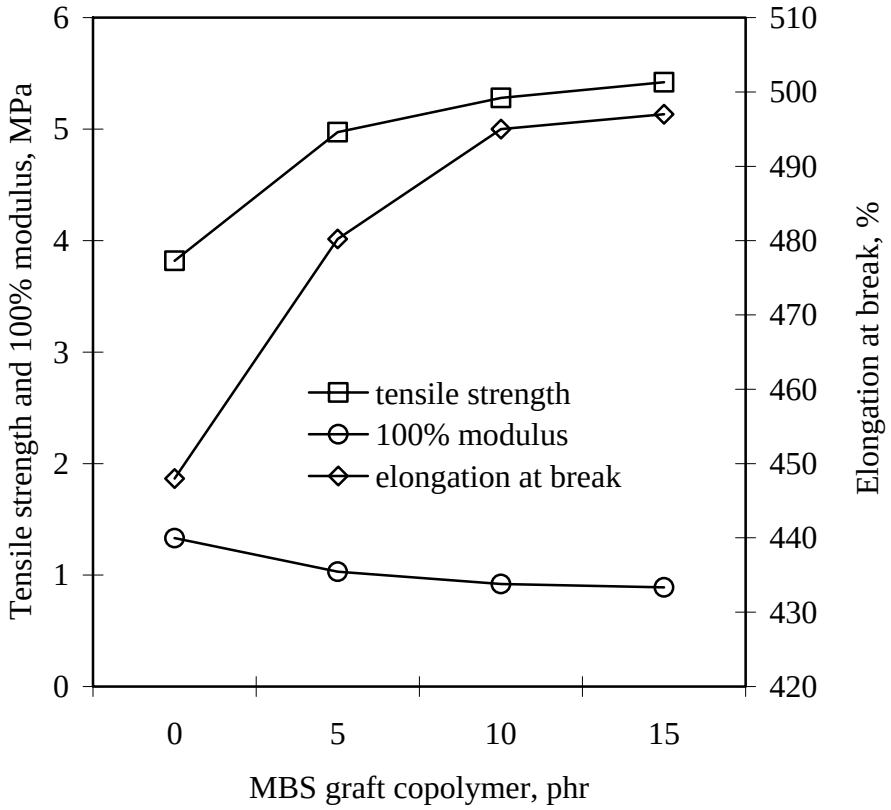


Fig. 9 Mechanical properties of the 50/50 NR/EPDM blends VS Compatibilizer loading

4. Conclusions

Processing, cure characteristics, and mechanical properties of NR/EPDM blends were studied as a function of blend ratio and compatibilizer concentration. Mooney viscosity decreased with increase in EPDM content in the NR/EPDM blend ratios whereas cure time showed an increase. The mechanical properties of the NR/EPDM blends are found to be influenced by the blend ratio. Tensile strength and elongation at break decreased with increase in EDPM content. However, the change of 100% modulus with increase of EPDM content in the NR/EPDM blend was quite small. SEM studies of the failure surface indicated that the adhesion between the components in the NR/EPDM systems. The absence of fibrils on the fracture surface of the NR/EPDM system indicated poor interface adhesion. This explains the reduction of tensile strength with an increase of EPDM content in the NR/EPDM blends. The incorporation of the EPDM in NR exhibits better stable mechanical properties as compared to the NR rich blend due to good thermal and weathering resistance of EPDM. The addition of graft copolymer into the 50/50 NR/EPDM blend increased the Mooney viscosity with an increase in graft copolymer concentration. The curing time t_{90} became shorter with increasing graft copolymer content. This is due to an increased compatibilizer interaction between NR and EPDM. Consequently, the tensile strength and elongation at break show improvement by the addition of the graft copolymer. Although, from overall mechanical properties, it could be suggested that the blending of NR with EPBM usually display inferior mechanical properties as compared to the average properties of the constituent rubbers; one may still be able to improve the weathering resistance of NR by blending it with EPDM for outdoor applications. Suitable application for the NR/EPDM blend could be in components demanding good weathering resistance and excellent dimension stability without significantly affecting the properties of interest in the blends.

Acknowledgement

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