Cure Characteristics, Morphology, and Mechanical Properties of Ethylene–Propylene–Diene–Monomer Rubber/Acrylonitrile Butadiene Rubber Blends

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ABSTRACT: Blends based on ethylene–propylene–diene monomer rubber (EPDM) and acrylonitrile butadiene rubber (NBR) was prepared. Sulfur was used as the vulcanizing agent. The effects of blend ratio on the cure characteristics and mechanical properties, such as stress–strain behavior, tensile strength, elongation at break, hardness, rebound resilience, and abrasion resistance have been investigated. Tensile and tear strength showed synergism for the blend containing 30% of NBR, which has been explained in terms of morphology of the blends attested by scanning electron micrographs. A relatively cocontinuous morphology was observed for 70 : 30, EPDM/NBR blend system. The experimental results have been compared with the relevant theoretical models. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 908–914, 2007

Key words: EPDM; NBR; blends; cure characteristics; mechanical properties; morphology

INTRODUCTION

In recent years, the production of elastomeric blends has markedly increased, due to their well-balanced physical and mechanical properties and the easy processability and relatively low cost. Blending of two or more types of polymers is a very useful technique for the preparation and development of materials with properties superior to those of the individual constituents.[1]

Interesting studies on polymer blends exists in the literature. For example, Kim and Hamed[2] prepared a vulcanizate based on a 50/50 natural rubber (NR)/*cis*-butadiene rubber (NR/*cis*-BR). This blend has been found to retain the rupture resistance property of NR vulcanizate and the resistances to slow fatigue crack growth property of *cis*-BR vulcanizate. Kundu et al.[3] investigated the solvent resistance of blends of poly [ethylene-*co*-vinyl acetate] (EVA) and polychoroprene (CR). The retention in tensile properties has been found to be maximum for CR and high CR content samples in solvent ageing. Wilmomala et al.[4] blended polyvinyl chloride (PVC) with NBR over a range of compositions, i.e., 5–40 wt % of the rubber. Morphological properties were studied as a function of rubber content and blending temperature. The ultimate tensile stress and modulus of the blends were found to decrease with rubber content. The maximum tensile toughness was obtained for the blend with a rubber content of 30% at a blending temperature of 155°C. Thiraphattaraphun et al.[5] prepared natural rubber-*g*-methyl methacrylate/poly(methyl methacrylate) [NR-*g*-MMA/PMMA] blends by melt mixing technique. The tensile strength, tear strength, and hardness were found to increase with increases in PMMA content. Saha[6] studied the rheological and morphological characteristics of PVC/CR blends. Experimental results showed that the CR could promote the processability and fusion of PVC. It was also found that the mixing sequence has a profound influence on the processability and compatibility of the melt blend system.

Ghosh and Basu[7] successfully prepared and studied the filled covulcanizates of an elastomer blend comprising NR and ethylene–propylene–diene rubber (EPDM) of commercial importance, using a multifunctional rubber additive, viz bis(diisopropyl) thiophosphoryl disulfide. A Two-stage vulcanization technique further improved the physicochemical properties of the blend vulcanizates. NR was blended with synthetic nonpolar rubbers such as styrene butadiene rubber (SBR), butadiene rubber (BR) and ethylene–propylene–diene rubber (EPDM), and polar rubbers such as NBR and CR by Saad and El-Sabbagh[8] NR/SBR and NR/BR blends were found to be compatible, while NR/EPDM, NR/NBR, and NR/CR blends were incompatible. SBR and PVC, which were tried as compatibilisers, improved the compatibility of the blends. The effects of different curing agents on the properties of EPDM/SBR blends were

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TABLE I
Properties and Specifications of EPDM and NBR

Product name	Herlene- 545 (EPDM)
Mooney Viscosity, ML_{1+4} @ 125°C	65.00
E/P[a], weight ratio	55/45
Molecular distribution	Broad
Specific gravity	0.86
Volatile matter, weight (%)	0.7
Ash, weight (%)	0.15
Color	Light amber
Product name	Aparene N-553-NS (NBR)
Moooney Viscosity, ML_{1+4} @ 100°C	47.00
Bound ACN[b], weight (%)	34.00
Volatile matter, weight (%)	0.70
Ash, weight (%)	0.50
Color	Light tan

[a] E/P, ethylene/propylene.
[b] ACN, acrylonitrile.

studied by Zhao et al.[9] They studied the effects of sulfur, peroxide and coagent curing systems. It was found that the addition of small amount of sulfur as a coagent to the peroxide cure system, remarkably improved the mechanical properties of the blends. Nasker et al.[10] prepared blends of carboxylated acrylonitrile-butadiene rubber (XNBR) and NR using bis(diisopropyl) thiophosphoryl trisulphide and bis (diisopropyl) thiophosphoryl tetrasulphide as novel coupling agent and accelerator respectively. The blend vulcanizates thus produced exhibited enhanced physical properties that could further be improved by adopting a two-stage vulcanization technique and also by the judicious selection of the NR/XNBR ratio.

Nitrile rubber (NBR) has good solvent resistance and abrasion resistance.[11] EPDM possesses excellent aging properties and the resistance to deterioration and retains good physical and mechanical properties even at higher temperature and in polar media[12] and has excellent ageing properties. The weather resistance of EPDM rubber is excellent so it is useful in many outdoor applications.[13] EPDM rubber does not require antioxidants and antiozonants during compounding, and the product has good heat resistance and electrical insulation properties.[14] Crosslinks can be introduced between polymer chains by using sulfur as vulcanizing agent. Raw rubber has poor physicochemical properties. To improve the properties some ingredients, such as accelerator, and activator should be introduced to the raw rubber in small quantities. The small quantity could affect the physical and mechanical properties of blends.[15]

The aim of the present work is to develop and characterize blends of EPDM and NBR vulcanized by sulfur. The cure characteristics such as scorch safety and cure rate have been analyzed. The morphology has been analyzed with the help of SEM photographs. The mechanical properties such as stress–strain behavior, tensile strength, tear strength, relative volume loss, and hardness of the blends were studied as a function of blend ratio. Attempts have also been made to correlate the mechanical properties with the existing theoretical models.

EXPERIMENTAL

Materials

Ethylene–propylene–diene monomer rubber (EPDM) used was Herlene-545 obtained from Herdillia Unimers Limited, Navi Mumbai, India. Acrylonitrile butadiene rubber (NBR) used was Aparene *N*-553-NS from Apar Industries, Mumbai, India. The characteristics of the blend components have been given in the Table I. All other ingredients such as sulfur, zinc oxide, stearic acid, and zinc diethyl carbamate used were of commercial grade.

Preparation of EPDM/NBR blends

EPDM/NBR blends were prepared in six different combinations. These were vulcanized by sulfur as the vulcanizing agent. The sample designations of the blend systems developed are given in Table II. The letters E and N represent EPDM and NBR, respectively. The subscript indicates the percentage of NBR in the blend. The compounding recipes of the blends are given in Table III. Mixes were sheeted out in a laboratory sized two-roll mixing mill having a friction ratio of 1 : 1.4. The cure characteristics were measured by using an elastograph, Monsanto Rheometer (MDR-2000) as per ASTM D-5289. The optimum cure time was determined at 170°C.[16] The compounded blends were then compression molded along the mill grain direction using an electrically heated hydraulic press (Indexpell, Kerala, India) under a pressure of 5 MPa for their optimum cure

TABLE II
Composition of EPDM/NBR Blends

Sample designation	EPDM (phr[a])	NBR (phr)
EN_0	100	0
EN_{20}	80	20
EN_{30}	70	30
EN_{50}	50	50
EN_{70}	30	70
EN_{100}	0	100

[a] phr, parts per hundred.

TABLE III
Formulation of Mixes

Ingredients	Quantity (phr[a])
Polymer	100
Zinc oxide	5.0
Stearic acid	1.5
Zinc diethyl carbamate	1.0
Sulphur	2.0

[a] phr, parts per hundred.

time (t_{90}) given in Table IV. These cured sheets were conditioned before testing (24 h maturation at room temperature).

Morphology

The morphological observations of the blends were made by a scanning electron microscope (JEOL-JS IN-T330-A-SEM; ISS Group, Whittington, Manchester, UK). For this the surfaces of crosslinked blends, after cryogenic breaking, were sputter coated with gold and examined under SEM.

Mechanical properties

Mechanical properties such as tensile strength, modulus (%), and elongation at break were examined on a Universal Testing Machine (series IX Automated Materials Testing System 1.38, model-441, Instron, USA) at a crosshead speed of 500 mm/min and at (25 ± 2)°C. The tensile properties of the blends were examined according to ASTM D-412. The tear test was conducted as per ASTM D-624 using 90° angle test pieces. The experimental conditions and equipment for the tear measurements were the same as that of the tensile testing. Five samples from each formulation were tested. The hardness of the samples was measured as per ASTM D-2240 using a Mitutoyo IRHD dead load apparatus. For hardness measurements, the sheets having an effective thickness of 6 mm were used. At least five measurements were taken and average values were reported. Rebound resilience measurements were performed using a Schob pendulum following the standard ISO 4662-1978 specifications.[2] Abrasion resistance was determined as relative volume loss in wear test using a Zwick DIN Abrader as per ASTM D-2228, employed rolling sliding test. Here, 0.1 kN load was applied to the rolling sliding cylinder on SiC paper. In addition, 400 mm stroke, 40 rpm speed of cylinder, (25 ± 2)°C test temperature, and 40% ± 5% humidity were used as test conditions. The density measurements were carried out using a Densimeter (ISO 2781), (Mirage MDS-200S, Resolution 0.001, A and D, Japan). Distilled water was used as the experimental liquid. The densities of samples were measured directly from the digital indicator of the scales.

TABLE IV
Cure Characteristics of EPDM/NBR Blends

Sample code	Optimum cure time t_{90} (min)	Scorch time t_2 (min)	Maximum torque (Nm)	Cure rate (at 170°C)
EN_0	5.10	0.4500	0.4922	0.0755
EN_{20}	4.40	0.4615	0.3838	0.0705
EN_{30}	3.67	0.6923	0.4111	0.1029
EN_{50}	3.20	0.5769	0.4297	0.1194
EN_{70}	3.05	0.6462	0.5186	0.1664
EN_{100}	3.36	0.6923	0.7041	0.2215

RESULTS AND DISCUSSION

Cure characteristics

Figure 1 shows torque–cure time graphs of sulfur vulcanized NBR/EPDM blends. The initial decrease in torque is due to the softening of the matrix. Torque then increases due to the formation of crosslinks between the macromolecular chains. It can be seen from Figure 1 that, as the percentage of NBR increases in the blend systems, the rheometric torque increases. Table IV shows the cure characteristics of the blends under investigation. Regular variations in maximum torque and optimum cure time (t_{90}) have been observed for the blends. Pure EPDM shows maximum optimum cure time. Optimum cure time decreases with an increase in NBR content in the blends. The t_{90} value has been found to be lowest for the blend having higher percentage of NBR. This shows that the rate of vulcanization was more in blends containing more NBR. Scorch time (t_2) is the time taken for the minimum torque value to increase by two units. It is a measure of the premature vulcanization of the material. As shown in Table IV, the

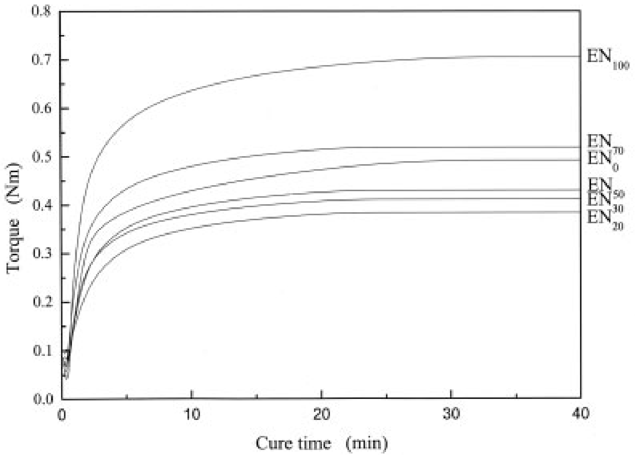
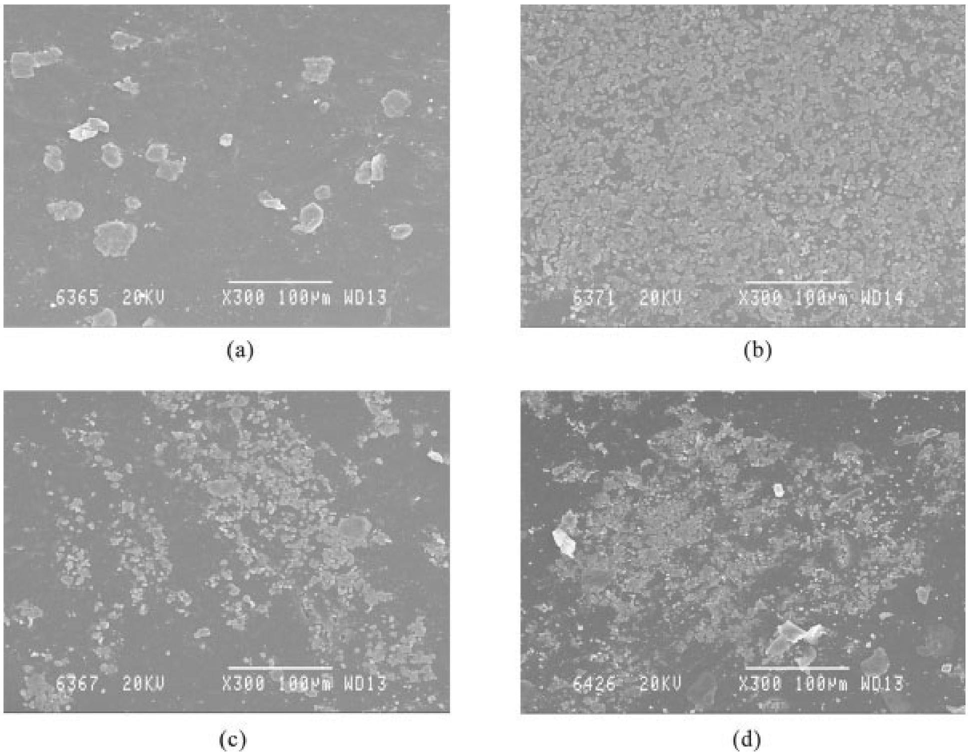


Figure 1 Torque–cure time graphs of EPDM/NBR blends.



(a) (b) (c) (d)

Figure 2 SEM of EPDM/NBR blends: (a) EN_{20}, (b) EN_{30}, (c) EN_{50}, and (d) EN_{70}.

maximum scorch time among the various blend systems is for EN_{30}. This shows that the scorch safety is highest for the blend with 70% EPDM and 30% NBR. Maximum torque, which is a measure of crosslink density, is also given in the Table IV. As the NBR content increases, the maximum torque increases, which indicate the enhancement in crosslink density of the blends.

Cure rate

$$\text{Cure rate} = (\text{cure time torque} - \text{scorch time torque})/(\text{cure time-scorch time}) \quad (1)$$

The calculated values of cure rate are also given in Table IV. The values show that the cure rate increases with increase in percentage of NBR content in the blend. This indicates that NBR is a cure activating component in various EPDM/NBR blends. This is due to the presence of unsaturation in the butadiene component of NBR. Sulfidic linkages are formed at the unsaturation sites between macromolecules during vulcanization. The increase in the number of NBR molecules (as weight percentage) increases the number of active sites for vulcanization.

Morphology

The SEM photographs of EN_{20}, EN_{30}, EN_{50}, and EN_{70} blends are shown in Figure 2(a–d). It has been found that the component dispersion nature in the blends is not uniform, which indicates their heterogeneous nature. The changes in the domain sizes of dispersed phase are due to the difference in the volume fractions and viscosities of the components. A relatively uniform distribution of the components has been found in EN_{30} blend. For EN_{70}, NBR becomes the continuous phase where EPDM rubber particles get dispersed.

Mechanical properties

The nature of deformation of the blends under an applied load can be understood from the stress–strain curves. The stress–strain curves of the sulfur-cured system as a function of blend ratio are given in Figure 3. It can be seen that EN_{30} with stands more stress. Figure 4 shows the variation of the tensile strength of blends with blend ratio. It can be seen that, as the percentage of NBR in the blend increases, the tensile strength increases to an optimum value, which then decreases. The tensile strength is maximum in the blend system containing 70% EPDM and 30% NBR. Beyond 30% NBR content, the tensile strength decreases. This is definitely associated with the relative uniform distribution of components for the 70/30, EPDM/NBR composition in the blend. Figure 5 shows the variation of tear strength with blend ratio. This also follows the same trend as that of tensile strength. The

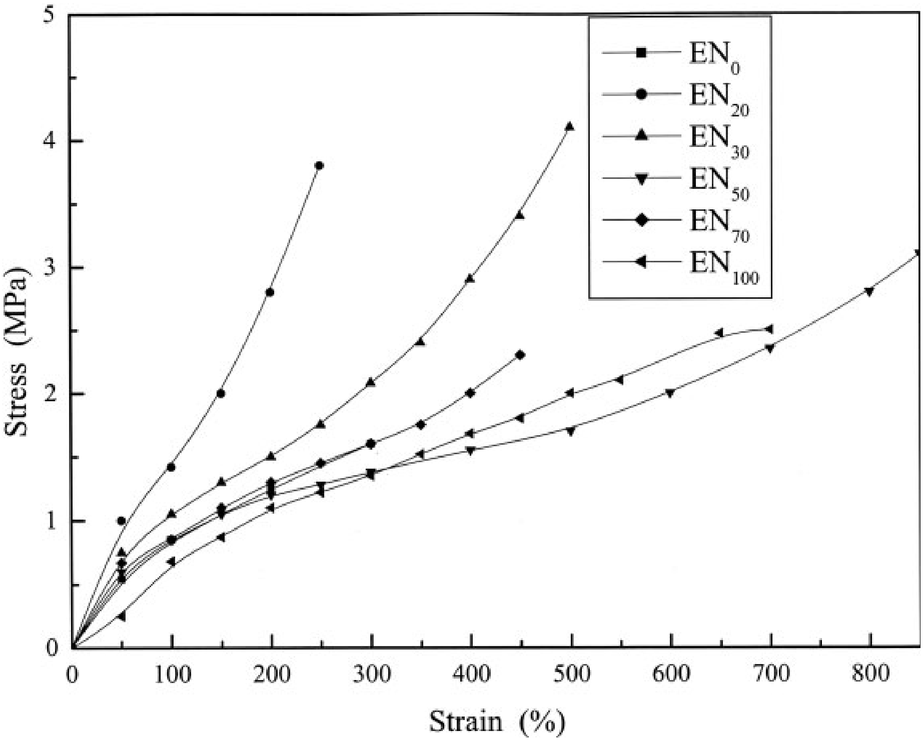


Figure 3 Effect of blend ratio on the stress–strain behavior of EPDM/NBR blends.

variations in elongation at break (%) for different blend ratios are given in Table V. Elongation at break is maximum for the blend containing 50 : 50, NBR and EPDM respectively. The variation of modulus (100%) with different blend ratio is shown in Table V. As in the case of tensile strength, modulus has been found to be maximum for EN_{30}. The values of hardness of the blends, as given in Table V, show that no considerable variation in hardness occurs, when the composition is varied. Table VI shows the percentage of rebound resilience for different EPDM/NBR blends. The different blends give an intermediate value between pure EPDM and pure NBR, with not much variation in their rebound resilience values. Pure EPDM gives the maximum and pure NBR gives the minimum percentage of rebound resilience. The abrasion resistances of the blends have been expressed in terms of relative volume loss. The relative volume loss decreases with increase in

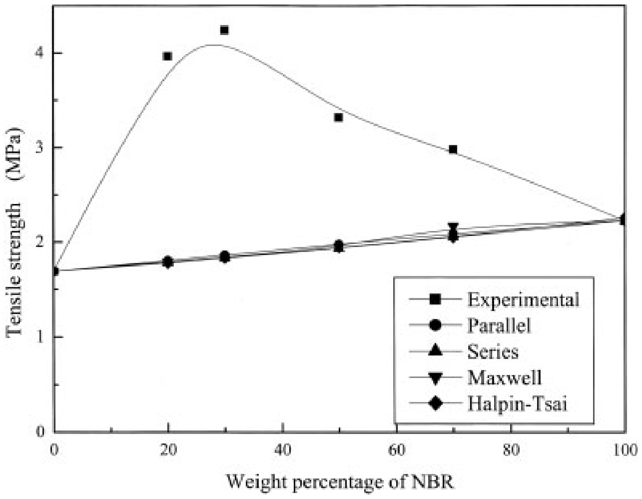


Figure 4 Comparison of experimental results with theoretical models for tensile strength of EPDM/NBR blends.

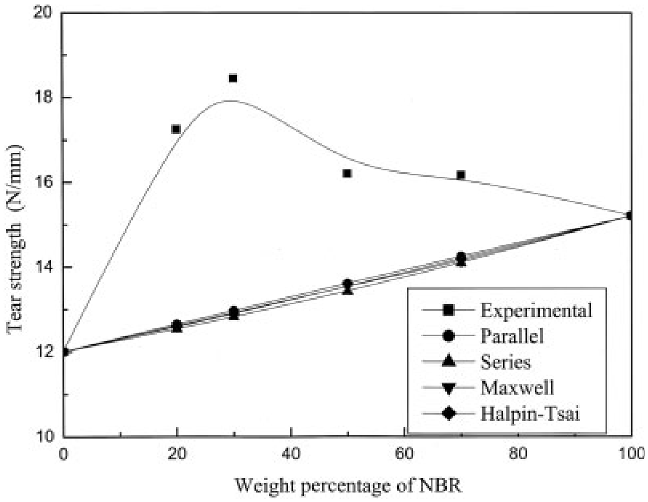


Figure 5 Comparison of experimental results with theoretical models for tear strength of EPDM/NBR blends.

TABLE V
Values of Modulus, Hardness, and Elongation at Break of EPDM/NBR Blends

Sample code	Modulus (100%) (MPa)	Hardness (IRHD)	Elongation at break (%)
EN_0	0.8535	49.8	295.5
EN_{20}	0.9969	50.9	318.8
EN_{30}	1.3200	51.2	570.3
EN_{50}	0.8008	51.2	808.3
EN_{70}	0.8198	50.9	726.6
EN_{100}	0.8677	51.2	458.3

TABLE VI
Values of Relative Density, Rebound Resilience, and Relative Volume Loss of EPDM/NBR Blends

Sample code	Relative density	Rebound resilience (%)	Relative volume loss (mm^3)
EN_0	0.9403	59.00	0.0551
EN_{20}	0.9457	35.00	0.1990
EN_{30}	0.9470	36.33	0.1453
EN_{50}	0.9657	34.33	0.0838
EN_{70}	0.9863	30.00	0.0758
EN_{100}	1.0367	26.33	0.1720

the NBR content in various EPDM/NBR blend systems also shown in Table VI.

Mechanical properties of blends are widely studied through a comparison of experimental results and predictions based on various theoretical models. Different theoretical models selected to predict the mechanical behavior of EPDM/NBR blend systems include parallel, series, Halpin-Tsai and Maxwell models.

The parallel model (highest upper bound model) is given by the equation,[17]

$$M = M_1\Phi_1 + M_2\Phi_2 \tag{2}$$

where M is the mechanical property of the blend, and M_1 and M_2 are the mechanical properties, and Φ_1 and Φ_2 are the volume fractions of the components 1 and 2, respectively. In this model the components are considered to be arranged parallel to one another so that the applied stress elongates each of the components by the same amount.

In the lowest lower bound series model, the components are arranged in series with the applied stress. The equation is[17]

$$1/M = \Phi_1/M_1 + \Phi_2/M_2 \tag{3}$$

where the variables are as mentioned above.

According to Halpin-Tsai equation[18]

$$M_1/M = (1 + A_iB_i\Phi_2)/(1 - B_i\Phi_2) \tag{4}$$

where

$$B_i = (M_1/M_2 - 1)/(M_1/M_2 + A_i) \tag{5}$$

A_i is a constant and is defined by the morphology of the system. $A_i = 0.66$ when a flexible component forms the dispersed phase in a continuous hard matrix. On the other hand, if the hard material forms the dispersed phase in a continuous flexible matrix, A_i becomes 1.5. Other variables are as mentioned above.

As per Maxwell model[19]

$$M = M_1([M_2 + 2M_1 - 2\Phi_2(M_1 - M_2)])/([M_2 + 2M_1 + \Phi_2(M_1 - M_2)]) \tag{6}$$

where the variables are as discussed earlier.

Figures 4 and 5 also show the comparison between experimental and theoretical curves of the tensile strength and tear strength of EPDM/NBR blends. All the four models show almost same positive trend for each and every composition. In the case of tensile strength, the experimental values show significant positive deviations, suggesting better properties for the present blend system than the theoretical predictions, both for the parallel and series models. The tear strength also gives the same synergistic trend to the parallel and series models.

CONCLUSIONS

The effects of blend ratio on the curing behavior, morphology and mechanical properties of blends of EPDM and NBR have been studied. The cure characteristics showed that the optimum cure time decreased with an increase in NBR content for the different blend ratios. The scorch time registered an increase up to 30% NBR in the blends and then decreased. Scorch safety has been found to be maximum for EN_{30} among the various blend ratios. The maximum torque increased with increase in the percentage of NBR content in the blends. The SEM analysis showed that the EPDM/NBR blends were of heterogeneous in nature. Tensile and tear strengths have been found to be highest for the EN_{30} system. The percentage of rebound resilience decreased with an increase in the NBR percentage. The experimental observations have been compared with relevant theoretical models highlighting the synergism shown by the EPDM/NBR blends. This highlights the feasibility of developing different products from the present blend system, which require a balance between good mechanical properties and oil resistance due to the different rubber components in the blend.

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