

# Cure Characteristics, Swelling Behaviors, and Mechanical Properties of Carbon Black Filler Reinforced EPDM/NBR Blend System

K. C. Manoj, Prajitha Kumari, G. Unnikrishnan

*Polymer Science and Technology Laboratory, Department of Chemistry, National Institute of Technology Calicut, Calicut 673601, Kerala, India*

Received 10 February 2010; accepted 3 October 2010

DOI 10.1002/app.33476

Published online 23 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The effect of carbon black fillers viz. semi-reinforcing furnace (SRF), high abrasion furnace (HAF) and intermediate super abrasion furnace (ISAF) carbon blacks on the cure, swelling and mechanical properties of 70/30 EPDM/NBR blend have been investigated. The maximum torque values have been found to be increased with increase in filler loading. Filled systems have been found to exhibit a reduced solvent uptake tendency compared to the unfilled sample. Blends loaded with ISAF exhibited the lowest toluene uptake among the carbon black filled systems due to the better filler reinforcement. A more uniform morphology has

been observed for ISAF-filled samples compared to the other filler loaded systems. The improvement in the mechanical properties has been observed to be the highest for ISAF-filled samples followed by HAF and SRF filled systems. This has been attributed to the smaller particle size of ISAF black. The experimental results of mechanical testing have been compared with various theoretical models. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2654–2662, 2011

**Key words:** blends; composites; cure characteristics; mechanical properties; swelling behaviors

## INTRODUCTION

Filler reinforcement is a conventional practice in rubber industry for improved physical properties.<sup>1,2</sup> Polymeric composites are finding applications in diverse fields; from house-hold appliances to spacecrafts. In comparison with single polymer systems, more possibilities for tailoring product performance have been brought about by the employment of polymer blends as matrices in composites.<sup>3–5</sup> Reinforcing filler like carbon black has significant influence upon the properties of an elastomer, often increasing its mechanical durability and elastic properties and modifying the sorption and permeability characteristics.<sup>6–12</sup>

Many scientists have studied the cure characteristics, morphology and mechanical properties of carbon black filled composites.<sup>13–17</sup> The structure development, rheological behavior, and viscoelastic properties of carbon black filled, dynamically vulcanized, thermoplastic elastomers based on ethylene-propylene–diene monomer rubber and polypropylene (PP), with the range of 50/50 to 80/20 weight ratios, have been studied.<sup>18</sup> Carbon black showed a tendency to stay mainly in the rubbery phase, which

leads to an increase in the viscosity difference between the blend components and to an increase in the rubber particle size. Tensile strength and rupture energy increased with carbon black loading.

El-Tantawy and Aal<sup>19</sup> evaluated the mechanical properties such as tensile strength, hardness, stiffness, and elongation at break of carbon black reinforced butyl rubber/high density polyethylene (HDPE) blends. The observed increase in mechanical properties was attributed to the increase in the cross-link density and the interfacial adhesion between the blend components. The mechanical properties of the blends of HDPE and acrylonitrile butadiene rubber (NBR), prepared by dynamic vulcanization using sulfur, peroxide, and a mixture of sulfur and peroxide curing systems, with fillers such as carbon black, silica, silane-treated silica and cork, have been evaluated.<sup>20</sup> All filled systems, except the cork filled one, exhibited superior mechanical properties. Ghoneim and Ismail<sup>21</sup> studied the physicomechanical properties of EPDM/natural rubber (NR) systems reinforced with carbon black. They justified the improvement in physicomechanical properties in terms of the good interaction between the blend components and carbon black. Desai et al.<sup>22</sup> showed that an increase in carbon black content in polyurethane (PU)/NR blends increased the stress-strain properties up to some extent. Composites of EPDM, HDPE and ground tire rubber powder (GTR) at

Correspondence to: G. Unnikrishnan (unnig@nitc.ac.in).

different ratios were subjected to mechanical testing in terms of blend composition.<sup>23</sup> The results indicated that the improvement in properties was inversely proportional to the substituted ratio of GTR; attributed to the development of a better interfacial adhesion between GTR and the blend components. The results have been confirmed by examining the fracture surfaces by SEM.

EPDM rubber is used in vibrators and seals; glass-run channel; radiator, garden and appliance hose; tubing; washers; belts; electrical insulation, and speaker cone surrounds. It is also used as a medium for water resistance in electrical cable-jointing, roofing membranes, geomembranes, rubber mechanical goods, plastic impact modification, thermoplastic, vulcanizates, and many other applications.

This report is intended as a reference for mount manufacturers in evaluating various types and loadings of carbon black in new-generation EPDM engine mount compounds. Increasingly hostile under-the-hood environments have led to an examination of EPDM as a replacement for natural rubber in automotive engine mounts.

Ethylene-propylene-diene monomer (EPDM) has excellent resistance to heat, oxidation and ozone, as well as to oils and chemicals, including ethylene glycol. The use of proper curatives and fillers can provide good compression set properties. It has been reported that EPDM rubber filled with excess carbon black has good aging and weathering properties as well as good, electrical properties.<sup>4,24,25</sup>

Nitrile rubber (NBR) has good resistance against oils and most type of fuels, such as petrol. This polymer has good mechanical properties, but somewhat lower resistance against weather and ozone. To reduce the cost, we selected to incorporate NBR, which can reduce the effective cost of the product.

The goal of this work is to investigate the effects of three types of carbon blacks viz. semireinforcing furnace (SRF), high abrasion furnace (HAF), and intermediate super abrasion furnace (ISAF) black on the cure, swelling, morphological and mechanical properties EPDM/NBR blends. The properties such as tensile strength, tear strength, modulus, rebound resilience, hardness, and abrasion resistance of the vulcanizates have been examined as a function of filler type and filler loading. Attempts have also been done 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

TABLE I  
Properties of the Carbon Black Fillers

Filler type	Grade	Surface area (m <sup>2</sup> /g)	Particle size (nm)
SRF	N 762	20	60
HAF	N 330	80	29
ISAF	N 220	120	23

Unimers Limited, Navi Mumbai, India (Mooney viscosity, ML<sub>1+4</sub> @ 125°C is 65.00, ethylene/propylene weight ratio is 55/45). Acrylonitrile butadiene rubber (NBR) used was Aparene N-553-NS from Apar Industries Ltd, Mumbai, India (Mooney viscosity, ML<sub>1+4</sub> @ 100°C is 47.00; bound acrylonitrile weight percentage is 34.00). The fillers used were ISAF (intermediate superabrasion furnace), HAF (high abrasion furnace) and SRF (semireinforcing furnace) carbon blacks, supplied by Rubo-Chem Industries, Mumbai, India. The properties of the fillers used are given in Table I. All other ingredients such as sulfur, zinc oxide (ZnO), stearic acid and zinc diethyl carbamate (ZDC) used were of commercial grade.

### Preparation of EPDM/NBR systems

Composites were prepared using 70/30 EPDM/NBR blend matrix (EN<sub>30</sub>) reinforced with ISAF, HAF, and SRF carbon blacks. Sulfur is used as the curing agent. The formulations of the mixes are given in Table II. The letters E, N, I, H, and S represent EPDM, NBR, ISAF, HAF and SRF respectively. The subscript indicates the percentage of the component present in the matrix. For example EN<sub>30</sub>I<sub>15</sub> represents, composite with 70/30/15 EPDM/NBR/ISAF system. The mixes were sheeted out in a laboratory sized two-roll mixing mill (150 mm × 300 mm) with a friction ratio 1 : 1.4 as per ASTM D15-627. The cure characteristics were monitored by means of an oscillating disc rheometer (Monsanto Rheometer, MDR-2000, USA) as per ASTM standard D-5289. The optimum cure time was determined at 170°C. 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. The cured sheets were conditioned before testing (24 h maturation at room temperature).

### Morphology

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

TABLE II  
Formulations of EPDM/NBR Systems

Sample code	EPDM (phr <sup>a</sup> )	NBR (phr)	ZnO (phr)	SA <sup>b</sup> (phr)	ZDC (phr)	SR <sup>c</sup> (phr)	ISAF (phr)	HAF (phr)	SRF (phr)
EN <sub>30</sub>	70	30	5.0	1.5	1.0	2.0	–	–	–
EN <sub>30</sub> I <sub>5</sub>	70	30	5.0	1.5	1.0	2.0	5	–	–
EN <sub>30</sub> I <sub>10</sub>	70	30	5.0	1.5	1.0	2.0	10	–	–
EN <sub>30</sub> I <sub>15</sub>	70	30	5.0	1.5	1.0	2.0	15	–	–
EN <sub>30</sub> I <sub>20</sub>	70	30	5.0	1.5	1.0	2.0	20	–	–
EN <sub>30</sub> H <sub>15</sub>	70	30	5.0	1.5	1.0	2.0	–	15	–
EN <sub>30</sub> S <sub>15</sub>	70	30	5.0	1.5	1.0	2.0	–	–	15

<sup>a</sup> phr, parts per hundred parts of rubber by weight.

<sup>b</sup> SA, stearic acid.

<sup>c</sup> SR, sulphur.

### Solvent sorption and swelling experiments

Circular test samples of diameter 1.94 cm, from compression molded sheets were punched out using a sharp steel die and dried overnight in a vacuum desiccator. The thickness of the sample was measured using a micrometer screw gauge with an accuracy of  $\pm 0.001$  cm. The samples were soaked in 20 mL of solvents contained in diffusion bottles kept in a thermostatically controlled oven. All the experiments are done at 28°C. The test samples were removed from the solvents at regular intervals, and then weighed after gently wiping the adhering solvent. Weight of the swollen samples was taken using an electronic balance (Shimadzu AW 220, Japan) with an accuracy of  $\pm 0.0001$  g. They were then immediately replaced in to the solvents in the diffusion bottles. The time of each weighing was kept to a maximum of 30 s to minimize the error due to the escape of solvent from the samples. The procedure was continued until equilibrium swelling was observed (ASTM D-417). The results of sorption experiments were expressed by plotting the mole percentage uptake at time “*t*” ( $Q_t$ ) of the liquid by 100 g of rubber sample against the square root of time. Value of  $Q_t$  was calculated according to the equation<sup>26,27</sup>:

$$Q_t = \frac{W_t/M_s}{W_p} 100 \quad (1)$$

where  $W_t$  and  $W_p$  are the mass of solvent absorbed at a given time ‘*t*’ and mass of the polymer sample, respectively.  $M_s$  is the molecular mass of the solvent used.

### 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 Corp., USA) at a crosshead speed of 500 mm/min

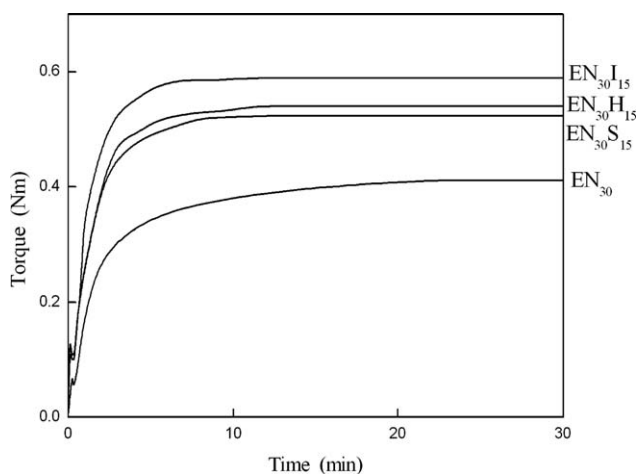
and at  $25 \pm 2^\circ\text{C}$ . Tensile properties of the blends were examined according to ASTM D-412. The experimental conditions and equipment for tear measurements were same as that of tensile testing. Tear test was conducted as per ASTM D-624 using 90° angle test pieces. Hardness of the samples was measured as per ASTM D-2240 using a Mitutoyo IRHD dead load apparatus. For hardness measurements, the sheets having an effective thickness of 6mm were used. Rebound resilience measurements were performed using a Schob pendulum following the standard ISO 4662-1978 specifications. 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,  $25 \pm 2^\circ\text{C}$  test temperature and  $40 \pm 5\%$  humidity were used as test conditions. Five samples from each formulation have been tested, and an average value has been presented.

## RESULTS AND DISCUSSION

### Cure characteristics

The cure characteristics and thus the processability of the carbon black filled 70/30 EPDM/NBR blend systems have been studied from torque-time graphs. Figure 1 shows the torque-time graphs of various sulfur vulcanized 70/30 EPDM/NBR and different types of carbon black filled 70/30 EPDM/NBR blend systems. It has been observed that the incorporation of carbon blacks into EN<sub>30</sub> matrix increases the maximum torque value ( $M_H$ ). This is definitely associated with the increase in the rigidity of the blend system due to filler loading which reduces the mobility of polymer chains in the matrix.<sup>28</sup>

The typical cure characteristics of carbon black filled blend systems have been presented in Table III. It is clear that the  $M_H$  values increase with an increase in the percentage of ISAF black. For a given



**Figure 1** Torque-time graphs of filled EPDM/NBR blends.

loading (15 phr), among the black fillers used, ISAF loaded mix shows the highest  $M_H$  value. The lowest  $M_H$  value is observed for SRF filled sample, and HAF-filled sample shows an intermediate behavior. This observation is associated with the difference in the extent of reinforcement by the three types of black particles. The highest reinforcement is observed in the case of ISAF black; associated with its smaller particle size.

The optimum cure time ( $t_{90}$ ) shows a regular variation with ISAF loading for a given blend ratio ( $EN_{30}$ ) as shown in Table III. The  $t_{90}$  decreases with an increase in the percentage of ISAF black in the composites up to 15 phr loading. At this loading the distribution of filler particles within the blend matrix is more uniform which provides a better reinforcement. However at a still higher filler loading,  $t_{90}$  value is lowered. This is due to the possible agglomeration of filler particles at higher filler concentrations. For a given percentage of filler loading (15 phr), SRF-filled system shows the highest  $t_{90}$  value compared with the other two systems.

Scorch time ( $t_2$ ), a measure of the premature vulcanization of a matrix, is an indication of scorch safety. As  $t_2$  increases, scorch safety increases.<sup>29</sup> As the percentage of ISAF black in  $EN_{30}$  matrix increases,  $t_2$  steadily increases up to a threshold value and then decreases. As shown in Table III, the highest  $t_2$  among the blend vulcanizates is for  $EN_{30}I_{15}$ ; hence this system possesses the highest scorch safety. Among the different filler loaded systems, for a given loading (15 phr), the ISAF-filled mix exhibits the highest scorch time. This indicates the better scorch safety of ISAF-filled composites.

The cure rate of the mixes has been computed using equation:

$$R_H = \frac{M_{90} - M_2}{t_{90} - t_2} \quad (2)$$

where  $M_{90}$  corresponds to the 90% of the maximum torque,  $M_2$  is the scorch time torque,  $t_{90}$  is the optimum cure time and  $t_2$ , the scorch time.

The values of cure rate are also given in Table III. The cure rate has been found to increase with an increase in the percentage of ISAF black as a typical case, up to a threshold value. The highest cure rate has been observed for 15 phr ISAF loaded sample; however, at still higher filler loading, the cure rate decreases. Among the black fillers used, for a given blend ratio (typically  $EN_{30}$ ) and for a given filler loading, the ISAF-filled sample shows the highest cure rate. These observations clearly indicate the better reinforcing efficiency of ISAF black in EPDM/NBR blends than HAF and SRF blacks.

Cotton<sup>30</sup> showed that the chemistry of the carbon black surface plays an important role in the initial steps preceding the actual crosslinking reaction. The reinforcing potential of the fillers can be evaluated from the rheological studies. The relative increase in reinforcement ( $\alpha$ ) due to the addition of the filler can be expressed by:

$$\alpha = \frac{\Delta M_{\max(\text{filler})} - \Delta M_{\max(\text{gum})}}{\Delta M_{\max(\text{gum})}} \quad (3)$$

where  $\Delta M_{\max}$  is the maximum change in torque during vulcanization. The values of  $\alpha$  and  $\Delta M_{\max}$  of sulfur cured 70/30 EPDM/NBR mix containing different carbon blacks of 15 phr loading and those of unfilled 70/30 EPDM/NBR are given in Table IV. The value  $\Delta M_{\max}$  as well as  $\alpha$  increases according to the reinforcing ability of the black fillers used.

## Morphology

SEM photographs of unfilled and filled EPDM/NBR blend systems are shown in Figures 2(a–d). Figure 2(a) shows the SEM photographs of unfilled 70/30 EPDM/NBR sample ( $EN_{30}$ ) and Figures 2(b–d) represent SRF, HAF and ISAF-filled 70/30 EPDM/NBR blends, respectively. Many domains in the matrix have been found to be fragmented into smaller sizes when the fillers are incorporated. This is due to the

**TABLE III**  
Cure Characteristics of Carbon Black Filled EPDM/NBR Blends

Sample code	Maximum torque, $M_H$ (Nm)	Optimum cure time, $t_{90}$ (min)	Scorch time, $t_2$ (min)	Cure rate, $R_H$ (Nm/min)
$EN_{30}$	0.41	3.67	0.69	0.103
$EN_{30}I_5$	0.48	4.10	0.46	0.097
$EN_{30}I_{10}$	0.52	3.90	0.56	0.111
$EN_{30}I_{15}$	0.59	3.23	0.58	0.181
$EN_{30}I_{20}$	0.66	3.60	0.54	0.139
$EN_{30}H_{15}$	0.54	3.80	0.51	0.117
$EN_{30}S_{15}$	0.52	3.85	0.42	0.112



**TABLE IV**  
**Values of  $\Delta M_{\max}$ ,  $\alpha$  and Swelling Coefficient Values for Carbon Black Filled EPDM/NBR Blend Systems**

Sample code	$\Delta M_{\max}$	$\alpha$	Swelling coefficient ( $\text{g}^{-1} \text{cm}^3$ )
EN <sub>30</sub>	0.33	–	4.94
EN <sub>30</sub> I <sub>15</sub>	0.49	0.48	3.50
EN <sub>30</sub> H <sub>15</sub>	0.45	0.35	3.52
EN <sub>30</sub> S <sub>15</sub>	0.44	0.33	3.59

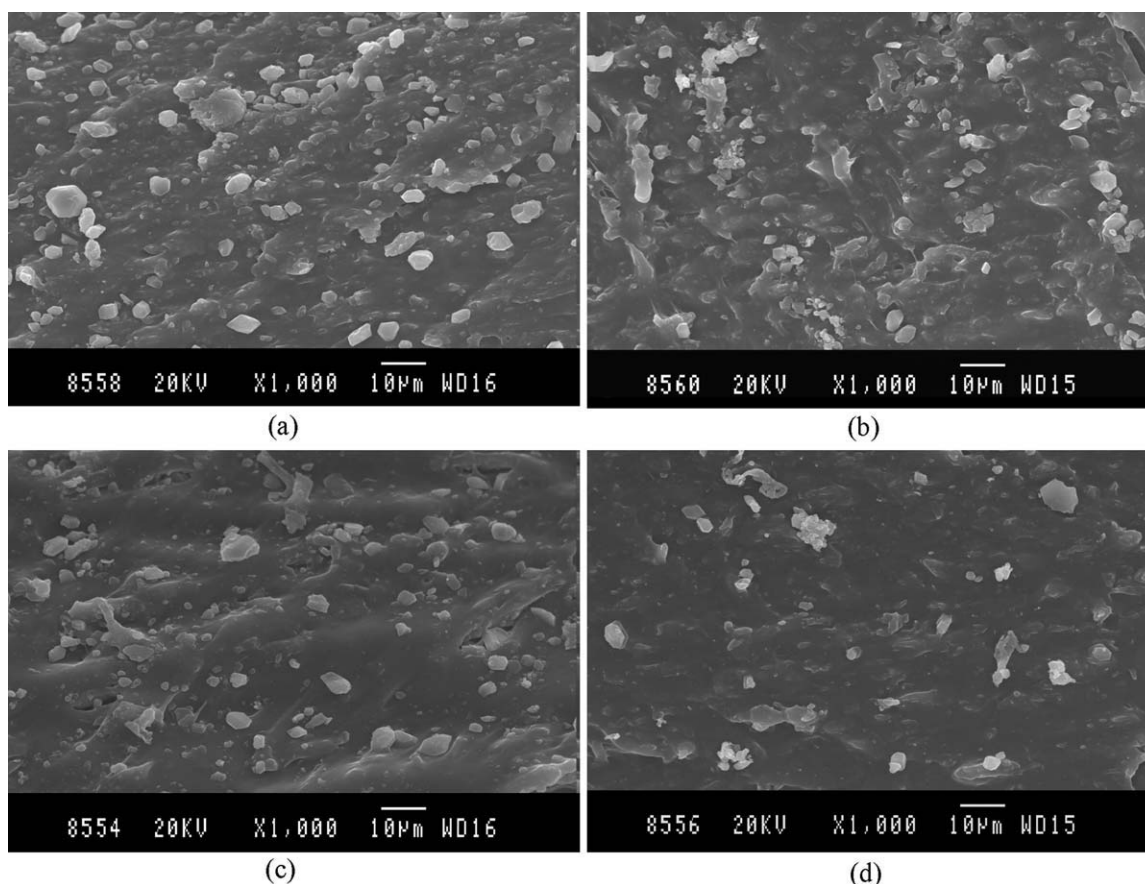
higher level of mechanical friction experienced during milling in carbon black filled samples compared to the unfilled system. An increase in homogeneity is observed when viewed from Figures 2(a–d). These morphological features contribute to the observed differences in the physical properties, as discussed in different sections.

### Comparison of barrier properties

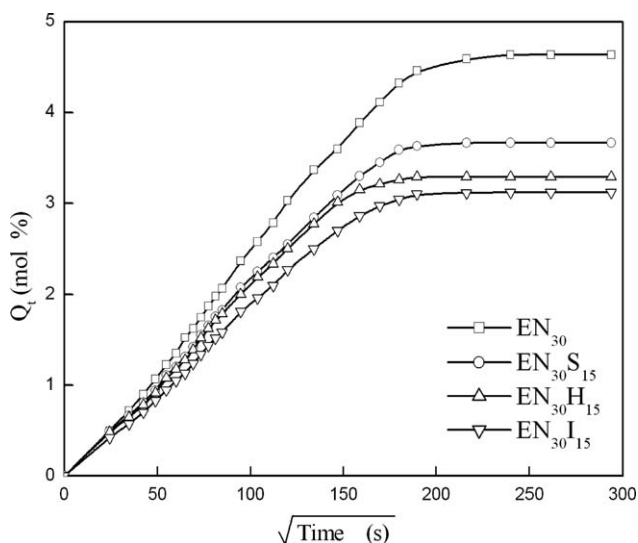
Figure 3 shows the comparison of mole percentage toluene uptake by 70/30 EPDM/NBR blend (EN<sub>30</sub>) and the EN<sub>30</sub> blend system filled with 15 phr of ISAF, HAF, and SRF respectively, vulcanized with sulfur. It is clear from the figure that filled system

shows a reduced solvent uptake tendency compared with the unfilled sample (EN<sub>30</sub>). The effective reinforcement in the blend matrix is evident from the above sorption curves. Vulcanization restricts the long-range movements of the polymer molecules but leaves their local segmental mobility high. Filler reinforcement modifies this condition. The attachment of chains to the surface of the filler has been accomplished through wetting. Carbon blacks can wet polymer segments, because of the increased probability of multiple adsorptions. The highest concentration of bound rubber is in the regions between carbon black particles. This reinforcement restricts the local freedom of movement of macromolecular chains and thereby improves the solvent resistance.

Among the different fillers used, EPDM/NBR loaded with ISAF shows the lowest penetrant interaction. It can be seen that the sorption follows the order: ISAF < HAF < SRF. This trend can be explained on the basis of the difference in the particle size of fillers reinforced to the matrix. For maximum reinforcement, the filler particles must be of the same size or smaller than the macromolecular chain end-to-end distance.<sup>31</sup> The degree of filler reinforcement increases with decrease in particle size or



**Figure 2** Scanning electron micrographs of 15 phr carbon black filled EPDM/NBR blends (a) EN<sub>30</sub> (b) EN<sub>30</sub>S<sub>15</sub> (c) EN<sub>30</sub>H<sub>15</sub> (d) EN<sub>30</sub>I<sub>15</sub>.



**Figure 3** Effect of carbon black on the mole percentage uptake of toluene.

increase in surface area.<sup>32</sup> Bound rubber increases as the surface area of carbon black increases. The ISAF black possesses the lowest particle size compared to other blacks used and hence executes higher degree of reinforcement. This causes a high resistance to the blend chain relaxation and thus the free volume within the matrix gets reduced, which subsequently restricts the diffusion of penetrants.

To assess the extent of the swelling behavior of the blends reinforced with carbon black, the swelling coefficients ( $\beta$ ) were calculated by equation<sup>33</sup>:

$$\beta = \frac{w_2 - w_1}{w_1} \rho_s^{-1} \quad (4)$$

where  $w_1$  and  $w_2$  are the weights of the samples before swelling and at equilibrium swelling and  $\rho_s$  is the density of the solvent.

Table IV shows the swelling coefficient values for different filled and unfilled blends in toluene. The higher swelling coefficient value is exhibited by the unfilled blend. The ISAF-filled blend shows the lowest swelling coefficient value.

Kraus<sup>34,35</sup> studied the degree of cure in particulate filler-reinforced vulcanizates by swelling method. The Kraus equation<sup>36</sup> has been applied to follow the extent of filler reinforcement. The degree of restriction exerted by reinforcing fillers has been given by the equation:

$$\frac{\phi_{puf}}{\phi_{pf}} = 1 - m \left[ \frac{\phi_f}{1 - \phi_f} \right] \quad (5)$$

where  $\phi_{puf}$  and  $\phi_{pf}$  are the volume fractions of the polymer blend in the fully swollen unfilled sample and in the fully swollen filled sample respectively.

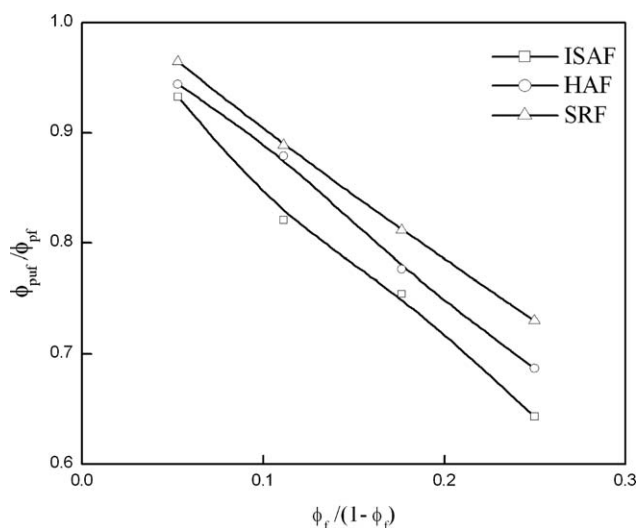
$\phi_f$  is the volume fraction of the filler and the slope  $m$  is a direct measure of the reinforcing capacity of the fillers in the matrix. According to Kraus theory, the curves with higher negative slope indicate a better reinforcing effect. From the Figure 4, it is observed that the negative value of the slope increases in the order: SRF < HAF < ISAF, indicating the degree of reinforcement in the same order. The order of reinforcement is complementary to the observed solvent uptake trend for the different filler loaded systems.

### Mechanical properties

#### Effect of filler loading

The effect of ISAF black filler loading on the tensile strength of EPDM/NBR blends is given in Table V. In general, the tensile strength of the filled systems is higher compared with the gum sample (EN<sub>30</sub>). It is due to the fact that, in carbon-filled samples, the rubber macromolecular chains bind tightly with carbon black.<sup>37</sup> The mechanism of reinforcement can be explained as follows.<sup>32</sup> A polymer sample has unequal distribution of chain lengths between the crosslinks. When an unfilled sample is subjected to a stress, the shortest chain will break first followed by the next most strained one leading to unequal distribution of stress. In the case of black filled samples, the most strained chains between two carbon black particles are given a chance of slipping to relieve the tension caused by stretching. Now the second chain shares the imposed load almost equally. This homogenous stress distribution gives an improvement in strength.

The tensile strength of the filled system in the present case shows an increase up to a loading of 15 phr, followed by a decrease at higher loading. The



**Figure 4**  $\phi_{puf} / \phi_{pf}$  against  $(\phi_f/1 - \phi_f)$  curves of filled 70/30 EPDM/NBR blends.

**TABLE V**  
Tensile Strength, Tear Strength, Elongation at Break and Modulus of Carbon Black Filled EPDM/NBR Blends

Sample code	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Modulus (100%) (MPa)
EN <sub>30</sub>	4.24	18.45	580.0	1.32
EN <sub>30</sub> I <sub>5</sub>	5.64	20.61	311.7	1.35
EN <sub>30</sub> I <sub>10</sub>	6.85	28.58	303.0	1.57
EN <sub>30</sub> I <sub>15</sub>	7.43	35.16	224.1	1.97
EN <sub>30</sub> I <sub>20</sub>	7.05	32.82	360.6	1.94
EN <sub>30</sub> H <sub>15</sub>	7.19	34.92	286.7	1.94
EN <sub>30</sub> S <sub>15</sub>	4.94	31.87	303.0	1.92

reinforcing effect of the filler gets counteracted and can finally be dominated by a dilution factor after a threshold value.<sup>28</sup> The observed maximum tensile strength observed at 15 phr ISAF black filled EPDM/NBR matrix is definitely associated with the relative uniform distribution of filler particles at this composition.

Table V also shows the variation of tear strength with different loadings of ISAF black. The tear strength also follows the same trend as that of tensile strength. Tear strength of the filled systems are higher than that of gum sample (EN<sub>30</sub>). As the filler concentration increases from 5 phr to 15 phr, the tear stress becomes more uniformly distributed in the polymer matrix and the blend exhibits improved tear strength.

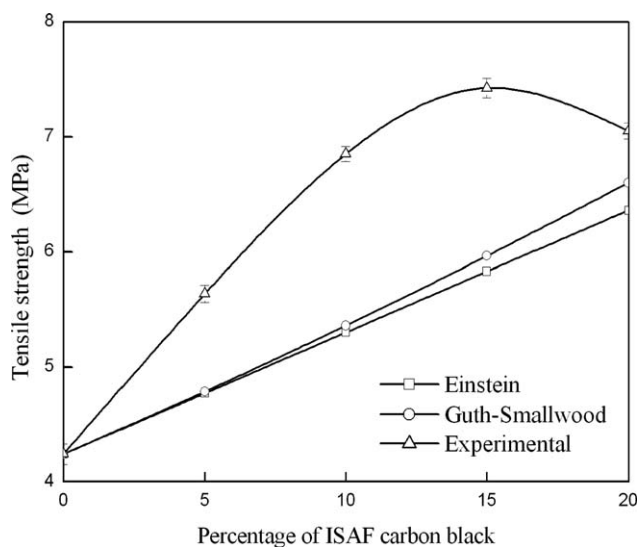
Table V shows the values of elongation at break of the mixes as a function of filler loading. The addition of filler reduces the elongation at break up to 15 phr loading. This also points towards the better reinforcement at this loading. Beyond this point, the agglomeration of carbon particles can occur which leads to an inferior filler-matrix interaction and thus to an increase in elongation tendency.

The 100% modulus values have been shown in Table V. The modulus also shows a steady increase up to 15 phr filler loading. This shows that EN<sub>30</sub>I<sub>15</sub> has the highest rigidity due to the uniform filler distribution in the matrix.

The hardness of the composites has also been analyzed and the results are presented in Table VI.

**TABLE VI**  
Hardness, Rebound Resilience and Relative Volume Loss of Carbon Black Filled EPDM/NBR Blends

Sample code	Hardness (IRHD)	Rebound resilience (%)	Relative volume loss (mm <sup>3</sup> )
EN <sub>30</sub>	51.2	36.33	0.15
EN <sub>30</sub> I <sub>5</sub>	52.0	36.00	0.23
EN <sub>30</sub> I <sub>10</sub>	53.0	34.00	0.22
EN <sub>30</sub> I <sub>15</sub>	53.5	33.67	0.21
EN <sub>30</sub> I <sub>20</sub>	55.4	33.33	0.22
EN <sub>30</sub> H <sub>15</sub>	53.0	34.00	0.26
EN <sub>30</sub> S <sub>15</sub>	52.3	34.67	0.37

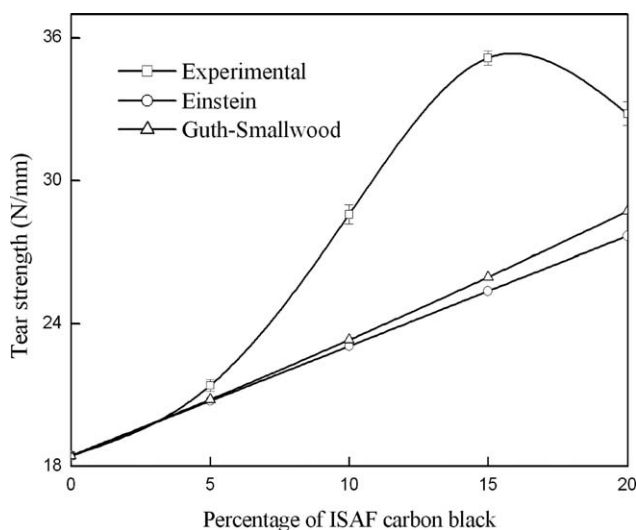


**Figure 5** Comparison of experimental results with theoretical models for tensile strength of carbon black filled EPDM/NBR blends.

It has been observed that the hardness of the composites is higher than the gum sample, EN<sub>30</sub>. The percentage rebound resilience of the composites has been observed to be decreasing with filler content. The abrasion resistance of the composites has been measured in terms of relative volume loss. A lower value of loss of volume indicates a higher abrasion resistance and vice versa. The relative volume loss of the composites is higher than that of the gum sample (Table VI).

#### Effect of filler type

The effect of filler type on the tensile strength of EPDM/NBR blends is shown in Table V. In comparison with the unfilled system, all the filled systems exhibit an improvement in tensile strength. This is due to the different degrees of reinforcement imparted by carbon black particles. However the values are different. For maximum reinforcement, the filler particles must be of the same size or smaller than the chain end-to-end distance. The degree of filler reinforcement increases with decrease in particle size or increase in surface area. In filled elastomers, the fillers act as stress concentrators. Smaller the particle size of fillers, more efficient will be the stress transfer from the matrix to the fillers.<sup>31</sup> The observed variation in tensile strength and tear strength, as shown in Table V, can thus be attributed to the different degrees of reinforcement of ISAF, HAF, and SRF in EPDM/NBR matrix. The variation in elongation at break (%) for the filled systems with different fillers is given in Table V. The presence of filler particles restricts the macromolecular chain



**Figure 6** Comparison of experimental results with the theoretical models for tear strength of carbon black filled EPDM/NBR blends.

elongation. Table V also shows the variation of modulus (100%).

The values of hardness of the composites are given in Table VI. The hardness is found to be highest for ISAF-filled sample followed by HAF and then SRF-filled sample for a given blend system. The resilience of the composites, also shown in Table VI, is found to be in the order: SRF > HAF > ISAF-filled composites, highlighting the degree of reinforcement in the same order. The relative volume loss of the composites increases with the decrease of reinforcement (Table VI).

#### Comparison with theoretical models

The theoretical models selected to predict the mechanical behavior of filled systems are those of Einstein and Guth-Smallwood.<sup>38,39</sup>

For filled systems, the simplest equation for reinforcement or for the increase in rigidity due to filler is given by Einstein. This equation can be represented as:

$$M = M_1(1 + 2.5\phi) \quad (6)$$

where  $M$  is the mechanical property of the filled system,  $M_1$  is the mechanical property of the unfilled system, and  $\phi$  is the volume fraction of the filler. Einstein's equation implies that the stiffening or reinforcing action of filler is independent of the size of the filler particles. The equation shows that the volume occupied by the filler is independent of the size of the filler particles. The volume occupied by the filler rather than its weight is the dominant variable. The equation also assumes that the filler is much more rigid than the matrix.

An extension of Einstein's theory, originally developed to explain rubber reinforcement, is due to Guth and Smallwood. Their equation for rigid spherical filler is:

$$M = M_1(1 + 2.5\phi + 1.41\phi^2) \quad (7)$$

Compared with the models used for tensile (Fig. 5) and tear (Fig. 6) strengths, the experimental values show significant positive deviations. This clearly highlights the reinforcing efficiency of black fillers, particularly by ISAF, in EPDM/NBR matrix.

#### CONCLUSIONS

The cure characteristics and mechanical properties of filler reinforced EPDM/NBR blend systems have been analyzed in terms of filler loading and filler types. The  $M_H$  values have been found to be increased with the filler loading. The  $t_{90}$  values decreased where as the cure rate increased with an increase in the percentage of black particles in the blend system up to a threshold level. The scorch safety has been found to be the highest for 15 phr loaded ISAF system. Filled samples have been found to show reduced solvent uptake compared with the unfilled sample for a given blend ratio. Blends loaded with ISAF exhibited the lowest liquid uptake among black filled systems which has been attributed to the better filler reinforcement. In comparison with the unfilled system, all the filled systems exhibited an improvement in tensile strength. Among the different filler types used, the ISAF-filled system showed the highest tensile strength and tear strength. This has been attributed to the better reinforcing efficiency of ISAF black. A relatively more uniform morphology has been observed for ISAF black filled samples as attested by SEM analysis. Two theoretical models were selected to predict the improvement in mechanical behavior. The experimental values showed significant positive deviations, suggesting the effective filler reinforcement in EPDM/NBR blends.

#### References

- Sadhan, C. J.; Alberto, P. *J Appl Polym Sci* 2002, 86, 2159.
- Ahmed, N. M.; El-Sabbagh, S. H. *Polym Plast Technol Eng* 2006, 45, 275.
- Das, N. C.; Chaki, T. K.; Khastgir, D. *Polym Int* 2002, 51, 156.
- Das, N. C.; Chaki, T. K.; Khastgir, D. *Carbon* 2002, 40, 807.
- Norman, R. H. *Conductive Rubber and Plastics*; Elsevier: London, 1970.
- Leblanc, J. L. *Prog Polym Sci* 2002, 27, 627.
- Park, S. J.; Kirm, J. S. *J Colloid Interface Sci* 2000, 232, 311.
- Kaempf, H. G.; Papenroth, W.; Holm, R. *J Paint Technol* 1974, 46, 56.
- Allen, N. S.; Edge, M. *Fundamentals of Polymer Degradation and Stabilization*; Chapman and Hall: Chichester, 1992.



10. Pokluda, I.; Palaskovas, M. *Int Polym Sci Technol* 1988, 15, 45.
11. Dannenberg, E. M. *Eur Polym J* 1985, 25, 167.
12. Ebell, P. C.; Hemsley, D. A. *Rubber Chem Technol* 1981, 54, 698.
13. Debapriya, D.; Debasish, D.; Singharoy, G. *Polym Eng Sci* 2007, 47, 1091.
14. Weili, W.; Chen, D. *Polym Compos* 2006, 27, 621.
15. Sombatsompop, N.; Wimolmala, E.; Markpin, T. *J Appl Polym Sci* 2007, 104, 3396.
16. Huang, J. C.; Muangchareon, P.; Grossman, S. J. *J Polym Eng* 2000, 20, 111.
17. Kozlowski, M.; Frekowiak, S. *Sens Actuators B* 2005, 109, 141.
18. Katbab, A. A.; Nazockdast, H.; Bazgir, S. *J Appl Polym Sci* 2000, 75, 1127.
19. El-Tantawy, F.; Aal, N. A. *J Appl Polym Sci* 2006, 101, 1237.
20. George, J.; Neelakantan, N. R.; Varughese, K. T.; Thomas, S. *J Appl Polym Sci* 2006, 100, 2912.
21. Ghoneim, A. M.; Ismail, M. N. *Polym Plast Technol Eng* 1999, 38, 979.
22. Desai, S.; Thakore, I. M.; Brennan, A.; Devi, S. *J Macromol Sci Pure Appl Chem* 2001, 38, 711.
23. Zeid, M. M. A.; Rabie, S. T.; Nada, A. A.; Khalil, A. M.; Hilal, R. H. *Nucl Instrum Methods Phys Res Sect B* 2008, 266, 111.
24. Ghosh, P.; Chakrabarti, A. *Eur Polym J* 2000, 36, 1043.
25. Mahapatra, S. P.; Sridhar, V.; Chaudhary, R. N. P.; Tripathy, D. K. *Polym Eng Sci* 2007, 47, 984.
26. Kumnuantip, C.; Sombatsompop, N. *Mater Lett* 2003, 57, 3167.
27. Mathai, S.; Thomas, S. *J Macromol Sci Phys B* 1996, 35, 229.
28. Sujith, A.; Unnikrishnan, G. *J Mater Sci* 2005, 40, 4625.
29. Haseena, A. P.; Priya, D. K.; Unnikrishnan, G.; Thomas, S. *Prog Rubber Plast Recycl Technol* 2005, 21, 155.
30. Cotton, G. R. *Kautsch Gummi Kunstst* 1969, 22, 477.
31. Wang, M. *J Rubber Chem Technol* 1998, 71, 520.
32. Blow, C. M.; Hepburn, C. *Rubber Technology and Manufacture*, 2nd Ed.; Butterworths: London, 1981.
33. Unnikrishnan, G.; Thomas, S. *Polymer* 1994, 35, 5504.
34. Kraus, G. *J Appl Polym Sci* 1957, 30, 928.
35. Kraus, G. *Rubber Chem Technol* 1964, 37, 6.
36. Kraus, G. *J Appl Polym Sci* 1963, 7, 861.
37. Soney, C. G.; Thomas, S. *Prog Polym Sci* 2001, 26, 985.
38. Guth, E. *J Appl Phys* 1945, 16, 20.
39. Smallwood, H. M. *J Appl Phys* 194, 15, 758.