

# Radiation-Processed Polychloroprene-*co*-ethylene-propene diene Terpolymer Blends: Evaluation of Blend Morphology, Miscibility, and Physical Properties

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**ABSTRACT:** The miscibility of polychloroprene rubber (CR) and ethylene-propylene-diene terpolymer rubber (EPDM) was studied over the entire composition range. Different blend compositions of CR and EPDM were prepared by initially mixing on a two-roll mill and subsequently irradiating to different gamma radiation doses. The blends were characterized by differential scanning calorimetry, Fourier transform infrared spectroscopy, density measurement, hardness measurement, and solvent permeability analysis. The compatibility of the blends was studied by measuring the glass transition temperature and heat capacity change of the blends. The immiscibility of blends was reflected by the presence of two glass transi-

tion temperatures; however, partial miscible domains were observed due to inter diffusion of phases. Permeation data fitted best with the Maxwell's model and indicated that in CR-EPDM blends, EPDM exists as continuous phase with CR as dispersed phase for lower CR weight fractions and phase inversion occurred in 40–60% CR region. It was observed that CR improved oil resistance of EPDM; however, the effect was prominent for blends of >20% CR content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3552–3559, 2008

**Key words:** blends; polychloroprene rubber; ethylene-propylene-diene terpolymer; radiation vulcanization

## INTRODUCTION

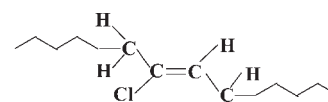
Blending of two or more polymers offers an economically viable and versatile way to produce new engineering materials with the desired properties.<sup>1–4</sup> Blends of rubber with other rubbers<sup>5–7</sup> or with plastics have been a subject of study for different groups, and there is growing interest in developing new methods to form blended polymers as well as characterize them.

Polymer-polymer compatibility has been extensively studied by several techniques such as differential scanning calorimetry (DSC), DMA, neutron scattering, electron microscopy, dilute solution viscometry, and other related techniques.<sup>8–10</sup> The morphology of blends and the interaction between polymer chain segments in a crosslinked polymer blend can also be investigated by solvent permeability study of the polymer matrix in a suitable solvent. This can provide important information about structural characteristics, chain flexibility, and segment packing density of the polymer.<sup>11–14</sup>

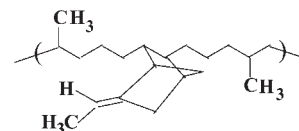
Elastomer-elastomer or elastomer-plastic blends are usually vulcanized by using conventional chemical method to improve their desired characteristics.

However, high-energy ionizing radiation has recently received a great deal of attention, primarily because of its ability to produce crosslinked networks in a wide range of polymers. The low-operation cost, additive-free technique, and room-temperature operations are among the added advantages of radiation vulcanization over the existing vulcanizing techniques.<sup>15–19</sup>

The blends of ethylene-propylene-diene terpolymer (EPDM) (nonpolar) with polychloroprene rubber (CR) (polar) have evinced special interest



Poly(Chloroprene) (CR)



Ethylene propylene diene terpolymer (EPDM)

because incorporation of suitable amount of CR is expected to impart oil resistance, heat resistance, and better adhesion characteristics to parent unsaturated matrix.<sup>20,21</sup> However, little information is available about the miscibility behavior of CR/EPDM blends. It would be important to investigate the

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**TABLE I**  
**Blend Compositions and Sample Designations**

CR (%)	EPDM (%)	Sample designation
00	100	CR00
20	80	CR20
40	60	CR40
60	40	CR60
80	20	CR80
100	00	CR100

miscibility behavior of this blend system, as most of the physio-mechanical properties are influenced by the miscibility behavior of the components of the blends. In this study, the compatibility, phase separation behavior, and interactions between the segments of CR and EPDM in their blends were investigated, as function of composition. The blend morphology was also interpreted by employing various theoretical models available for observed solvent permeability pattern.

## EXPERIMENTAL

### Materials

CR and EPDM were procured from a local supplier M/s Polystar chemicals in block form. Chloroform used for swelling studies was of Analar grade.

### Sample preparation and characterization

A series of blends of CR and EPDM was prepared by initially mixing the two components homogeneously on a two-roll mixing mill. The homogeneous mix was cut to small pieces and compressed into sheets of size  $12 \times 12 \text{ cm}^2$  of different thicknesses in range 1–4 mm using compression-molding machine at  $150 \text{ kg/m}^2$  pressure for 2 min at  $130^\circ\text{C}$ . The blend compositions and sample designations have been represented in Table I. Irradiation was carried out under aerated condition using a gamma chamber 5000 (GC-5000) having Co-60 gamma source supplied by M/s BRIT India. The dose rate of gamma chamber was ascertained to be  $5 \text{ kGy/h}$  using Fricke dosimetry prior to irradiation of samples.

For the sorption studies, radiation crosslinked blends irradiated to a dose of  $250 \text{ kGy}$  were Soxhlet extracted at elevated temperature for 12 h to extract any sol content using xylene as solvent. The insoluble gel part was then dried initially under room conditions and later in a dissector. The dried blend so obtained was cut into uniform square pieces ( $1 \times 1 \text{ cm}^2$ ) using a sharp edged die and used for swelling studies. Preweighed samples were placed in a 200-mesh stainless steel compartment and immersed in excess xylene. The swelled samples were periodically removed, blotted free of surface xylene using

laboratory tissue paper, weighed on Mettler analytical balance (accuracy  $0.00001 \text{ g}$ ) in stopper bottles and returned to the swelling medium. Measurements were taken until the samples reached constant weight.

Fourier transform infrared spectroscopy (FTIR, JASCO 660) was used for compositional characterization of the blends. Spectra were recorded at  $4 \text{ cm}^{-1}$  resolution and averages of at least 16 scan in the standard wave number range  $400\text{--}4000 \text{ cm}^{-1}$ .

The density in  $\text{g cm}^{-3}$  was determined by using density balance from M/s AND, Japan (Least count  $0.00001 \text{ g}$ ) using suitable liquids.

DSC (DSC-822 from M/s Mettler) was used to observe glass transition temperature of the blends. All DSC thermograms were recorded at heating rate of  $20^\circ\text{C min}^{-1}$ , under inert atmosphere. Prior to DSC run, the instrument was calibrated for temperature and heat flow using high-purity indium standard. The mid point of the slope change of heat capacity plot of second scan was taken as the glass transition temperature.

The gel content was determined by refluxing the samples with xylene for 24 h. The remaining insoluble portion was dried in vacuum oven at  $60^\circ\text{C}$  to a constant weight. Gel content was evaluated using following relationship [eq. (1)].

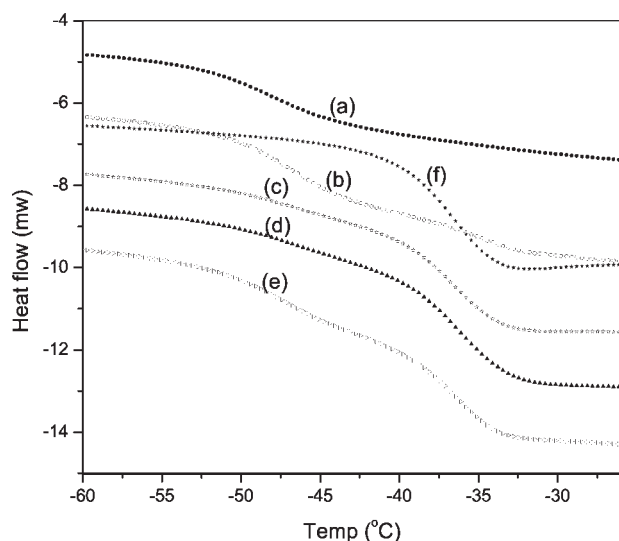
$$\text{Gel content} = \left( \frac{W_g}{W_i} \right) \quad (1)$$

where  $W_g$  and  $W_i$  are the weight of insoluble fraction and initial weight, respectively.

## RESULTS AND DISCUSSION

### Glass transition and heat capacity measurement

The effect of specific interactions between the blend segments was studied by measuring the glass transition temperature ( $T_g$ ). The DSC thermograms recorded for different blends are shown in Figure 1. EPDM shows a broad transition, whereas CR shows a narrow transition. In general, the miscibility of two blends is indicated by presence of single glass transition temperature; however, in the present CR/EPDM system, the blend compositions were found to have two distinct transitions, reflecting immiscibility of the system. As evident from the Figure 1, the glass transition temperature was a function of blend composition, indicating either partial compatibility or significant interfacial interactions between the components of blends. It has been reported that under such circumstances,  $T_g$  model applicable for miscible blends can be employed for each glassy phase, and it is possible to calculate phase composition of blends and proportion of material in each phase.<sup>22,23</sup>



**Figure 1** DSC thermograms recorded at  $20^{\circ}\text{C min}^{-1}$ , under inert atmosphere. (a) CR00, (b) CR20, (c) CR40, (d) CR60, (e) CR80, and (f) CR100.

The Fox equation [eq. (2)] is often used as a  $T_g$  additive model for miscible polymer blend systems<sup>24</sup>

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

where 1 and 2 represents CR and EPDM, respectively,  $w_1$  and  $w_2$  are the weights of Components 1 and 2, and  $T_g$  is the glass transition temperature of pure component.

The Fox equation can be modified for the present blend system, for the weight fraction of one component in other phase, in the following form.<sup>24</sup>

$$W_{bl} = \left[ \frac{(T_{gab1} - T_{ga})}{(T_{gb} - T_{ga})} \right] \times \frac{T_{ga}}{T_{gab1}} \quad (3)$$

$$W_{a1} = (1 - W_{b1}) \quad (4)$$

where  $T_{gab1}$  and  $T_{gab2}$  are the blend  $T_g$ 's in the two phases, and  $T_{ga}$  and  $T_{gb}$  are pure component's  $T_g$ 's. Assuming that the subscripts  $a$  and  $b$  are assigned to two components and subscripts 1 and 2 to the two glassy phases;  $X_1$ , the weight fraction of total polymer in Phase 1;  $X_2$ , the weight fraction of total polymer in Phase 2;  $W_{a1}$ , the weight fraction of Component 1 in Phase 1;  $W_{a2}$ , the weight fraction of Component 1 in Phase 2;  $W_{b1}$ , the weight fraction of Component 2 in Phase 1;  $W_{b2}$ , the weight fraction of Component 2 in Phase 2; and  $W_{at}$ , the weight fraction of Component 1 in total polymer blend.

The equation given earlier can also be applied for Phase 2. The weight fraction of total component in each phase is

$$X_1 = \frac{(W_{a1} - W_{a2})}{(W_{a1} - W_{a2})} \quad (5)$$

$$X_2 = (1 - X_1) \quad (6)$$

Moreover, a relatively simpler additive model can also be derived from Gordon-Taylor equation, in which the thermal expansion in the liquid and glassy phases is considered to be constant for all polymers<sup>25,26</sup>

$$T_g = T_{ga} \cdot W_1 + T_{gb} \cdot W_2 \quad (7)$$

It results in the following form:

$$W_{b1} = \frac{(T_{gab1} - T_{ga})}{(T_{gab1} - T_{ga})} \quad (8)$$

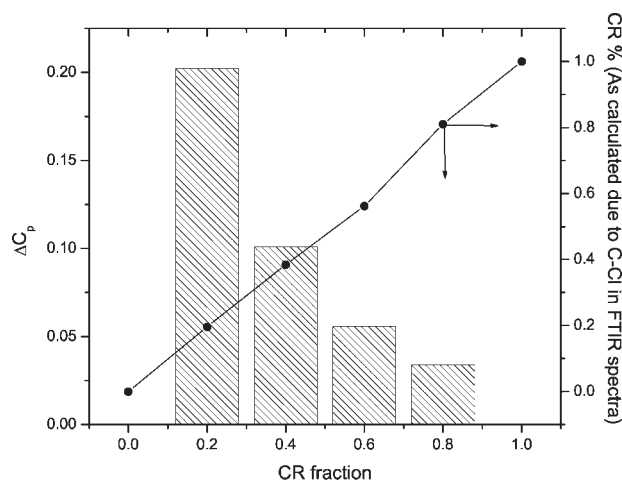
The modified Fox and Gordon-Taylor equations were used to calculate, CR or EPDM components in EPDM or CR rich domains of blends. The values found by two equations were in good agreement. Table II shows the results based on modified Fox equation. It is clear from the tabulated values that CR and EPDM rubber show partial miscibility, and the extent of diffusion of the two components does not show a consistent trend. However, values are lower for the EPDM diffusion in CR phase at higher CR content. The effect is very prominent for blend with 80% CR which shows a very low extent of EPDM interdiffusion. This variation in partial miscibility of CR/EPDM system was further established by estimation of heat of mixing for the blends.

The change in heat capacity near glass transition provides information about the size of dispersed phase, that is, miscible characteristics of the blend composition. From the experimental values of  $\Delta C_{pi}$ , heat capacity change at the glass transition of each component of the blend, it is possible to calculate  $(\Delta C_p)_{cal}$  value for each blend using the following relationship<sup>27,28</sup>:

$$(\Delta C_p)_{cal} = W_a(\Delta C_p)_a + W_b(\Delta C_p)_b \quad (9)$$

**TABLE II**  
Miscibility Parameters Estimated Using Modified Fox Equation

Sample	Phase 1 (EPDM rich)			Phase 2 (CR rich)		
	$X_1$	$W_{CR}$	$W_{EPDM}$	$X_2$	$W_{CR}$	$W_{EPDM}$
CR00	–	0	1	–	–	–
CR20	0.84	0.10	0.90	0.15	0.73	0.27
CR40	0.61	0.15	0.85	0.39	0.79	0.21
CR60	0.42	0.26	0.74	0.58	0.84	0.16
CR80	0.20	0.21	0.79	0.80	0.95	0.05
CR100	–	–	–	–	1	0



**Figure 2** (a) Variation in difference between experimental and theoretical  $C_p$  values and absorbance due to incorporation of CR in EPDM for blends (b) variation of normalized absorbance of C—Cl FTIR band with composition.

The value obtained can then be compared with the experimental value  $(\Delta C_p)_{\text{exp}}$  for both miscible and immiscible systems with one or two  $T_g$ 's. Any difference observed can be expressed as an excess value [eq. (10)].

$$(\Delta C_p)_E = (\Delta C_p)_{\text{exp}} - (\Delta C_p)_{\text{cal}} \quad (10)$$

As the miscible blends show only one glass transition, the difference in experimental and calculated heat capacity is expected to be very small. On the other hand, for immiscible blends, the  $(\Delta C_p)_E$  values are expected to be significantly high, indicating repulsive interactions between the polymeric segments. The  $(\Delta C_p)_E$  values, for the current CR/EPDM system plotted in Figure 2, suggest the presence of weak-interfacial interactions between CR and EPDM segments. FTIR technique was used to evaluate the compositional characteristic of blends to substantiate these observations. Compositional characterization of polymer blends was done by following the vibration because of C—Cl, (at  $650 \text{ cm}^{-1}$ ) because of introduction of CR in the EPDM matrix. The results from normalized peak height showed a close agreement between calculated and expected value of CR weight fraction (Fig. 2). Therefore, it is evident that the EPDM/CR system is incompatible with partially miscible interdiffused domains; furthermore, the interfacial adhesion between two components is not significant as evident from heat capacity variation with blend composition.

#### Effect of gamma radiation on CR/EPDM blends

The CR/EPDM blends were covalently crosslinked using gamma radiation. Figure 3 shows the change in the gel content of CR/EPDM blends on irradiation.

Unirradiated samples were found to be soluble in hot xylene; however, blends irradiated to a dose  $> 30 \text{ kGy}$  were insoluble due to the formation of a three-dimensional network.<sup>29</sup>

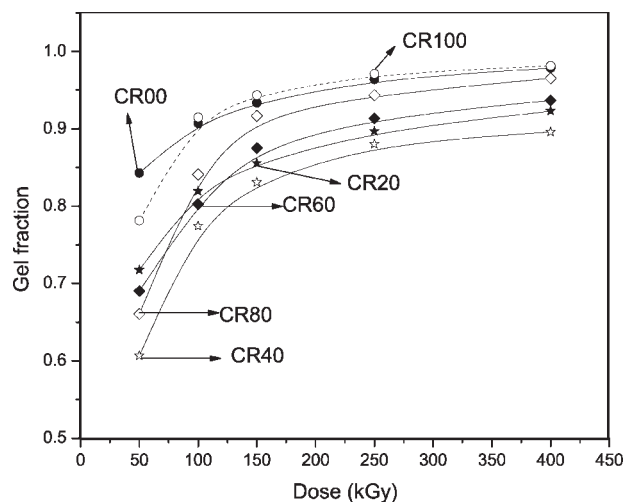
For a noninteracting type of system, gel fraction values for the blends are expected to follow additive rule, that is, it should vary in proportion to the pure components present in the matrix. However, in the present system, the ratio of ruptured to crosslinked chains shows higher value (i.e., low gel fraction) than pure components for blends containing 20–60% CR. We have recently reported that elastomer blends system may exhibit inconsistent or poor gelation characteristics when compared with their parent polymers.<sup>9</sup> This behavior has been attributed to relatively poor radical–radical interactions in polymer blends due to increase in free volume on blending with second component, this is in accordance with the observation of glass transition temperature and heat capacity variation.

#### Interaction parameter and heat of polymer mixing

The effect of polymer–polymer interaction on the solvent transport mechanism was investigated by studying the polymer–polymer interaction parameter between CR and EPDM ( $\chi_{12}$ ) using from the equilibrium solvent uptake (CR/ $\text{CHCl}_3$ /EPDM) behavior.

$$\begin{aligned} \ln a_c &= 0 \\ &= \ln \phi_c + (1 - \phi_c) + (\chi_{c1}\phi_1 + \chi_{c2}\phi_2)(1 - \phi_c) - \chi_{12}\phi_1\phi_2 \end{aligned} \quad (11)$$

where  $a_t$  is the activity of the chloroform absorbed into a blend of Polymers 1 and 2, and  $\phi_c$ ,  $\phi_1$ , and  $\phi_2$  are the volume fractions of chloroform, Polymers 1 and 2 in ternary system.<sup>30</sup>  $\chi_{c1}$  and  $\chi_{c2}$  are the



**Figure 3** Effect of radiation dose on the gelation behavior of different blends.



TABLE III  
Properties of CR and EPDM

Rubber	$\delta$ (J/cc) <sup>1/2</sup>	$\rho$ (g/cc)	Mol. wt.
CR	19.22	1.23	87.5
EPDM	16.17	0.86	70

polymer–toluene interaction parameter determined from the equilibrium solvent uptake of the neat polymers

$$\ln a_c = 0 = \ln \phi_c + (1 - \phi_c) + \chi_{cl}(1 - \phi_c)^2 \quad (12)$$

To study, the intrinsic miscibility behavior of CR/EPDM system (in the absence of solvent), the heat of mixing of CR/EPDM blend system was calculated according to the following equation.<sup>31</sup>

$$\Delta H_m = (1 - w_b)M_a\rho_a(\delta_a - \delta_b)^2 \times \left[ \frac{w_b}{(1 - w_b)M_b\rho_b + w_bM_a\rho_a} \right] \quad (13)$$

where  $M$ ,  $w$ ,  $\delta$ , and  $\rho$  are the molecular weight of monomer unit, weight fraction, solubility parameter, and the polymer density, respectively, and subscripts  $a$  and  $b$  refer to CR and EPDM, respectively. The parameters of CR and EPDM related to equation are shown in Table III.

The behavior of heat of mixing demonstrates the heterogeneity of CR/EPDM blend system over the major composition range (Fig. 4).  $\Delta H_m$  values were found to lie between 0.02 and 0.06 J and increased with increase in weight fraction of CR in the blend attaining a maximum value at  $\sim 65\%$  and decreasing afterward. Schneider<sup>31</sup> has calculated the  $\Delta H_m$  value for many polymer pairs and showed for compatible polymer pairs, the value lies in the range 0.004–0.04 J. Considering this  $\Delta H_m$  values for compatibility, a miscibility gap is expected to exist in 30–90% CR region. These assumptions support the possibility of interdiffusion of phases between 0 and 30 CR and  $>90\%$  region, as observed in the DSC analysis.

The interaction parameter derived from equilibrium chloroform uptake was found to be negative and showed compositional dependence (Fig. 4), indicating improvement in the specific interactions between CR and EPDM at higher EPDM fraction and also reflecting increase in the level of mixing with increase in the EPDM fraction in the blends as indicated by heat of mixing and calorimetric studies.

### Diffusion in crosslinked blends

The permeability of solvents provides insight into the morphological characteristics of blends. It has been suggested that the rate of approach to solvent can be characterized by a diffusion coefficient value “ $D$ ” which can be calculated from the eq. (14)<sup>32</sup>

$$M_t/M_\infty = 4/\pi^{0.5} (Dt/L_o^2)^{0.5} \quad (14)$$

where “ $D$ ” is the diffusion coefficient in a polymer-fixed reference frame, and  $L_o$  is initial thickness of the sample. The value of  $D$  determined using eq. (14) depends on the polymer segmental mobility and holds good for systems without appreciable swelling. For considerable swelling, as is the case of swelling of CR-EPDM blends in chloroform, a corrected equation has been suggested incorporating a new parameter  $\phi$ , the volume fraction of the polymer in the swollen mass,<sup>31</sup> thus giving the intrinsic diffusion coefficient,  $D^*$  given by

$$D^* = \frac{D}{\phi^{7/3}} \quad (15)$$

The volume fraction of polymer  $\phi$  in the solvent swollen sample can be calculated by using the eq. (16)

$$\phi = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \quad (16)$$

where  $w_1$  and  $\rho_1$  are the weight and the density of the polymer sample, respectively; and  $w_2$  and  $\rho_2$  are the weight and the density of the solvent.

The permeation of small molecules through polymers generally occurs through solution diffusion kinetics, i.e., the penetrant molecules are first absorbed by polymer followed by diffusion through the polymer. However, the net transport through the polymer depends on the difference in the amount of penetrant molecule between two surfaces and the permeability of penetrant in a polymer depends on diffusivity as well as on sorption of the penetrant in the polymer. Permeability has been defined as<sup>31</sup>

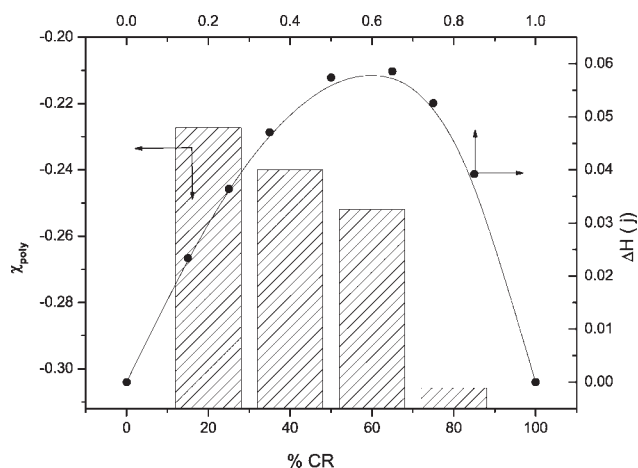
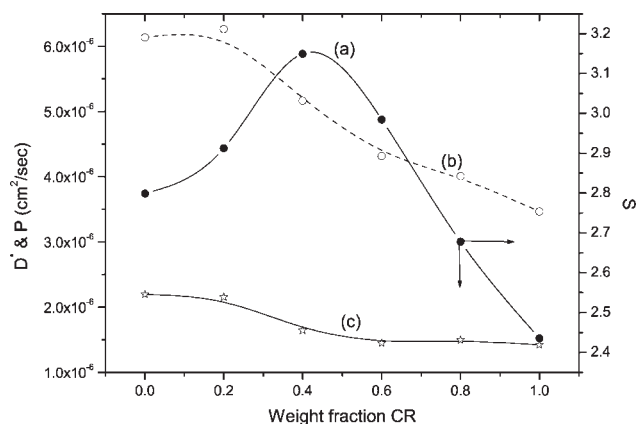


Figure 4 (a) Variation of heat of mixing for blends of different composition (b) Variation of polymer–polymer interaction parameter for blends of different composition.



**Figure 5** Variation in (a) sorption coefficient, (b) permeability coefficient, and (c) intrinsic diffusion coefficient of chloroform in blends irradiated to a dose of 250 kGy.

$$P = D \cdot S \quad (17)$$

where  $S$  is the sorption coefficient that is related to the equilibrium sorption of the penetrant and can be calculated as,

$$S = M_s/M_p \quad (18)$$

where  $M_s$  is the mass of the solvent at equilibrium, and  $M_p$  is the mass of polymer sample. The variation in the intrinsic diffusion coefficient, sorption coefficient, and permeability coefficient with fraction of CR is illustrated in Figure 5. It is clear from the figure that intrinsic diffusion coefficient and permeability coefficient decrease with increase in CR fraction; however, the sorption coefficient profiles are concave toward  $x$  axis, with maxima at around 40% CR. This clearly indicates that the sorption and diffusion were not exactly in accordance with each other, the lag between the two phenomena may be due to initial absorption of solvent by polymer chains to relax followed by actual diffusion of solvent into the blends. As irradiation affects the final properties of the blend by causing permanent effects like crosslinking, degradation, IPN, or semi-IPN formation, a close correlation is expected between the radiation responses of the components of the blend with the sorption behavior of the system. The delayed formation of aldehydic, acidic, alcoholic, and other oxygenated groups due to diffusion of oxygen to residual radical sites has also been reported to be an important factor affecting sorptive activity of the polymer matrices.<sup>12,16</sup>

### Blend morphology

The permeation of the penetrant into polymer matrix depends on the polymer morphology, which controls the propagation of molecule from one side to another. Any morphological factor that modifies

either the structure or the flexibility of the polymer chains is expected to change the permeability of the solvent molecules in the polymer matrix. An attempt was made to interpret the permeability results in terms of various theoretical models generally used for the morphological analysis of heterogeneous polymeric blends.

Robeson's two limiting models, namely series and parallel models, are generally used in case of polymer blends.<sup>33</sup> According to the Parallel model,

$$P_c = P_1\phi_1 + P_2\phi_2 \quad (19)$$

and by Series model

$$P_c = \frac{P_1P_2}{\phi_1P_2 + \phi_2P_1} \quad (20)$$

where  $P_c$ ,  $P_1$ , and  $P_2$  are the permeation coefficients of the blend, Components 1 and 2, respectively, and  $\phi_1$  and  $\phi_2$  are the volume fractions of the Components 1 and 2, respectively.

To describe the effect of permeating component on the overall blend permeability, Maxwell suggested the following equation.<sup>30</sup>

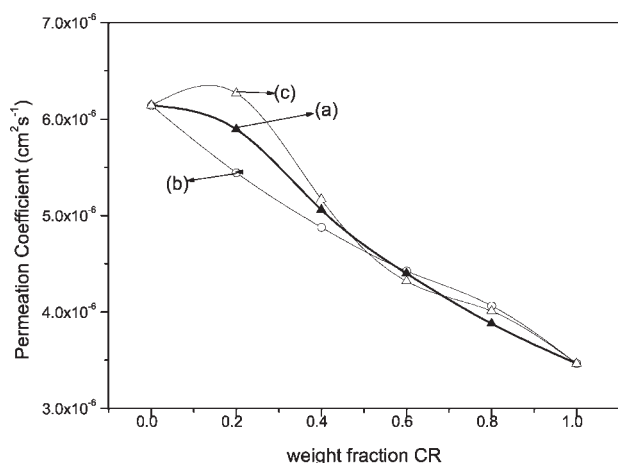
$$P_c = P_m \left[ \frac{P_d + 2P_m - 2\phi_d(P_m - P_d)}{P_d + 2P_m + \phi_d(P_m - P_d)} \right] \quad (21)$$

where subscripts "d" and "m" correspond to the dispersed phase and matrix, respectively.

Robeson extended Maxwell's analysis to include the continuous and discontinuous characteristics of both phases at intermediate compositions and expressed the equation as,

$$P_c = x_a P_1 \left[ \frac{P_2 + 2P_1 - 2\phi_2(P_1 - P_2)}{P_2 + 2P_1 + \phi_2(P_1 - P_2)} \right] + x_b P_2 \left[ \frac{P_2 + 2P_1 - 2\phi_1(P_1 - P_2)}{P_2 + 2P_1 + \phi_1(P_1 - P_2)} \right] \quad (22)$$

where  $x_a$  and  $x_b$  are the fractional contributions to the continuous phase so that  $x_a + x_b = 1$ . It is known that permeability of the blend, in which the more permeable polymer is in continuous phase will approach the parallel model, whereas permeability data will approach to the series model when the less permeable polymer is continuous phase.<sup>30</sup> The experimental data (Fig. 6) was found to be in close agreement with Maxwell's model, indicating for CR/EPDM radiation crosslinked blends, CR is a continuous phase at higher CR fractions, whereas at lower CR content EPDM forms the continuous phase. This clearly indicates that phase inversion takes for CR/EPDM blends depending on the proportion of the two components.

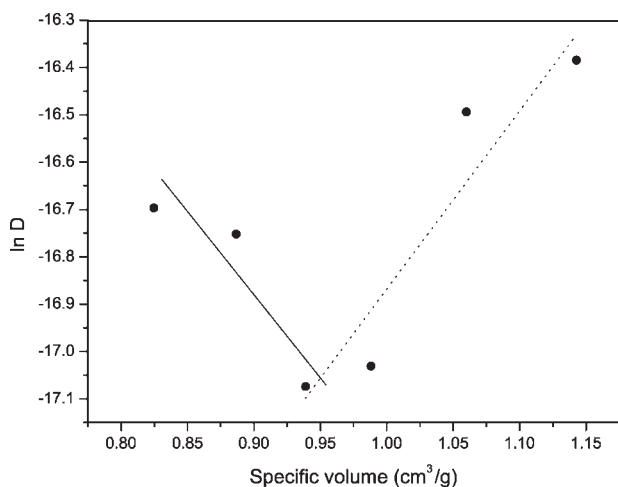


**Figure 6** Permeation coefficient ( $P$ ) profiles calculated using different models, for blends irradiated to a dose of 250 kGy. (a) experimental, (b) Maxwellian (EPDM as disperse phase), and (c) Maxwellian (CR as disperse phase).

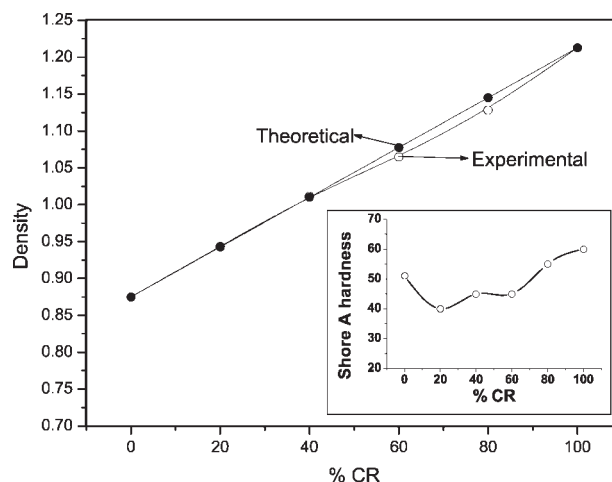
The correlation shown between specific volume and diffusion coefficient of blend composition in Figure 7 indicates the change in diffusion coefficient with specific volume of the blends. The specific volume in turn depends on the composition of the blend and on the interactions between CR and EPDM segments in amorphous phase. The intersection of two straight lines is located around 50% CR blend composition, indicating phase inversion at this composition as concluded from similar studies earlier.<sup>34</sup> This inference further supports that higher component exists as a continuous phase as reflected from permeability model fitting.

### Effect of blend composition on the physical properties

The difference between experimental density and calculated density (additive) of the blends can also

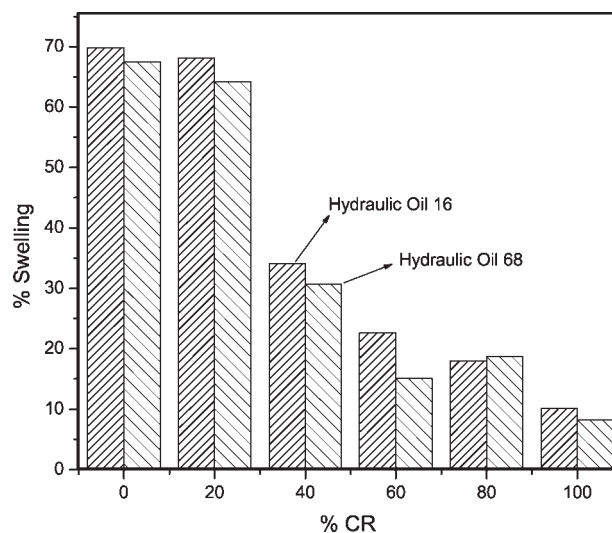


**Figure 7** Variation of diffusion coefficient with blend composition.



**Figure 8** Variation of density of blends with blend composition. Inset: variation of hardness with blend composition.

provide an estimation of the extent of the miscibility of blends. Figure 8 represents the variation of calculated density and experimental density with blend composition. It is clear on comparison of the two profiles that for all the blends, there is negative deviation indicating that all blends have some free volume. The increased free volume would lead to decreased poor miscibility and lesser overlapping of free radicals generated on irradiation and hence resulting in poor crosslinking. The radiation-induced crosslinking of rubber samples would be reflected as increase in hardness of the blends on irradiation. Inset of Figure 8 shows the compositional dependence of hardness of the blends. It was found that initially the hardness of the CR/EPDM blend increased with the incorporation of CR in the matrix. Hardness is generally referred to the resistance of material to the local deformation, and the results proved that



**Figure 9** Oil resistance of blends.

the blends with higher CR content were more resistant toward local deformation consequently leading to increase in hardness values.<sup>9</sup>

The effect of the incorporation of CR in EPDM upon the oil (hydraulic oil 16 and 68) resistance of nonpolar EPDM has been shown in Figure 9. It is clear that addition of CR enhances the oil resistance of EPDM; however, the effect is prominent for blends with CR content >20%. The not so significant increase in oil resistance up to 20% CR content may be due to the compensation of the surface polarity enhancement, with increase in the oil uptake due to increased free volume of the blends. It seems at higher CR content, the phobicity of blends for oil due to polar contribution from CR is able to overcome the ease of solvent access due to free volume. The anomalous behavior in some physical properties of CR/EPDM blends may be due to overall changes that occurred due to free volume and also depend on intrinsic radiation response of blend component. Thus, a simplistic model to represent the radiation response may not be adequate to explain the observations.

### CONCLUSION

The results obtained in this study have highlighted the immiscibility of CR/EPDM blends in general. The glass transition and heat capacity studies indicated partial miscibility. Radiation induced changes in the properties and the extent of changes in the properties were a function of the miscibility of the two components of the blends. A phase inversion around 50 : 50 CR/EPDM blend composition was observed as indicated by diffusion coefficient and specific volume studies. Morphological analysis by solvent permeability also revealed the phase inversion and predicted higher component as a continuous phase in the blends. The difference in experimental density and calculated density of the blends was found to be small with a negative deviation indicating immiscibility of blends. The oil resistance of blends was found to be dependent on blend morphology and improved for blends containing higher fractions of CR > 20%.

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