

Radiation-Processed Styrene–Butadiene-*co*-Ethylene–Propylene Diene Rubber Blends: Compatibility and Swelling Studies

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ABSTRACT: Radiation-induced compatibility behavior of SBR–EPDM blends of different composition has been investigated using dilute solution viscometry. The results show that at a threshold dose of 10 kGy, good interaction between the components of the blends is achieved. Higher radiation doses lead to formation of crosslinked three-dimensional copolymer network, whose swelling depends on the radiation dose imparted. The anomalous diffusion of solvent into

the gels was confirmed by rigorous treatment of the swelling data. Permeation data agreement with the series model indicated that in SBR–EPDM blends EPDM exists as continuous phase and SBR as dispersed phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3638–3649, 2006

Key words: radiation; compatibility; blends; viscosity; dynamic swelling

INTRODUCTION

Polymer blends are physical mixtures of structurally different polymers, which interact through secondary forces with no covalent bonding.¹ Blending of two or more components offers an economically viable and versatile way to produce new engineering materials with the desired properties from the parent components.^{2,3} Therefore, blends of rubber with other rubbers^{4–6} or with plastics^{7–9} have been a subject of study for different groups. The blends of unsaturated rubbers with ethylene–propylene–diene rubber (EPDM) are of special interest because incorporation of suitable amount of EPDM imparts significant heat and ozone resistance to the parent unsaturated matrix.¹⁰ However, a thorough knowledge of polymer–polymer compatibility and phase separation behavior is essential to ensure desired properties in the blend. Polymer–polymer compatibility has been extensively studied by several techniques such as DSC, DMA, neutron scattering, electron microscopy, and other related techniques,¹¹ which are time-consuming and involve expensive instrumentation. Dilute solution viscometry (DSV) offers alternative simple, inexpensive but equally reliable method to analyze polymer miscibility in solution.^{12,13} The effectiveness of DSV is based on

the assumption that mutual interaction of macromolecules in solution has a great influence on the viscosity of ternary systems and it in turns provides the information about miscibility behavior of macromolecules.¹⁴ The interaction between polymer chain segments in a crosslinked polymer blend can be studied by dynamic and equilibrium sorption kinetic studies of the polymer matrix in a suitable solvent. It provides important information about structural characteristics, chain flexibility, and segment packing density of the polymer.^{15–17}

In the present study, DSV technique has been used to study the compatibility and phase separation behavior of SBR/EPDM blends upon exposure to high-energy radiation and monitor change in the compatibility behavior induced due to mutual radiation grafting of polymeric segments. Further, the interactions between covalently crosslinked polymer segments were investigated by studying the rate of solvent transport in the radiation-crosslinked polymer matrix. In the present investigation, various viscosity parameters and molecular transport properties have been correlated with the miscibility of blends.

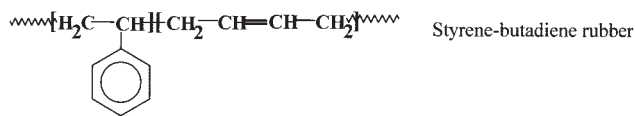
EXPERIMENTAL

Materials

Styrene-butadiene rubber (SBR) (Synaprene-1502, styrene content 25%) and ethylene–propylene–diene monomer (EPDM) (Kelton-512, ethylene content 55%)

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were supplied by local supplier, in block form. Toluene used for viscosity and swelling studies was of AR grade. Ubbelohde-type capillary viscometer was used for all viscometry measurements. A Cobalt-60 gamma chamber GC-5000, having a dose rate of 5 kGy h⁻¹ as measured using Fricke dosimeter, was used for irradiation purpose.



Structures of SBR and EPDM

Sample preparation

A series of blends of SBR and EPDM was prepared by initially mixing the two components homogeneously on two-roll mixing mill. The homogeneous mix was cut to small pieces and compressed into sheets of size 12 × 12 cm² of different thicknesses in range 1–4 mm, using compression-molding machine (at 150 kg m⁻² pressure for 2 min at 130°C). The samples were seal packed in polyethylene bags and then put for irradiation in gamma chamber.

All viscosity measurement for ternary or binary systems were performed at (25 ± 0.1)°C in a temperature bath. Appropriate amount of polymer was dissolved in toluene (0.5 g dL⁻¹) to prepare stock solutions of ternary or binary systems. Dilutions to yield at least six lower concentrations were made by adding appropriate aliquots of solvent. The elution time of each solution was determined as an average of at least five readings.

For the sorption studies, radiation-crosslinked blends were Soxhlet extracted at elevated temperature for 12 h to extract any sol content, using toluene as solvent. The insoluble gel part was then dried initially under room conditions and later in a desiccator. The dried blend so obtained was cut into uniform square pieces (1 × 1 cm²), 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 toluene. The swelled samples were periodically removed, blotted free of surface toluene (using laboratory tissue paper), weighed (in stopper bottles) on Mettler analytical balance (accuracy 0.00001 g) and returned to the swelling medium. Measurements were taken until the samples reached constant weight.

Theory of DSV and swelling kinetics

Theory of DSV⁹ and dynamic and equilibrium swelling kinetics¹⁸ are described elsewhere in detail; however, a brief description of these theories is given here.

Dilute solution viscometry

The classical Huggins equation when adapted to polymer-solvent system has the following form

$$\left(\frac{\eta_{sp}}{C_i}\right) = [\eta]_{sp} + b_{ii}C_i \quad (1)$$

where, the interaction parameter, b_{ii} is related to Huggins coefficient K_i by $b_{ii} = K_i[\eta]^2$, and $[\eta]_i$ is the intrinsic viscosity defined as

$$[\eta]_i = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C_i}\right) \quad (2)$$

$\left(\frac{\eta_{sp}}{C_i}\right)$ and C_i represent the specific viscosity and polymer concentration respectively.

For a solvent/polymer 1/polymer 2 system, the intrinsic viscosity of the mixture $[\eta]_m$ denotes the coil dimensions, which can be altered by contraction or expansion of coil depending on the interaction (which may be attractive or repulsive) between unlike polymer segments. The viscometric interaction parameter b_m characterizes the overall interaction (hydrodynamic as well as thermodynamic) between polymer chains and can be used to determine polymer-polymer miscibility. On the basis of $[\eta]_m$ and b_m values, many criteria have been proposed to predict the polymer-polymer compatibility by DSV.

For a mixture of natural or uncharged polymer in a common solvent, a theoretical relationship between the intrinsic viscosity and interaction parameter of mixture and individual component can be given as

$$[\eta]_{mix} = [\eta]_2w_2 + [\eta]_3w_3 \quad (3)$$

where w denotes the weight fraction of the component, subscript 2 and 3 denotes polymer 1 and polymer 2 respectively, and subscript 23 (used in equation below) corresponds to unlike molecular interaction pair.

A criteria can be proposed based on the difference between the experimental and ideal values of $[\eta]_{mix}$ assuming that the intrinsic viscosity can be treated as an excess property by similarity with those of real solutions. Therefore,

Blends are compatible if $\Delta[\eta]_{mix} = [\eta]_{mix}^{exp}$

$$- [\eta]_{mix}^{id} < 0$$

Blends are incompatible if $\Delta[\eta]_{mix} = [\eta]_{mix}^{exp}$

$$- [\eta]_{mix}^{id} > 0$$

The above criterion takes care of change in hydrodynamic volume of polymer due to mutual attraction or repulsion between polymeric segments. However, another important criteria is ΔB , which is based on viscometric interaction parameter (Huggins parameter) can be defined as

$$b_m^{\text{exp}} = b_{22}w_2^2 + 2b_{23}^{\text{exp}}w_2w_3 + b_{33}w_3^2$$

$$b_{23}^{\text{id}} = b_{22}^{1/2}b_{33}^{1/2}$$

Blends are compatible if $\Delta B_{\text{mix}} = (b_{23}^{\text{exp}} - b_{23}^{\text{id}}) > 0$

Blends are incompatible if $\Delta B_{\text{mix}} = (b_{23}^{\text{exp}} - b_{23}^{\text{id}}) < 0$

Sun et al.¹⁹ and Jiang and Wang⁸ proposed a thermodynamic parameter (α), which includes viscometric interaction parameter (Huggins parameter) as well as intrinsic viscosity of the system, for polymer-polymer miscibility. It has been defined as

$$\alpha = K_m$$

$$K_m = \frac{(k_2w_2^2[\eta]_{22} + 2(k_2k_3)^{1/2}w_2w_3[\eta]_2[\eta]_3 + k_3w_3^2[\eta]_{33})}{(w_2[\eta]_2 + w_3[\eta]_3)^2} \quad (4)$$

where

$$K_m = \frac{(k_2w_2^2[\eta]_{22} + 2k_{23}w_2w_3[\eta]_2[\eta]_3 + k_3w_3^2[\eta]_{33})}{(w_2[\eta]_2 + w_3[\eta]_3)^2} \quad (5)$$

Blends are compatible if $\alpha > 0$

Blends are incompatible if $\alpha < 0$

Sorption kinetics of crosslinked blends

The transport mechanism, which indicates the relative importance of diffusion and relaxation, was identified through the empirical equation (6)¹⁸

$$M_t/M_\infty = Kt^n \quad (6)$$

where M_t is the mass of solvent absorbed at time t , M_∞ is the mass of the solvent absorbed at equilibrium, K is the rate constant, and n is an empirical number called transport exponent. The transport exponent values were obtained by linear regression of the $M_t/M_\infty < 0.6$ versus t^n plot. A value of $n = 0.5$ is considered as an indication that the process is diffusion controlled (Fickian diffusion) or Case I transport, whereas transport is considered to be relaxation controlled (Case II)

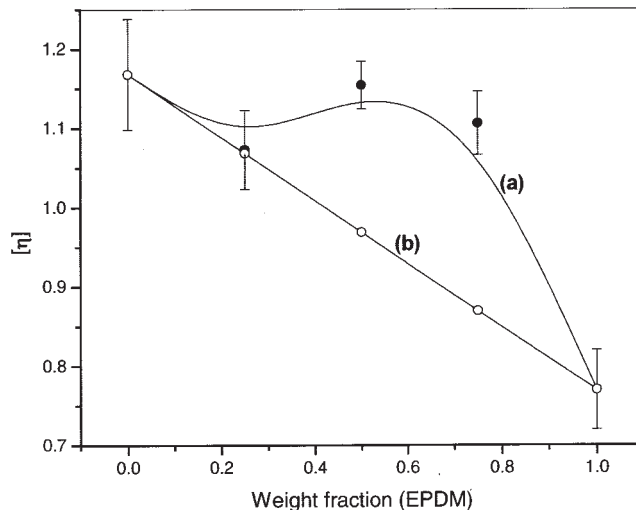


Figure 1(a) Intrinsic viscosity variation for unirradiator SBR-EPDM blends in toluene: (a) experimental profile and (b) theoretical profile.

for $n = 1.0$ and as anomalous when the value of n lies between 0.5 and 1.0.

RESULTS AND DISCUSSION

Miscibility studies

The viscosity measurements were used as a principal tool for examining the compatibility of the SBR/EPDM rubber blends. The specific viscosity (η_{sp}) for different concentrations was measured by measuring the elution time of the solutions. The intrinsic viscosities as well as the viscometric interaction parameters were determined from the intercept and the slope of the plot between η_{sp}/C and C respectively.

Miscibility studies of SBR-EPDM blends

Figure 1(a) represents the variation of $[\eta]_{\text{mix}}^{\text{exp}}$ with change in composition of blends for unirradiator blends; the straight line represents the additive value of intrinsic viscosity of mixture ($[\eta]_{\text{mix}}^{\text{id}}$). It can be seen that in the composition range studied the experimental value of intrinsic viscosity is higher than the theoretical value calculated on the basis of ideal behavior assumption. According to the assumption, positive deviation from ideal solution behavior means repulsive interaction between the two polymers, indicating that unirradiator SBR/EPDM blends are incompatible over the whole composition range. Figure 1(b) shows the plot of α and ΔB as a function of weight fraction of EPDM. Based on the sign convention, it is clear that miscibility criteria are not satisfied for the SBR/EPDM blends in the composition range of present study.

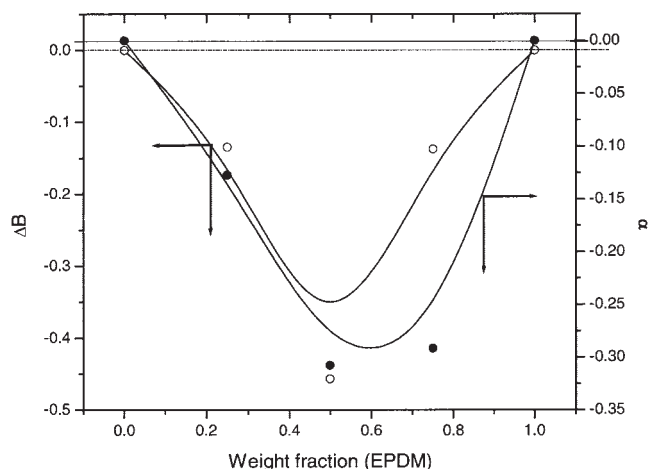


Figure 1(b) Variation in miscibility parameters ΔB and α of unirradiated blends in toluene.

The heterogeneity of SBR/EPDM blend system can also be demonstrated by the heat of mixing of SBR/EPDM blend system, which can be calculated according to the following equation²⁰:

$$\Delta H_m = (1 - w_b)M_a\rho_a(\delta_a - \delta_b)^2x \times \left[\frac{w_b}{(1 - w_b)M_b\rho_b + w_bM_a\rho_a} \right] \quad (7)$$

where M , w , δ , and ρ are the molecular weight of monomer unit, weight fraction, solubility parameter, and the polymer density, respectively, and subscript a and b refers to SBR and EPDM, respectively. The parameters of SBR and EPDM related to eq. (7) are given in Table I.²¹ The behavior of heat of mixing over the whole composition range is shown in Figure 2, it was found to lie between 0.05 and 0.13 J. It is clear that ΔH_m increases with increase in weight fraction of EPDM in the blend, attains maximum value at $\sim 70\%$ and decreases afterwards. Scheneir²² has calculated the ΔH_m value for many polymer pairs and showed for compatible polymer pairs, the value lies in the range $4 \times 10^{-3} - 4 \times 10^{-2}$ J. Therefore, it was clear that SBR-EPDM blends were immiscible over the entire composition range studied.

Effect of gamma radiation on the miscibility behavior

Figure 3(a) represents the variation of $[\eta]_{\text{mix}}^{\text{exp}}$ with change in composition of blends for blends irradiated

TABLE I
 δ and ρ Values for SRR and EPDM

Rubber	δ (J/cc) ^{1/2}	ρ (g/cc)	M
SBR	7.9	0.90	168
EPDM	8.5	0.86	70

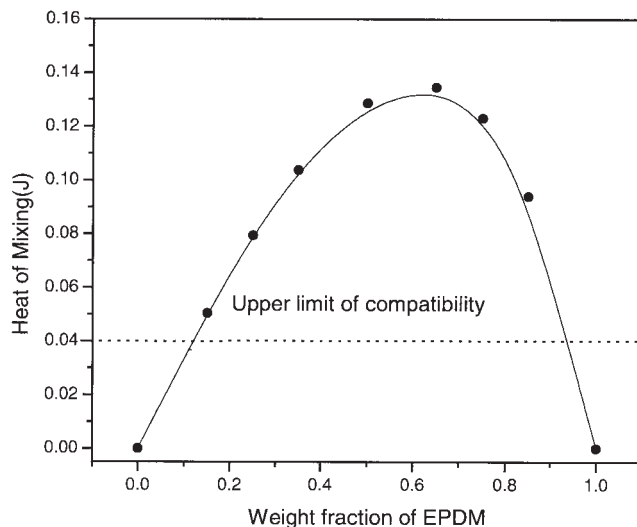


Figure 2 Variation of heat of mixing for blends of different composition.

to a dose of 5 kGy. It can be seen that the experimental value of intrinsic viscosity is higher than the theoretical value over the entire composition range. The values of α and ΔB are found to be negative over the entire composition range as shown in Figure 3(b). The general trend observed with all of the three criteria is similar to the unirradiated blends and it denotes the incompatibility of blends over the entire composition range even after irradiation at 5 kGy, but with a quantitative difference to unirradiated blends.

The miscibility behavior of blends was further probed by irradiating the blends to higher radiation doses. Figures 4(a) and 4(b) show profiles for the

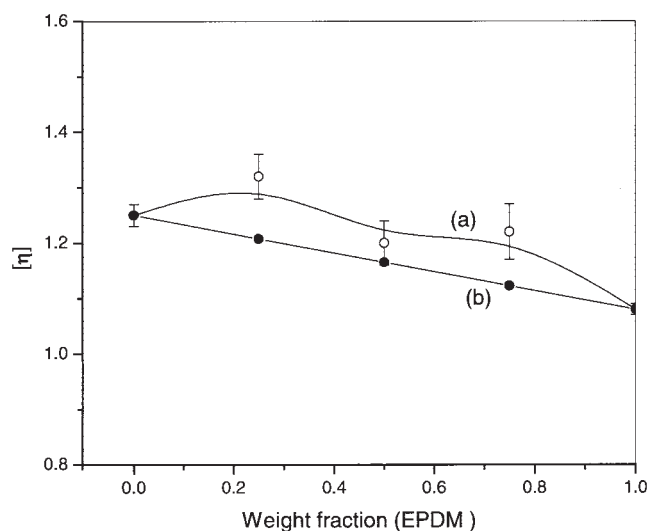


Figure 3(a) Intrinsic viscosity variation for SBR-EPDM blends irradiated to a dose of 5 kGy: (a) experimental profile and (b) theoretical profile.

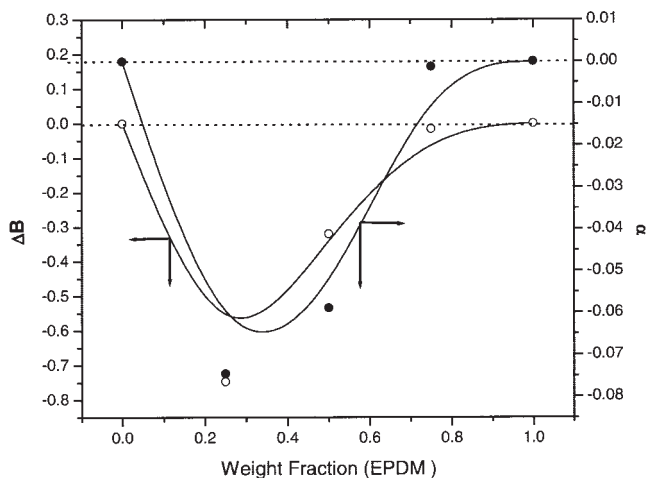


Figure 3(b) Variation in miscibility parameters ΔB and α of blends irradiated to a dose of 5 kGy.

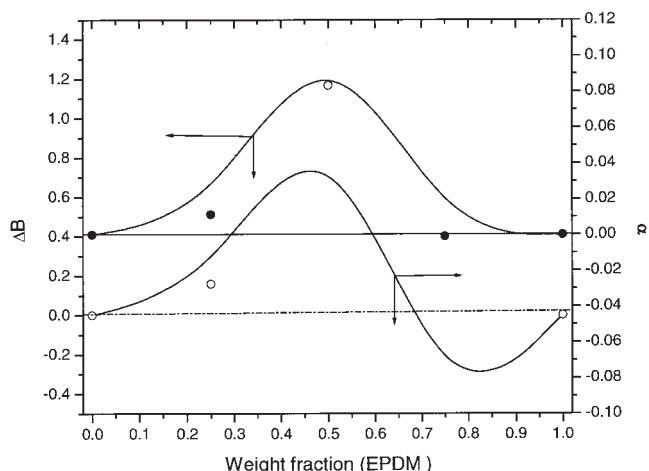


Figure 4(b) Variation in miscibility parameters ΔB and α of blends irradiated to a dose of 10 kGy.

blends irradiated to a dose of 10 kGy. The experimental value of intrinsic viscosity was found to be lower than theoretical value for blends up to 60% EPDM content and it was greater than $[\eta]_{mix}^{id}$ values for blends of higher EPDM content. The values of α and ΔB values were also found to be positive up to 60% of EPDM. As all of the three miscibility criteria are satisfied in the composition range 0–60% of EPDM, it was concluded that the SBR–EPDM blends are compatible in the aforementioned range, when it is preirradiated to an absorbed dose of 10 kGy.

Irradiation to higher doses lead to the gel formation, hence viscometric behavior and miscibility behavior

of blends irradiated to higher doses could not be investigated by DSV.

Mechanism of compatibility enhancement by radiation in SBR–EPDM blends

The formation of random macromolecular complex of SBR and EPDM during mechanical mixing of SBR and EPDM constitutes the first step of the process. The dissolution of such macromolecular complex in solvent like toluene would result in a ternary mixture SBR + EPDM + toluene. However, after gamma irradiation it would be a multi component system, as gamma irradiation would lead to the formation various macromolecular arrangements as shown in Scheme 1.

The multicomponent system in the present study can be designated as $S_n(S_x-E_y)E_n$ it involves

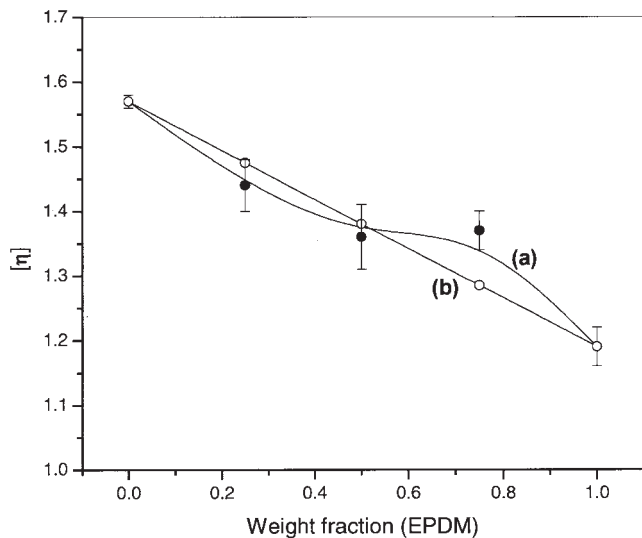
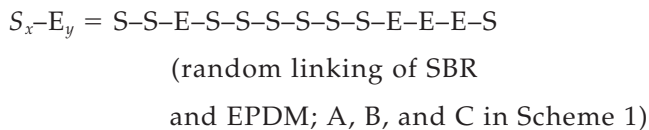
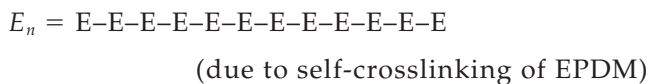
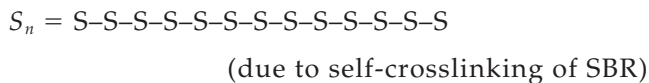
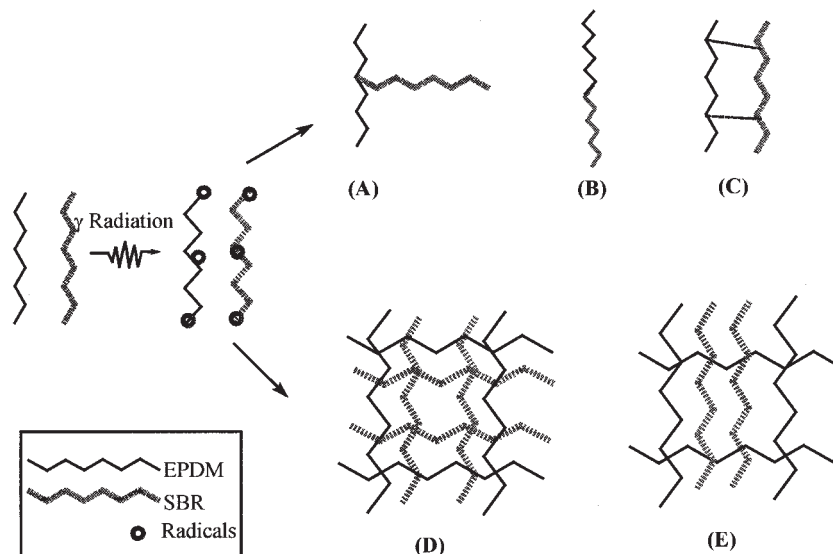


Figure 4(a) Intrinsic viscosity variation for SBR-SPDM blends irradiated to a dose of 10 kGy: (a) experimental profile and (b) theoretical profile.

where S represents SBR chain and E represents EPDM chain. The presence of D and E type arrangements of Scheme 1 are ruled out during viscometric studies, as the blends have been irradiated to pre gel doses. D and E type of arrangements would result in the gel



A=Graft copolymer, B=Block copolymer, C=crosslinked chains, D= IPN, E=semi IPN

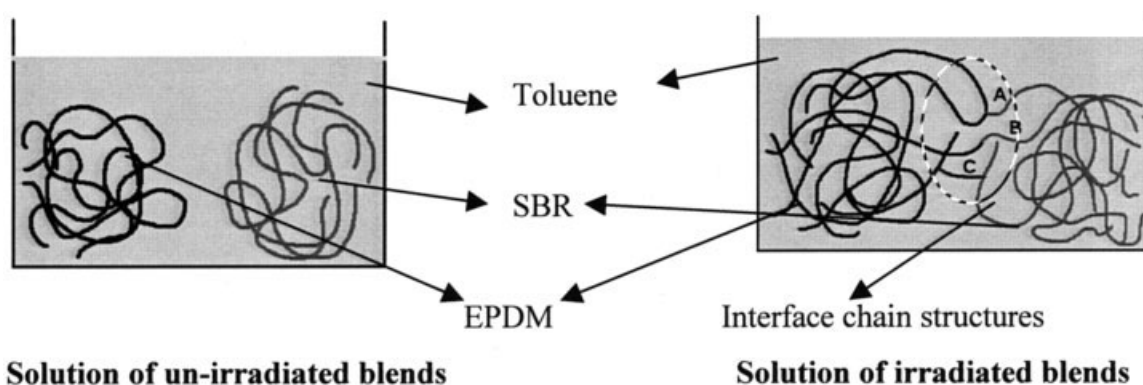
Scheme 1

formation and their properties are discussed in the next section.

The macromolecular complexes are expected to have random conformation in such dilute solution, the structural change induced after radiation grafting (A, B, and C) would affect the competition between the hydrodynamic deforming stress ($\sim \eta_m \delta\gamma/\delta t$) and interfacial restoring stresses ($\sim \alpha/R$) and decide the ultimate hydrodynamics of the system (where η_m and $\delta\gamma/\delta t$ are the viscosity and deformation rate of the matrix, and α and R are interfacial tensions and characteristic size). Clearly, the dynamic effects of the graft polymer would affect the interfacial tension between the polymeric components ($S_n/(S_x-E_y)/E_n/\text{toluene}$). The grafting of SBR onto EPDM or *vice versa* may reduce the deformation between EPDM and SBR segments by decreasing inter-

facial tension, and thereby lowering the overall hydrodynamic stress and the macromolecular complex viscosity. Thus, the enhanced compatibility of the irradiated system can be attributed to the functioning of S_x-E_y as interfacial agent, where segments of SBR and EPDM are present, thereby acting as a coupling agent between SBR and EPDM phase, i.e., formation of structures A, B, and C on irradiation provides an interface between pure SBR and EPDM domains. Presence of such structures in the copolymer blends allows uniform dispersal of chains when the blends are dissolved in toluene as shown pictorially in Scheme 2.

This is also supported by many other reports on the significant changes in the surface properties like interfacial tension because of radiation grafting and block polymer formation.²³⁻²⁵ However, the over all interac-



Scheme 2

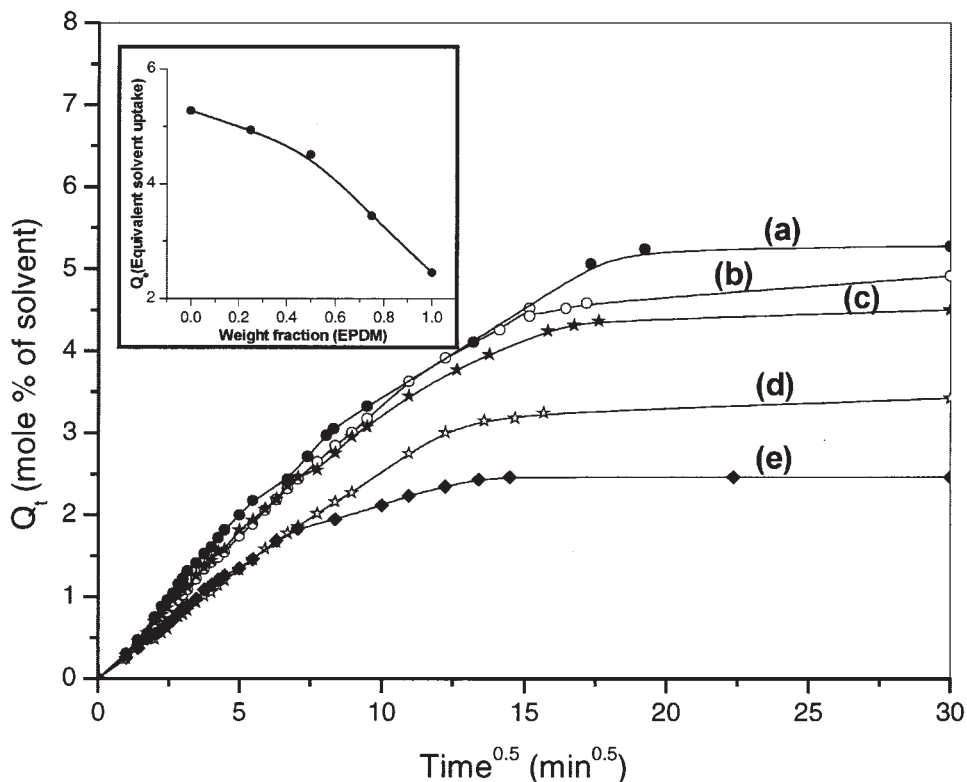


Figure 5 Solvent uptake of SBR-EPDM crosslinked blends irradiated to a total dose of 400 kGy: (a) EPDM 0%, (b) EPDM 25%, (c) EPDM 50%, (d) EPDM 75%, and (e) EPDM 100%. Inset: equivalent solvent uptake of SBR-EPDM blends.

tion between the copolymer chains (S_x-E_y) and individual polymer segments depends strongly on the ratio of copolymer chains to individual chains. The cooperative interaction increases rapidly only after a threshold value of this ratio is achieved. It seems that this threshold concentration is achieved only after the blends are irradiated to a dose of 10 kGy since the blends irradiated to lower radiation dose of 5 kGy did not show any miscibility, whereas blends irradiated to 10 kGy were found to be miscible in 0–60% regime. It may also be mentioned that chemical sequence in S_x-E_y is statistical and the ratio of S and E units present in it must not be much larger than 1 to observe compatibility behavior. Further, such systems can only be compatible with well-defined periodicities in the chemical sequence of E and S chains and it is very difficult to establish a quantitative correlation of the miscibility with the radiation dose, as the structure, statistical variation, steric hindrance, molecular asymmetry of the polymeric component has to be further probed for quantitative correlation.

Swelling behavior of irradiated SBR-EPDM crosslinked blends

Swelling mechanism of blends

For swelling studies, the solvent uptake by a known weight of crosslinked blends was monitored as a func-

tion of time. Blend irradiated to a dose of 400 kGy were chosen for swelling studies because this dose has been recommended for vulcanization of most of the elastomers.^{26,27} Figure 5 shows change in the swelling ratio for a series of blends. It is clear that extent of solvent uptake decreases with increase in EPDM content of the blend. This can be attributed to two reasons; first, due to increase in the crosslink density of the blend with increase in the EPDM content, as EPDM is more prone to radiation effect in comparison to SBR and predominantly undergoes crosslinking. Second, it is known that EPDM exhibits both, toughness of the plastic and the elasticity of gum elastomers phase due to its tightly packed structure, and thereby, this intrinsic property of EPDM might restrict the free movement of penetrant molecules causing the lower value of swelling ratio. However, the equilibrium swelling data does not provide an actual insight into the dynamic swelling mechanism of the blends, therefore the swelling kinetics of these blends was investigated.

To understand the type of process controlling the dynamic swelling, values of k and n (eq. (6)) were determined. Table II gives the values of these parameters for different blends. The n values tend to a value 0.5 with increase in the content of EPDM in the matrix; however, in none of the cases the value was perfectly 0.5 for process of swelling to be called Fickian (diffusion controlled). In earlier works²⁴ for n values of even

0.55–0.63, it was assumed that the diffusion is nearly Fickian, though it has been clearly stated that mere n values are not sufficient to categorize swelling to be Fickian and more rigorous treatment of the swelling data is needed to confirm the swelling process to be Fickian.^{18,25}

It has been suggested that for the cases of Fickian transport, the rate of approach to equilibrium can be characterized by a diffusion coefficient value D , which can be calculated from eq. (8)²⁵

$$M_t/M_\infty = 4/\pi^{0.5} (Dt/L_0^2)^{0.5} \quad (8)$$

where D is the diffusion coefficient in a polymer-fixed reference frame and L_0 is initial thickness of the sample. The presence of dimensionless time factor (Dt/L_0^2) in this equation also suggests that a plot of M_t/M_∞ versus $t^{0.5}/L_0$ (diffusion plot) should be independent of sample thickness. Also, when a sorption curve is computed from eq. (9),¹⁸ using D value obtained experimentally, and compared with the experimentally determined diffusion plot, beyond linear region, the absorption curve is concave towards the x -axis.

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} \{8/(2n+1)^2\pi^2\} \times \exp\{- (2n+1)^2\pi^2(Dt/L_0^2)\} \quad (9)$$

Figure 6 shows swelling kinetics of one of the blends (50:50) for samples of different initial thicknesses. It can be seen that swelling kinetics is a function of the thickness of sample for the blends, indicating the swelling cannot be designated as Fickian on basis of nonfulfillment of thickness criteria. To further substantiate these findings, since for n values, $1 > n > 0.5$, the diffusion is said to be anomalous and rate of diffusion approximately equal to the rate of relaxation, value of D obtained using eq. (8) were compared with k_r (rate of relaxation values) obtained using eq. (10)²⁸

$$M_t/M_\infty = \tilde{1} - \exp(-k_r t) \quad (10)$$

TABLE II
 k and n Values for Blends Irradiated
to a Dose of 400 kGy

Blend composition	$\log k$	n
EPDM 0%	-2.28	0.6
EPDM 25%	-2.19	0.55
EPDM 50%	-2.15	0.55
EPDM 75%	-2.07	0.52
EPDM 100%	-1.93	0.54

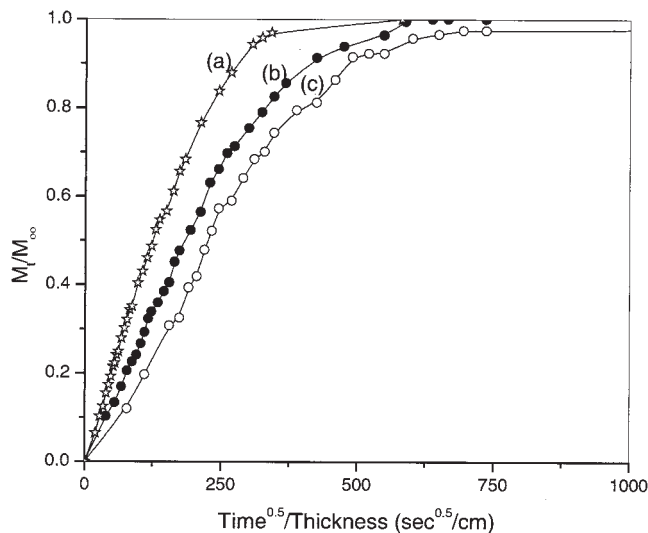


Figure 6 Swelling kinetics of SBR-EPDM (50:50) blend irradiated to a dose of 400 kGy. Initial thickness: (a) 0.4 cm, (b) 0.2 cm, and (c) 0.1 cm.

Figure 7 shows variation in rate of diffusion (D) and rate of relaxation (k_r) with time. It is clear that the shape of the profiles is dissimilar for these parameters; the k_r values decrease continuously till equilibrium swelling is reached (inset Fig. 7), whereas D value increases initially and decrease subsequently. Further, the D values are about 3 orders lower than the k_r value over the entire time range indicating the swelling is diffusion controlled. Probably due to very low diffusion rate values, earlier workers reported²⁴ the diffusion to be Fickian. Also, the diffusion curve obtained from eq. (8) was not concave to x -axis. Thus, from these studies, it is clear that swelling of blends does not confirm to any criteria for Fickian diffusion and it will be fair to categorize it as anomalous.

The value of D determined using eq. (8) depends on the polymer segmental mobility and holds good for systems without appreciable swelling. For considerable swelling as is the case of swelling of SBR-EPDM blends in toluene, a better corrected equation has been suggested incorporating ϕ ,²⁹ the volume fraction of the polymer in the swollen mass, thus giving the intrinsic diffusion coefficient, D^* given by

$$D^* = \frac{D}{\phi^{7/3}} \quad (11)$$

where volume fraction of polymer ϕ in the solvent swollen sample can be calculated using eq. (12)

$$\phi = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \quad (12)$$

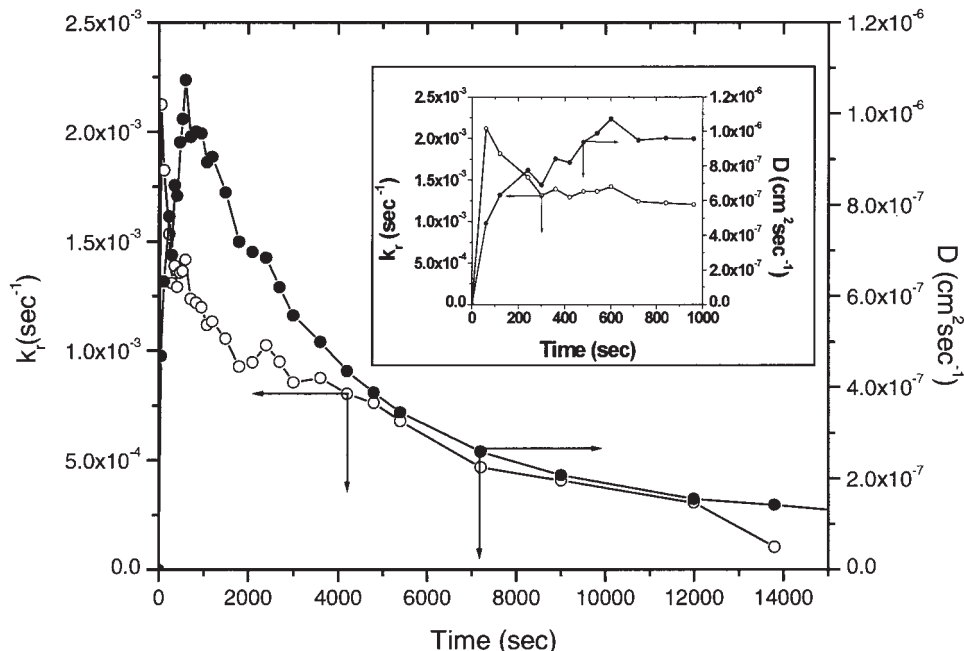


Figure 7 k_p and D values for SBD:EPDM (50:50) blend irradiated to a dose of 400 kGy.

where w_1 and ρ_1 are the weight and the density of the polymer sample, respectively; and w_2 and ρ_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 as³⁰

$$P = D \times S \tag{13}$$

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

$$S = M_s/M_p \tag{14}$$

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 volume fraction of EPDM is illustrated in Figure 8. It is clear from the figure that the intrinsic diffusion coefficient, sorption coefficient, and permeability coefficient follows the trend $EP_{00} > EP_{25} > EP_{50} > EP_{75} > EP_{100}$; however, the sorption coefficient profiles is

concave towards x -axis, whereas permeability coefficient profile is convex towards x -axis. This clearly indicates that both of these processes are not exactly in accordance with each other, the lag between the two phenomenon's may be due to initial absorption of solvent by the polymer chains to relax, followed by actual diffusion of solvent into the blends. Also since irradiation affects the final properties of the blend by causing permanent effects like crosslinking, degradation, IPN or semi-IPN formation therefore a close correlation is expected between the radiation responses of the components of the blend

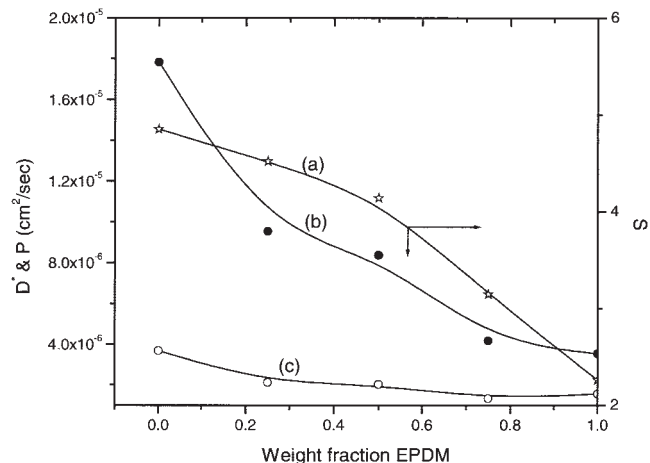


Figure 8 Variation in D^* , S , and P values for blends irradiated to a dose of 400 kGy.

with the sorption behavior of the system. Further, 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 deciding sorptive activity of the polymer matrices.^{31,32} The sorptive activity and diffusion rate will depend not only on the nature and number of polar groups, but also on their position in the polymer chains, hence, the extent to which the groups are shielded is significant, along with the other factors like microporosity and crosslinking density of the matrix.

Crosslinking density of radiation processed blends

The key parameters that determine the amount of solvent absorbed by crosslinked network are the crosslink density and the extent of polymer-solvent interaction that is reported as the value of Flory-Huggins parameter χ . The diffusion into solid samples depends on the availability of appropriate molecular size holes in the network; however, it may be mentioned that the kinetic response which includes solvent sorption rate, the rate of approach to equilibrium, and the transport mechanism controlling the solvent sorption may also depend upon additional factors like history of the samples and its composition.^{18,33,34} To gain further insight into sorption process in relation to the morphological characteristics of the polymer, the molecular weight between crosslinks (M_c) has been estimated using the following relation, based on the theory initially proposed by Flory and Rehner³⁵:

$$\bar{M}_c = -V_1 \rho_p \frac{\phi_p^{1/3} - \phi_p^{1/2}}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} \quad (15)$$

where, v_l is the molar volume of the solvent, ρ_p is the polymer density, ϕ_p is the volume fraction of the polymer in the swollen matrix and χ is the Flory-Huggins interaction parameter between solvent and polymer which can be calculated using following relation³⁵:

TABLE III
Variation of M and Crosslink Density with EPDM Content for Blends Irradiated to a Total Dose of 400 kGy

EPDM (%)	M_c (g mol ⁻¹)	Crosslinking density (10 ⁵ mol g ⁻¹)
0	13564.41	3.69
25	5325.44	9.39
50	2834.60	17.64
75	1140.16	43.85
100	449.48	111.00

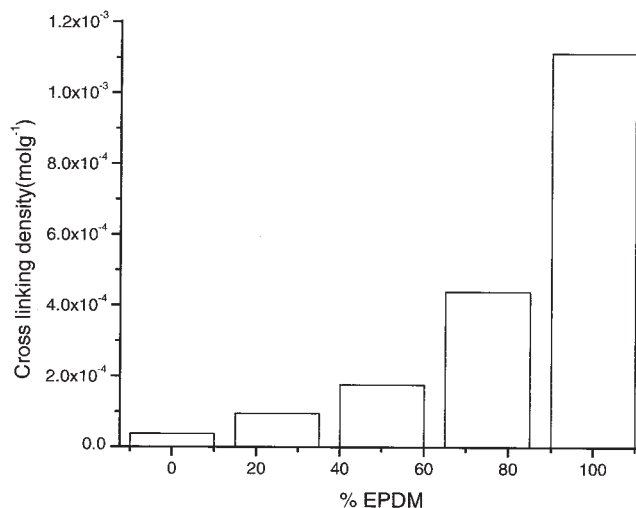


Figure 9 Crosslink density of blends irradiated to radiation dose of 400 kGy.

$$\chi = \beta + \frac{V_1}{RT} (\delta_s - \delta_p)^2 \quad (16)$$

where δ_s and δ_p are the solubility parameters of the solvent and the polymer, β is the lattice constant whose value is taken as 0.34, R is the universal gas constant, and T is the absolute temperature.

The behavior of crosslinking density ($1/2M_c$) with EPDM weight fraction is shown in Table III and Figure 9. These values are in order of EP₀₀ > EP₂₅ > EP₅₀ > EP₇₅ > EP₁₀₀, indicating predominantly crosslinking behavior of EPDM on irradiation.

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; hence an attempt has been made to interpret the permeability results in terms of various theoretical models generally used for heterogeneous polymeric blends.³⁶

Robeson's two limiting models, namely series and parallel models, are generally used in case of polymer blends.³⁶

According to the parallel model

$$P_c = P_1 \phi_1 + P_2 \phi_2 \quad (17)$$

and by series model

$$P_c = \frac{P_1 P_2}{\phi_1 P_2 + \phi_2 P_1} \quad (18)$$

where P_c , P_1 , and P_2 are the permeation coefficients of the blend, component I, and component II, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the components I and II, respectively.

To describe the effect of permeating component on the overall blend permeability, Maxwell suggested the following equation³⁷:

$$P_c = P_m \left[\frac{P_d + 2P_m - 2\phi_d(P_m - P_d)}{P_d + 2P_m + \phi_d(P_m - P_d)} \right] \quad (19)$$

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

$$P_c = x_a P_1 \left[\frac{P_2 + 2P_1 - 2\phi_2(P_1 - P_2)}{P_2 + 2P_1 + \phi_2(P_1 - P_2)} \right] + x_b P_2 \left[\frac{P_2 + 2P_1 - 2\phi_1(P_1 - P_2)}{P_2 + 2P_1 + \phi_1(P_1 - P_2)} \right] \quad (20)$$

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.³⁴ The experimental data (Fig. 10) is found to be in close agreement with series model indicating for SBR-EPDM radiation crosslinked blends EPDM is a continuous phase.

CONCLUSION

In summary, our studies show that gamma irradiation of SBR-EPDM blends to a threshold dose induces good compatibility between the two components SBR and EPDM, which otherwise show poor compatibility. The change in the miscibility behavior with irradiation has been attributed to the cooperative interaction phenomenon between the copolymer SBR-EPDM and SBR/EPDM segments. Swelling kinetics of crosslinked blend matrices indicates that rate of diffusion in these blends is much slower than the rate of relaxation of chains but other criteria for designating diffusion to be Fickian are not fulfilled. Permeation studies of these blends established that in SBR-EPDM blends EPDM is a continuous phase and SBR is a

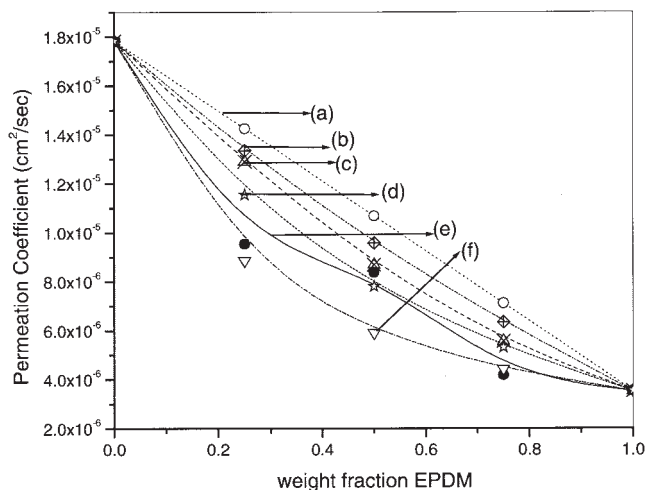


Figure 10 Permeation coefficient (P) value profiles calculated using different values for blends irradiated to a dose of 400kGy: (a) Parallel model, (b) Maxwellian (EPDM as disperse phase), (c) Robeson model, (d) Maxwellian (SBR as disperse phase), (e) experimental profile, and (f) series model.

dispersed phase. The results also indicate that significant degree of complexities can be expected when analyzing such blend system and a more comprehensive picture of graft polymer architecture, i.e., overall molecular weight, molecular weight of the grafts, and their asymmetry is required to fully understand anatomy of such blends.

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