Evidences of Solvent-Induced Miscibility in Polychloroprene-*co*-Ethylene-Propene Diene Terpolymer Blends

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ABSTRACT: Solvent dependent changes in the compatibility behavior of Polychloroprene/Ethylene–propylene–diene terpolymer blends (CR/EPDM) have been investigated using dilute solution viscometry and solvent permeability analysis. To predict the compatibility of rubber blends of different compositions in solvents of different cohesive energy densities, Huggins interaction parameter (ΔB), hydrodynamic interaction ($\Delta\eta$) and Sun's parameter (α) were evaluated from the analysis of the specific and reduced viscosity data of two and three-component polymer solutions. Miscibility criteria were not satisfied for CR/EPDM blends over the entire composition range in toluene, xylene, and carbon tetrachloride (CCl_4), however, a narrow miscibility domain was observed in chloroform ($CHCl_3$) for CR/EPDM/$CHCl_3$ system. These results were further corroborated with the analysis of heat of mixing (ΔH_m) and polymer–polymer interaction parameter (χ_{12}), for all rubber blend compositions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1884–1891, 2009

Key words: polychloroprene; ethylene-propene-diene terpolymer; blends; compatibility; dilute solution viscosity

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 of 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-propene-diene terpolymer rubber (EPDM) have evinced special interest because incorporation of appropriate amount of EPDM imparts significant heat and ozone resistance to parent unsaturated matrix.[10] However, knowledge regarding compatibility of blend components and their phase separation behavior is essential to ensure desired properties of 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 an 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.[14–17] In the present study DSV technique has been used to investigate whether the presence of suitable solvent is able to induce some positive interaction between the two components to enhance their miscibility. The change in miscibility of two components has been proposed to occur predominantly due to change in polymer–solvent interaction.

EXPERIMENTAL

Materials

Poly chloroprene rubber (CR) and Ethylene–propylene–diene terpolymer (EPDM) (Kelton-512, Ethylene content 55%) were procured from a local supplier M/s Polystar chemicals in block form. All solvents used for viscosity and swelling measurements were of AnalaR grade. Ubbelholde type capillary viscometer was used for all viscometry studies. A Cobalt-60 gamma chamber GC-5000 having a dose rate of 5 $kGyh^{-1}$ as measured using Fricke dosimeter, was used for irradiation purpose (Structure 1).

Sample preparation

A series of blends of CR and EPDM were prepared by initially mixing the two components
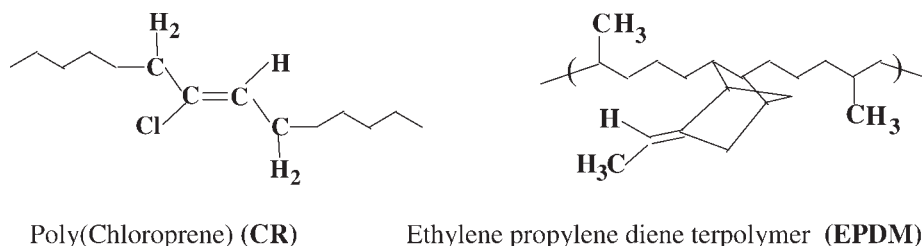
Poly(Chloroprene) **(CR)**   Ethylene propylene diene terpolymer **(EPDM)**

Structure 1 Structures of rubbers used for studies

homogeneously on two-roll mixing mill. The composition of various blends studied is shown in Table I. The homogeneous mix was cut to small pieces and compressed into sheets of size 12 × 12 cm^2 of different thicknesses in range 1–4 mm using compression-molding machine at 150 kg/m^2 pressures for 2 min at 130°C.

All viscosity measurements for binary or ternary systems were performed at 25°C ± 0.1°C in a temperature bath. Appropriate amount of polymer was dissolved in solvent (0.5 g dL^{-1}) to prepare stock solutions of binary or ternary 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 estimation of polymer–polymer interaction parameter, radiation crosslinked blends, irradiated to a dose of 400 kGy, were Soxhlet extracted using toluene at elevated temperature for 12 h to extract any sol content. The insoluble gel part was then dried initially under room conditions and later in a dessicator. The dried blend so obtained was cut into uniform square pieces (1 cm × 1 cm) 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 on Mettler analytical balance (accuracy 0.00001 g) in stopper bottles and returned to the swelling medium. Measurements were taken until the samples reached constant weight.

Dilute solution viscometry

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

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

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

$$[\eta]_i = \lim_{c \to 0}\left(\frac{(\eta_{sp})_i}{C_i}\right) \tag{2}$$

$((\eta_{sp})_i/C_i)$ and C_i represents the specific viscosity and polymer concentration respectively.

For a solvent/polymer 1/polymer 2 system, the intrinsic viscosity of the mixture $[\eta]_{mix}$ denotes the coil dimensions, which can be altered by contraction or expansion of coil depending on the attractive or repulsive interaction 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. Based on $[\eta]_{mix}$ and b_m, many criteria have been proposed to predict the polymer–polymer compatibility by DSV.[8,9,18–20]

For a mixture of neutral 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

TABLE I
Composition and Viscometric Parameters of Blends

Designation	CR (%)	EPDM (%)	CCl$_4$		Chloroform	
			$[\eta]$	b	$[\eta]$	b
EP00	100	00	0.82865	0.58776	0.78405	0.62214
EP20	80	20	0.88361	0.62349	0.66546	0.82942
EP40	60	40	0.95389	0.79488	0.72909	0.70915
EP60	40	60	0.99330	1.05919	0.67434	0.83159
EP80	20	80	1.05514	1.27665	0.72196	0.76318
EP100	00	100	1.01445	1.98695	0.65266	1.10592

$$[\eta]_{mix} = [\eta]_2 w_2 + [\eta]_3 w_3 \qquad (3)$$

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 into consideration the 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,

$$b_m^{exp} = b_{22} w_2^2 + 2 b_{23}^{exp} w_2 w_3 + b_{33} w_3^2$$
$$b_{23}^{id} = b_{22}^{1/2} b_{33}^{1/2}$$

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

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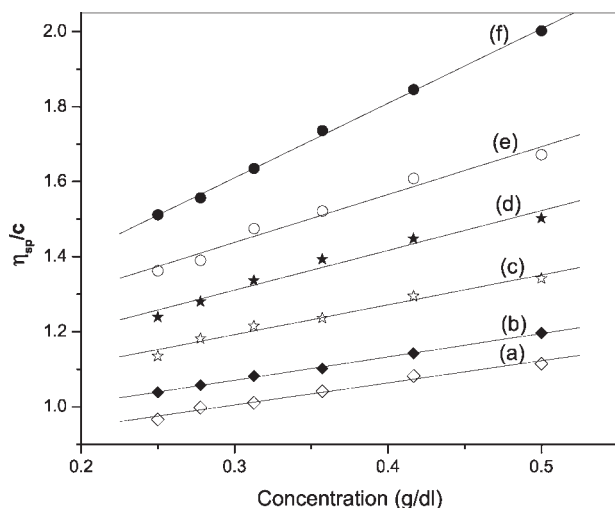

Figure 1 η_{sp}/c versus c profiles of blends in CCl$_4$ (a) EP00, (b) EP20, (c) EP40, (d) EP60, (e) EP80, and (f) EP100.
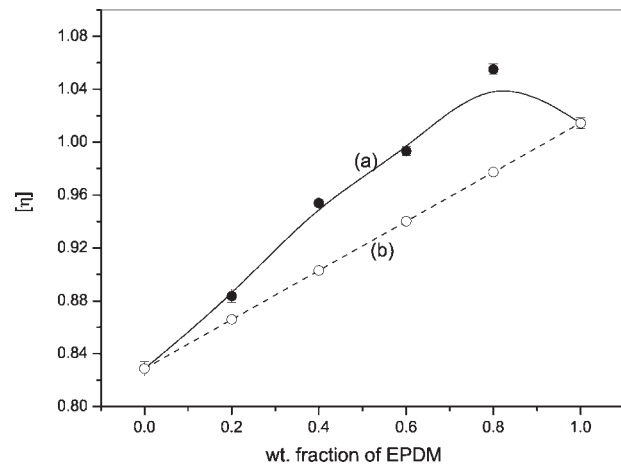
Figure 2 Variation of $[\eta]$ with amount of CR in blend in CCl$_4$ (a) Experimental and (b) Theoretical.

$$\alpha = K_m$$
$$- \frac{\left(k_2 w_2^2 [\eta]_{22} + 2(k_2 k_3)^{1/2} w_2 w_3 [\eta]_2 [\eta]_3 + k_3 w_3^2 [\eta]_{33} \right)}{\left(w_2 [\eta]_2 + w_3 [\eta]_3 \right)^2} \qquad (4)$$

where,

$$K_m = \frac{(k_2 w_2^2 [\eta]_{22} + 2 k_{23} w_2 w_3 [\eta]_2 [\eta]_3 + k_3 w_3^2 [\eta]_{33}}{\left(w_2 [\eta]_2 + w_3 [\eta]_3 \right)^2} \qquad (5)$$

Blends are compatible if, $\alpha > 0$.
Blends are incompatible if, $\alpha < 0$.

RESULTS AND DISCUSSION

Figure 1 shows reduced viscosity profiles of different blend compositions of CR/EPDM in CCl$_4$. It can be seen from the figure that all profiles are linear over the whole composition range. Limiting viscosity numbers (intrinsic viscosity, $[\eta]$), and Huggins interaction parameters determined by Huggins extrapolated lines (linear regression coefficients > 0.99) are listed in Table I.

Figure 2 represents the variation of $[\eta]_{mix}{}^{exp}$ with change in composition of blends. The straight line represents the additive value of intrinsic viscosity of mixture ($[\eta]_{mix}{}^{id}$).The deviations exceed experimental error and are assumed to be indicative of change in coil conformation, depending upon the interactions among the components of the ternary system. 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,
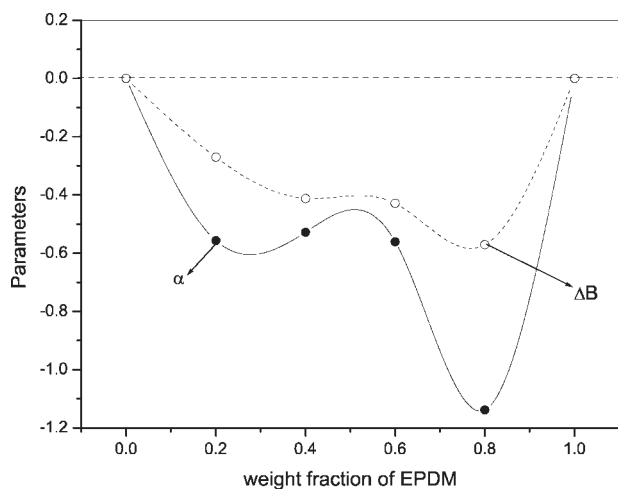
Figure 3 Variation of miscibility parameters α and ΔB for blends in CCl$_4$.

which clearly indicates that CR/EPDM blends are incompatible over the whole composition range in CCl$_4$. To further substantiate the observation the miscibility parameters α and ΔB were assessed for different blends. Figure 3 shows the plot of these parameters as a function of CR in the blends. Based on the sign convention, it is clear that miscibility criteria are not satisfied for the CR/EPDM/CCl$_4$ system in the blend composition range studied.

Reduced viscosity profiles for the CR/EPDM blends in polar solvent chloroform have been shown in Figure 4. It is clear from the figure that all the profiles are linear in the complete composition range; however Huggins extrapolated lines (linear regression coefficients >0.99) did not show any systematic pattern with the blend composition. The anomaly in the behavior was further revealed when intrinsic viscosity values [η] (from intercept of profiles) were
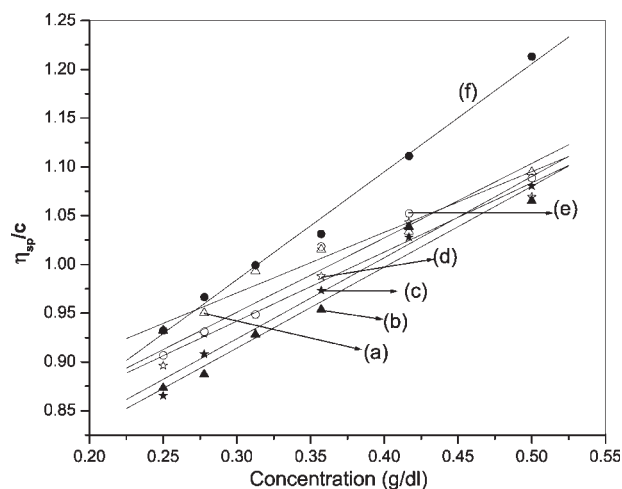
found to be 0.65 for pure EPDM and 0.78 for pure chloroprene, whereas [η] values for intermediate blends were random not showing any consistent trend between the above two values for pure EPDM and pure CR. On the other hand ''b'' values were found to be lowest for pure chloroprene and highest for pure EPDM, though the intermediate compositions did not show consistent trend. It is to be noticed that for CR/EPDM/Chloroform ternary system [η] values are strikingly different from the CR/EPDM/CCl$_4$ ternary system, which shows highest [η] value for pure EPDM and lowest for pure CR. The thermodynamic interaction parameter (b) though followed approximately the similar trend in both the cases; the values were much different, lower for higher EPDM fraction in CR/EPDM/CHCl$_3$ system (Table I).

The variation of [η]$_{mix}^{exp}$ and [η]$_{mix}^{id}$ with composition of blends in chloroform is shown in Figure 5. It can be seen that up to 40% EPDM, a sharp negative deviation in [η] is observed, indicating better miscibility in comparison to CR/CCl$_4$/EPDM system. However for blends containing 40–80% EPDM intrinsic viscosities were comparable with the theoretical values calculated on the basis of ideal behavior assumption. At >80% EPDM content the blend systems were immiscible as reflected from positive deviation from viscosity parameter. Figure 6 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 satisfied for the CR/EPDM blends in the composition range 0–40% EPDM in CR/EPDM/CHCl$_3$ system.

The miscibility of blends was further investigated in other solvents of intermediate cohesive energy densities (CED). Table II shows CED values for some of the solvents used for studies.[21] Figures 7 and 8, represents the deviation in viscometric miscibility
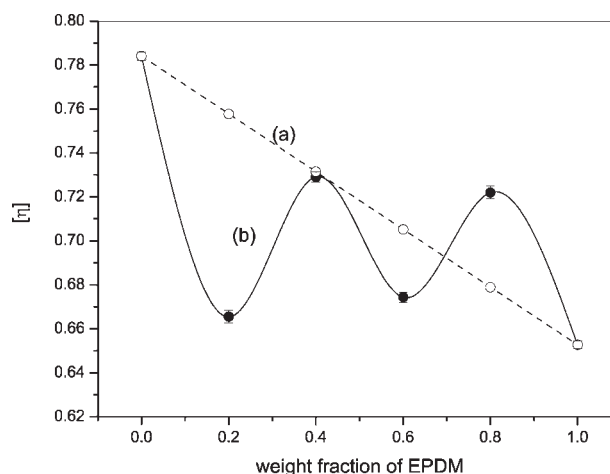

Figure 4 η$_{sp}$/c versus c profiles of blends in Chloroform (CHCl$_3$) (a) EP00, (b) EP20, (c) EP40, (d) EP60, (e) EP80, and (f) EP100.

Figure 5 Intrinsic viscosity variation for CR/EPDM blends in chloroform (a) Theoretical profile and (b) Experimental profile.

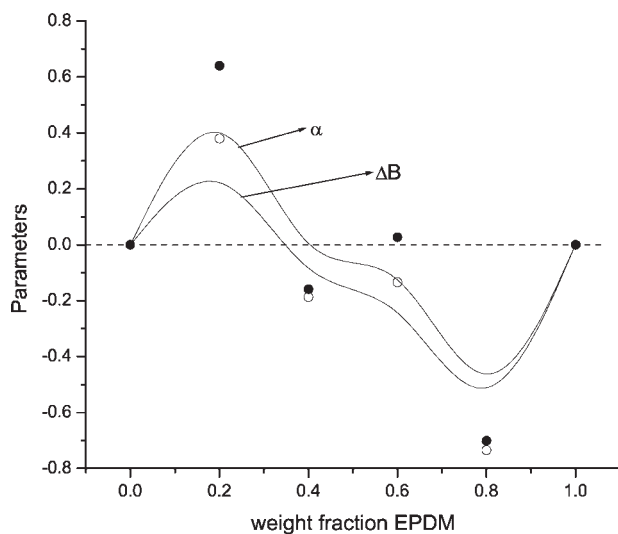**Figure 6** Variation of miscibility parameters α and ΔB for blends in chloroform.

Figure 7 Variation of miscibility parameters Δ[η], α and ΔB for blends in xylene.

parameters Δ[η], ΔB, and α with CR content in the blends, when xylene and toluene were used as solvent respectively. It is clear from the figures that blends are immiscible over complete compositional range in toluene and xylene, though the extent of deviation between experimental and theoretical values are different from that in CCl₄. Such changes in the miscibility behavior of CR and EPDM with solvent indicate that cohesive energy density of solvent plays a decisive role in the interaction between polymer components. It is evident from the results that the general assumption that polymer–polymer interactions dominate over polymer-solvent ones, is virtually invalid in this case.[14,17] It is to be further emphasized that in the miscibility of CR/Solvent/EPDM system, the thermodynamic interactions plays major role in addition to the hydrodynamic interactions between segments. The thermodynamic interactions include interaction between segments of the same polymer, interaction between each component polymer and solvent, and the interaction between two component polymers.

The intrinsic viscosity values for different blend compositions in different solvents have been plotted in Figure 9. For pure EPDM [η] was observed to be

highest in CCl₄ and lowest in CHCl₃, indicating about the better solvation of EPDM in CCl₄. On the other hand, pure CR had highest value of [η] in xylene, and lowest in CHCl₃. Figure 9 clearly indicates that among the various solvents chosen for this study, CHCl₃ was least preferred solvent for both the components of blend, i.e., polymer solvent interactions are weakest in CHCl₃, resultingin the dominance of repulsive forces (between rubber and solvent) over attractive ones. These repulsive intermolecular interactions result in increase in the intermolecular excluded volume effect. The polymer chains thus possess shrunken-coiled conformation with decrease in size, which is reflected as decrease in the intrinsic viscosity of EPDM and CR solution in chloroform. Since the macromolecular complexes have random conformation in such dilute solution, this solvent dependent

TABLE II
CED (Cohesive Energy Density) Values of Solvents Used for Studies

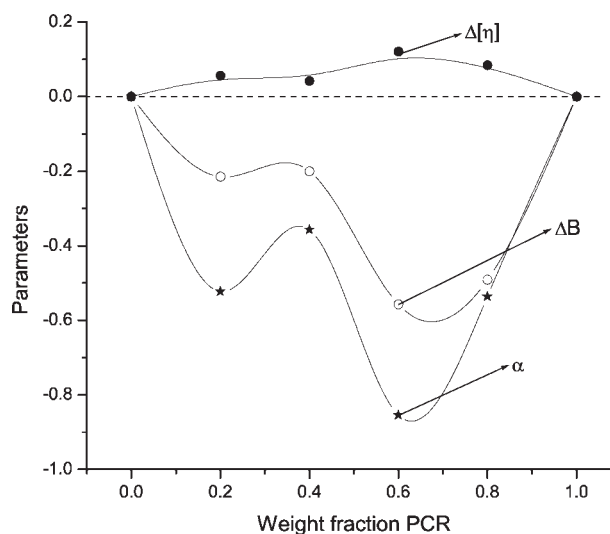| Solvent	δ_0	δ_D	δ_P	δ_H (J/cc)$^{1/2}$
Benzene	21.3	18.7	8.6	5.3
Toluene	18.2	18.0	1.9	2.0
Xylene	18.0	17.7	1.0	3.1
Chloroform	18.8	17.7	3.1	5.7
Acetone	20.0	15.5	10.4	7.0
CCl₄	17.7	17.7	00	00

Figure 8 Variation of miscibility parameters Δ[η], α and ΔB for blends in toluene.
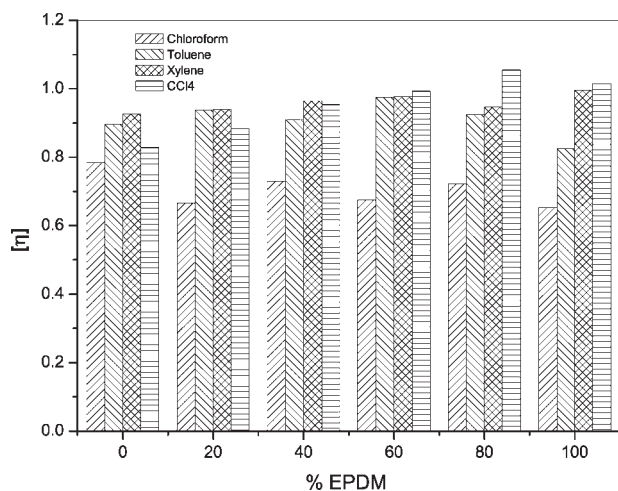
Figure 9 Intrinsic viscosity of blends in chloroform, toluene, xylene, and CCl$_4$.

behavior 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). These observations clearly indicate solvent can significantly affect the interfacial tension between the polymeric components; poor solvent may reduce the deformation between EPDM and CR segments by decreasing interfacial tension due to lower polymer solvent interaction.

The observed viscometric results can be corroborated by dilute solution density measurements[9]. Therefore density measurement studies were carried out. However, no significant information was obtained from these studies as the deviation observed in the density were not significant in view of the very low concentration range of study (Table III).

To study, the intrinsic miscibility behavior of CR/EPDM system (i.e., in the absence of solvent), the heat of mixing of CR/EPDM blend system was calculated according to the following equation.[22]

$$\Delta H_m = (1 - w_b)M_a\rho_a$$

$$\times (\delta_a - \delta_b)^2 x \left[\frac{w_b}{(1 - w_b)M_b\rho_b + w_bM_a\rho_a} \right] \quad (6)$$

where M, w, δ, and ρ are the molecular weight of monomer unit, weight fraction, solubility parameter,

TABLE III
Densities (g/cc) of Rubber Solutions in Solvents
(Concentration = 0.5 g/dl)

	CHCl$_3$	CCl$_4$	Xylene	Toluene
Chloroprene	1.489	1.591	0.870	0.869
EPDM	1.486	1.587	0.868	0.866
Pure solvent	1.488	1.590	0.868	0.866

TABLE IV
Thermodynamic Parameters for Two Components of Blends

Rubber	δ (J/cc)$^{1/2}$	ρ (g/cc)	Mol. wt.
CR	19.22	1.23	87.5
EPDM	16.17	0.86	70

and the polymer density respectively, and subscript a and b refer to CR and EPDM respectively. The parameters of CR and EPDM related to equation are shown in Table IV.

The behavior of heat of mixing for CR/EPDM blend system is shown in Figure 10. ΔH_m values were found to lie between 0.02 and 0.06 J, it increases with increase in weight fraction of EPDM in the blend, attaining maximum value at $\sim$ 75% and decreasing afterwards. Schneier[22] has calculated the ΔH_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 ΔH_m values for compatible components a miscibility gap is expected to exist in 30–90% EPDM region. However in most of the solvents studied, the miscible region was a function of CED value of the solvent used. Such a deviation from the predicted ΔH_m values may exist in presence of solvent as the, thermodynamics of a ternary system (polymer1/polymer2/solvent) will be different than a pure binary polymer (polymer1/polymer2) system due to interaction of polymer and solvent.

Sorption coefficient (S) that is related to the equilibrium sorption of the penetrant, and interaction parameter between CR and EPDM (χ_{12}) that is related to the associative interactions between polymeric components in a ternary system, can provide an estimation of interaction among blends components. These parameters can be calculated using eqs. (7) and (8)
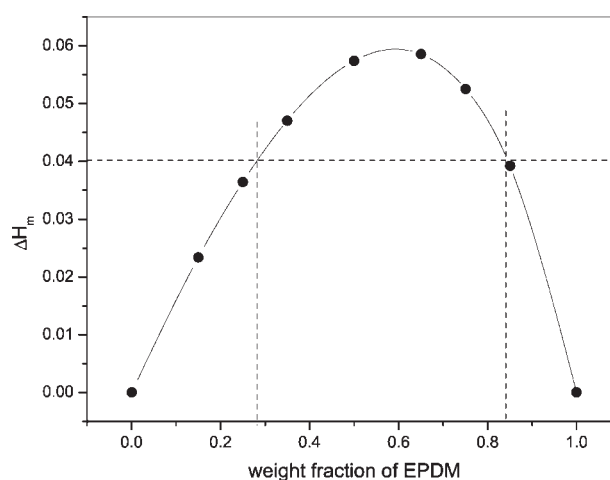
$$S = M_s/M_p \quad (7)$$

Figure 10 Variation of heat of mixing for blends of different composition.

where M_s is the mass of the solvent at equilibrium and M_p is the mass of polymer sample

$$\ln a_t = 0$$
$$= \ln \phi_t + (1 - \phi_t) + (\chi_{t1}\phi_1 + \chi_{t2}\phi_2)(1 - \phi_t)$$
$$- \chi_{12}\phi_1\phi_2 \qquad (8)$$

where a_t is the activity of the solvent absorbed into a blend of polymer 1 and 2, and ϕ_t, ϕ_1, and ϕ_2 are the volume fractions of solvent, polymer 1 and 2 in ternary system. χ_{t1} and χ_{t2} are the polymer solvent interaction parameter determined from the equilibrium solvent uptake of the neat polymers

$$\ln a_t = 0 = \ln \phi_t + (1 - \phi_t) + \chi_{ti}(1 - \phi_t)^2 \qquad (9)$$

For the sorption studies, radiation crosslinked blends were investigated for uptake of different solvents. Figure 11 shows change in the swelling ratio for a series of blends in different solvents. From the swelling data, the interaction parameter for different solvents has been plotted in Figure 12. The interaction parameter derived from equilibrium solvent uptake was found to be negative and shows compositional dependence in all the solvents. It indicates improvement in the specific interactions between CR and EPDM at higher EPDM fraction in chloroform and also reflects increase in the level of mixing with increase in the EPDM fraction in the blends. The χ_{12} values for CCl_4 system are nearly zero, corresponding to nearly immiscible blends.

The values obtained from swelling and viscometric techniques were in good agreement in majority of the cases, however, some anomaly was found in the equilibrium swelling maximum swelling and highest intrinsic viscosity of CR in xylene and chloroform.
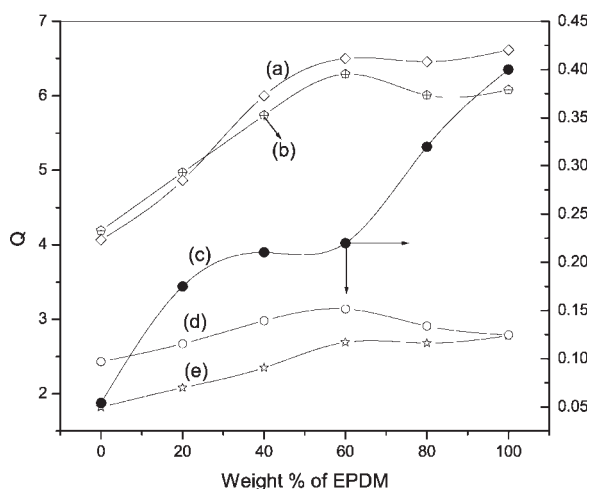

Figure 11 Swelling ratios of blends in different solvents (a) CCl_4, (b) chloroform, (c) acetone, (d) toluene, and (e) benzene.
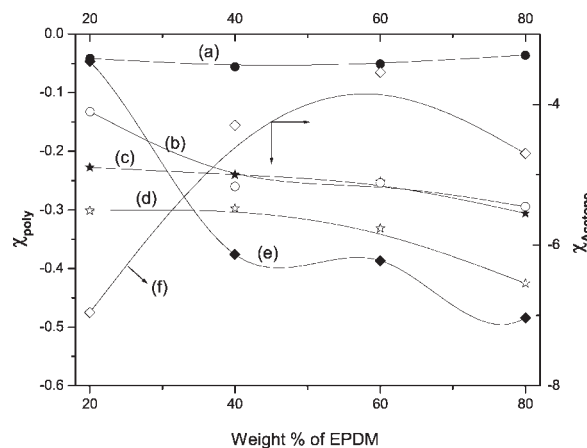

Figure 12 Variation of interaction parameter with composition of blends. (a) CCl_4, (b) xylene, (c) toluene, (d) benzene, (e) chloroform, and (f) acetone.

This anomaly can be attributed to the microscopic changes that occurred in the samples on irradiation. It is well known that 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 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.[23,24] The sorptive activity and diffusion rate 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.

These results indicate that phase separation is not prevalent in all of the solvents. Since the internal repulsion effect is known to promote the miscibility in similar systems, the weak polymer solvent interaction in chloroform will lead to better miscibility of CR and EPDM. The plausible explanation for the observed variation in the miscibility behavior in solutions with the change in solvent is that, though the solution of the pure polymers and their blends are homogeneous, the coils would expand to different extents in each solvent depending upon the χ_{12} values. Several studies have been reported on the effect of solvents on various miscible and immiscible blends using different analytical techniques.[25–31] In most of the cases, the nature of the solvent was found to affect the polymer–polymer interaction of blends and which in turn affects the miscibility of the blend. In the miscibility analysis of polymer blends in solution phase, it is important that

individual fractional parameters are considered instead of considering the cumulative value of solubility parameter. Ha et al.[32] in their study on the PMMA/PVAc system have shown that if δ_h of the solvent is higher than 6.5 $J^{1/2}$ $cm^{3/2}$, the cast blends of PMMA/PVAc are immiscible. This explanation seems valid for the polymers having higher contribution from polar groups. However in the present study one component of the blend system namely EPDM, is nonpolar having over all interaction parameter close to CCl_4, thus it is highly likely that this component would tend to remain in its own coils in such a solvent, and extent of interaction with other polymer present in the system will be lower. On the other hand, in the chloroform, the weaker polymer-solvent interaction, originating from interactions of the solvent and polymeric species, could allow the formation of an intermacromolecular complex of high conformational energy, whereas, such specific interaction between the components and the solvent were not possible in other solvents used for the study.

CONCLUSIONS

The significant changes in the miscibility behavior and inter molecular interactions between CR and EPDM were observed with change in cohesive energy density of the solvent. Dilute-solution viscometry (DSV) revealed that the blends are immiscible over the entire composition range in toluene, xylene and CCl_4, but miscibility was observed in chloroform for blends having upto 40% EPDM. Heat of mixing for the CR/EPDM system indicated the immiscibility, as the ΔH_m values were found to lie between 0.02 and 0.06 J with maximum value at $\sim$ 75% EPDM. Polymer–polymer interaction parameter in different solvents indicated improvement in the specific interactions between CR and EPDM at higher EPDM fraction in chloroform and also reflects increase in the level of mixing with increase in the EPDM fraction in the blends, whereas, χ_{12} values for CCl_4 system were found to be nearly zero.

References

1. Krause, S. In Polymer Blends; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, p 1.
2. George, S. C.; Ninan, K. N.; Greonincks, G.; Thomas, S. J Appl Polym Sci 2000, 78, 1280.
3. McDonel, E. T.; Baranwal, K. C.; Andries, J. C. In Polymer Blends; Paul, D. R., Newman, S. Eds., Academic Press: New York, 1978; Vol. 2, Chapter 19, p 287.
4. Shershnev, V. A. Rubber Chem Technol 1982, 55, 537.
5. Woods, M. E.; Davidson, J. A. Rubber Chem Technol 1976, 49, 112.
6. Gardiner, J. B. Rubber Chem Technol 1968, 41, 1312.
7. Pingping, Z. Eur Polym Mater 1997, 33, 411.
8. Jiang, W. H.; Han, S. J. Eur Polym Mater 1998, 34, 1579.
9. Mathew, M.; Ninan K. N.; Thomas, S. Polymer 1998, 39, 6235.
10. El-Sabbagh, S. H. Polym Test 2003, 22, 93.
11. Olabisi, O.; Robeson L. M.; Shaw, M. T. In Polymer–Polymer Miscibility; Academic Press: New York, 1979; p 57.
12. Kulshrestha, A. K.; Singh, B. P.; Sharma, Y. N. Eur Polym Mater 1988, 24, 29.
13. Kulshrestha, A. K.; Singh, B. P.; Sharma, Y. N. Eur Polym Mater 1988, 24, 33.
14. Chee, K. K. Eur Polym Mater 1990, 26, 423.
15. Khinnavar, T.; Aminabhavi, M.; Balundge, R. H.; Shukla, S. S.; Kutac, A. J Hazard Mater 1991, 28, 281.
16. Cooke, N. E. J Polym Sci Part B: Polym Phys 1991, 29, 1633.
17. Lucht, I. M.; Peppas, N. A. J Appl Polym Sci 1987, 33, 1557.
18. Crank, J., Ed. The Mathematics of Diffusion, 2nd ed.; Oxford University Press: Clarendon, 1975.
19. Sun, Z.; Wang, W.; Feng, Z. Eur Polym Mater 1992, 28, 1259.
20. Zhong-Yu, W. J Polym Sci Part B: Polym Phys 2003, 41, 2296.
21. Gardon, J. L. In Encyclopedia of Polymer Science and Technology, Mark, H. F., Gaylord, N. G., Bikales, N. M., Eds.; Interscience: New York, 1965, Vol. 3, p 833.
22. Schneier, B. J Appl Polym Sci 1973, 17, 3175.
23. Dubey, K. A.; Bhardwaj, Y. K.; Chaudhari, C. V.; Bhattacharya, S.; Gupta, S. K.; Sabharwal, S. J Polym Sci Part B: Polym Phys 2006, 44, 1676.
24. Anelli, P.; Baccaro, S.; Carenza, M.; Palma, G., Radiat Phys Chem 1995, 46, 1031.
25. Haiyang, Y.; Pingping Z.; Feng, R.; Yuanyuan, W.; Tiao, Z. Eur Polym Mater 2000, 36, 21.
26. Tewari, N.; Srivastava, A. K. Macromolecules 1992, 25, 1013.
27. Papanagopoulos, D.; Dondos, A. Macromol Chem Phys 1994, 195, 439.
28. Danait, A.; Deshpande, D. D. Eur Polym Mater 1995, 31, 122.
29. Inai, Y.; Takenouchi, S.; Yokota, K. Polym J 1996, 28, 365.
30. Papanagopoulos, D.; Dondos, A. Polymer 1996, 37, 1053.
31. Tang, M.; Liau, W.-R. Eur Polym Mater 2000, 36, 2597.
32. Ha, C. S.; Lee, W. K.; Cho, W. J. Macromol Symp 1994, 84, 279.