

Viscosity Behavior of PVC-Modified Liquid Natural Rubber Blends

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SYNOPSIS

Compatibility of poly(vinyl chloride) (PVC) with liquid natural rubber (LNR) and epoxidized liquid natural rubber (ELNR) has been studied by solution viscometric methods. The relative viscosity versus composition plots for PVC/LNR and PVC/ELNR-20 blends are found to be nonlinear. The corresponding intrinsic viscosity values show negative deviation from ideal behavior when plotted against composition. The modified Krigbaum and Wall parameter, Δb , also shows negative values for all compositions of these blends studied. The results indicate that PVC/LNR and PVC/ELNR-20 blends are incompatible systems. On the other hand, PVC/ELNR-50 blends yielded linear plots when relative viscosity was plotted against composition. The intrinsic viscosity composition plots for this system showed positive deviation from ideal behavior. The Δb values are positive for all compositions of these blends studied. These results are characteristic of a compatible blend system. Hence it is concluded that liquid natural rubber can be made compatible with PVC when the former is epoxidized to a sufficient level. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Blending as a route to enhance specific material properties has been widely accepted for polymers and exploited in a variety of commercial products.^{1,2} For a polymer blend to show superior properties, compatibility of the two homopolymers is required to an optimum extent. The compatibility is attributed to specific interactions among the component molecules. This specific interaction can be of different types, namely, dipole-dipole, ion-dipole, hydrogen bonding, etc. The complimentary dissimilarity of their structures also leads to the compatibility of the two polymers.

Many experimental and theoretical methods have been used to study polymer compatibility. Heat of mixing, viscometry, glass transition temperature, morphology studies by optical and electron microscopy, light scattering, infrared spectroscopy, neutron scattering, and dynamic mechanical analysis are some of the methods extensively reported in the literature.¹⁻³

An insight to interactions in polymers and hence to compatibility can be obtained by the simple viscometric technique.⁴⁻⁹ The determination of compatibility by viscometry depends on the fact that the repulsive interaction among polymer molecules causes their shrinkage, leading to a lowering of solution viscosity, while attractive interaction increases the viscosity. The estimation of compatibility of different pairs of polymers based on viscosity data for ternary systems involving polymer/polymer/solvent has been attempted by several authors.¹⁰⁻¹⁶

Kulshreshtha, Singh, and Sharma¹⁰ applied this method to the PVC/ABS blend system to assess the compatibility. They found that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility. Chee¹¹ also applied this method for identifying the compatibility of poly(vinyl chloride)/poly(methyl methacrylate) (PVC/PMMA), poly(methyl methacrylate)/poly(isobutyl methacrylate) (PMMA/PiBMA), and PVC/PiBMA. The compatibility of polycarbonate (PC) and poly(hexamethylene sebacate) (PHMS) blends having different molecular weight has been characterized by viscometry using the Krigbaum and Wall parameter, Δb , by Shih and Beatty.¹⁵ The val-

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ues for Δb for PC/PHMS mixtures were negative, and therefore they concluded that these blends were not thermodynamically compatible under equilibrium conditions.

Theoretical Consideration

Basically, the dilute solution viscometry depends on the classical Huggins equation¹⁷ that expresses the specific viscosity $[\eta_{sp}]$ of the polymer as a function of concentration C , when one of the components is alone in solution.

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \quad (1)$$

where $[\eta]$ is the intrinsic viscosity. If we put $k[\eta]^2 = b$ the Huggins equation becomes

$$\frac{[\eta]_{sp}}{C} = [\eta] + bC \quad (2)$$

where b is the interaction term.

The theoretical consideration starts from the derivation by Krigbaum and Wall.¹⁶ The specific viscosity, $\eta_{sp,m}$, of a mixed polymer solution can be expressed as follows:

$$\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (3)$$

where $[\eta_1]$ is the intrinsic viscosity of the component 1 alone in solution and $[\eta_2]$ is the intrinsic viscosity of the component 2 in solution. C_1 and C_2 are the concentration of component 1 and 2, respectively, in mixed polymer solution, and b_{12} is the interaction coefficient for the mixture of components 1 and 2. For mathematical convenience Krigbaum and Wall¹⁶ defined the interspecific interaction coefficient b_{12} as

$$b_{12} = \sqrt{b_{11}b_{22}} \quad (4)$$

The values of b_{11} and b_{22} are obtained from comparison of eq. (1) and (2).

$$k[\eta_1]^2 = b_{11} \quad (5)$$

$$k[\eta_2]^2 = b_{22} \quad (6)$$

But the definition of b_{12} according to eq. (4) is not valid for systems that have negative values for b_{11} or b_{22} . Therefore, the modification by Williamson

and Wright¹⁸ is used to evaluate b_{12} , which can be expressed as

$$b_{12}^* = \frac{b_{11} + b_{22}}{2} \quad (7)$$

The value of b_{12} can be theoretically calculated from eq. (7) and can also be obtained from (3).

According to Krigbaum and Wall,¹⁶ information on the interaction between polymer 1 and 2 can be obtained by comparison of experimental b_{12} and theoretical b_{12}^* values. Here the compatibility is characterized by a parameter, b , expressed as

$$\Delta b = b_{12} - b_{12}^* \quad (8)$$

where b_{12} is the experimental value and b_{12}^* is the theoretical value. Negative values of Δb are found for solutions of incompatible polymer systems, while positive values refer to attractive interaction in compatible systems. We can reduce eq. (3) to the following form when total concentration of the mixture (C) approaches zero

$$(\eta_{sp,m}/C)_{C \rightarrow 0} = [\eta_1] \left(\frac{C_1}{C} \right)_{C \rightarrow 0} + [\eta_2] \left(\frac{C_2}{C} \right)_{C \rightarrow 0} \quad (9)$$

In this paper our studies of compatibility of polyvinyl chloride with liquid natural rubber (PVC/LNR) and polyvinyl chloride with epoxidized liquid natural rubber (PVC/ELNR) of varying degree of epoxidation have been discussed. Equations (8) and (9) are used to characterize the compatibility.

EXPERIMENTAL

Materials

PVC (K -value 65, \bar{M}_w 140,000, density 1.37) was supplied by M/s Chemicals and Plastics Ltd., Madras. ISNR-5 was supplied by Rubber Research Institute of India, Kottayam. Liquid natural rubber (LNR) with \bar{M}_n 5000 was obtained by the method reported by Ravindran, Nair, and Francis.¹⁹ Epoxidized liquid natural rubber with 20 and 50 mol % of epoxidation (ELNR-20 and ELNR-50), were prepared by the *in situ* epoxidation of LNR in our laboratory. 2-Butanone supplied by Merck was used as the solvent for blending. This was dried with calcium chloride and distilled before use. Glacial acetic acid, toluene, methanol, and hydrogen peroxide were of reagent grade.

Preparation of Liquid Natural Rubber¹⁹

A 7% solution of natural rubber (100 g) in toluene was prepared in a two liter flask made up of borosil glass, and it was mixed with 100 mL of hydrogen peroxide. This was partly homogenized with the addition of 50 mL methanol. The solution was then placed in sunlight and irradiated with stirring for 50 h. After the irradiation, the organic layer was separated and the solvent was removed by distillation. The liquid natural rubber was then precipitated by the addition of methanol and dried in vacuum.

Preparation of Epoxidized Liquid Natural Rubber

ELNR-50

LNR (25 g) dissolved in 166 mL of toluene to obtain a 15% solution was stirred at 50°C for 10 h with 1.1 mol of H₂O₂ and 0.35 mol of glacial acetic acid. At the end of the reaction the product was isolated by precipitating from methanol and dried in vacuum. It was then characterized by titrimetric, IR, NMR, and DSC techniques.

ELNR-20

LNR (25 g) dissolved in 166 mL of toluene to obtain a 15% solution was stirred at 50°C for 3 h with 0.55 mol of H₂O₂ and 0.35 mol of glacial acetic acid. Isolation and characterization were done as above.

Blending and Viscosity Measurements

Polymer solutions were prepared by dissolving accurately weighed samples in a calculated amount of solvent. Polymer mixtures of desired proportion were prepared by mixing measured volumes of individual polymer solutions. Compositions of the blends are given in Table I. The blends were designated as follows: PVC/LNR (60/40) means a blend

of 60 parts PVC with 40 parts LNR, PVC/ELNR-20 (60/40) means a blend of 60 parts PVC with 40 parts epoxidized liquid natural rubber of 20 mol % epoxidation, etc.

The relative viscosities of the polymer solutions and their mixtures were determined by an Ubbelohde Viscometer (Schott Gerate AVS 400-Viscometer). The measurements were carried out at constant temperature of 28.9°C and were achieved in a water bath with a thermostat (Schott Gerate CT 1450/2 thermostat).

RESULTS AND DISCUSSION

The intrinsic viscosity values of PVC and LNR were obtained from the plots of η_{sp}/C versus concentration as shown in Figure 1. The corresponding values for ELNR-20 and ELNR-50 were obtained from plots given in Figures 2 and 3, respectively. The intercept of the plots with abscissa gives the intrinsic viscosity of the corresponding polymers and the values are shown in Table II. The γ^2 values are correction factors in linear regression analysis. These values are almost equal to unity, which shows perfect fit of the data. Plots for the polymer mixtures are also shown in Figures 1–3. The intrinsic viscosity values of the blends were obtained from these plots and they are tabulated in Table II.

PVC/LNR System

Blends of PVC and liquid natural rubber were prepared in different compositions as shown in Table I. The viscosity behavior of these blends in solution has been followed with a view to assess the extent of compatibility between the individual polymers. Generally, PVC is expected to be incompatible with liquid natural rubber due to the solubility parameter mismatch between them. The results obtained in

Table I Composition of PVC–Rubber Blends

Blends	PVC	LNR	ELNR-20	ELNR-50
PVC/LNR (60/40)	60	40	—	—
PVC/LNR (50/50)	50	50	—	—
PVC/LNR (30/70)	30	70	—	—
PVC/ELNR-20 (60/40)	60	—	40	—
PVC/ELNR-20 (50/50)	50	—	50	—
PVC/ELNR-20 (30/70)	30	—	70	—
PVC/ELNR-50 (60/40)	60	—	—	40
PVC/ELNR-50 (50/50)	50	—	—	50
PVC/ELNR-50 (30/70)	30	—	—	70

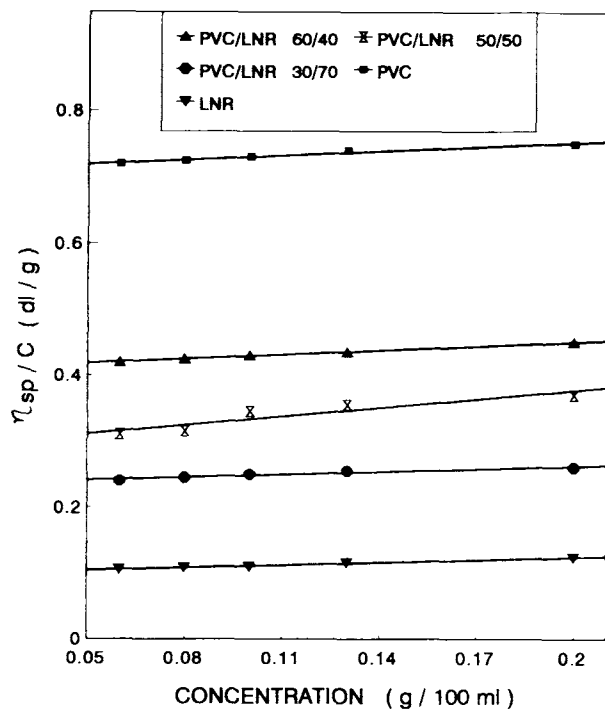


Figure 1 η_{sp}/c versus C for PVC, LNR, and PVC/LNR blends.

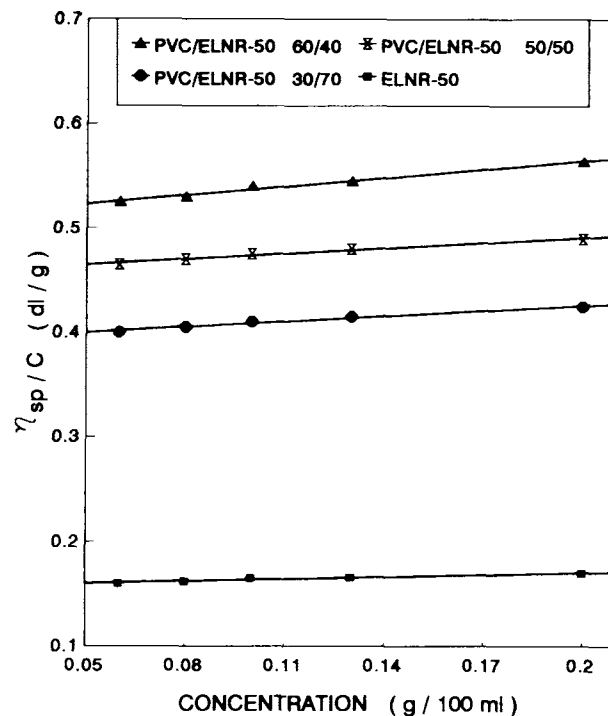


Figure 3 η_{sp}/c versus C for ELNR-50 and PVC/ELNR-50 blends.

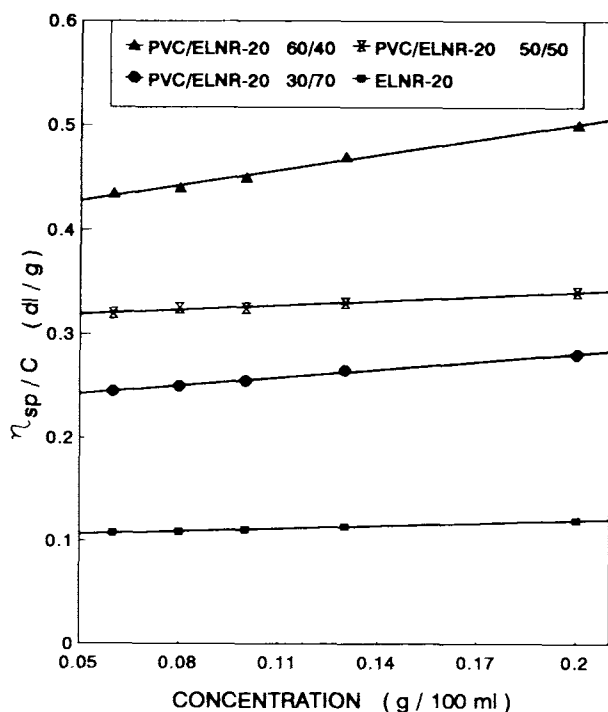


Figure 2 η_{sp}/c versus C for ELNR-20 and PVC/ELNR blends.

the viscosity studies are also consistent with this view. Figure 4 shows a plot of intrinsic viscosity versus composition of these blends. The plot shows a negative deviation from ideal behavior. Ideal systems always give straight line plots. Many authors¹⁵ have studied immiscible systems by this method and found that the intrinsic viscosity always shows a negative deviation due to repulsive interaction between the component polymers. The repulsive in-

Table II Intrinsic Viscosity of the Component Polymers and the Blends

Polymer/Blends	γ^2	$[\eta]$ [dL/g]
PVC	1.0	0.7078
LNR	0.9889	0.1001
ELNR-20	1.0	0.1019
ELNR-50	1.0	0.1584
PVC/LNR (60/40)	1.01	0.4735
PVC/LNR (50/50)	1.0	0.3119
PVC/LNR (30/70)	1.0	0.2345
PVC/ELNR-20 (60/40)	1.0	0.4046
PVC/ELNR-20 (50/50)	1.0	0.3156
PVC/ELNR-20 (30/70)	0.989	0.2202
PVC/ELNR-50 (60/40)	1.01	0.5133
PVC/ELNR-50 (50/50)	1.0	0.4652
PVC/ELNR-50 (30/70)	1.0	0.3901

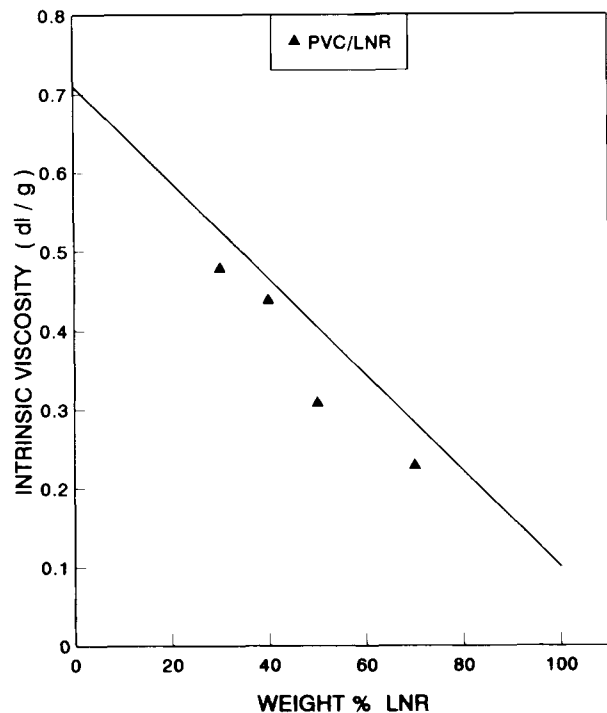


Figure 4 Intrinsic viscosity versus composition for PVC/LNR blends.

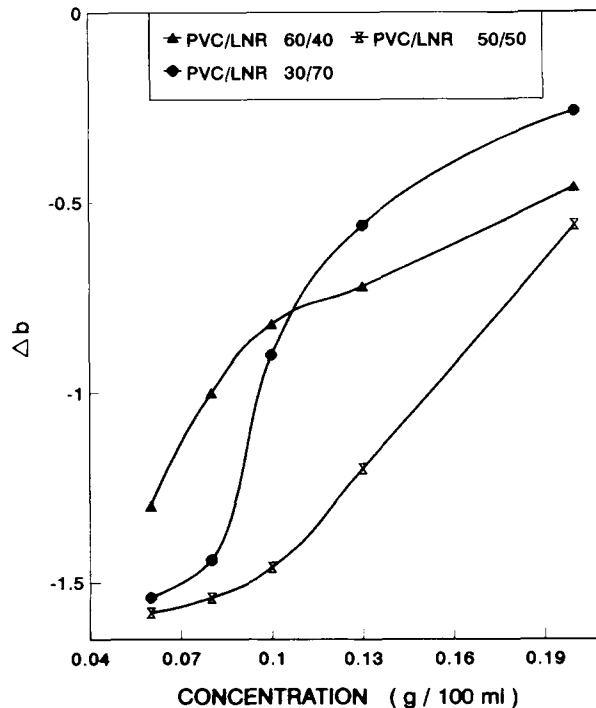


Figure 5 Δb versus total concentration for PVC/LNR blends.

teraction causes a reduction in the hydrodynamic volume of the polymer molecules, and hence the viscosity of the solution is diminished.

The values of Δb as per eq. (8) have been plotted for different total concentrations of PVC/LNR (Fig. 5). The curve lies in the negative region for the composition range studied. These negative values indicate repulsive interaction among the component polymers characteristic of an incompatible system. The values of Δb decrease as the total concentration of the mixture decreases, as shown in the figure. This may be due to the increase in polymer-solvent interaction with an increase in solvent concentration. In other words the polymer-solvent interaction exceeds the polymer-polymer interaction at high dilution. The lowest value for Δb was obtained in the case of 50% PVC.

The relative viscosity-composition plots of PVC/LNR blends are given in Figure 6. The graphs show a deviation from linearity and it takes up an S-shape. This indicates incompatibility of the components. Kulshreshtha, Singh, and Sharma¹⁰ also showed that such a behavior is characteristic of incompatible systems.

It was also found that these blend systems in solution turn turbid at moderate concentrations, showing phase separation. All these observations

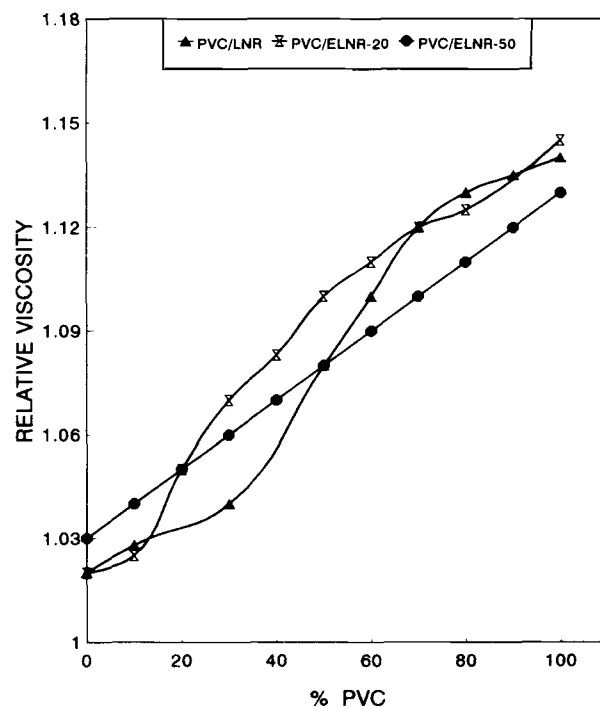


Figure 6 Relative viscosity versus composition for blends of PVC/LNR, PVC/ELNR-20, and PVC/ELNR-50.

indicate that PVC/LNR blends are incompatible in all composition ranges studied.

PVC/ELNR-20

Polar groups have been introduced into liquid natural rubber in order to enhance its miscibility with PVC. Thus the liquid natural rubber has been subjected to epoxidation to a level of 20 mol % and the product was mixed with PVC in different compositions, as shown in Table I. The intrinsic viscosity versus composition plots are given in Figure 7. All the compositions show negative deviation from ideal behavior. It suggests that the system is incompatible. Hence the introduction of 20 mol % epoxy group into liquid natural rubber is found to be insufficient to bring about the miscibility.

Figure 8 shows the plots of Δb versus total concentration for all the three compositions. The negative values indicate that the systems are incompatible. However, Δb value for the PVC/ELNR-20 (60/40) blend approaches zero at higher total concentration, namely, 0.2%. Also, the values of Δb increase with a decrease in the proportion of rubber content in the blends when compared at the same total concentration of different composition. These observations suggest that the PVC/ELNR-20 blend systems become more compatible at lower concen-

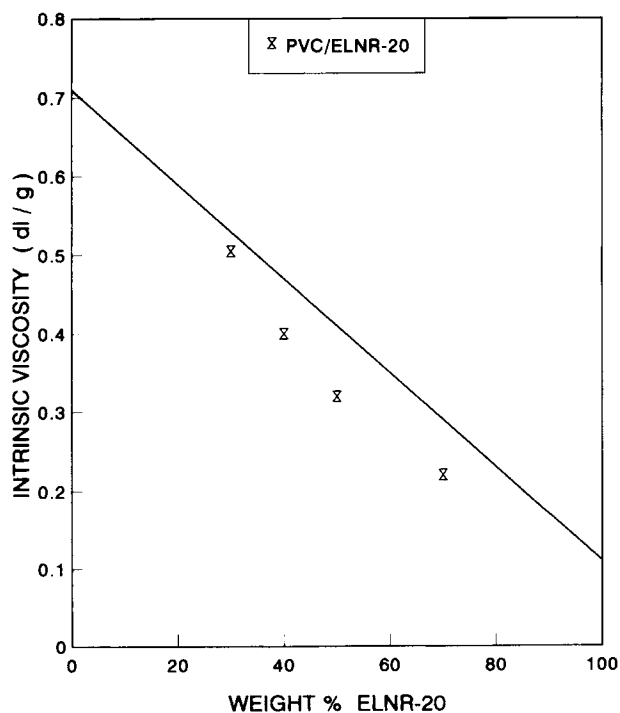


Figure 7 Intrinsic viscosity versus composition for PVC/ELNR-20 blends.

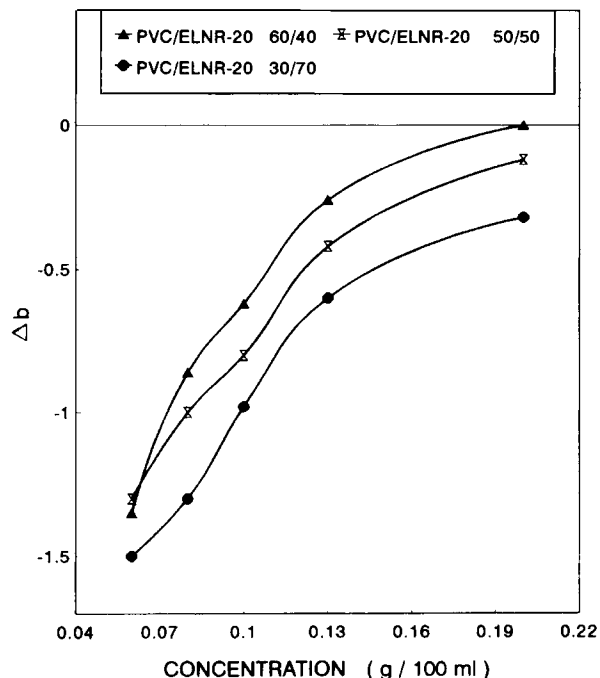


Figure 8 Δb versus total concentration for PVC/ELNR-20 blends.

tration of ELNR-20 in the mixture. In all the cases the values of Δb decrease with decrease in the total concentration of the blends. This is because the polymer-polymer interaction is being replaced by the polymer-solvent interaction at higher dilution.

The above results were corroborated by the relative viscosity-composition plots as in Figure 6. The curve shows an S-type pattern indicating two-phase formation with an inversion in phases at intermediate composition (60/40). The increase in the level of compatibility is attributed to variation in the solubility parameter of liquid natural rubber due to the presence of epoxy groups, which enhance its polarity and, hence, interaction with PVC.

PVC/ELNR-50

Since 20 mol % epoxidation of liquid natural rubber was found to be inadequate in bringing about compatibility with PVC, the degree of epoxidation was further raised to 50 mol %. The ELNR-50 was then mixed with PVC, and blends of varying composition were prepared as shown in Table I. A plot of intrinsic viscosity versus composition of these blends has been presented in Figure 9. All the compositions showed positive deviation from ideal behavior. This indicates the commencement of attractive interaction with PVC when the level of epoxidation is increased.

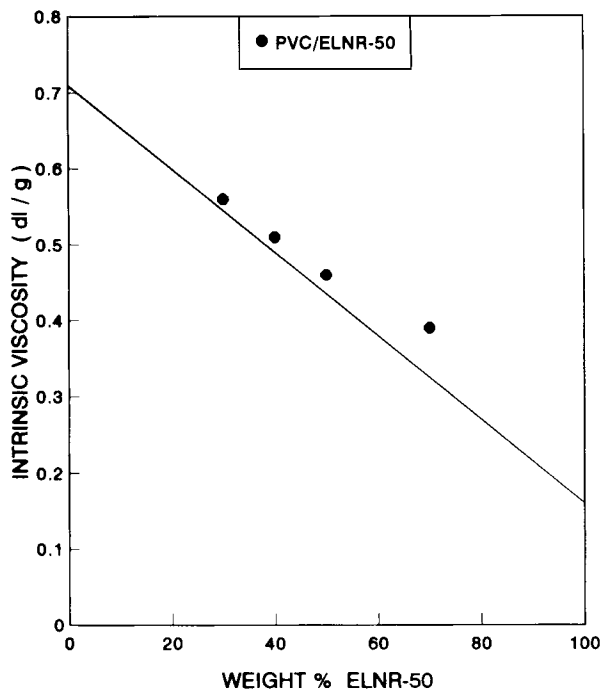


Figure 9 Intrinsic viscosity versus composition for PVC/ELNR-50 blends.

Hence, the blends comprising of PVC and ELNR-50 can be considered as compatible systems.

The values of Δb according to eq. (8) have been computed for the three compositions. These values are plotted against total concentration of the blends and are shown in Figure 10. In all the cases the Δb values are found to be positive, indicating attractive interaction between the components. This observation is characteristic of compatible blends as reported in the case of many other systems.^{15,16} Unlike the previous two cases, the Δb values for the present system increase with decrease in the total concentration. The Δb values for PVC/ELNR-50 (50/50) were found to be slightly higher than those of the other two compositions.

The relative viscosity–composition plots for the PVC/ELNR-50 blends are shown in Figure 6. The plots are linear at all the composition ranges studied. This again indicates that PVC/ELNR-50 is a compatible system. The compatibility is attributed to the matching of solubility parameters caused by the presence of higher concentrations of epoxy groups in the liquid natural rubber.

A comparative account of all three systems studied in this work, namely, PVC/LNR, PVC/ELNR-20, and PVC/ELNR-50 suggests that liquid natural rubber can be made compatible with PVC by increasing the polarity of the liquid rubber with the help of sufficient numbers of epoxy groups.

CONCLUSION

The intrinsic viscosity–composition plots for three series of blends, namely, PVC/LNR, PVC/ELNR-20, and PVC/ELNR-50, have been examined with a view to study the extent of compatibility of the blend components. The PVC/LNR and PVC/ELNR-20 blend systems showed negative deviation from ideal behavior, indicating incompatibility when intrinsic viscosity values were plotted against composition. PVC/ELNR-50 has shown positive deviation characteristic of a compatible system.

Similar results were obtained when Δb values were examined. PVC/LNR and PVC/ELNR-20 blend systems gave negative values of Δb for all compositions studied. This indicates repulsive interaction between component polymers, and hence they are considered as incompatible systems. However, the values of Δb for one of the systems, *viz.*, PVC/ELNR-20, are found to be higher than those of PVC/LNR when compared at the same composition and total concentration. This indicates that there is an increase in the compatibility of the blend components with the introduction of epoxy groups in liquid natural rubber. This is further confirmed by the fact that PVC/ELNR-50 blend showed positive values of Δb characteristic of a compatible system.

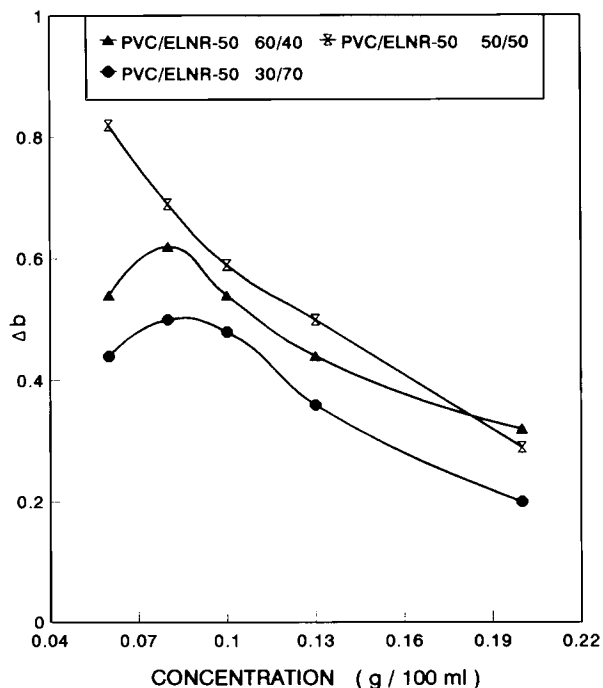


Figure 10 Δb versus total concentration for PVC/ELNR-50 blends.

The relative viscosity-composition plots for PVC/LNR and PVC/ELNR-20 are found to deviate from linearity. PVC/ELNR-50 gave a linear plot. Earlier workers have shown that incompatible blends always yielded nonlinear plots and compatible blends yielded linear plots.

All the above observations suggest that PVC/ELNR-50 is a compatible blend system, whereas PVC/LNR and PVC/ELNR-20 remain incompatible. In other words, higher concentrations of epoxy groups in liquid natural rubber increase its miscibility with PVC.

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