

Compatibility studies of polymer–polymer systems by viscometric techniques: nitrile-rubber-based polymer blends

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(Revised 7 October 1997)

Interactions in binary polymer systems have been analysed from the viscosity behaviour. Dilute solution viscosity measurements were made on three different ternary polymer (1)/polymer (2)–solvent (3) systems, *i.e.* acrylonitrile–butadiene rubber (NBR)/polystyrene, NBR/poly(styrene–*co*–acrylonitrile), NBR/poly(acrylonitrile–*co*–butadiene–styrene) in chloroform, as a function of blend composition. The polymer–polymer interaction parameter $\chi_{i(p-p)}$ and the corresponding polymer–solvent interaction parameter $\chi_{i(p-s)}$ were determined for all the blend systems. In order to predict compatibility, the interaction parameter term Δb , obtained from modified Krigbaum and Wall theory, and the difference in the intrinsic viscosities of the polymer mixtures and the weight-average intrinsic viscosities of the two polymer solutions taken separately are used. These results were correlated with the experimentally determined densities and were found to be in agreement. Finally, the results are correlated with spectroscopic evidence. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: blend compatibility; dilute solution viscometry; Krigbaum and Wall interaction parameter)

INTRODUCTION

Polymer blends are physical mixtures of structurally different polymers which interact through secondary forces with no covalent bonding¹. Blending of the polymers may result in a reduction in the basic cost and improved processing, and also may enable properties of importance to be maximised. However, the mechanical, thermal, rheological and other properties of a polymer blend depend strongly on its state of miscibility².

The compatibility of polymer blends is calculated theoretically as well as being estimated experimentally by dynamic mechanical, thermal, electron-microscopic, neutron scattering, light scattering, spectroscopic and viscometric techniques^{1,2}. Because of its simplicity, viscometry is an attractive and very useful method for studying the compatibility of polymer blends. Additional advantages, *i.e.* that no sophisticated equipment is necessary and that the crystallinity or the morphological states of the polymer blends do not affect the result³, make the viscometric method more convincing for characterising polymer mixtures. Also, the retarded diffusion of polymers in the solid state makes it difficult to attain a condition of true thermodynamic equilibrium, and so the behaviour of a polymer mixture in solution is the best method of assessing the miscibility⁴.

Estimation of the compatibility of different pairs of polymers based on dilute solution viscosity for a ternary polymer/polymer–solvent system has been attempted by several authors, including Mikhailov and Zeilkman⁵, Bohmer and Florian⁶, Feldman and Rusu⁷, Krigbaum and Wall⁸, and Catsiff and Hewett⁹. The compatibility of

polycarbonate (PC) and poly(hexamethylene sebacate) (PHMS) blends has been characterised by a viscosity technique using the Krigbaum and Wall parameter, Δb , by Shih and Beatty¹⁰. The values of Δb for PC/PHMS mixtures were negative, and therefore they concluded that these blends were not thermodynamically compatible under equilibrium conditions. Using the glass transition temperature, T_g , of the blend as a measure of the bulk solid-state compatibility, a correlation was obtained with the Krigbaum and Wall parameter Δb . The versatility of the viscometric technique is not affected by the choice of solvent, as was shown by Kulshreshta *et al.*¹¹. Lizymol and Thomas¹² have reported that for the three binary systems poly(vinyl chloride)/poly(ethylene vinyl acetate) (PVC/EVA), PVC/styrene–acrylonitrile (SAN) and EVA/SAN, the Krigbaum and Wall model modified by Williamson and Wright was more applicable than the Catsiff and Hewett model. The compatibility in the solution state was correlated to that in the solid state for these blends, and was found to be in agreement^{13–15}.

The present work discusses in detail our investigation into the compatibility of the three binary polymer blends poly(acrylonitrile–*co*–butadiene)/polystyrene, poly(acrylonitrile–*co*–butadiene)/poly(styrene–*co*–acrylonitrile) and poly(acrylonitrile–*co*–butadiene)/poly(acrylonitrile–*co*–butadiene–*co*–styrene). An attempt has been made to extend the most applicable viscometric theories to these three polymer blend systems, which exhibit different levels of compatibility.

EXPERIMENTAL

The basic characteristics of the polymers used are given in Table 1. Chloroform (CHCl₃), cyclohexanone,

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Table 1 Details of materials used

Material	Source	Characteristic ^a	Value
Nitrile rubber (Aparene N553NS; NBR)	Gujarat Apar Polymer Ltd., Bombay	Volatile matter (%)	0.130
		Antioxidant (%)	1.400
		Organic acid (%)	0.250
		Soap (%)	0.004
		Mooney viscosity, ML ₁₊₄ 100°C	40.00
		Bound –CN (wt%)	34.00
		Density (g cm ⁻³)	0.911
		Mol. wt, <i>M_w</i> (g mol ⁻¹)	13.49 × 10 ⁴
Polystyrene, atactic (PS)	Polychem India Ltd., Bombay	Density (g cm ⁻³)	1.021
		Mol. wt, <i>M_w</i> (g mol ⁻¹)	10.62 × 10 ⁴
Styrene–acrylonitrile (SAN)	Anoopam India Pvt. Ltd., New Delhi	Density (g cm ⁻³)	1.087
		–CN (wt%)	24.00
		Mol. wt, <i>M_w</i> (g mol ⁻¹)	15.59 × 10 ⁴
Acrylonitrile–butadiene–styrene (ABS)	Anoopam India Pvt. Ltd., New Delhi	Density (g cm ⁻³)	1.041
		–CN (wt%)	18.00
		Butadiene (wt%)	41.00
		Styrene (wt%)	41.00
		Mol. wt, <i>M_w</i> (g mol ⁻¹)	5.64 × 10 ⁴

tetrahydrofuran (THF), vinyl acetate, trichloroethylene and toluene (A.R. grade; Merck) were used as solvents for the various experiments in the present work. The solvents were dried over calcium chloride and double-distilled before use.

The individual polymer solutions were prepared by dissolving the polymers in the specified solvents, followed by stirring for 24 h. For preparing the blend solutions, the polymer solutions were subsequently blended in the appropriate proportions.

The specific viscosities of the polymers and their mixtures in the specified solvents were determined with use of an automated Ubbelohde-type viscometer (Schott Gerate AVS 400). The measurements were carried out in a closed system to minimise solvent evaporation. The measurement temperature was 30 ± 0.01°C, and this was achieved in a water-bath fitted with a thermoregulator (Schott Gerate CT-1450/2 thermostat). The various dilutions required during the viscosity measurements were performed in the bulb of the viscometer. At least five observations were made for each measurement.

The densities of all the dilute solutions (prepared in chloroform with a concentration of 0.25 g dl⁻¹) were measured using a specific gravity bottle at 30°C. The densities are accurate to three decimal places. Infrared spectra of the different blend compositions were obtained with use of a Perkin-Elmer FTi.r. (1600 series) spectrophotometer. The blend solutions (5% (w/v) in chloroform) were cast on a mercury surface at ambient temperature in order to obtain a uniform film thickness. In all cases, same-volume aliquots of the blends were poured onto same-diameter areas of the mercury surface. After ensuring solvent evaporation, the cast films were carefully washed using non-solvent methanol. Dried films about 30 μm thick were used for the spectral analysis.

RESULTS AND DISCUSSION

Traditionally, the concept of the Hildebrand solubility parameter has been employed to estimate the miscibility of two materials¹. The measure of the interaction between a polymer blend and a solvent in a polymer–solvent system is the interaction parameter χ_i , given by the following relationship¹⁴

$$\chi_i = \frac{V_i}{RT}(\delta_2 - \delta_1)^2 \quad (1)$$

where δ_2 and δ_1 are the solubility parameters of the polymer and solvent, respectively, and V_i , R and T are the molar volume of the solvent (reference volume), gas constant and absolute temperature, respectively.

In the case of polymer blends, the solubility parameter of the blends for the blend–solvent system is calculated using the following expression^{3,12}.

$$\delta_b = x_1\delta_1 + x_2\delta_2 \quad (2)$$

where x_1 and x_2 are the weight fractions of the component polymers of the blends, and δ_1 and δ_2 are their solubility parameters. Equation (1) has been modified for calculating the polymer–polymer interaction parameters in polymer blends^{12,14}. For this purpose, δ_2 and δ_1 are the solubility parameters of the respective polymer components.

The solubility parameters of the polymer, required in the above expression, were measured by determining the intrinsic viscosities in a series of solvents^{2,13}. The solubility parameter of the solvent in which the intrinsic viscosity of the polymer is highest is taken as the solubility parameter of the polymer. The intrinsic viscosities of acrylonitrile–butadiene rubber (NBR), polystyrene (PS), SAN and acrylonitrile–butadiene–styrene (ABS) in various solvents are tabulated in Table 2.

All the polymer–solvent systems used in our investigation were incapable of exhibiting any strong interactive forces, such as hydrogen bonding. The obtained solubility parameter values of the polymers are presented in Table 3. Table 4 tabulates the polymer–polymer interaction parameters of all the blend systems, while Table 5 tabulates the interaction parameters of polymer blends with the

Table 2 Intrinsic viscosities of the polymers in various solvents

Solvent ^a	Intrinsic viscosity (dl g ⁻¹)			
	NBR	PS	SAN	ABS
Toluene (8.9)	2.509 ^b	0.383	0.143	0.421
Vinyl acetate (9.0)	– ^c	– ^c	0.448	0.512
Tetrahydrofuran (9.1)	0.315	0.524	0.730 ^b	0.583
Trichloroethylene (9.2)	– ^c	– ^c	0.719	0.597 ^b
Chloroform (9.3)	1.663	0.769 ^b	0.712	0.571
Cyclohexanone (9.9)	0.494	0.112	0.209	0.108

^aThe solubility parameters (cal^{1/2} cm^{-3/2}) are given in parentheses

^bThe highest $[\eta]$ value among the various polymer/solvent systems

^cNot measured

Table 3 Solubility parameters ((cal cm⁻³)^{1/2}) for the polymers

NBR	PS	SAN	ABS
8.9	9.3	9.1	9.2

Table 4 Interaction parameters for the polymer (1)/polymer (2) systems

System	Polymer as component I	Molar vol. of component I ^a (cm ³ mol ⁻¹)	Interaction parameter
NBR/PS	NBR	78.6	0.021
	PS	129.2	0.034
NBR/SAN	NBR	78.6	0.005
	SAN	104.2	0.007
NBR/ABS	NBR	78.6	0.012
	ABS	55.4	0.008

^aThe molar volume of the monomer unit was taken as the reference volume

Table 5 Interaction parameters for the NBR (1)/PS (2) blend–CHCl₃ (3) systems

System	Solubility parameter of blend ^a ((cal cm ⁻³) ^{1/2})	Interaction parameter ^b
<i>NBR/PS</i>		
0/100	9.3	0
30/70	9.2	0.002
50/50	9.1	0.005
70/30	9.0	0.010
100/0	8.9	0.021
<i>NBR/SAN</i>		
0/100	9.1	0.005
30/70	9.0	0.009
50/50	9.0	0.012
70/30	8.9	0.015
100/0	8.9	0.021
<i>NBR/ABS</i>		
0/100	9.2	0.053
30/70	9.1	0.089
50/50	9.0	0.012
70/30	9.0	0.015
100/0	8.9	0.021

^aValues for the blends calculated using equation (2) have been quoted only to the first decimal place. However, for the determination of χ , δ_{blend} values obtained as such were employed

^bThe molar volume of chloroform was taken as the reference volume in equation (1)

solvent. Molecular mixing of two high molecular weight polymers can occur only when χ_1 is very close to zero. The effect of this parameter is to require that the solubility parameter difference is less than 0.1 cal^{1/2} cm^{-3/2}. From *Table 4*, it can be seen that the polymer–polymer interaction parameter χ_i for all the three systems is very small, suggesting partial miscibility.

However, the χ_1 values for the NBR/SAN and NBR/ABS blends are much lower than the interaction parameter for the NBR/PS blends. Therefore, the tendency for the NBR/SAN and NBR/ABS blends to be miscible is greater than for the NBR/PS blends. The reason lies in the smaller difference in the solubility parameters of the component polymers in the polymer blend, as given in *Table 3*. The value of $\delta_2 - \delta_1$ for the NBR/PS blends is 0.4 cal^{1/2} cm^{-3/2}, while $\delta_2 - \delta_1$ for NBR/SAN and NBR/ABS is 0.2 cal^{1/2} cm^{-3/2} and 0.3 cal^{1/2} cm^{-3/2}, respectively.

Table 5 gives the interaction parameters of the blends with the solvent. It is evident that for the NBR/PS system, the polymer–polymer interaction is less than the

polymer–solvent interaction since $\chi_{\text{NBR-PS}} > \chi_{\text{NBR/PS-CHCl}_3}$. Also, as the weight per cent of PS increases, the polymer–solvent interaction increases. For the NBR/CHCl₃ system, as well as the NBR/PS systems, the $\delta_2 - \delta_1$ value is 0.4 cal^{1/2} cm^{-3/2}, while for the PS/CHCl₃ systems, the $\delta_2 - \delta_1$ value is 0. Hence, increasing the concentration of PS in the blend favours a polymer–solvent interaction larger than a polymer–polymer interaction.

However, for the NBR/SAN systems, the polymer–polymer interaction is greater than the polymer–solvent interaction since $\chi_{\text{NBR/SAN-CHCl}_3} > \chi_{\text{NBR-SAN}}$. Again, as the concentration of SAN increases in the blend, the polymer–solvent interaction increases. Here too, the reason lies in the lower $\delta_2 - \delta_1$ value of 0.2 cal^{1/2} cm^{-3/2} for the SAN/CHCl₃ system, while NBR/CHCl₃ has a $\delta_2 - \delta_1$ value of 0.4 cal^{1/2} cm^{-3/2}. The NBR/ABS blends demonstrate similar behaviour to that of the NBR/SAN blends, which is evident from *Tables 4 and 5*.

Dilute solution viscosity theories for compatibility studies of polymer blends

Earlier studies indicate that the interaction in binary polymer systems can be analysed accurately by studying the viscosity behaviour^{10,13,16}. To this end, a different theoretical approach has been formulated with reference to an ideal, binary polymer system.

A completely empirical equation for predicting the ideal behaviour of mixed solutions based on the additivity concept was developed by Catsiff and Hewett⁹. According to these workers

$$\eta_{\text{sp,m}} = [C_1(\eta_{\text{sp,1}}) + C_2(\eta_{\text{sp,2}})]/C \quad (3)$$

where $\eta_{\text{sp,m}}$ is the specific viscosity of the mixed polymer solution, $\eta_{\text{sp,1}}$ and $\eta_{\text{sp,2}}$ are the specific viscosities of the polymer components 1 and 2, respectively, at a concentration $C = C_1 + C_2$, and C_1 and C_2 are the concentrations of components 1 and 2, respectively.

Using the above equation, Catsiff showed that the higher apparent specific viscosity of the mixed polymer solution than the expected ideal $\eta_{\text{sp,m}}$ value may give a measure of the attractive interactions in the system.

However, the classical Huggins¹⁸ equation expresses the specific viscosity η_{sp} of a single polymer solution as a function of the concentration C , *i.e.*

$$\eta_{\text{sp}}/C = [\eta] + K_{\text{H}}[\eta]^2 C \quad (4)$$

where $[\eta]$ is the intrinsic viscosity. The term $K_{\text{H}}[\eta]^2$ is termed the specific interaction coefficient b , arising from the polymer interactions at finite concentrations. A Huggins plot of $\eta_{\text{sp}/c}$ versus C of the polymer solution should yield a straight line with intercept and gradient equal to $[\eta]$ and b , respectively. Krigbaum and Wall⁸ have adapted the Huggins equation for an ideal polymer/polymer mixed solution as

$$\eta_{\text{sp,m}} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (5)$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of polymer components 1 and 2, respectively, C_1 and C_2 are the concentrations of the respective components in the mixed polymer solution, and b_{12} is the interaction coefficient for the mixture with components 1 and 2.

The interaction coefficient between the two polymers, b_{12} , in a polymer blend, according to Williamson and Wright¹⁷, can be calculated theoretically as

$$b_{12} = b_{11} + b_{22}/2 \quad (6)$$

According to Krigbaum and Wall, information on the interaction between polymer molecules 1 and 2 should be obtainable from a comparison of experimental b_{12} and theoretical $(b_{12})^*$ values. The experimental b_{12} values are obtained from equation (5) while the theoretical $(b_{12})^*$ value is computed from equation (6). The compatibility of the polymer mixture can be characterised by a parameter Δb (hereafter referred to as the Krigbaum and Wall parameter), which is given by

$$\Delta b = b_{12_{\text{exp}}} - b_{12_{\text{theor}}} \quad (7)$$

Negative values of Δb are found for solutions of systems containing incompatible polymers, while positive values of Δb refer to an attractive interaction and compatibility.

An alternative definition of ideal solution behaviour may be obtained by considering the intrinsic viscosities of a mixed polymer solution, derived from the equation

$$[\eta_{\text{sp,m}}/C]_{C \rightarrow 0} = [\eta_1](C_1/C)_{C \rightarrow 0} + [\eta_2](C_2/C)_{C \rightarrow 0} \quad (8)$$

Here also, if the apparent intrinsic viscosity of the blend determined experimentally is larger than the ideal value (obtained from equation (8)), a strong attractive interaction between the two polymers is indicated.

In fact, the basis of studying the viscosity for assessing the compatibility rests on the assumption that repulsive interactions may cause shrinkage of the random coils of the polymer molecules, resulting in a viscosity of the polymer mixture that is reduced below the value calculated from viscosities of the pure components on the basis of additivity¹⁰. If there is an attractive interaction, the viscosity increases and the system is compatible, while the opposite may suggest incompatibility.

Additivity concept of intrinsic viscosity for assessing miscibility

It has been shown that the maximum concentration for the validity of equation (8) is 2.0 g dl^{-1} . The highest concentration used in this study was 0.5 g dl^{-1} . The intrinsic viscosity of the polymer system, $[\eta]$, is obtained from the intercept of the plot of η_{sp}/C versus C by the method of linear regression, and a perfect fit is obtained when $\gamma^2 = 1$. The data for the various blend systems are given in Table 6.

It can be seen that the 50/50 NBR/PS system exhibits a higher intrinsic viscosity value than the value calculated on the assumption of ideal behaviour. However the NBR/PS 70/30 and 30/70 systems demonstrate a lower value than the calculated value. According to the assumption that a negative deviation from ideal solution behaviour means

repulsive interactions between the two polymers, it can be concluded that the NBR/PS 70/30 and 30/70 systems are incompatible, whereas the 50/50 system shows a positive deviation from ideal behaviour, suggesting compatibility.

The observed intrinsic viscosity of the NBR/SAN 30/70 system is slightly lower than the ideal value. However, the NBR/SAN 70/30 and 50/50 blend compositions demonstrate a strong positive deviation from ideal behaviour, indicating compatibility in the polymer solution regime.

The observed $[\eta]$ values for the NBR/ABS 30/70 and 50/50 blends show a slight negative deviation while that for the 70/30 blend shows a positive deviation from the expected ideal value.

Specific viscosity as given by the Catsiff and Hewett model

The observed and calculated specific viscosities (according to equation (3)) of the various blend systems were determined. The differences between the observed and calculated values, $\Delta\eta_{\text{sp,m}}$, are plotted as a function of blend composition in Figure 1. According to the Catsiff and Hewett concept^{9,17}, for an ideal blend system, the $\Delta\eta_{\text{sp,m}}$ value should be zero throughout.

For the NBR/PS 30/70 and 70/30 systems, the $\Delta\eta_{\text{sp,m}}$ values are negative, while the NBR/PS 50/50 blend has a positive $\Delta\eta_{\text{sp,m}}$ value. Thus, only the 50/50 blend system suggests a positively deviating blend (PDB) behaviour, and hence this system can be considered as being compatible.

The $\Delta\eta_{\text{sp,m}}$ values for NBR/SAN are positive for the 70/30 and 50/50 blends, implying miscibility with increasing weight per cent of NBR in the blend. However, the 30/70 blend value suggests immiscibility behaviour. The NBR/ABS blends show a positive deviation only in the case of the 70/30 blend.

The behaviour predicted by the Catsiff model was found to be in agreement with the conclusion drawn from other viscosity theories on polymer blends. Thus the Catsiff and Hewett model is found to be applicable to the understanding of miscibility for all the blend systems studied in our work.

Table 6 Observed and calculated intrinsic viscosities of NBR-based blends in chloroform as solvent

Polymer system	Correlation coefficient, γ^2	Intrinsic viscosity (dl g^{-1})	
		Observed	Calculated
NBR	0.99	1.663	–
PS	1.00	0.769	–
SAN	0.99	0.712	–
ABS	0.99	0.571	–
NBR/PS	30/70	0.99	0.9431.038
NBR/PS	50/50	0.99	1.2811.216
NBR/PS	70/30	0.99	1.3411.395
NBR/SAN 30/70	0.99	0.947	0.998
NBR/SAN 50/50	1.00	1.221	1.188
NBR/SAN 70/30	1.00	1.394	1.378
NBR/ABS 30/70	0.99	0.856	0.899
NBR/ABS 50/50	0.99	1.065	1.117
NBR/ABS 70/30	0.99	1.556	1.336

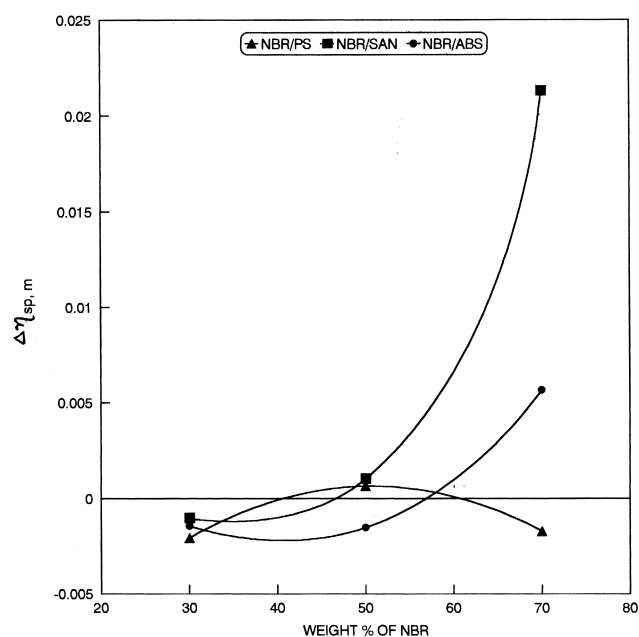


Figure 1 Effect of blend composition on the $\Delta\eta_{\text{sp,m}}$ values of different NBR-based blends

Krigbaum and Wall parameter, Δb

The values of Δb according to equation (7) for different total concentrations of NBR/PS mixtures are given in Figure 2. It is seen that the Δb values for the 50/50 blend are positive and show a positive deviation from ideal behaviour over almost all dilutions, indicating an attractive interaction. The Δb values for the NBR/PS 70/30 blend progressively become negative with increasing dilution, indicating incompatibility in solution. The Δb values for the NBR/PS 30/70 composition steadily become negative with dilution, indicating a repulsive interaction after a critical concentration of the polymer blend solution. The decrease of Δb with total concentration of the mixture may arise because the interaction between solvent and polymer increases as the amount of solvent increases, and ultimately exceeds the polymer–polymer interaction.

The Δb values for the NBR/SAN blends are shown in Figure 3. The Δb values for the NBR/SAN 50/50 and 70/30 compositions steadily become increasingly positive with dilution of the polymer solution, implying a stronger attractive interaction with dilution. However the Δb values of NBR/SAN 30/70, initially positive, gradually decrease and become negative with dilution. The reason for this contradictory behaviour with dilution is probably due to the capability of the individual acrylonitrile chain segments of the SAN phase to penetrate into the nitrile rubber phase, since they are chemically identical, or *vice versa*. As the weight per cent of NBR increases in the blend, the concentration of acrylonitrile segments increases, and hence the interaction due to the resulting penetration into the other phase increases. Evidently, with increasing dilution of the polymer blend solution, the polymer blend molecules will become disentangled more spaciouly, resulting in a greater interaction between the structurally similar acrylonitrile segments. However, in the case of the 30/70 NBR/SAN phase, the acrylonitrile concentration is probably not optimum enough to induce a greater interaction with dilution.

The Δb values of the NBR/ABS blends are plotted as a

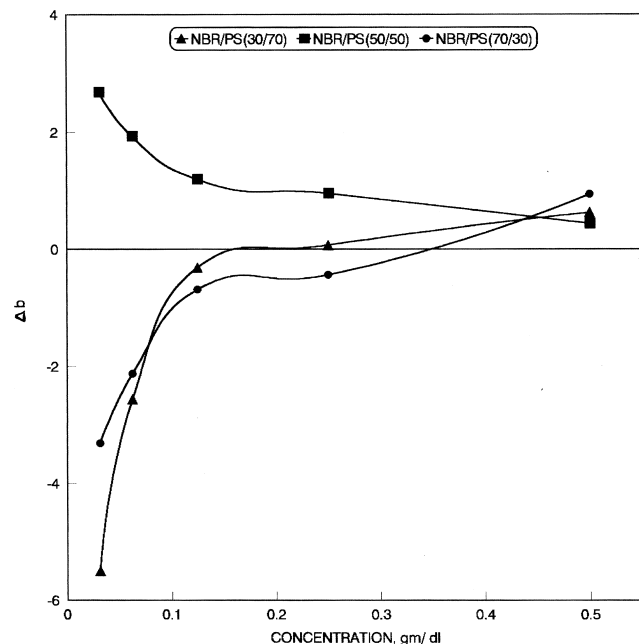


Figure 2 Effect of blend composition and concentration on the Δb values of the NBR/PS blends

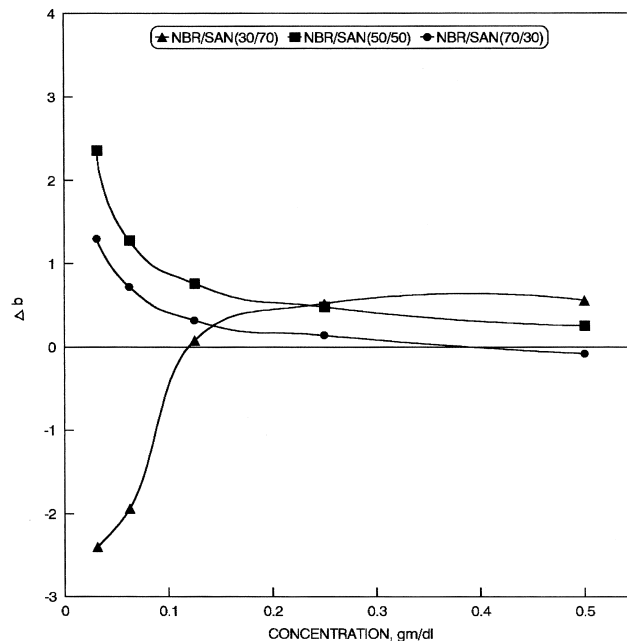


Figure 3 Effect of blend composition and concentration on the Δb values of the NBR/SAN blends

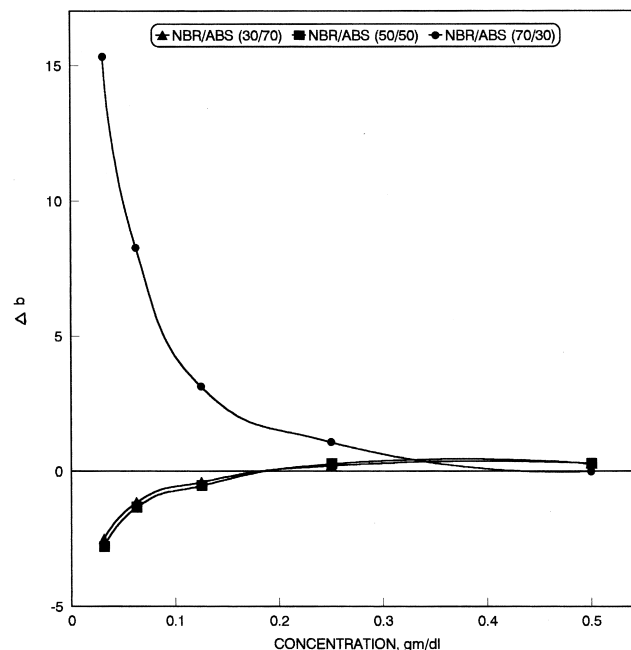


Figure 4 Effect of blend composition and concentration on the Δb values of the NBR/ABS blends

function of concentration in Figure 4. This indicates that with increasing dilution, the 30/70 and 50/50 compositions steadily exhibit larger negative values, suggesting increasingly repulsive interactions, while the 70/30 NBR/ABS blend shows increasingly positive values of Δb with dilution. Thus, the 70/30 NBR/ABS blend becomes miscible at a higher concentration. In the case of the NBR/ABS blends, also, the reason for the strange behaviour of Δb with dilution cited for NBR/SAN holds good.

Dilute solution density measurements

The concept of miscibility predicted by viscometry has been correlated to the findings of dilute solution density

Table 7 Observed and calculated densities of various NBR-based polymer blend–chloroform solutions^a

Polymer system	Observed density (g cm ⁻³)	Calculated density (g cm ⁻³)
NBR	0.980	—
PS	0.984	—
SAN	0.989	—
ABS	0.986	—
NBR/PS 30/70	0.982	0.983
NBR/PS 50/50	0.984	0.982
NBR/PS 70/30	0.980	0.981
NBR/SAN 30/70	0.986	0.986
NBR/SAN 50/50	0.986	0.984
NBR/SAN 70/30	0.983	0.982
NBR/ABS 30/70	0.985	0.984
NBR/ABS 50/50	0.983	0.983
NBR/ABS 70/30	0.982	0.981

^aConcentration, 0.25 g dl⁻¹; temperature, 30°C**Table 8** FTi.r. data for different blend compositions: –CN absorption frequency

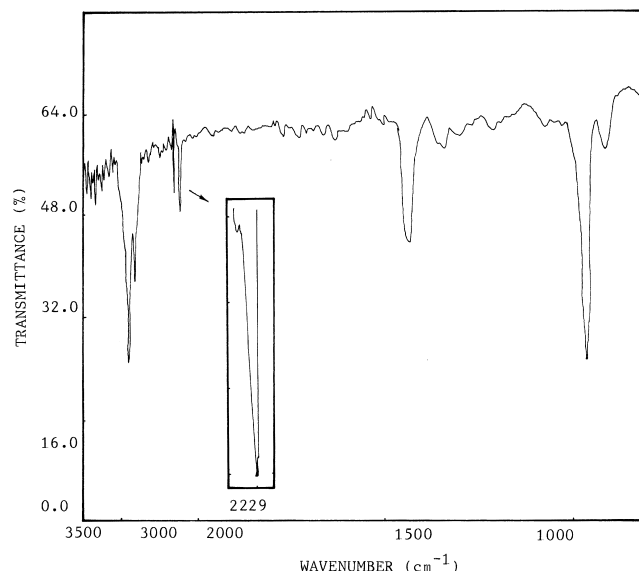
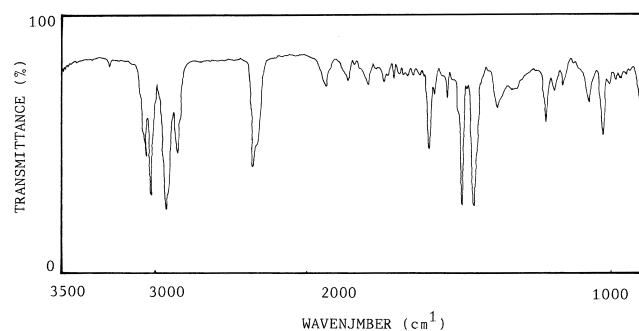
Blend composition	ν_{-CN} (cm ⁻¹)
NBR	2229
SAN	2229
ABS	2229
NBR/PS 30/70	2236
50/50	2233
70/30	2237
NBR/SAN 30/70	2227
50/50	2222
70/30	2226
NBR/ABS 30/70	2212
50/50	2211
70/30	2208

measurements on polymer mixtures. If a system is miscible, an attractive interaction will cause an increase in the density of the resulting blend. Hence, a greater observed density would imply miscibility^{19,20}. However, our intention was to seek a correlation in the dilute solution regime, corresponding to our viscometric findings. Hence the concentration chosen of the polymer mixture solution was 0.25 g dl⁻¹. It seems quite natural that the deviation observed in the density may not be very substantial for this concentration regime. The density was calculated from the density values of individual polymers assuming an additive contribution, according to the weight fraction of the components.

The observed and calculated densities (according to the concept of additivity) of the polymer blend solutions are given in Table 7. The observed densities are higher than the calculated values for the NBR/PS 50/50 blend. This densification of the 50/50 blend suggests miscible behaviour. The observed densities are found to be higher than the calculated values for the NBR/SAN 50/50 and 70/30 blends, while the 30/70 blend has almost identical values. This confirms that the NBR/SAN 70/30 and 50/50 blends are miscible systems. The observed densities of the NBR/ABS 30/70 and 70/30 blends show higher values than calculated, implying miscibility, whereas the 50/50 blend results suggest immiscibility behaviour. The miscibility behaviour for the NBR/PS, NBR/SAN and NBR/ABS blends for the various compositions studied is in agreement with our predictions based on viscometry theories.

Spectroscopic studies of the blend films

FTi.r. spectroscopy has been used as a potential tool for

**Figure 5** FTi.r. spectrum of NBR**Figure 6** FTi.r. spectrum of PS

the investigation of mutual interactions of various polymers^{21,22}. The PMMA/poly(vinylidene fluoride) system exhibits specific interactions involving the carbonyl group, as derived from the infrared spectroscopic studies performed by Coleman *et al.*²³. The very small spectral changes that are introduced as a result of the interactions were detected by noticeable shifts in the ν_{-CN} absorption peak with blend composition in our studies (Table 8).

The FTi.r. spectra of NBR and PS are shown in Figures 5 and 6, respectively. The band at 1375 cm⁻¹ is due to the C–H stretching of the polybutadiene segment of NBR. The C=C and C–H stretching give rise to the bands at 837 cm⁻¹ and 1244 cm⁻¹, respectively. The sharp band at 2229 cm⁻¹ is due to the –CN absorption. However, in the spectrum of the NBR/PS 50/50 blend (Figure 7), the ν_{-CN} shifts to 2233 cm⁻¹. The other bands at 1646–1600 cm⁻¹, 1493 cm⁻¹ and 1557–1521 cm⁻¹ in the spectrum originate from the skeletal ring breathing modes (C=C) of the aromatic rings of the PS segments. The bands at 1493, 1472 and 1452 cm⁻¹ correspond to the stretching modes of the aliphatic C–H groups of the PS segments. The C–H aromatic stretching vibrations produce bands at 1810 cm⁻¹, which is the overtone of the out-of-plane C–H deformation vibration at 907 cm⁻¹ of styrene.

Thus, the frequency shift (towards the higher energy region) from 2229 cm⁻¹ for pure NBR to 2233 cm⁻¹ for the NBR/PS 50/50 blend strongly suggests some repulsive interaction of a polar nature involving the –C=N group.

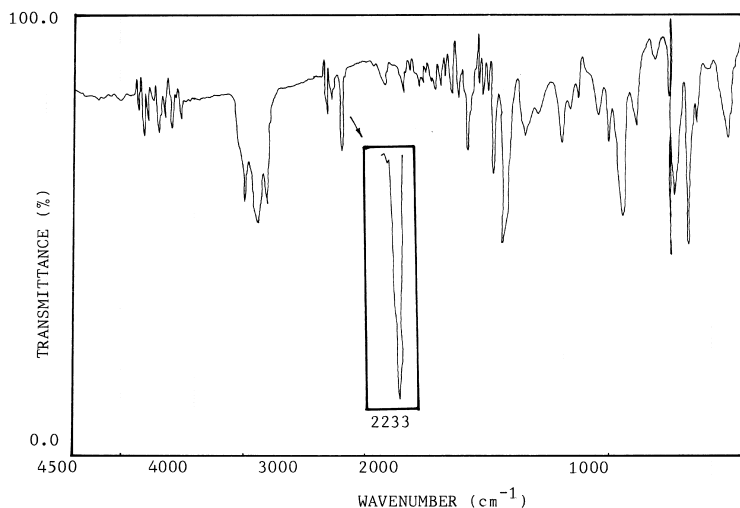


Figure 7 FTIR spectrum of the NBR/PS 50/50 blend

This may increase the $\text{C}=\text{N}$ bond order or, conversely, strengthen the bond, thus absorbing at a higher energy. Similarly, ν_{CN} for the other NBR/PS compositions also shows a similar trend, as given in Table 8.

The ν_{CN} of the NBR/SAN 50/50 blend was found to be at 2222 cm^{-1} . The corresponding ν_{CN} absorption frequencies of pure NBR and pure SAN were 2229 cm^{-1} . This suggests that there is some attractive polar interaction involving the CN bond. This may weaken the $\text{C}=\text{N}$ bond, resulting in its absorption at lower energy. The 30/70 and 70/30 NBR/SAN blends also show a similar shift in ν_{CN} . The trend in the shift of ν_{CN} for the NBR/ABS blends is similar to that for the NBR/SAN blends discussed earlier.

The repulsive interaction in the NBR/PS blends confirms our previous viscometric findings. However, the repulsive interaction seems to be least for the 50/50 blend among the NBR/PS blends, as inferred from ν_{CN} in Table 8. Our studies have already predicted a compatible behaviour for the 50/50 NBR/PS blend in the solution state. For the NBR/SAN blends, the ν_{CN} values suggest that there is an attractive interaction in all compositions, with the maximum interaction in the 50/50 blend, corresponding to the lowest ν_{CN} value. In the case of the NBR/ABS blends also, there is an attractive interaction involving the ν_{CN} group, as shown by the decreasing value of ν_{CN} . The 70/30 NBR/ABS blend shows the lowest ν_{CN} value or the maximum attraction involving the CN group, which has been already found to be compatible on the basis of our viscometric technique. The attractive nature of the interaction, and hence the resulting compatible nature of the NBR/SAN and NBR/ABS blends may result from the identical segmental and structural aspects of their respective components.

CONCLUSIONS

The present investigation indicates clearly that the interaction in the blends studied by simple measurements based on viscometry, solubility parameter, interactions and solution density provide valuable information about the compatibilities of the blends which is generally obtained from sophisticated techniques such as thermal and dynamic mechanical methods. The Δb value, the Catsiff and Hewett based $\Delta\eta_{\text{sp,m}}$ value, the intrinsic viscosities and the densities suggest that the NBR/PS systems are largely incompatible due to repulsive interactions, while the NBR/SAN and NBR/ABS blends are mostly compatible as a result of an

attractive interaction involving the acrylonitrile segments. The results have been correlated with those of spectroscopic studies on these blends. However, spectroscopy can only substantiate the findings from the other methods for demonstrating compatibility, rather than being a speculative tool in its own right. Finally, it is important to mention that the viscosity parameters used in this work have been found to be highly sensitive and useful for characterising the compatibility of binary polymer blends.

ACKNOWLEDGEMENTS

M. M. gratefully acknowledges financial support from the University Grants Commission, New Delhi, for carrying out this research programme.

REFERENCES

1. Krause, S., Polymer–polymer compatibility, in *Polymer Blends*, Vol. 1, ed. D. R. Paul and S. Newman. Academic Press, New York, 1978.
2. Olabisi, O., Robeson, L. M. and Shaw, M. T., *Polymer–Polymer Miscibility*. Academic Press, New York, 1979.
3. Kulshreshtha, A. K., Singh, B. P. and Sharma, Y. N., *Eur. Polym. J.*, 1988, **24**, 29.
4. Irvine, K., Robert E., *Synthetic Polymeric Membranes*. John Wiley and Sons, CA, 1985.
5. Mikhailov, N. V. and Zeilkman, S. G., *Kolloid Z.*, 1957, **19**, 465.
6. Bohmer, B. and Florian, S., *Eur. Polym. J.*, 1970, **6**, 471.
7. Feldman, D. and Rusu, M., *Eur. Polym. J.*, 1970, **6**, 627.
8. Krigbaum, W. R. and Wall, F. J., *J. Polym. Sci.*, 1950, **5**, 505.
9. Catsiff, E. H. and Hewett, W. A., *J. Appl. Polym. Sci.*, 1962, **6**, 530.
10. Shih, K. S. and Beatty, C. L., *Br. Polym. J.*, 1990, **22**, 11.
11. Kulshreshtha, A. K., Singh, B. P. and Sharma, Y. N., *Eur. Polym. J.*, 1988, **2**, 191.
12. Lizymol, P. P. and Thomas, S., *Eur. Polym. J.*, 1994, **30**, 1135.
13. Lizymol, P. P. and Thomas, S., *J. Appl. Polym. Sci.*, 1994, **51**, 635.
14. Singh, Y. P. and Singh, R. P., *Eur. Polym. J.*, 1983, **19**, 535.
15. Lizymol, P. P. and Thomas, S., *Polym. Degrad. Stabil.*, 1993, **41**, 59.
16. Monteiro, E. E. C. and Thaumatorgo, C., *Polym. Bull.*, 1993, **30**, 697.
17. Williamson, W. R. and Wright, B., *J. Polym. Sci.*, 1950, **5**, 505.
18. Huggins, M. L., *J. Am. Chem. Soc.*, 1942, **64**, 2716.
19. Wang, Y. Z., Hsieh, K. H., Chen, L. W. and Tseng, H. C., *J. Appl. Polym. Sci.*, 1994, **53**, 1191.
20. Kawahara, S., Sato, K. and Akiyama, S., *J. Polym. Sci. Polym. Phys. Ed.*, 1994, **32**, 15.
21. Xiaojiang, Z., Pu, H. H., Yanheng and Junfeng, L., *J. Polym. Sci. Part C: Polym. Lett.*, 1989, **27**, 223.
22. Lim, J. C., Park, J. K. and Song, H. Y., *J. Polym. Sci., Polym. Phys. Ed.*, 1994, **32**, 29.
23. Coleman, M. M., Zarian, J., Varnell, D. F. and Painter, P. C., *J. Polym. Sci., Polym. Lett. Ed.*, 1977, **15**, 745.