

# Compatibility Studies on Solution of Polymer Blends by Viscometric and Phase-Separation Technique

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**ABSTRACT:** Solution blending of polystyrene (PS) and natural rubber (NR) was carried out in toluene and chloroform to determine the compatibility. Experimental evidence for the compatibility of these blends was derived from viscometric and phase-separation studies. The viscometric method was based on the intrinsic viscosities of transfer of polymer in pure and "mixed" solvents. The compatibility of these blends based on the heat of mixing was also examined theoretically. All the experimental and theoretical evidence show that the blends are incompatible at the compositions studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 880–889, 2000

**Key words:** polymer blend; intrinsic viscosity; phase separation; heat of mixing; miscibility; compatibility

## INTRODUCTION

Polymeric blends are dominating various application areas because of their tailor-made properties. However, their performance depends on the compatibility of the blend components. Therefore, determination of the compatibility of polymer blends is of considerable importance. Superior properties of blends are determined by compatibility or miscibility of the constituent homopolymers at a molecular level. Many experimental and theoretical methods have been used to investigate polymer compatibility.<sup>1</sup> The determination of the heat of mixing, glass transition temperature, morphology by electron microscopy, and dynamic mechanical response are some of the methods extensively reported in the literature.<sup>1</sup> But it is still needed to find simpler and quicker meth-

ods for determining compatibility.<sup>2</sup> Homogeneous mixing at a molecular scale is a prerequisite for polymer compatibility. Several blending methods are available such as melt, dry, and solution blending. Blending the polymers in solution ensures effective attainment of equilibrium between the different polymer components in solution. Furthermore, viscosity can be measured effectively. A large number of investigations have been carried out on polymer blend miscibility using viscosity measurements of the corresponding ternary (polymer–polymer–solvent) systems.<sup>3–11</sup> This method, based on dilute solution viscometry (DSV), relies on the assumption that repulsive interaction may cause shrinkage of the macromolar coils, giving a negative deviation of viscosity from additivity. Thakore et al.<sup>9</sup> applied the viscosity method to the poly(vinyl chloride)/starch acetate (PVC/STAc) polyblend system to study the compatibility. They have found that the plots of relative viscosity versus composition are not linear, indicating incompatibility of the two polymers. The miscibility of two stiff polymers (cellulose and alginate) has been characterized by the DSV technique and a modified treatment based on Chee's method<sup>10</sup> by Zhang et al.<sup>11</sup> Cellulose

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and alginate formed either a miscible or an immiscible blend depending on the blend ratio.

In phase-separation techniques, Molau<sup>12,13</sup> presented the mechanism of the action of graft and block copolymers at the interface of the two polymer components in a dilute solution. A solution of an immiscible polymer pair *A* and *B* in a mutual solvent separated into two phases and demixes to form two layers. When a small amount of a suitable graft or block copolymer is added as an emulsifier, a stable polymeric oil in oil emulsion results and the emulsifier locates at the interface.

Blends of polystyrene (PS) and natural rubber (NR) form a new class of thermoplastic elastomers (TPEs) of much importance. PS exhibits superior processing characteristics. However, it is extremely brittle. On the other hand, NR is characterized by good elastomeric properties, good resilience, and damping behavior but poor chemical resistance and processability. TPEs from PS and NR blends are expected to exhibit good processability, impact strength, good flexibility, and a rubbery nature. The properties of the resulting blend depend on the compatibility of the individual blend components. The solid-state compatibility of PS/NR blend components was recently analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and FTIR in this laboratory.<sup>14</sup>

In this article, the compatibility of PS and NR blends in solution was investigated using viscometric and phase-separation studies. In latter method, compatibility of these blends by the addition of a block copolymer of styrene and isoprene [poly(styrene-*b*-isoprene)] was studied as function of the phase-separated NR layer and time for phase separation. The influence of the molecular weight of the block and homopolymer, concentration of the block copolymer, effect of solvent, and mode of addition of the block copolymer on phase separation were studied.

## EXPERIMENTAL

### Materials

Commercial PS (SC-206E) was supplied by Supreme Plastics (Bombay, India). NR (ISNR-5) was supplied by the Rubber Research Institute (Kerala, India). Linear diblock copolymers of styrene and isoprene (PS-*b*-PI) were synthesized in the laboratory by living anionic polymerization

**Table I Characteristics of the Materials Used**

Materials	$[\eta]^a$ (dL/g)	Solubility Parameter (cal/cc) <sup>1/2</sup>	$M_v \times 10^{-5}$
NR <sub>0</sub>	5.38	7.75	11.0
NR <sub>20</sub>	2.20	7.75	2.94
PS	0.79	8.56	2.30
Diblock Copolymer ( <i>B</i> )	$\bar{M}_n^c \times 10^{-5}$	MWD <sup>d</sup> of PS- <i>b</i> -PI	Wt % Composition (S : I) <sup>e</sup>
<i>B</i> <sub>1</sub>	2.58	1.09	50 : 50
<i>B</i> <sub>2</sub>	0.96	1.26	50 : 50

<sup>a</sup> Determined in toluene at 25°C.

<sup>b</sup> NR suffix indicates time of mastication in minutes.

<sup>c,d</sup> Determined by GPC, in THF at 30°C.

<sup>e</sup> Determined by <sup>1</sup>H-NMR.

methods. The synthesis and characterization of copolymers were described elsewhere.<sup>14</sup> The characteristics of the materials used are given in Table I.

### Dilute Solution Viscometry (DSV) Measurements

Solutions, 0.2% (w/v), of each polymer in toluene were prepared. The various blends of PS and NR were made by mixing solutions of the polymer in toluene in the required proportions. The total concentration of the blend was kept constant for all the blend systems. Similarly "mixed solvents" containing a constant concentration of 0.2 g/dL of polymer B (either PS or NR) in toluene were prepared.

A suspended-level Ubbelohde viscometer was fabricated. All viscosity measurements were made using a Schott Gerate AVS 440 automatic viscosity measuring system. The temperature was maintained constant at 25°C. The intrinsic viscosity ( $[\eta]$ ) and slopes were determined from the plots of reduced viscosity versus concentration. Intrinsic viscosities of polymers in pure and "mixed solvent,"  $[\eta]^0$  and  $[\eta]^*$ , respectively, and their difference,  $\Delta[\eta]$ , were estimated. Chee's parameters  $\Delta B$  and  $\mu$  were also calculated.

Phase-separation experiments were carried out by preparing the solution of 50/50 wt % PS/NR blends in chloroform with and without the addition of the block copolymer. The blend solution was stirred for 24 h and kept standing.

## RESULTS AND DISCUSSION

## Theory

Chee<sup>10</sup> proposed a simple method to predict the miscibility of PVC/PMMA, PVC/PiBMA, and PMMA/PiBMA blends using DSV. The results were confirmed by DSC studies of these blends. Basically, DSV is based on the classical Huggins equation,<sup>15</sup> which expresses the specific viscosity ( $\eta_{sp}$ ) of a single-solute solution as a function of the concentration  $C$ . For a nonelectrolyte dilute solution, a plot of  $\eta_{sp}/C$  versus  $C$  should yield a straight line with an intercept and slope equal to  $[\eta]$  and  $b$ , respectively. For a ternary system, where the solvent is component 1 and two polymers are components 2 and 3,  $[\eta]$  and  $b$  in the Huggins equation assumes the form

$$[\eta] = w_2[\eta]_2 + w_3[\eta]_3 \quad (1)$$

and

$$b = w_2^2 b_{22} + w_3^2 b_{33} + 2w_2 w_3 b_{23} \quad (2)$$

$$b_{23} = \frac{(b - w_2^2 b_{22} - w_3^2 b_{33})}{2w_2 w_3} \quad (3)$$

where  $[\eta]_2$  and  $[\eta]_3$  are the intrinsic viscosities of polymers 2 and 3 in a pure solvent, respectively.

Chee<sup>10</sup> proposed a differential parameter  $\Delta B$  as a measure of intermolecular interactions which can be written as

$$\Delta B = b_{23} - \frac{(b_{22} + b_{33})}{2} \quad (4)$$

Here,  $b_{22}$  and  $b_{33}$  are the specific interaction coefficients of polymers 2 and 3 in single polymer solutions, respectively;  $b$ , the specific interaction coefficient between the two polymers; and  $w_2$  and  $w_3$ , the weight fractions of the two polymers in the blend.

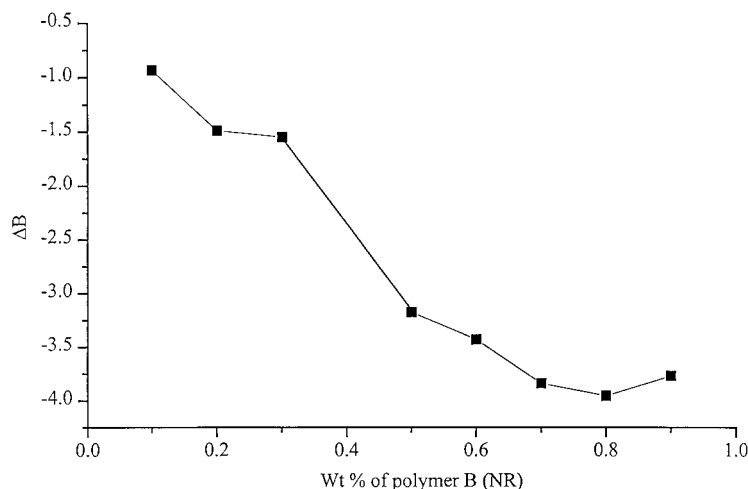
Accordingly,  $\Delta B \geq 0$  signifies miscibility and  $\Delta B < 0$  indicates phase separation. However, if  $[\eta]_2$  and  $[\eta]_3$  are sufficiently far apart, a more effective parameter  $\mu$  has been suggested, which is given as

$$\mu = \frac{\Delta B}{([\eta]_3 - [\eta]_2)^2} \quad (5)$$

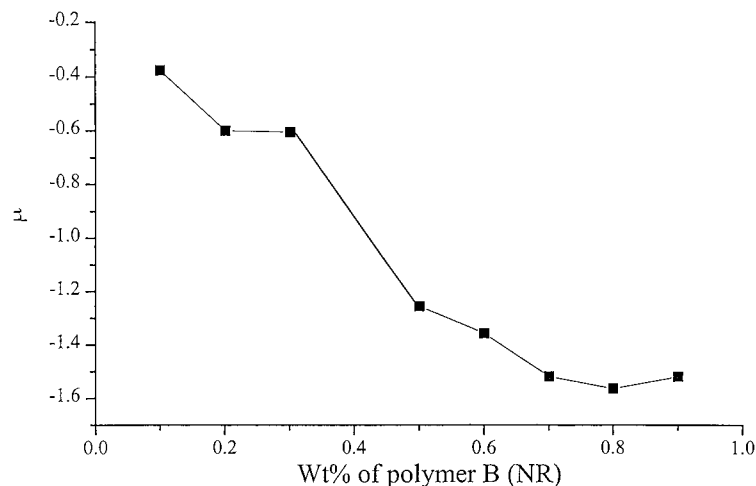
Equation (5) is valid for  $[\eta]_2 \neq [\eta]_3$ .

The dimensionless quantity  $\mu$  can be conventionally determined using eq. (5). However, Chee considered  $\Delta B$  and  $\mu$  to be equal to zero for the pure components of the blend.

Hugelin and Dondos<sup>16</sup> studied the influence of the nature of the solvent on the miscibility of a polymer. They observed that the  $[\eta]$  of polymer A, measured in a solution of polymer B in solvent S, was lower than that of the same polymer A measured in the pure solvent S. Danait and Deshpande<sup>4,5</sup> proposed a simple method which is a slight modification of that proposed by Hugelin and Dondos. In their approach, the  $[\eta]$  of a polymer is measured when transferred from a pure



**Figure 1** Plot of Chee's factor  $\Delta B$  versus weight fraction of polymer B (NR) for PS/NR (polymer A/polymer B) blends in toluene at 25°C.

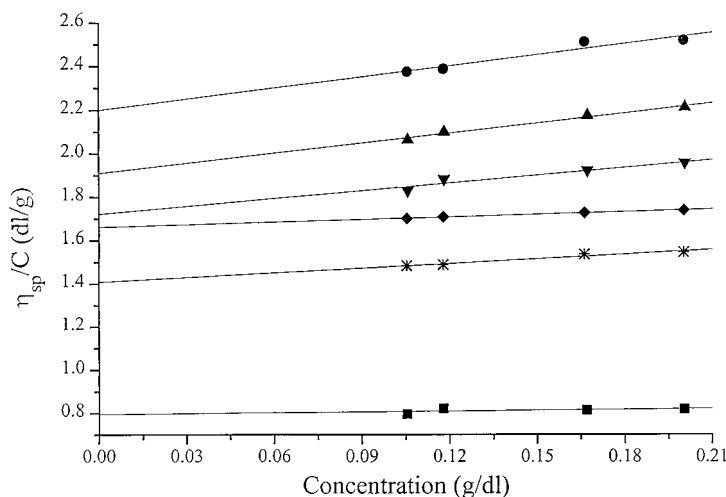


**Figure 2** Plot of Chee's factor  $\mu$  versus weight fraction of polymer NR (polymer B) for PS/NR (polymer A/polymer B) blends in toluene at 25°C.

solvent to a "mixed solvent," that is, the intrinsic viscosity of polymer 2 is determined separately in a pure solvent ( $[\eta]^0$ ) and also in a solvent containing a constant concentration ( $C^*$ ) of polymer 3 ( $[\eta]^*$ ). In the latter case, the "solvent" is now a solution of concentration  $C^*$  of polymer 3 in solvent  $S$  and the flow time of this "mixed solvent" is determined and taken as the reference. A plot of reduced viscosity ( $\eta_{sp}/C_2$ ) versus the concentration of polymer 2 ( $C_2$ ) is made. On extrapolating to zero concentration, one can get  $[\eta]^0$ , the intrinsic viscosity of polymer 2 in solvent  $S$ , and  $[\eta]^*$ , the intrinsic viscosity of polymer 2 in a mixed solvent ( $3 + S$ ). Thus, the difference ( $[\eta]^* - [\eta]^0$ )

$= \Delta[\eta]$  gives a measure of the interaction between polymers 2 and 3 in a solvent  $S$ , which is called the intrinsic viscosity of transfer. Depending on the strength of the interaction, the magnitude of  $\Delta[\eta]$  varies.  $\Delta[\eta] < 0.1$  dL/g suggests very little or no interaction and, hence, immiscible blends. A high positive value of  $\Delta[\eta]$ , that is,  $\geq 0.1$  dL/g, indicates an increase in the hydrodynamic volume due to strong associative interactions and, hence, miscible blends.

Chee's method was applied to blends of PS and NR. Plots of  $\Delta B$  and  $\mu$  versus the weight fraction of one of the blend components (NR) are shown in Figures 1 and 2, respectively. Over the entire



**Figure 3**  $\eta_{sp}/C$  versus  $C$  for PS/NR blend solution of different compositions in toluene at 25°C. Solid lines drawn through the experimental data points are for (■) PS, (●) NR, (▲) PS/NR 20/80, (▼) PS/NR 30/70, (◆) PS/NR 40/60, and \* PS/NR 50/50.

**Table II** Intrinsic Viscosity of Transfer for Different Blend Systems

Blend System	$[\eta]^0$ (dL/g)	$[\eta]^*$ (dL/g)	$\Delta[\eta]$ (dL/g)
PS in (NR + toluene)	0.79	0.72	-0.07
NR in (PS + toluene)	2.20	1.40	-0.80

composition range,  $\Delta B$  and  $\mu$  have negative values, indicating that this blend exhibits phase separation and, hence, is immiscible.

### Intrinsic Viscosity of Transfer

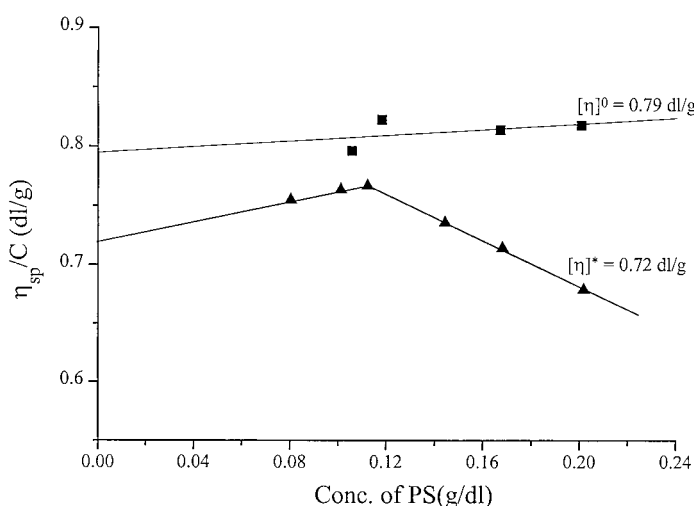
Plots of the reduced viscosities of polymers in pure solvent are found to be linearly increased with respect to concentration (Fig. 3). The plots of the change in the viscosity in a “mixed solvent” show very interesting results. The values of  $[\eta]^0$ ,  $[\eta]^*$ , and  $\Delta[\eta]$  for the blend system are given in Table II. The change in the reduced viscosity of PS in a “mixed solvent” for PS/NR is shown in Figure 4. Similarly, the change in the reduced viscosity of NR in a “mixed solvent” for PS/NR is shown in Figure 5. In the (NR + toluene) solvent, the reduced viscosity of PS is found to increase slowly with increase in the PS concentration. Also, as the concentration reaches a certain limit, above 0.11 g/dL, the reduced viscosity decreases very sharply. But over the concentration range of PS, the viscosity of the solution is lower as compared with that in the pure solvent (Fig. 4). It can

therefore be concluded that at the higher concentration of PS in the blend the PS/NR blend becomes more and more immiscible.

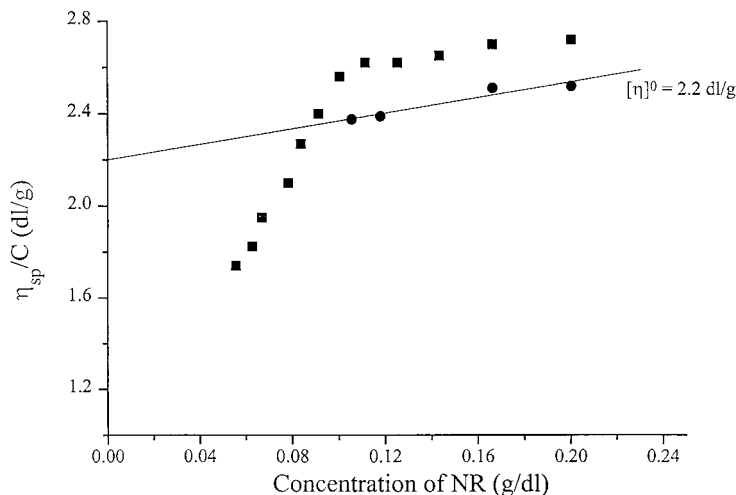
The behavior of NR in a “mixed solvent” (PS + toluene) is different compared to PS in NR + toluene. In both cases,  $\Delta[\eta]$  is found to be negative. At a low concentration of NR, there is an initial decrease in the viscosity of the solution as compared with that in the pure solvent, but a slight increase at a higher concentration of NR (Fig. 5). As the concentration reaches a certain limit up to 0.1 g/dL, the viscosity remains almost the same and a further increase in concentration does not show any change in the viscosity. Based on the negative  $\Delta[\eta]$  value, the PS/NR blend can be considered as an immiscible blend system. From the study of the solid-state compatibility of the binary polymer blends of PS and NR by DSC,<sup>14</sup> it is found that they are immiscible over the entire composition range. Two distinct glass transition temperatures ( $T_g$ 's) are observed at around 104 and  $-63^\circ\text{C}$ . The higher  $T_g$  is attributed to the PS phase and the lower one to the NR phase. That at higher concentration of NR the  $T_g$ 's are shifted to 98 and  $-57^\circ\text{C}$ , correspondingly, indicates there may be a tendency toward partial miscibility at a very low extent. A viscometry study pointed in this direction as well.

### Heat of Mixing and Compatibility

Schneier<sup>17</sup> calculated the heat of mixing ( $\Delta H_m$ ) for a number of compatible and incompatible polymer blends. The heat of mixing is an approx-



**Figure 4** Plots of  $\eta_{sp}/C$  versus  $C$  of PS for PS/NR blends in (■) pure and (▲) “mixed” solvents at  $25^\circ\text{C}$ . (■) and (▲) correspond to the solvent toluene and NR + toluene, respectively.



**Figure 5** Plots of  $\eta_{sp}/C$  versus  $C$  of NR for PS/NR blends in (●) pure and (■) “mixed” solvents at 25°C. (●) and (■) correspond to the solvent toluene and PS + toluene, respectively.

imate measure of the free energy of mixing<sup>18,19</sup> and, thus, may indicate the degree of compatibility. Schneier suggested the following equation for two-component polymer blends from the formulation of Gee<sup>20</sup>:

$$\Delta H_m = \left[ x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left\{ \frac{x_2}{(1-x_2)M_2\rho_2 + (1-x_1)M_1\rho_1} \right\}^2 \right]^{1/2} \quad (6)$$

where  $x$  is the weight fraction of the polymer;  $\rho$ , the polymer density;  $M$ , the molecular weight of the monomer unit; and  $\delta_1$  and  $\delta_2$ , the solubility parameters of polymers  $A$  and  $B$ , respectively.

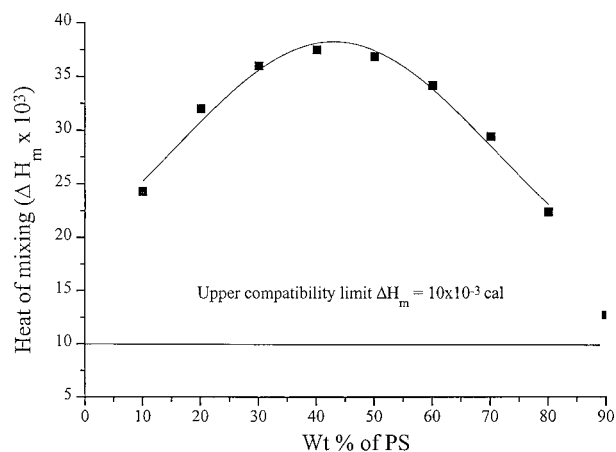
The above method was successfully used for predicting the miscibility of a blend of PVC/STAc by Thakore et al.<sup>9</sup> and for an NR/PMMA blend by Oommen and Thomas.<sup>3</sup> Figure 6 shows the variation of the calculated heat of mixing with the blend composition. The calculated values of  $\Delta H_m$  of PS/NR blends are found to be above the compatibility limit ( $10 \times 10^{-3}$  cal/mol) for all compositions, confirming that the PS/NR blends are incompatible in all compositions.

## Phase-Separation Behavior

### Effect of Block Copolymer Concentration

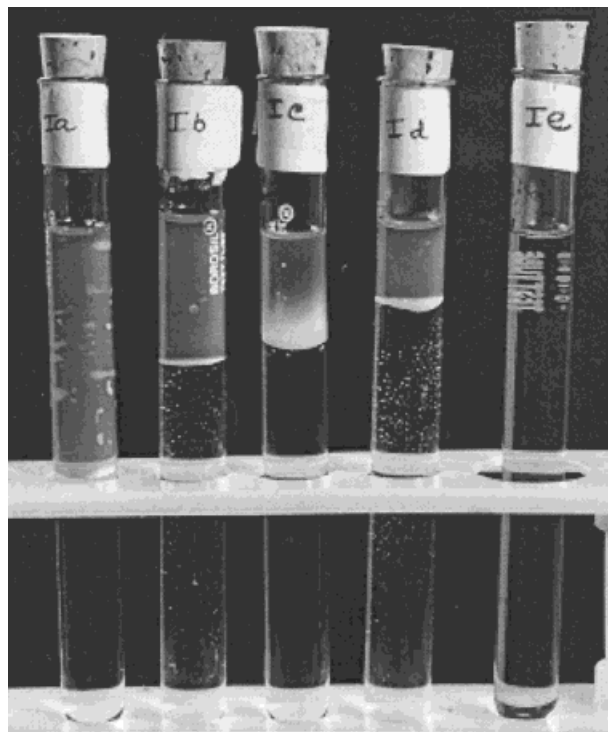
The PS/NR forms a heterogeneous system and a solution of these two in chloroform separates into two phases with a sharp interface after an inter-

val of 12 h. This clearly shows that PS and NR have no chemical interaction, and they are incompatible even after stirring the solution for 24 h in a common solvent. But in the presence of a 1 wt % linear diblock copolymer (PS-*b*-PI), phase separation took place after a period of 55 h compared to 12 h in the system without the block copolymer. Again, the extent of the volume fraction of NR separated at equilibrium is found to be smaller than the system with no compatibilizer. The influence of copolymer concentration on the phase-separation process visible to the naked eye is shown in Figure 7. The volume of the NR phase-separated layer decreases from left to right as the amount of the copolymer increases from 0 to 5 wt



**Figure 6** Heat of mixing ( $\Delta H_m$ ) versus weight percent of PS (polymer  $A$ ) in PS/NR blends.





**Figure 7** Optical photograph of the influence of block copolymer on phase separation of 50/50 PS/NR blends.

%. When the copolymer content reaches 5 wt %, no phase separation can be observed. As the amount of the block copolymer increases, the time required for phase separation increases sharply.

The time required for phase separation and the volume fraction of the phase-separated NR layer for the PS/NR blend containing up to 7.5 wt % of the block copolymer are given in Tables III and IV. The times required for phase separation are

108, 252, and 290 h for a 2, 3.5, and 5 wt % block copolymer concentration, respectively, using chloroform as a solvent. On further addition of the block copolymer (7.5 wt %), no phase separation was observed even for a period of 6 weeks. This happens when the copolymer content reaches above the equilibrium concentration, which can be considered as the “critical micelle concentration” (CMC). The same trend can be obtained by observing the volume fraction of the phase-separated NR layer with the block copolymer concentration. In chloroform, the volume fraction of the phase-separated NR layer decreases with the block copolymer concentration and no phase separation occurs after 5 wt % of the block copolymer, indicating interfacial saturation.

These experimental observations are in quantitative agreement with the theory of Noolandi and Hong.<sup>21–23</sup> As the copolymer content increases, the time of phase separation increases and the volume fraction of the phase-separated NR layer decreases. Finally, the system reaches interfacial saturation. At this point, no phase separation could be observed. The long time required for phase separation is due to the decrease in the interfacial tension between the homopolymers by the localization of the block copolymer in the interfacial area. The interfacial activity of the copolymer, in fact, decreases the interaction energy and, hence, the polymer–polymer solution does not undergo any phase separation.

#### Effect of Nature of Solvent on Phase Separation

Phase separation was studied by changing the solvent from chloroform to toluene. In both cases, phase-separation behavior is similar and the sat-

**Table III** Phase-separation Times for Various PS/NR Blends (Time in Hours)

% of PS- <i>b</i> -PI (Compatibilizer)	System I <sup>a</sup> PS/NR <sub>20</sub> <sup>d</sup> /B <sub>1</sub>	System II <sup>b</sup> PS/NR <sub>0</sub> /B <sub>1</sub> <sup>e</sup>	System III <sup>b</sup> PS/NR <sub>20</sub> /B <sub>1</sub>	System IV <sup>b</sup> PS/NR <sub>20</sub> /B <sub>2</sub>	System V <sup>c</sup> PS/NR <sub>20</sub> /B <sub>1</sub>
0	12	7	12	12	14
1.0	64	40	55	53	58
2.0	118	73	108	82	114
3.5	294	146	252	240	278
5.0	**	230	290	272	**
7.5	**	**	**	**	**

\*\* : No phase separation.

<sup>a</sup> Chloroform as solvent and two-step mixing.

<sup>b</sup> Chloroform as solvent and one-step mixing.

<sup>c</sup> Toluene as solvent and one-step mixing.

<sup>d</sup> The suffix of NR indicates the time of mastication in minutes.

<sup>e</sup> The  $\bar{M}_n$  of B<sub>1</sub> (PS-*b*-PI) =  $2.58 \times 10^5$  and  $\bar{M}_n$  of B<sub>2</sub> =  $0.96 \times 10^5$ .

**Table IV** Volume Fraction of the Phase-Separated NR Layer

% of PS- <i>b</i> -PI (Compatibilizer)	System I <sup>a</sup> PS/NR <sub>20</sub> <sup>d</sup> /B <sub>1</sub>	System II <sup>b</sup> PS/NR <sub>0</sub> /B <sub>1</sub> <sup>e</sup>	System III <sup>b</sup> PS/NR <sub>20</sub> /B <sub>1</sub>	System IV <sup>b</sup> PS/NR <sub>20</sub> /B <sub>2</sub>	System V <sup>c</sup> PS/NR <sub>20</sub> /B <sub>1</sub>
0	0.5273	0.5502	0.5273	0.5273	0.5805
1.0	0.3182	0.4262	0.3206	0.3612	0.3086
2.0	0.2072	0.3463	0.2208	0.2362	0.2174
3.5	0.1636	0.2180	0.1697	0.1780	0.1647
5.0	**	0.1960	0.1040	0.1280	**
7.5	**	**	**	**	**

<sup>a-e</sup> See footnotes a–e to Table III.

uration point is attained at a copolymer content 3.5 wt %, which is lower in toluene compared to a value of 5 wt % in chloroform (Table III). The demixing time of the polymer blend in toluene is also correspondingly higher. The volume fraction of the NR layer separated in toluene is small compared to the chloroform system (Table IV). Toluene solvates the polymer species more effectively compared to chloroform because the solubility parameter difference between PS and toluene ( $\Delta\delta = 0.34$ ) is less than that between PS and chloroform ( $\Delta\delta = 0.74$ ). Again, the difference in the solubility parameter between NR and toluene is 1.15 ( $\Delta\delta$ ) and that between NR and chloroform is 1.55 ( $\Delta\delta$ ). So, in both the cases, toluene is a better solvent compared to chloroform. Therefore, the polymer-blend solution made in toluene takes a longer time for demixing.

#### **Effect of Mode of Addition on Phase Separation**

While studying the morphology of nylon/rubber blends, Cimmino et al.<sup>24</sup> observed an additional size reduction when the blends were prepared in two steps in comparison to one-step mixing. The same conclusion was drawn by Asaletha et al.<sup>25</sup> for the NR/PS blend system using NR-*g*-PS as the compatibilizer.

Two-step mixing was carried out by blending the dispersed phase with the compatibilizer first and then blending it with the matrix polymer. By preblending the modifier with the dispersed phase, it was possible to increase the interaction between the copolymer and the dispersed phase. Preblending with the dispersed phase helps to locate the copolymer at the interface.<sup>26,27</sup> A similar observation was reported by Oommen and Thomas.<sup>3</sup>

The effect of the mode of addition of the block copolymer on phase separation of the blends was

studied. It was found that in two-step mixing the time required for phase separation is relatively higher and the amount of the block copolymer required for interfacial saturation is less compared to one-step mixing (Table III). It is also seen in two-step mixing that the volume fraction of the phase-separated layer is less than that of one-step mixing (Table IV). By preblending the block copolymer with a minor phase, the amount of the copolymer that can defuse into the interface can be increased.

#### **Effect of Block Copolymer/Homopolymer Molecular Weight on Phase Separation**

The influence of the block copolymer and the homopolymer molecular weight on the phase-separation behavior of the blends was studied using block copolymers of molecular weights  $2.58 \times 10^5$  and  $0.96 \times 10^5$  and NR of molecular weights  $11 \times 10^5$  and  $2.94 \times 10^5$ . As the molecular weight of the block copolymer decreases, the time taken for phase separation decreases and the volume fraction of the phase-separated NR layer increases (Tables III and IV). According to Riess and Jolivet,<sup>28</sup> the emulsification efficiency of the copolymer can be compared by the ratio of the molecular weight of the homopolymer and the block copolymer. If

$$\alpha = \frac{\text{Molecular weight of PS homopolymer}}{\text{Molecular weight of PS component in the block copolymer}}$$

$$\beta = \frac{\text{Molecular weight of NR homopolymer}}{\text{Molecular weight of NR component in the block copolymer}}$$

then the copolymer is less efficient as an emulsifier for  $\alpha > 1$  and  $\beta > 1$ . The emulsifying property



of the copolymer is optimum when  $\alpha < 1$  and  $\beta < 1$ . In an ideal case, when  $\alpha = \beta < 1$ , the copolymer has no preferential solubility.

For system III, the values of  $\alpha$  and  $\beta$  are less compared to system IV as the block copolymer molecular weight decreases from  $2.58 \times 10^5$  to  $0.96 \times 10^5$ , keeping the homopolymers' (PS and NR) molecular weight constant. As a result, efficient emulsification is obtained. In fact, this is reflected by the demixing time as well as by the volume fraction of the phase-separated layer (Tables III and IV).

The value of  $\beta$  is higher for system II compared to system III as the homopolymer's (NR) molecular weight decreases from  $11 \times 10^5$  to  $2.94 \times 10^5$ , keeping the PS and the copolymer molecular weights constant. So, the demixing time is less and the volume fraction of the phase-separated layer is more in the case of system II than that of system III (Tables III and IV). Noolandi and Hong<sup>21-23</sup> pointed out that the molecular weight of the copolymer is important in reducing the interfacial tension of immiscible polymer blends. Our result is in accordance with Noolandi and Hong's theory. The reduction in interfacial tension is clear from the higher time for phase separation and the low amount of the phase-separated NR layer.

#### **Effect of Block Copolymer Composition on Phase Separation**

The effect of block copolymer composition on the phase separation of the blend was studied. It was found that by using a symmetrical diblock copolymer as a compatibilizer the time required for phase separation is relatively higher and the amount of the block copolymer required for interfacial saturation is less. Therefore, block copolymers with an equal segment length (50/50 wt %) show a superior compatibilizing action compared to other block copolymers of unequal segment length (e.g., 30/70, 70/30, 15/85, and 85/15). A symmetrical diblock copolymer is more or less located at the interface and leads to a large reduction in interfacial tension.<sup>29</sup> In contrast, asymmetric block copolymers are not able to improve the interfacial properties even at higher concentration. Therefore, phase-separation experiment data using symmetrical diblock copolymers ( $B_1$  and  $B_2$ ) as a compatibilizer are only presented in Tables III and IV.

## **CONCLUSIONS**

Polymer–polymer interactions in blends were studied by viscometry, heat of mixing, and phase-separation techniques. PS/NR blends are found to be incompatible from the results obtained for Chee's parameters  $\Delta B$  and  $\mu$ . The negative values of  $\Delta B$  and  $\mu$  is an indication of the incompatibility of PS/NR blends in all compositions. The heat of mixing values ( $\Delta H_m$ ) of the PS/NR blends further support the incompatibility of the blends. The "intrinsic viscosities of transfer" approach provides a qualitative picture of the interaction among the polymers and, hence, the miscibility. The incompatibility causes the phenomenon of phase separation of the polymer-blend solutions. A block copolymer compatibilizer acts as the emulsifier which locates at the interface and extends into the homopolymer phases with which it is compatible.

The time required for the phase separation is an indication of the extent of compatibilization. The presence of small amounts of the block copolymer increases the time for phase separation substantially. No phase separation is observed once the critical micelle concentration has been attained. Two-step mixing helps the preferential location of the block copolymer at the interface during mixing and promotes better interfacial interactions. The extent of localization of the block copolymer at the interface and, hence, the efficiency of the compatibilizer at the interface can be enhanced by the selection of block copolymers of suitable molecular weight.

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