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# Compatibility studies of natural rubber/poly(methyl methacrylate) blends by viscometry and phase separation techniques

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The compatibility of binary blends of natural rubber (NR) and poly(methyl methacrylate) (PMMA) has been analysed from the viscosity behaviour. For this, the equations developed by both Krighbaum and Wall, and their modified forms by Williamson and Wright, were used. The interaction between polymers in solution has been interpreted qualitatively based on the heat of mixing ($\Delta H$) and interaction parameter ($\chi_1$). Viscometry and spectroscopy studies and calculation of the heat of mixing and the interaction parameter indicated the heterogeneous nature of NR/PMMA blends. The effects of graft copolymer of natural rubber and poly(methyl methacrylate) (NR-g-PMMA) as an emulsifying agent on the interfacial properties of NR/PMMA blends were studied based on the phase separation behaviour. The demixing behaviour is found to be a function of graft copolymer concentration, mode of mixing, nature of solvent and molecular weight of homopolymers and graft copolymers. The demixing behaviour has been studied by noting the phase separation time and volume of the phase separated region. The addition of graft copolymer decreases the demixing behaviour of the blends.

## 1. Introduction

Industrially important thermoplastic elastomers can be developed by blending suitably chosen rubber and plastic. These materials combine the excellent processability characteristics of plastics and the technical properties of rubbers. But the manifestation of superior properties depends on the miscibility of the constituent homopolymers. Most of the thermoplastic–elastomer blends are incompatible and the compatibility can be enhanced by the addition of graft or block copolymers.

Several studies have been carried out to investigate the polymer compatibility [1–4] and the interfacial activity of copolymers in heterogeneous polymer blends. Heat of mixing, dynamic mechanical analysis, thermal analysis (DSC, DMA), light, X-ray and neutron scattering, infrared spectroscopy, nuclear magnetic resonance spectroscopy, fluorescence spectroscopy, etc., are some of the methods used to study the polymer–polymer compatibility [5, 6]. Since the above methods are sophisticated in nature, attempts were made to check compatibility by simple techniques [7–11]. In this respect viscometry becomes an attractive method for studying the compatibility of polymers in solution. The basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blends lies in the fact that while in solution the repulsive interaction may cause shrinkage of polymer coils resulting in a viscosity of the polymer mixture which is lower than the value calculated from viscosities of pure components, on the assumption of additivity law. On the other hand attractive interaction increases the viscosity of the system.

Kulshreshtha *et al.* [13, 14] reported a quick and simple method to determine the compatibility in poly(vinyl chloride)/acrylonitrile butadiene styrene (PVC/ABS) system. It is reported that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility. Chee [15] also proved viscometry as a simple and reliable tool for understanding the compatibility of poly(vinyl chloride)/poly(methyl methacrylate) (PVC/PMMA) and poly(methyl methacrylate)/poly(isobutyl methacrylate) (PMMA/PiBMA) system. Williamson and Wright [16] carried out dilute solution viscosity measurements on ternary polymer systems (two polymers and one solvent). They reported that Krighaum and Wall treatment is not generally applicable to the calculation of polymer–polymer interaction and therefore used empirical relationship derived by Catsiff and Hewett [17].

Recently Thomas and co-workers [18, 19] reported on the intrinsic viscosities of poly(vinyl chloride)/

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poly(ethylene-co-vinyl acetate) (PVC/EVA), poly(vinyl chloride)/poly(styrene-co-acrylonitrile) (PVC/SAN) and poly(ethylene-co-vinyl acetate/poly(styrene-co-acrylonitrile) (EVA/SAN) blends. In order to predict the compatibility of a polymer pair in solution, the interaction parameter term, $\Delta b$, obtained from the modified Krigbaum and Wall theory and the difference in intrinsic viscosities of the polymer mixtures and the weight average intrinsic viscosities of the two polymer solution taken separately were used. Shih and Beatty [20] also studied the compatibility of solutions of polycarbonate and poly(hexamethylene sebacate) blends using the Krigbaum and Wall parameter, $\Delta b$.

Phase separation of polymer mixtures in a dilute solution provides another method to detect the compatibility. Molau [2, 3] presented a mechanism of the action of graft or block copolymer at the interface of two components in solution. A solution of incompatible polymer pairs, A and B, in a mutual solvent separates into two phases and demixes to form two layers. When a small amount of graft or block copolymer is added as an emulsifier a stable polymeric oil-in-oil emulsion results.

The suitably chosen graft copolymer molecule locates itself in the interface between the polymer A solution and the polymer B solution. The graft copolymer molecules can be so arranged that polymer A backbone of the copolymer are located in the polymer A solution with which they are compatible, while the polymer B side chains are located in the polymer B solution with which they are also compatible. Thus the reason for the accumulation of the graft copolymer in the interface appears to be not an attraction between like polymer chains, but a repulsion between different polymer chains. It is also suggested that the only place at which the graft copolymer molecule becomes thermodynamically stable is at the interface. The molecular weight, length of the backbone, number of side chains per backbone, etc., influence the stabilizing action of these materials in polymeric oil-in-oil emulsions. Molau [2] also indicated the fact that the graft or block copolymer must be oriented in a definite manner for the stabilization mechanism. Molau analysed the emulsification with a radiated graft copolymer. The demixing times were found to be a function of the radiation dose which the emulsifier has already received.

Hughes and Brown [21] have studied the influence of styrene grafted poly(ethyl acrylate) on the phase separation of poly(ethyl acrylate) and polystyrene in a common solvent. Addition of a graft copolymer of poly(ethyl acrylate) and styrene did not give two liquid layers.

Recently Fayt and co-workers [22–24] reported a large number of systems in which beneficial effects of polymeric emulsifiers in polymer blends have been illustrated. Fayt and co-workers clearly demonstrated that the emulsifier is uniformly adsorbed at the interface between the two polymers.

Studies by Coumans *et al.* [25] and Paul and co-workers [25, 27] discuss the emulsification of heterogeneous polyethylene/polystyrene (PE/PS) blends by the addition of block copolymers. Bristow [28] and Merrett [29] studied the effect of interpolymer reactions on polymer–polymer–solvent systems. Bristow observed a marked reduction in the speed of phase separation in phase equilibrium studies in polymer–polymer–solvent systems. Merrett [29] found that colloidal suspensions of solid polymer particles in organic solvents can be stabilized by graft copolymers.

Noolandi and Noolandi and Hong [31, 32] have proposed thermodynamic theories concerning the emulsifying effect of copolymers in binary polymer blends. When the copolymer is added to a binary system, the copolymer localizes at the interface and it broadens the interfacial area leading to a lowering of the interaction energy and decrease in the total free energy. The localization of block copolymer with the homopolymers and the separation of blocks are mainly responsible for the reduction in the interfacial tension. Noolandi and Hong reported that both copolymer concentration and molecular weight are equally important in reducing the interfacial tension.

In this paper we present two simple methods to predict the compatibility between natural rubber/poly(methyl methacrylate) (NR/PMMA) blends. In the first technique viscosity measurements have been carried out and the polymer–polymer interaction parameter is calculated using the modified Krigbaum and Wall theory. In the second method compatibility of NR/PMMA by the addition of a graft copolymer is followed as a function of volume fraction of the phase-separated PMMA and the time for phase separation. The influence of the molecular weight of the graft and homopolymers, composition of the blends, concentration of the graft copolymer, effect of solvents and mode of addition of the graft copolymer on the properties have been studied.

## 2. Experimental details

The characteristics of the materials used are given in Table I. The poly(methyl methacrylate) (PMMA) was synthesized in our laboratory by polymerizing methyl methacrylate using benzoyl peroxide. $PMMA_2$ was supplied by Gujarat State Fertilizer Corporation Limited. Natural rubber (NR), (ISNR5, Indian Standard Natural Rubber-5) was supplied by the Rubber Research Institute of India, Kottayam. $NR_3$, $NR_8$, PMMA-g-$NR_5$ and PMMA-g-$NR_{10}$ were obtained by mastication of the respective materials (natural rubber and graft copolymer) for 3, 8, 5 and 10 min,

TABLE I Characteristics of the polymers

| Materials | Density $(g\,cm^{-3})$ | Solubility parameter $(I\,cm^{-3})^{1/2}$ | Molecular weight $\bar{M}_W$ | $\bar{M}_W/\bar{M}_n$ |
|---|---|---|---|---|
| $PMMA_1$ | 1.1 | 49.4 | $2.09 \times 10^5$ | 2.39 |
| $PMMA_2$ | 1.1 | 42.7 | $1.05 \times 10^5$ | 2.09 |
| NR | 0.9 | 32.4 | $7.02 \times 10^5$ | 1.35 |
| $NR_3$ | 0.9 | 32.4 | $5.15 \times 10^5$ | – |
| $NR_8$ | 0.9 | 32.4 | $4.03 \times 10^5$ | – |
| NR-g-PMMA | 1.04 | – | $8.76 \times 10^5$ | – |
| NR-g-$PMMA_5$ | 1.04 | – | $4.39 \times 10^5$ | – |
| NR-g-$PMMA_{10}$ | 1.04 | – | $1.79 \times 10^5$ | – |

respectively. The preparation and characterization of the graft copolymer (PMMA-g-NR) are reported elsewhere [33]. Toluene and chlorobenzene distilled and dried over $CaCl_2$ were used as the solvent. The relative viscosities of the polymer solution of different concentrations and their mixtures were determined by an Ubbelohde-type viscometer (Schott Gerate AVS 400 viscometer). The measurements were carried out at constant temperature of $28.9 \pm 0.01\,^{\circ}C$ and was achieved in a water bath with a thermostat (Schott Gerate CT 1450/2 thermostat). Blends of NR and PMMA having 100, 70, 50, 30 and 0% PMMA at a maximum concentration of $0.1\ g\,dm^{-3}$ in toluene was prepared for viscometric experiments.

Phase separation experiments were carried out by preparing the solution of 50/50, 60/40 and 70/30 NR/PMMA in toluene with and without the addition of graft copolymer. The blend solution was stirred for 12 h and kept standing. The sample was examined for phase separation as a function of time and graft copolymer concentration. The volume fraction of the phase-separated PMMA layer was observed at different time intervals and graft copolymer concentration. The experiment was repeated with chlorobenzene solvent, with graft and homopolymers of various molecular weights and also by changing the mode of addition of the graft copolymer.

## 3. Results and discussion

The theoretical considerations to explain the compatibility in terms of intrinsic viscosity and concentrations begin from the Krigbaum and Wall [34] equation. Specific viscosity, $\eta_{spm}$, of a mixed polymer solution is given by the equation

$$\eta_{spm} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \qquad (1)$$

where $[\eta_1]$ is the intrinsic viscosity of component 1. $C_1$ is the concentration of the component in the mixed polymer solution. $b_{12}$ is the interaction coefficient for the mixture of components 1 and 2. Similarly $[\eta_2]$ and $C_2$ correspond to the second component in the polymer solution. The coefficient $b_{11}$ is related to the constant $k$ in the Huggins equation. It expresses the specific viscosity ($\eta_{sp}$) of the polymer as a function of concentration $C$ when one component alone is in the solution. According to Huggin's equation

$$\eta_{sp}/C = [\eta] + k[\eta]^2C \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity and $k$ is the Huggin's constant. If we put $k[\eta]^2 = b$, the Huggin's equation becomes

$$\eta_{sp}/C = [\eta] + bc \qquad (3)$$

where $b$ is the interaction term. The interaction coefficient between the two polymers, $b_{12}^*$, according to Williamson and Wright is

$$b_{12}^* = \frac{b_{11} + b_{22}}{2} \qquad (4)$$

The value of $b_{12}$ can be theoretically calculated from Equation 4 and can also be obtained from Equation 1.

According to Krigbaum and Wall [33] the information on the interaction between polymer molecules 1 and 2 should be obtained from comparison of experimental $b_{12}$ and theoretical $b_{12}^*$ values. Here the compatibility of the polymer mixture is characterized by a parameter $\Delta b$, given by

$$\Delta b = b_{12} - b_{12}^* \qquad (5)$$

$b_{12}$ is obtained from Equation 1 and $b_{12}^*$ from Equation 4. Negative values of $\Delta b$ are obtained for solutions of incompatible polymer systems while the positive values of $\Delta b$ are for compatible solutions with attractive interactions.

Specific viscosity, $\eta_{sp}$, and reduced viscosity, $\eta_{sp/C'}$ of NR, PMMA, 50/50, 70/30 and 30/70 NR/PMMA are determined experimentally. The intrinsic viscosities are obtained from the plot of $\eta_{sp/C}$ versus concentration. The plots of $\eta_{sp/C}$ versus $C$ for NR, PMMA and blends are given in Figs 1–3. The graphs are linear and the data fitted to the straight line very well. The intercept of the line with the $y$-axis gives the intrinsic viscosities, $[\eta]$, of the corresponding polymer solutions. The experimental and calculated values of the blends are given in Table II. The $\gamma^2$ values are correction factors in linear regression analysis. The values are almost equal to unity which show a perfect fit. The observed values are lower than the calculated values (Table II and Fig. 4) which again provide an indication that NR/PMMA blends are immiscible. All the compositions show a negative deviation from the ideal behaviour which is in agreement with the fact that NR/PMMA blends are incompatible. The values of $\Delta b$ at different concentrations were calculated from $b_{12}$ and $b_{12}^*$ values. The

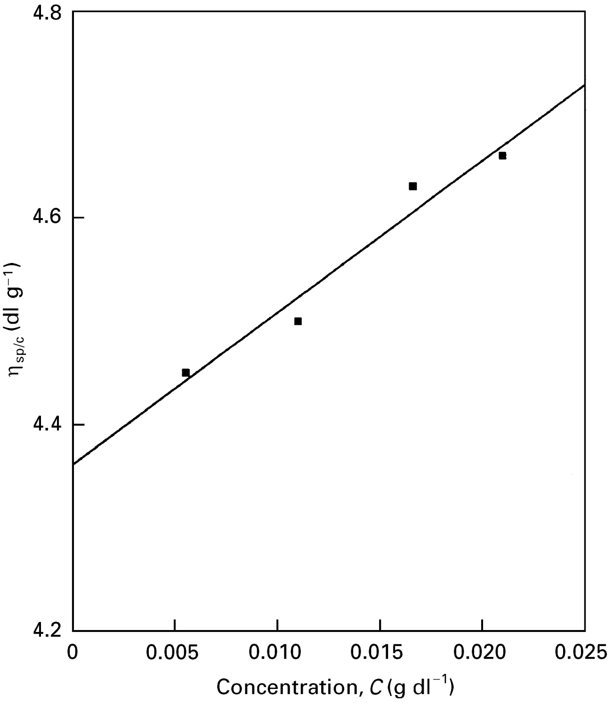

*Figure 1* $\eta_{sp/c}$ versus concentration for NR.

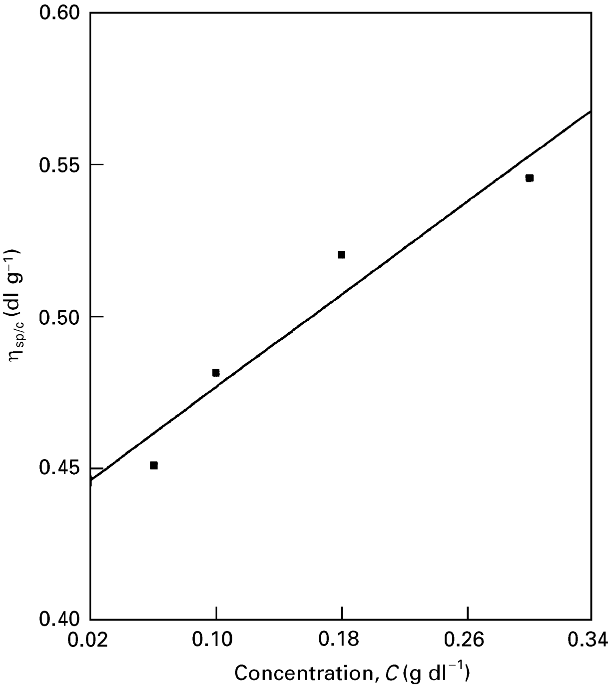

*Figure 2* $\eta_{sp/c}$ versus concentration for PMMA.

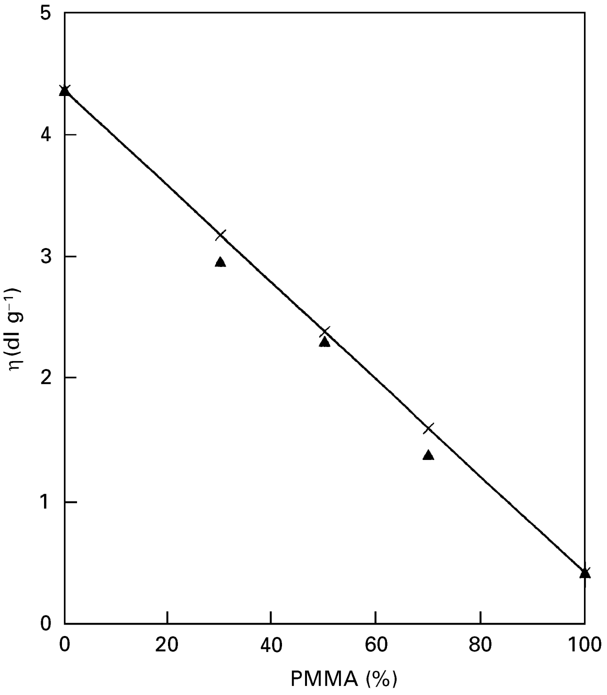

*Figure 4* Experimental (▲) and calculated (×) intrinsic viscosities [η] of NR/PMMA polymer blends.

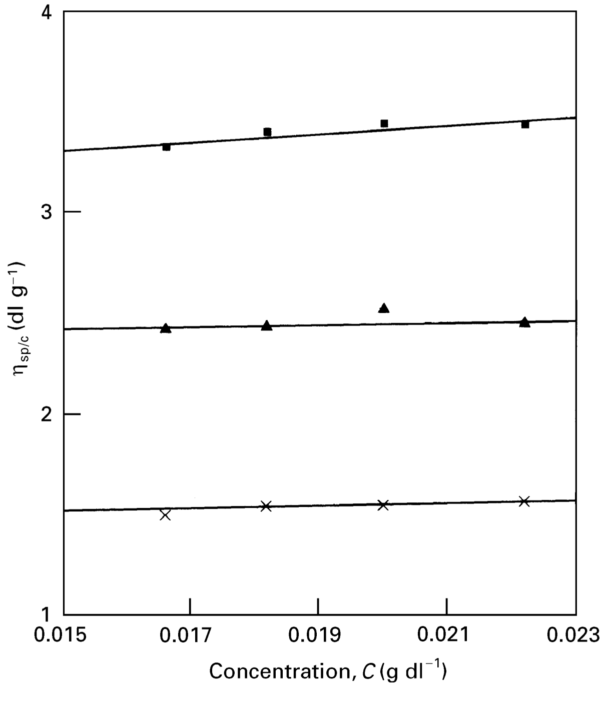

*Figure 3* $\eta_{sp/c}$ versus concentration for 70/30 (■), 50/50 (▲) and 30/70 (×) NR/PMMA blends.

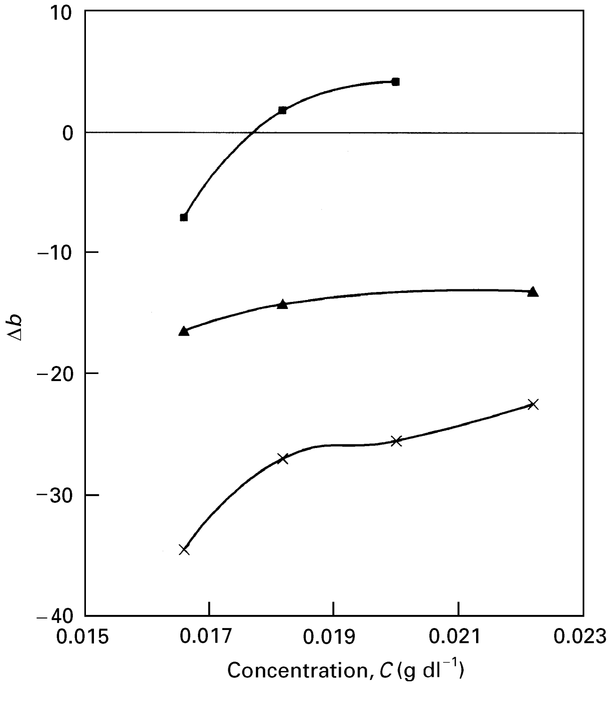

*Figure 5* $\Delta b$ versus concentration for 70/30 (■), 50/50 (▲) and 30/70 (×) NR/PMMA blends.

TABLE II Experimental and calculated values of [η] for NR/PMMA blends.

| NR | PMMA | $\gamma^2$ | $\eta_{exp}$ (dl g$^{-1}$) | $\eta_{cal}$ (dl g$^{-1}$) |
|---|---|---|---|---|
| 0 | 100 | 0.9903 | 0.44 | – |
| 30 | 70 | 0.9905 | 1.40 | 1.614 |
| 50 | 50 | 0.9899 | 2.32 | 2.399 |
| 70 | 30 | 0.9717 | 2.97 | 3.183 |
| 100 | 0 | 0.9153 | 4.36 | – |

values of $\Delta b$ at different compositions of NR/PMMA are given in Fig. 5. The values are mostly negative indicating immiscibility of the blends. It is also interesting to note that for 70/30 and 50/50 NR/PMMA blend system, the values decrease as the concentration decreases. This is probably because the interaction between the solvent and the polymers increases as the solvent concentration increases [18]. In other words the systems are less compatible at high dilution. Again it is seen that $\Delta b$ values decrease as the composition of the NR increases in the system. The results suggest

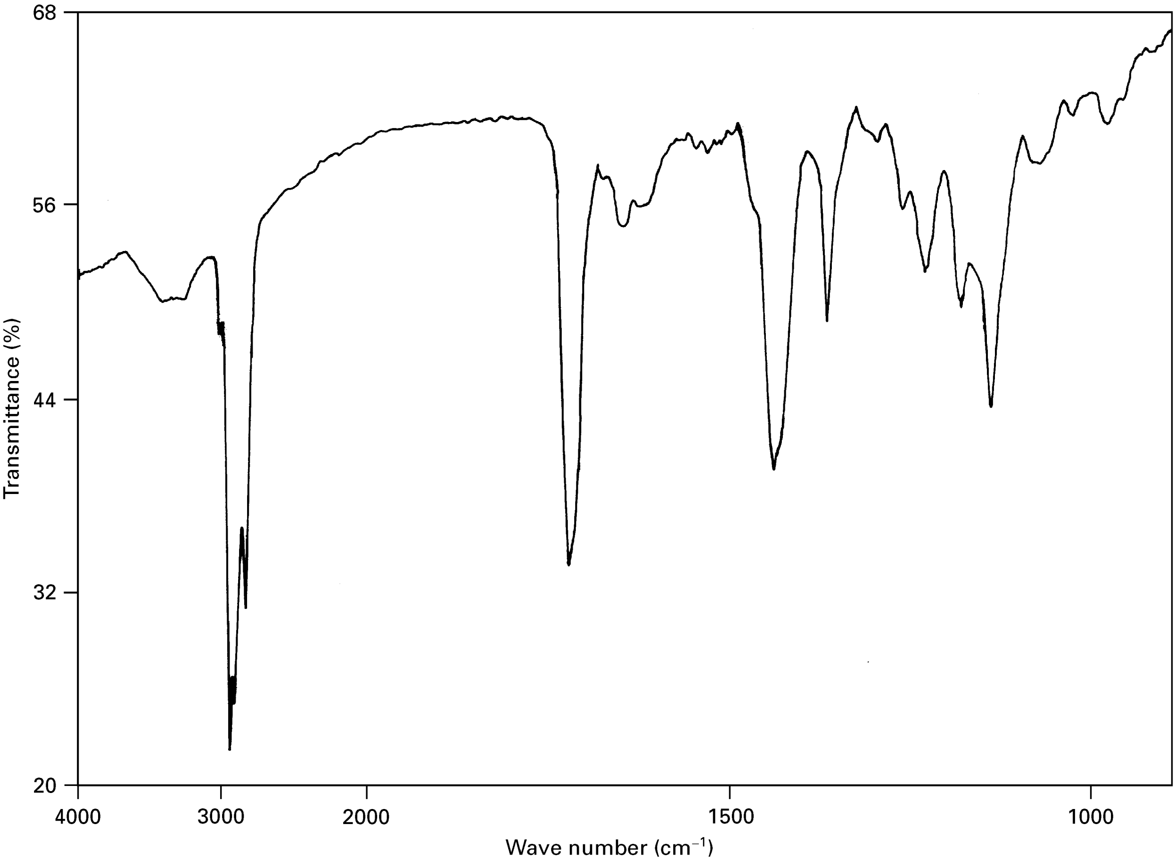

*Figure 6* Infrared spectrum of 50/50 NR/PMMA blend.

that NR/PMMA blend systems are more compatible as the amount of NR increases. The infrared spectrum of 50/50 NR/PMMA blend (Fig. 6) does not show any indication of miscibility. The carbonyl peak of PMMA at 1740 cm$^{-1}$ remains unaffected in the blend suggesting no interaction between NR and PMMA.

## 3.1. Heat of mixing and compatibility

The heat of mixing, which may be an approximate measure of the polymer–polymer compatibility [35, 36] was calculated using the equation developed by Schneier [37].

$$\Delta H_m = [X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 (X_2/(1 - X_2) M_2 \rho_2 + (1 - X_1) M_1 \rho_1)^2]^{1/2} \quad (6)$$

where $X$, $\rho$ and $M$ are the weight fraction of the polymer, polymer density and molecular weight of the monomer, respectively. $\delta_1$ and $\delta_2$ are the solubility parameters of polymers 1 and 2, respectively.

Fig. 7 shows the variation of the calculated heat of mixing with composition. The calculated values of NR/PMMA blends are found to be above the compatibility limit [38] for all compositions confirming the fact that NR/PMMA blends are incompatible in all compositions.

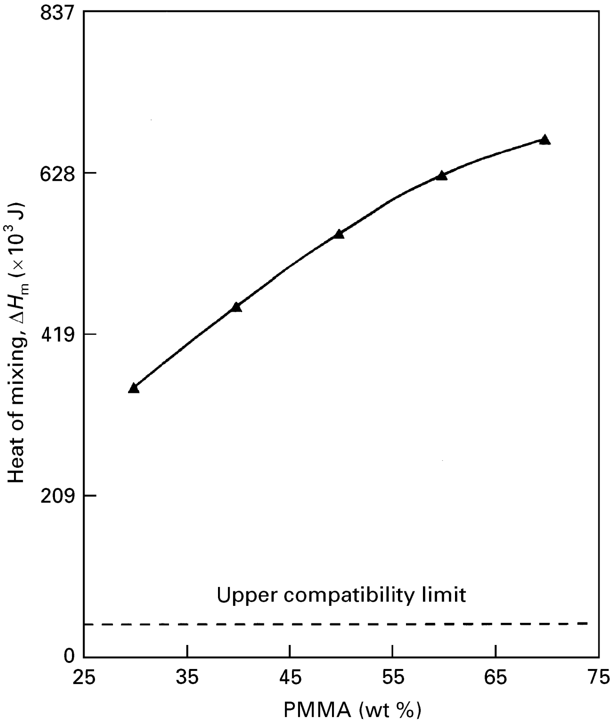

*Figure 7* Heat of mixing ($\Delta H$) versus weight percentage of PMMA in the blend.

## 3.2. Polymer/polymer and polymer blend/ solvent interactions

The interaction parameters between polymer and polymer, and polymer blend and solvent are a measure of compatibility. The interaction parameters $X_i$ are given by the following expression [39].

$$X_i = V_i/RT(\delta_2 - \delta_1)^2 \quad (7)$$

$V_i$ is the reference volume of the solvent, $R$ is the gas constant and $T$ is absolute temperature. $\delta_2$ and $\delta_1$ are solubility parameters of solvent and polymer, respectively.

The same expression has also been used for calculating the interaction parameter between polymers in polymer blends [40, 41]. The blend/solvent interaction parameters have also been calculated according to the method adopted by Singh and Singh [39]. The solubility parameters of the blend ($\delta$) can be calculated knowing the weight fractions $X_1$ and $X_2$ and the individual solubility parameters ($\delta_1$ and $\delta_2$)

$$\delta = X_1\delta_1 + X_2\delta_2 \tag{8}$$

The interaction parameter of NR/PMMA blend and that of the NR/PMMA blends and solvent are given in the Tables III and IV. The incompatibility between polymer pairs in solution is evident from the fact that the interaction parameter between NR and PMMA exceeds that of the NR/PMMA blend and toluene. It is also important to mention that all interaction parameter values that are positive indicate immiscibility. In order to check further the extent of miscibility the $\chi$ critical values are calculated using the equation.

$$(\chi_{\mathrm{AB}})_{\mathrm{C}} = \frac{1}{2}\left[\frac{1}{X_{\mathrm{A}}^{1/2}} + \frac{1}{X_{\mathrm{B}}^{1/2}}\right] \tag{9}$$

The values are given in Table III. The $\chi$ critical values are less than the $\chi$ values of the polymer–polymer pair. This further implies that NR/PMMA is completely immiscible.

## 3.3. Phase separation behaviour

### 3.3.1. *Effect of graft copolymer concentration*

The NR/PMMA forms a heterogeneous system and a solution of these two in toluene separates into two phases with a sharp interface after an interval of 11 h. This clearly shows that PMMA and NR have no chemical interaction and are incompatible even after stirring the solution for 12 h. The situation changes by the addition of 1% graft copolymer. In the presence of copolymer the phase separation took place after a period of two days as against 11 h in the system with no graft. Again, the extent of volume fraction of PMMA separated at equilibrium is found to be smaller than the system with no emulsifier. An optical photograph showing the influence of copolymer concentration on the phase separation process is given in Fig. 8. The volume of PMMA layer separated decreases from right to left as the amount of graft copolymer increases from 0 to 15%. One can see from the photograph that when the copolymer content reaches 15% no phase separation could be observed. The graft copolymer concentrates at the interface and exhibits a well defined orientation and the homopolymer molecules are grouped together with corresponding chains of graft copolymer. As the amount of graft copolymer increases, the time required for phase separation increases sharply. This can be understood from Tables V and VI where the time required for phase separation and the volume fraction of the phase separated PMMA layer are given for NR/PMMA blends containing up to 20% of graft copolymer. There is a sharp increase in the time of phase separation with the addition of a small amount of graft copolymer. The time required for phase separation is 264, 270 and 288 h for 5, 7.5 and 10% graft copolymer concentration, respectively, in toluene solvent. On further addition of graft copolymer (12.5, 15 and 20%), no separation could be observed for several weeks (observed for 8 weeks). This happens when the copolymer content reaches above the equilibrium concentration which can be considered to be the so-called critical micelle concentration. The same trend can be obtained by observing the volume fraction of the phase-separated PMMA layer with graft copolymer concentration. In toluene the volume fraction of phase-separated PMMA layer decreases with graft copolymer concentration and no phase separation

TABLE III Interaction parameter for polymer–polymer system.

| System | Polymer as component 1 | Molar volume | Interaction parameter | Critical interaction parameter $(\chi_{\mathrm{AB}})_{\mathrm{C}}$ |
|---|---|---|---|---|
| NR/PMMA | NR | 75.5 | 2.07 | $9.75 \times 10^{-3}$ |
| | PMMA | 90.9 | 2.50 | $9.75 \times 10^{-3}$ |

TABLE IV Interaction parameter for polymer blend–solvent system (toluene)

| System | Solubility parameter of the blend $(\mathrm{J\,cm^{-3}})^{1/2}$ | Solubility parameter of the solvent $(\mathrm{J\,cm^{-3}})^{1/2}$ | Interaction parameter |
|---|---|---|---|
| 50/50 NR/PMMA | 40.9 | 37.2 | 0.1347 |
| 60/40 NR/PMMA | 39.2 | 37.2 | 0.03932 |
| 70/30 NR/PMMA | 37.5 | 37.2 | 0.00075 |

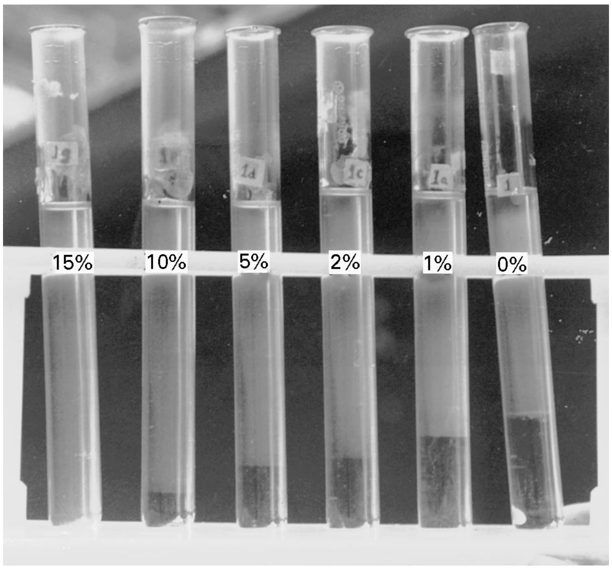

*Figure 8* Optical photograph showing influence of graft copolymer on phase separation of 50/50 NR/PMMA blends.

TABLE V Phase separation times for various NR/PMMA blends

| % of graft | Time (h) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NR/PMMA$_1^a$ NR-g-PMMA (System I) | NR/PMMA$_1^b$ NR-g-PMMA | NR/PMMA$_1^c$ NR-g-PMMA | NR/PMMA$_2^a$ NR-g-PMMA (System II) | NR$_3$/PMMA$_2^a$ NR-g-PMMA (System III) | NR$_8$/PMMA$_2^a$ NR-g-PMMA (System IV) | NR/PMMA$_1^a$ NR-g-PMMA$_5$ (System V) | NR/PMMA$_1^a$ NR-g-PMMA$_{10}$ (System VI) |
| 0 | 11 | 10 | 11 | 14 | 6 | 3 | 11 | 11 |
| 1 | 48 | 72 | 73 | 52 | 28 | 18 | 24 | 18 |
| 2 | 50 | 96 | 110 | 60 | 72 | 190 | 13 | 26 |
| 3 | 62 | 120 | 140 | 72 | 180 | ** | 40 | 30 |
| 5 | 264 | 192 | 211 | 271 | 210 | ** | 73 | 52 |
| 7.5 | 270 | 244 | 280 | 278 | ** | ** | 140 | 123 |
| 10 | 288 | 294 | ** | ** | ** | ** | 182 | 192 |
| 12.5 | ** | ** | ** | ** | ** | ** | 215 | 201 |
| 15 | ** | ** | ** | ** | ** | ** | ** | 289 |
| 20 | ** | ** | ** | ** | ** | ** | ** | ** |

** No separation.

[a] Toluene solvent and one-step mixing.

[b] Chlorobenzene solvent and one-step mixing.

[c] Toluene solvent and two-step mixing.

TABLE VI Volume fraction of the phase separated PMMA layer

| % of graft | Volume fraction | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NR/PMMA$_1^a$ NR-g-PMMA (System I) | NR/PMMA$_1^b$ NR-g-PMMA | NR/PMMA$_1^c$ NR-g-PMMA | NR/PMMA$_2^a$ NR-g-PMMA (System II) | NR$_3$/PMMA$_2^a$ NR-g-PMMA (System III) | NR$_8$/PMMA$_2^a$ NR-g-PMMA (System IV) | NR/PMMA$_1^a$ NR-g-PMMA$_5$ (System V) | NR/PMMA$_1^a$ NR-g-PMMA$_{10}$ (System VI) |
| 0 | 0.3437 | 0.5777 | 0.3437 | 0.3546 | 0.3456 | 0.3546 | 0.3437 | 0.3437 |
| 1 | 0.2913 | 0.2820 | 0.328 | 0.2718 | 0.3210 | 0.2610 | 0.3017 | 0.312 |
| 2 | 0.281 | 0.273 | 0.210 | 0.2612 | 0.1980 | 0.190 | 0.293 | 0.298 |
| 3 | 0.228 | 0.218 | 0.192 | 0.220 | 0.170 | ** | 0.258 | 0.272 |
| 5 | 0.197 | 0.182 | 0.178 | 0.186 | 0.156 | ** | 0.282 | 0.2913 |
| 7.5 | 0.176 | 0.134 | 0.162 | 0.166 | ** | ** | 0.198 | 0.289 |
| 10 | 0.114 | 0.102 | ** | 0.112 | ** | ** | 0.188 | 0.212 |
| 12.5 | ** | ** | ** | ** | ** | ** | 0.124 | 0.188 |
| 15 | ** | ** | ** | ** | ** | ** | ** | 0.128 |
| 20 | ** | ** | ** | ** | ** | ** | ** | ** |

** No separation.

[a] Toluene solvent and one-step mixing.

[b] Chlorobenzene solvent and one-step mixing.

[c] Toluene solvent and two-step mixing.

occurs after 15% of graft copolymer which indicates interfacial saturation.

There are several studies on the interfacial saturation of binary blends by the addition of graft and block copolymer in immiscible polymer blends. Many polymer pairs are incompatible in a solution of moderate concentrations. The immiscibility is evident from the phase separation of the mixture into two distinct layers. It is well established that the graft copolymer has the ability to make the immiscible blend compatible in a common solvent [21]. The compatibilizer decreases the interfacial tension between the matrix and the dispersed phase. Many papers report on the so-called interfacial saturation of binary polymer blends by the addition of compatibilizer. Anastasiadis *et al.* [42] have observed a sharp decrease in interfacial tension with the addition of a small amount of poly(styrene-*b*-butadiene) in PS/1,2 polybutadiene blends followed by a levelling off at higher concentrations of copolymer. Fayt *et al.* [43] observed an equilibration in the dispersed phase dimension with increasing block copolymer concentration in PE/PS blends. Willis and Favis [44] also reported that an equilibrium concentration of 5% ionomer was sufficient to compatibilize polyolefine/polyamide blends. Gailard *et al.* [45, 46] have examined the surface activity of copolymers by studying the interfacial tension reduction in demixed polymer solutions. Addition of poly(styrene-*b*-butadiene) to polystyrene/polybutadiene/styrene ternary systems first showed a characteristic decrease in interfacial tension followed by levelling off. The effect of addition of poly(dimethyl siloxane-*b*-oxy methylene) on the interfacial tension between methyl terminated poly(dimethyl siloxane) and poly(oxy ethylene-*b*-oxy propylene) has been studied by Patterson *et al.* [47]. They found that less than 2% of the block copolymer was sufficient to saturate the interface and to reach the limiting interfacial tension value. Inoue *et al.* [48] reported on the mechanism of domain formation on a ternary system consisting of polystyrene/poly(styrene-*b*-isoprene)/polyisoprene. The domain structure was investigated by light and electron microscopies using an osmium tetroxide fixation technique. They concluded that when the molecular weight of the homopolymer is much higher than that of the corresponding arm of the copolymer, the block copolymer can no longer act as an emulsifier.

All these experimental observations and the present study suggest that there is an optimum amount of compatibilizer which can saturate the interface. Further amounts of compatibilizer above the optimum amount will not modify the interface any more but promote micelle formation which is undesirable.

The present work can be related to Noolandi and Hong's [30–32] theoretical prediction that there is a maximum quantity of compatibilizer which can saturate the interface of the binary blend. An expression for interfacial tension reduction upon the addition of the copolymer was developed by Noolandi and Hong based on thermodynamics to explain the emulsifying effect of the A–b–B in immiscible A/B blends. The expression for interfacial tension reduction ($\Delta\gamma$) in a binary blend upon the addition of a divalent copolymer is given by [42]

$$\Delta\gamma = d\phi_{\mathrm{C}}[(\tfrac{1}{2}\chi + 1/Z_{\mathrm{C}}) - 1/Z_{\mathrm{C}}\,\mathrm{Exp}(Z_{\mathrm{C}}\chi/2)] \qquad (10)$$

where $d$ is the width of half height of the copolymer profile reduced by Kuhn statistical segment length, $\phi_{\mathrm{C}}$ is the bulk volume fraction of the copolymer in the system, $\chi$ is the Flory–Huggin's interaction parameter between A and B segments of the copolymer. $Z_{\mathrm{C}}$ is the degree of polymerization of the copolymer. According to this theory, the interfacial tension reduction decreases linearly upon the addition of the copolymer followed by a levelling off at higher concentrations. Although the theory was developed for symmetric block copolymers, it has been found that the theory can be applied to graft copolymer as well [41]. Our experimental observations are in agreement with Noolandi's findings on a qualitative basis. As the copolymer content increases, the time of phase separation increases and the volume fraction of the phase-separated PMMA layer decreases and finally the system reaches interfacial saturation. At this point no phase separation could be seen. The long time required for phase separation is due to the decrease in the interfacial tension between the homopolymers by the localization of the graft copolymer in the interfacial area. The interfacial activity of the copolymer infact decreases the interaction energy and hence the polymer–polymer solution does not undergo any phase separation.

## 3.4. Effect of nature of solvent on phase separation

Phase separation has been studied by changing the solvent system from toluene to chlorobenzene. In both cases the phase separation trend is same and the saturation point is attained at a copolymer content of 10%. But the time required for demixing in chlorobenzene is higher than that for toluene. The volume fraction of the PMMA layer separated in chlorobenzene is small compared to the toluene system. This is shown in Tables III and IV. Chlorobenzene solvates the polymer species much more than that of toluene and consequently the interaction between chlorobenzene and the NR/PMMA blend is higher. The difference in behaviour between the solvent is due to the difference in solubility parameter. The solubility parameter difference between PMMA and chlorobenzene ($\Delta\delta C_1 = 2.3$) is less than that between PMMA and toluene ($\Delta\delta t_1 = 2.9$). Again the difference in solubility parameter between NR and chlorobenzene is 1.75 ($\Delta\delta C_2$) and that between NR and toluene is 1.15 ($\Delta\delta t_2$). The $\Delta\delta C_1 - \Delta\delta C_2$ and $\Delta\delta t_1 - \Delta\delta t_2$ values between the homopolymers and solvent are 0.55 and 1.75 for chlorobenzene and toluene, respectively. This indicates that chlorobenzene is a good solvent for the polymer pair. Therefore, polymer–polymer solution made in chlorobenzene took more time for demixing.

## 3.5. Effect of mode of addition on phase separation

In the morphological study of nylon/rubber blends Cimmino *et al.* [49] observed additional size reduction when blends were prepared in two steps in comparison to one-step mixing. Two-step mixing was carried out by blending the dispersed phase with the compatibilizer first and then blending it with the matrix polymer. By pre-blending the modifier with the dispersed phase, it was possible to increase the interaction between the copolymer and the dispersed phase. Pre-blending with the dispersed phase helps to locate the copolymer at the interface [50, 51]. Similar observations have been reported by Willis and Favis [52] and Thomas and co-workers [53, 54].

The effect of mode of addition of the graft copolymer on phase separation of the blends has been studied. It was found that in two-step mixing, the time required for phase separation is relatively greater and the amount of graft copolymer required for interfacial saturation is less compared to one-step mixing (Table V). It is also seen that in two-step mixing the volume fraction of the phase-separated layer is less than that of one-step mixing (Table VI). By pre-blending graft copolymer with the minor phase the amount of copolymer that can diffuse into the interface can be increased and the distance travelled by the copolymer to reach the interface can be minimized. This will help the preferential location of the graft copolymer at the NR/PMMA interface during mixing and thus leads to better interfacial interactions.

## 3.6. Effect of graft copolymer/homopolymer molecular weight on phase separation

The influence of graft copolymer molecular weight and homopolymer molecular weight on the phase separation behaviour of the blends has been studied by using graft copolymers of molecular weight $8.76 \times 10^5$, $4.39 \times 10^5$ and $1.79 \times 10^5$, NR of molecular weight $7.02 \times 10^5$, $5.15 \times 10^5$ and $4.03 \times 10^5$ and

PMMA of molecular weight $2.09 \times 10^5$ and $1.05 \times 10^5$. As the molecular weight of the graft copolymer decreases the time taken for phase separation decreases and the volume fraction of the phase-separated PMMA layer increases (Table V and VI). The effect of molecular weight of the copolymers on the demixing process can be explained by theories of Riess and Jolivet [55]. According to them emulsification efficiency of the copolymer can be compared by defining the ratio of the molecular weight of the homopolymer and the graft copolymers. If

$$\alpha = \frac{\text{Molecular weight of PMMA homopolymer}}{\begin{array}{c}\text{Molecular weight of PMMA component}\\ \text{in the graft copolymer}\end{array}}$$

and

$$\beta = \frac{\text{Molecular weight of NR homopolymer}}{\begin{array}{c}\text{Molecular weight of NR component}\\ \text{in the graft copolymer}\end{array}}$$

then, the copolymer is less efficient as an emulsifier if $\alpha > 1$ and $\beta > 1$. The emulsifying properties 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.

The $\alpha$ and $\beta$ values of the graft copolymer and homopolymers are given in the Table VII. It can be seen that and values decrease as the molecular weight of the graft copolymer increases. For systems I, II, III and IV, the $\alpha$ and $\beta$ values are either close to and or less than one [55]. Therefore the tendency of the graft copolymer to stay at the interface increases and strengthens the compatibilization. In fact, the extent of compatibilization is maximum in system IV (Table V) where the $\alpha$ and $\beta$ values are the lowest. For other systems (V and VI) the $\alpha$ and $\beta$ values are greater than unity showing inefficiency of the compatibilizer to locate at the interface which is inconsistent with the experimental results, i.e. the time required for phase separation is less and a large amount of graft copolymer is required for compatibilization. It should be noted that the time for demixing increases and the system becomes more stable as the molecular weight of the graft polymer increases. Noolandi and Hong [30–32] pointed out that the molecular weight of the copolymer is important in reducing the interfacial tension of immiscible polymer blends. The localization of the copolymer at the interface and the separation of the blocks into corresponding homopolymer phases lead to various phenomena such as lowering of the interaction energy between the two immiscible polymers. the broadening of the interface between the homopolymers and reduction in entropy of the system. In our study, as the molecular weight of graft copolymer increases or homopolymer molecular weight decreases, $\alpha$ and $\beta$ values become less than unity and hence a greater reduction in interfacial tension. The reduction in interfacial tension is clear from the higher time required for phase separation and the low amount of phase-separated PMMA layer (Tables V and VI).

## 4. Conclusion

Simple techniques like viscometry and phase separation studies have been used to test the compatibility between polymers. Krigbaum and Walls equations have been successfully applied to explain the compatibility in terms of intrinsic viscosity and concentration. The observed viscosity values are lower than the calculated values, thus indicating a lack of interaction between the NR/PMMA blend system. $\Delta b$ is a parameter obtained from the solution viscosities of the polymer blend system representing the interaction of the individual molecules. A negative value of $\Delta b$ is an indication of incompatibility of NR/PMMA blends in all compositions. The heat of mixing values and the interaction parameter ($\chi$) of NR/PMMA blends further support the incompatibility of these blends.

The effect of graft copolymer on the compatibility between polymer–polymer solution and the amount of copolymer required for compatibilization have been evaluated. The incompatibility causes the phenomenon of phase separation of the polymer blend solutions. The graft copolymer identical to the component homopolymers 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 used to evaluate the extent of compatibilization. The phase separation took place quickly (5–11 h) for blends with no graft copolymer. Presence of small amounts of graft copolymer increases the phase separation time to a considerable extent. No phase separation was observed once the critical micelle concentration was attained. The experimental results are qualitatively in agreement with the theoretical predictions of Noolandi and Hong. Chlorobenzene is found to be a better solvent because its solubility parameter is more close to that of the

TABLE VII $\alpha$ and $\beta$ values of the NR/PMMA blends

| System | | Molecular weight of PMMA | Molecular weight of PMMA in the graft | $\alpha$ | Molecular weight of NR | Molecular weight of NR in the graft | $\beta$ |
|---|---|---|---|---|---|---|---|
| I | (NR/PMMA$_1$/NR-g-PMMA) | $2.09 \times 10^5$ | $2.27 \times 10^5$ | 0.93 | $7.02 \times 10^5$ | $6.48 \times 10^5$ | 1.09 |
| II | (NR/PMMA$_2$/NR-g-PMMA) | $1.05 \times 10^5$ | $2.27 \times 10^5$ | 0.46 | $7.02 \times 10^5$ | $6.48 \times 10^5$ | 0.75 |
| III | (NR$_3$/PMMA$_2$/NR-g-PMMA) | $1.05 \times 10^5$ | $2.27 \times 10^5$ | 0.46 | $5.15 \times 10^5$ | $6.48 \times 10^5$ | 0.79 |
| IV | (NR$_8$/PMMA$_2$/NR-g-PMMA) | $1.05 \times 10^5$ | $2.27 \times 10^5$ | 0.46 | $4.03 \times 10^5$ | $6.48 \times 10^5$ | 0.62 |
| V | (NR/PMMA$_1$/NR-g-PMMA$_5$) | $2.09 \times 10^5$ | $1.41 \times 10^5$ | 1.47 | $7.02 \times 10^5$ | $3.24 \times 10^5$ | 2.16 |
| VI | (NR/PMMA$_1$/NR-g-PMMA$_{10}$) | $2.09 \times 10^5$ | $0.46 \times 10^5$ | 4.49 | $7.02 \times 10^5$ | $1.32 \times 10^5$ | 5.31 |

homopolymers. Two-step mixing helps the preferential location of the graft copolymer at the interface during mixing and promotes better interfacial interactions. The extent of localization of the graft copolymer at the interface and hence the efficiency of the compatibilizer at the interface can be enhanced by the selection of graft copolymers of suitable molecular weight.

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