Miscibility between PS and PSAN Affected by Solvent and Temperature of the System[*]

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Abstract The influence of solvent on the miscibility of polystyrene (PS) and poly (styrene-*co*-acrylonitrile) (PSAN) blends has been investigated viscometrically. The miscibility of different PS/PSAN blend (30/70, 50/50 and 70/30) compositions in acetone and benzene at 20, 30, and 40 °C was investigated on the basis of the sign of Chee (ΔB and μ), and Sun's (α) criteria. The values of these parameters were evaluated from the analyses of reduced viscosity data of binary (solvent/polymer) and ternary (solvent/polymer1/polymer2) polymer systems. These investigations indicated partial miscibility for both the blend systems. However, PS/PSAN/acetone blend system showed somewhat higher partial miscibility than the PS/PSAN/Benzene blend system highlighting the impact of solvent over the polymer-polymer interactions and hence their miscibility. The results obtained through viscometry were also corroborated by the refractive index and density results for the blends under study. The effect of temperature on miscibility in both the cases was almost negligible.

Keywords: Miscibility; Polystyrene; Poly(styrene-*co*-acrylonitrile); Viscosity; Density; Refractive index.

INTRODUCTION

Modern technology needs new types of polymeric materials, whose properties are not only tailored for a particular application but may be even modified in a thoughtful manner. Polymer blends are the best alternatives to satisfy the growing needs of new polymer materials with targeted properties[1]. They, therefore, are receiving more attention due to low cost alternatives to the development of totally new polymers or copolymers with improved properties[2]. Polymer blends are physical mixtures of two or more polymers and/or copolymers that interact through secondary forces with no covalent bonding[3]. They are dominating different application areas due to simplicity, versatility, economical and tailor-made properties. However, the performance of polymer blends depends on their end properties which in turn depend on the component polymers, composition, solvent used and, mainly, on the miscibility of blend components at molecular level[4–7]. The extensive applications of polymer blends have led to an increasing research effort on their miscibility[4]. Several works have been developed in the last 35 years on polymer-polymer miscibility[8, 9]. The presence of some favorable interaction between component polymers is essential for miscibility of the blend[1, 4]. The polymer-polymer miscibility[10, 11] may be due to various specific interactions, such as hydrogen bonding[12], dipole-dipole interactions[13], charge transfer complexes[14], or segment-segment repulsion inside the blends in addition to the similarity in chemical structure. Different techniques have been used for investigation of the miscibility of polymer blends which include dynamic mechanical analysis (DMA), thermal analysis, electron microscopy, neutron scattering, light

scattering, spectroscopy, and viscometry[3, 4]. Because of its simplicity, viscometry, refractometry and density are attractive techniques for studying the polymer-polymer miscibility in solution. Dilute solution viscometry (DSV) is based on the assumption that the viscosity of ternary system (polymer 1/polymer 2/solvent) can either be lower or higher than that of the binary system (polymer 1/solvent or polymer 2/solvent) depending upon the nature of interactions (attractive or repulsive) involved. In case of presence of attractive forces between the constituent polymers, swelling of the polymeric coils and, hence, increase in viscosity will occur and *vice versa*[15, 16].

The present work, a continuation of our previous investigation[17], further reports on the results about the influence of solvent on miscibility of PS/PSAN blend. In this paper, acetone and benzene have been used as common solvents due to considerable differences in their structures.

We selected PS as a base polymer due to its good properties, such as good processability, rigidity, transparency, low water absorbability, and that it can be produced at low costs. However, PS has some drawbacks, such as sensitivity to chemicals and food materials with high oil content, poor UV-resistance and brittleness. PS finds its main applications in the packaging industry[18, 19]. The second base polymer, PSAN, which is a copolymer of styrene and acrylonitrile, has excellent chemical and heat resistances in addition to superior mechanical properties. Moreover, it is also recommended for prolonged outdoor applications without any color changes due to better weather, UV resistance, and thermal stability[20].

THEORETICAL

Dilute solution viscometry (DSV) is based on the classical Huggins equation[21] that can be expressed as

$$\frac{\eta_{sp}}{c} = [\eta] + bc \tag{1}$$

where η_{sp} is the specific viscosity of a single solute solution, $[\eta]$ is the intrinsic viscosity and c is the mass concentration of the solute, b indicates the polymer-solvent binary interactions, and k, the Huggins coefficient, reflects binary interactions between polymer segments. b can be related to the Huggins coefficient k by

$$b = k[\eta]^2 \tag{2}$$

An analogue of the classical Huggins equation proposed by Krigbaum and Wall[22] can be applied to ternary systems (polymer 1/polymer 2/solvent).

They proposed the following approach for probing the miscibility of polymer blend;

$$\frac{(\eta_{sp})_m}{c_m} = [\eta]_m + b_m C_m \tag{3}$$

where c_m is the total concentration of the component polymers $c_1 + c_2$, $(\eta_{sp})_m$ is the specific viscosity and b_m is the global interaction between the component polymers of the blend. b_m can be related to the Huggins coefficient k_m of the polymer blend by

$$b_m = k_m [\eta]_m^2 \tag{4}$$

where $[\eta]_m$ is the weight average of the intrinsic viscosity of the two component polymers since the molecules have no influence on each other in dilute solution, thus

$$[\eta]_m = w_1 [\eta]_1 + w_2 [\eta]_2 \tag{5}$$

The term b for a blend of polymer 1 and polymer 2 can be written as

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12} \tag{6}$$

where w_1, w_2 are the weight fractions of polymer 1 and polymer 2, respectively, b_{11}, b_{22} and b_{12} are the interaction parameters of the polymer 1 and polymer 2, and polymer blend with solvent respectively that are obtained from the slopes of the plots of reduced viscosity versus concentration.

K.K. Chee Criterion

Chee[23] suggested the following criteria to characterize polymer-polymer miscibility in a solution;

$$\Delta B = \frac{b - 5}{2 w_1 w_2} \tag{7}$$

where $\bar{b} = w_1 b_{11} + w_2 b_{22}$, in which w_1, w_2 are the weight fractions of polymer 1 and polymer 2 respectively, in a given solution and b_{11}, b_{22} are the slopes of the reduced viscosity versus concentration curves of the pure polymer solutions. For the ternary system, 'b' can be written as:

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12}$$

where b_{12} is the slope of the reduced viscosity versus blend concentration plot.

$\Delta B \geq 0$ indicates miscibility whereas $\Delta B < 0$ indicates immiscibility of the polymer blend.

Chee developed another novel parameter, μ, for the determination of polymer-polymer miscibility and is giver by,

$$\mu = \frac{\Delta B}{\left([\eta]_2 - [\eta]_1 \right)^2} \tag{8}$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of pure component solutions. The blend is miscible if $\mu \geq 0$ and immiscible if $\mu < 0$.

Sun's Criterion

Sun *et al.*[24] proposed the α criterion to determine the miscibility of polymer blends;

$$\alpha = k_m - \frac{\left[\left(\sqrt{k_1} \right) \eta_1 w_1 + \left(\sqrt{k_2} \right) \eta_2 w_2 \right]^2}{\left[\eta_1 w_1 + \eta_2 w_2 \right]^2} \tag{9}$$

$$k_1 = \frac{b_{11}}{[\eta]_1^2}, k_2 = \frac{b_{22}}{[\eta]_2^2} \text{ and } k_m = \frac{b_m}{[\eta]_m^2}$$

Here k_1, k_2, k_m are the Huggins' constants for component 1, 2, and the blend and b_m is the slope of the reduced viscosity versus concentration of the blend, respectively. $\alpha \geq 0$ signifies mutual attraction between the constituent polymers in the solution and, hence, miscibility, while $\alpha < 0$, signifies mutual repellency and, hence, immiscibility of the polymer blend.

EXPERIMENTAL

Materials

The two polymers used in this study, polystyrene and poly(styrene-*co*-acrylonitrile) having 25 wt% AN contents, were purchased from Aldrich, USA; they had weight-average molar mass, M_w, of 1.87×10^5 and 1.96×10^5 g/mol, respectively. The solvents acetone and benzene, purchased from Acros (Spain) and were of analytical grade and used as- received.

Sample Preparation

Stock solutions of PS/PSAN blends with compositions 0/100, 30/70, 50/50, 70/30, and 100/0 were prepared by dissolving the required amount of polymers separately in acetone and benzene. The mixtures were then allowed to stand for 36 h at ambient temperature until homogeneous solutions were obtained. The total mass of the component polymers in the stock solutions was maintained at 1.0 g/dL. The stock solutions of neat polymers and their blends for each solvent were diluted with appropriate amount of the respective solvent to get the desired lower concentrations (0.25, 0.5 and 0.75 g/dL). The first numeral of the blend composition, throughout this paper, indicates the PS fraction.

Methods

Viscosity

The viscosity measurements of PS, PSAN and their blend solutions were made at three different temperatures, 20, 30 and 40 °C, using an Ostwald type capillary viscometer. All the measurements were made in a LAUDA Thermostat (Model E-200 Germany), with a thermal stability of (± 0.01) °C. The flow times were initiated after approximately 15−20 min equilibration time and were continued until several flow time readings agreed with one another. The flow time of each solution was taken as the average of three subsequent readings.

Refractive index

The refractive indices of the PS, PSAN and their blend solutions were measured with a digital Abbe's refractometer, Bellingham + Stanley (BS) London UK, with a thermostated water circulating system at the three different temperatures, 20, 30 and 40 °C. The uncertainty in the refractive index measurements was (± 0.0001).

Density

The densities of the PS, PSAN and their blend solutions were measured with a Mettler-Toledo Digital Density Meter, Model DE40, Switzerland at three different temperatures, 20, 30, and 40 °C. The temperatures of the measurements were within an uncertainty of (± 0.1) °C. The instrument was calibrated with the standard density water supplied with the instrument. The estimated error in the density measurements was within (± 0.05)%.

RESULTS AND DISCUSSION

The reduced viscosity (η_{sp}/c) versus concentration plots for PS, PSAN, and their blends of different compositions (30/70, 50/50 and 70/30) in acetone and benzene at 20, 30, and 40 °C, are presented in Figs. 1(a−c) and 2(a−c), respectively.
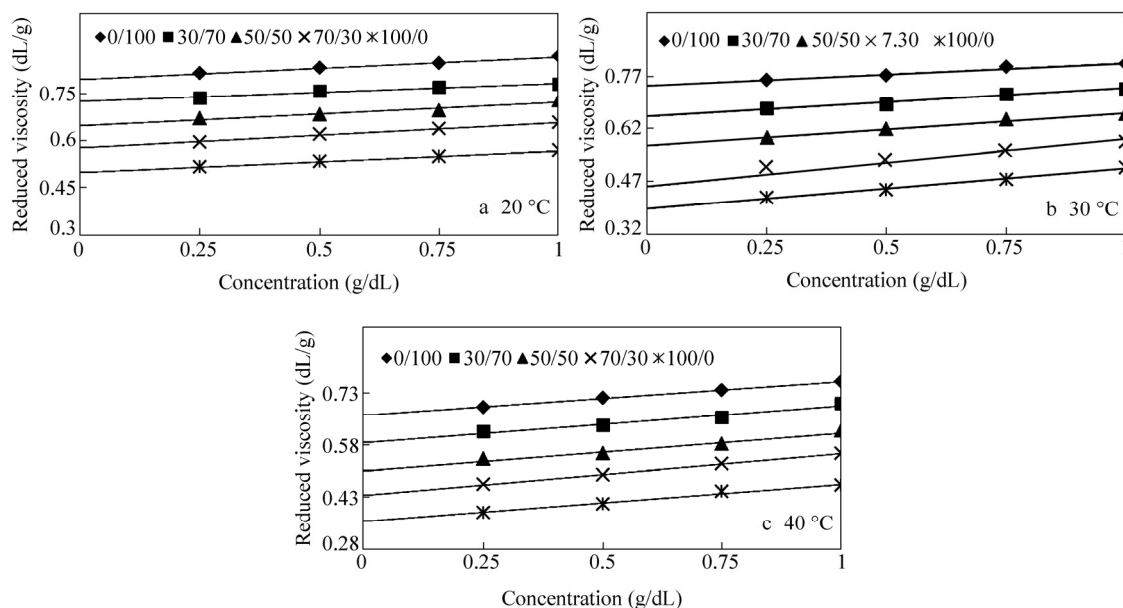

Fig. 1 (a−c) Huggins plots for PS, PSAN and their blends in acetone at various temperatures

    The Huggins plots for PS/PSAN/acetone were linear having no cross overs in the investigated concentration range indicating miscibility for the said blend system. However, the Huggins plots for PS/PSAN/benzene blend system were not parallel and showed cross overs at 40 °C only, indicating immiscibility of the blend[25].
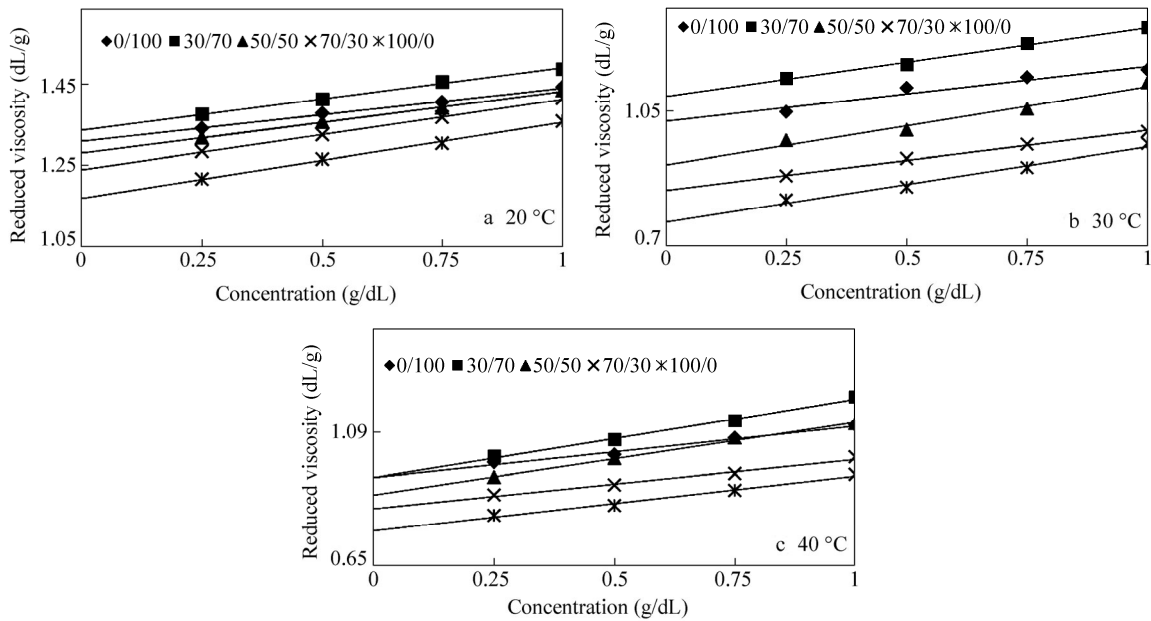
Fig. 2 (a–c) Huggins plots for PS, PSAN and their blends in benzene at various temperatures

The values of the various viscometric parameters such as ΔB, μ[23], and α[24] were computed using Eqs. (7), (8), and (9) respectively.

The plots of these parameters versus weight fraction of PS in the PS/PSAN/acetone and PS/PSAN/benzene blend systems at 20, 30, and 40 °C for various blend compositions are shown in Figs. 3(a–d) and 4(a–d), respectively.
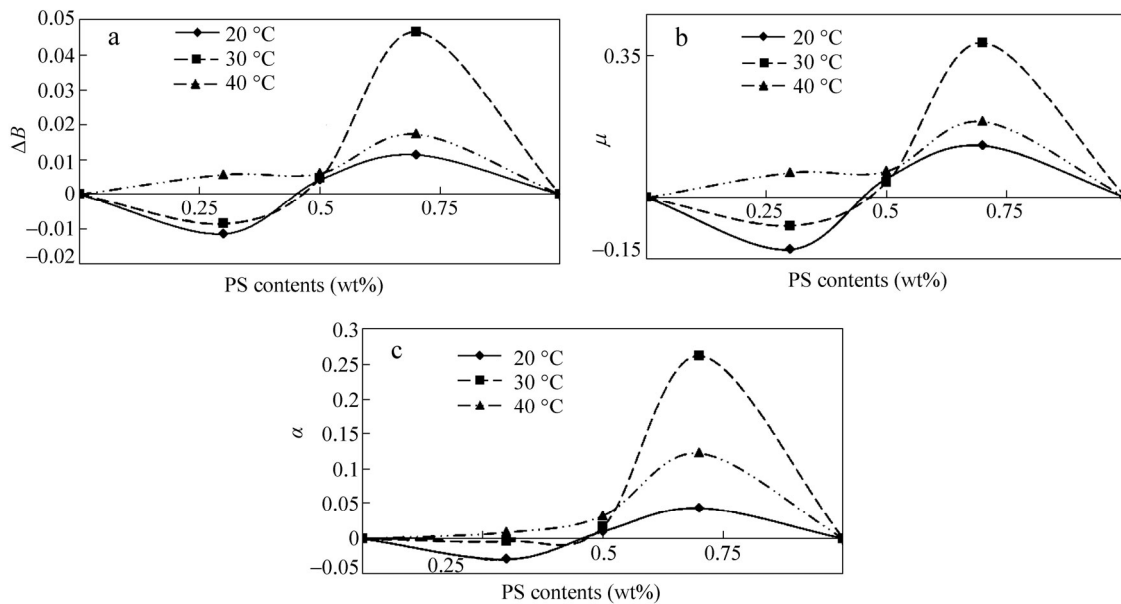

Fig. 3 (a–c) Plots of interaction parameters versus weight fraction of PS in PS/PSAN/acetone blends

Based on the sign convention described earlier in the theoretical section, the results for the ΔB, μ, and α parameters showed miscibility over the entire composition and temperature range for PS/PSAN/acetone system

with the only exception of 30/70 blend composition at 20 °C and 30 °C. There was a complete agreement among different interaction parameters (ΔB, μ, and α) regarding miscibility and/or immiscibility of PS/PSAN/acetone blend system for various blend compositions at all temperatures. The effect of composition and temperature on miscibility was quite clear for the PS/PSAN/acetone blend system because the magnitude of different parameters' values increased with increase in PS contents of the blend and rise in temperature indicating increased strength of polymer-polymer interactions and hence enhancement in miscibility. The results of these parameters (ΔB, μ, and α) for the PS/PSAN/benzene system were more composition and almost temperature independent. The only disagreement observed between Chee (ΔB and μ) and Sun's (α) parameters in terms of the miscibility, for the PS/PSAN/benzene system, was for the composition, 70/30 at 20 °C. Similar disagreement were also observed by Jayaraju *et al.* and Varada *et al.* for chitosan/poly(vinyl pyrrolidone) and epoxy/unsaturated polyester resin, respectively[26, 27]. Since parameter, α, is more reliable than the parameters, ΔB and μ, and hence decision regarding miscibility of the composition, 70/30, at 20 °C was made on the basis of parameter, α[28]. The PS/PSAN/benzene blend system showed miscibility only for compositions, 30/70 and 50/50 at 30 °C and 40 °C. On the other hand, the same blend system showed immiscibility for compositions, 30/70, 50/50 at 20 °C only and for 70/30 at all the investigated temperatures. Though, the small magnitude of positive values of various parameters for both the blend systems indicate the weak nature of the secondary forces present between the blend components, but at the same time the relatively greater magnitude of positive values for the PS/PSAN/acetone blend system than the PS/PSAN/benzene blend system also confirm the impact of solvent on miscibility.
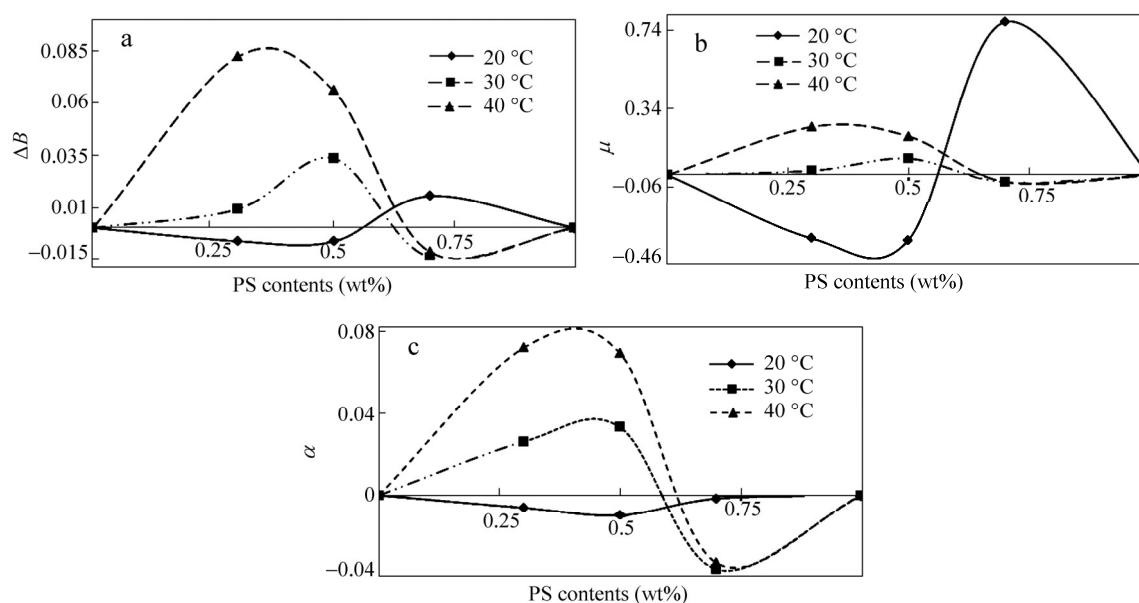

Fig. 4 (a–c) Plots of interaction parameters versus weight fraction of PS in PS/PSAN/benzene blends

For further confirmation, we measured refractive index and density of both the blend systems at various temperatures.

The variation of refractive index and density versus weight percent of PS in the PS/PSAN/acetone blend shows both linear and non-linear parts thereby confirming its partial miscibility. The variations are linear for the said blend system when PS contents are equal to or more than 50 wt% at all the investigated temperatures as shown in Figs. 5(a) and 5(b).
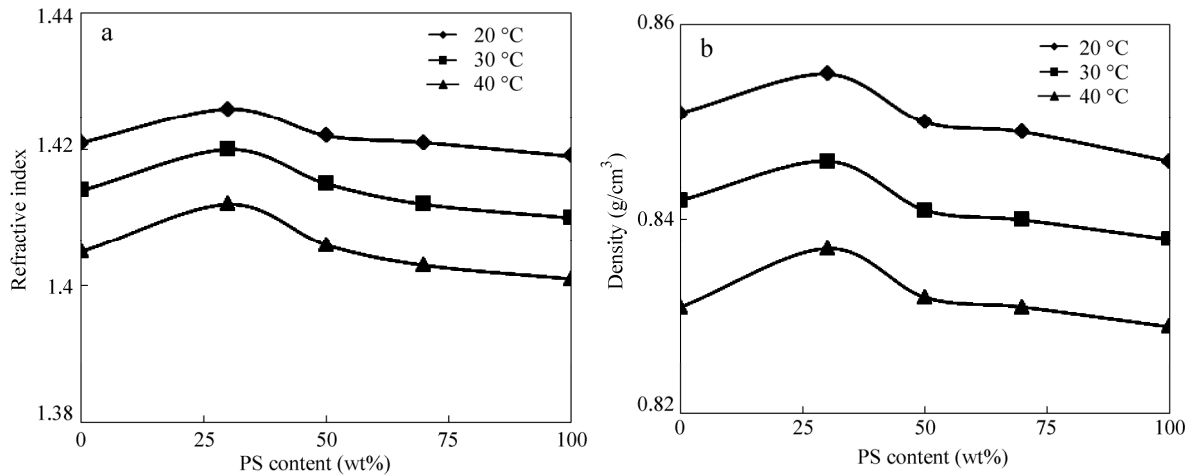
Fig. 5 Plots of refractive index (a) and plots of density (b) versus wt% of PS in PS/PSAN/acetone blends at various temperatures

These findings for the PS/PSAN/acetone blend system not only support the results of different interaction parameters but also indicate miscibility window for the said system.

On the other hand, the refractive index and density versus weight percent of PS in the PS/PSAN/benzene plots are non-linear indicating immiscibility of the said blend system (Figs. 6a and 6b), which seem to be in contradiction with the findings of various interaction parameters for the PS/PSAN/benzene blends.
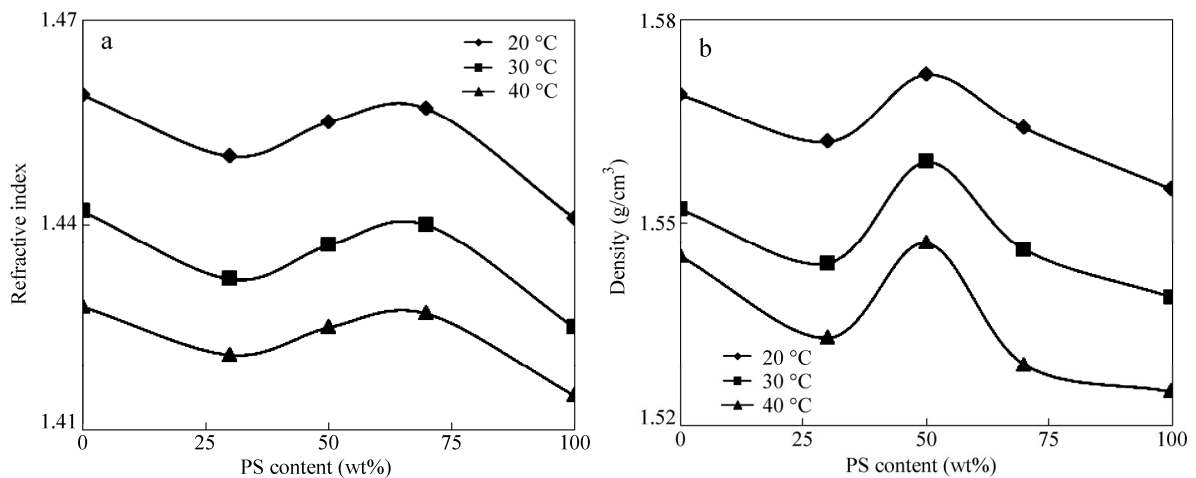

Fig. 6 Plots of refractive index (a) and plots of density (b) versus wt% of PS in PS/PSAN/benzene blends at various temperatures

Different viscometric parameters, though, indicate semi compatibility for the said blend system but to a very small extent due to very small magnitude of the positive values. Although, the density and refractive index results agree to some extent with those of Huggins' plots showing cross overs and hence immiscibility for the said blend system[25]. This contradiction in the results may be attributed to the very weak nature of interactions between the blend components in benzene. Acetone is, therefore, classified a better solvent than benzene, regarding miscibility of the PS/PSAN blend system.

CONCLUSIONS

The miscibility characterization of PS/PSAN blend in acetone and benzene was made at various temperatures by employing density, refractive index, and viscometric techniques. Variations in miscibility for both the PS/PSAN/acetone, and PS/PSAN/benzene blend systems were composition dependent though the effect of composition on the miscibility was totally different for both the systems. In the former case, the miscibility increased with the increase in PS contents whereas in the latter case it decreased with increase in PS contents of the blend. The results obtained through various physical techniques were almost in close agreement for the former system, whereas some disagreements were found regarding miscibility and/or immiscibility for the latter blend system. The study also revealed almost negligible effect of temperature over the miscibility. On the basis of these results, both the blend systems are classified as semi compatible, though semi compatibility was quite pronounced in PS/PSAN/acetone than PS/PSAN/benzene.

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