Compatibility Studies on Polystyrene and Poly-*n*-Butyl Methacrylate

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ABSTRACT: Polystyrene (PS) was a solution blended with poly-*n*-butyl methacrylate (PnBMA) at different compositions and the interactions between the two polymers were studied by using viscometry, ultrasound studies, and mechanical properties. All the properties show a characteristic variation in three stages. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2322–2330, 2002

Key words: compatibility; viscometry; ultrasound; mechanical properties

INTRODUCTION

Polymer blending is one of the most commercially significant areas for the development of new polymeric materials. The major advantage and usefulness of the blend is that it allows the manufacturers to respond more rapidly at a reduced cost to new market requirements. Properties of an existing blend are the function of the composition and it can be easily be modified to meet performance and cost objectives required by new or changing markets. Blends offer an improvement in processibility and performance.

Poly blends are physical mixtures of polymers and because the mixing of polymers is normally an endothermic process, the obtained poly blends are of a heterogeneous nature. Blending of two polymers usually leads to a class of materials whose properties are due to the presence of two phases or domains. The size of the domains that constitute the dispersed phase can vary in multiphase materials. If the polymers comprising the mixture have a strong affinity for one another, they will be compatible and mutually soluble.

Such mixtures form homogeneous poly blends, which have a single phase. The size and distribution of the phases determine the degree of compatibility. Although high compatibility is desirable for ease of blending, some degree of incompatibility often leads to useful properties. A completely homogeneous poly blend tends to average the properties of the two polymers comprising the polyblend in direct proportion to the volume fraction of each polymer blended, whereas a multiphase poly blend often provides a superior balance of useful properties. The ultimate goal of polymer blending is a practical one of achieving commercially viable polymers through either unique properties or lower costs than some other means might provide.

A basic understanding of the interactions between the materials will aid in the modification of the properties for specific application and also effectively reduce the cost. Development of newer properties depends on the degree of compatibility of the polymers at the molecular level. There have been various techniques, such as heat of mixing, glass transition temperature, morphology, and dynamic mechanical studies, for studying the miscibility of the polymer blend. Chee and Sun et al.[1,2] suggested the viscometric method to study polymer–polymer miscibility. The viscosity method

is simple and offers very useful information about the relationship between dilute solution properties and bulk structure of the polymer blend. The advantage of using ultrasound velocity[3–11] measurements for investigating polymer miscibility has been shown by many workers. The present investigation aims to understand the interactions between polystyrene (PS) and poly-n-butyl methacrylate (PnBMA) at various blend compositions by using viscometry and ultrasound studies of the blend solutions and the mechanical properties of the blend films.

EXPERIMENTAL

PS obtained from SISCO (India) was used in this study. The molecular weight of the sample was found to be 2.5×10^5. PnBMA was synthesized by emulsion polymerization technique. n-Butyl methacrylate (SD fine, India) (2 mole), sodium lauryl sulphate (0.25 g), and water (164 ml) were formed into an emulsion and potassium peroxy disulphate (Merck) (0.55 g) was used as initiator; the reaction was performed at 60°C. The polymer was precipitated by using brine solution, and then filtered, washed, and dried. The molecular weight of PnBMA was found to be 6.95×10^4. Analytic reagent (AR) grade toluene (Merck) was used as solvent for blending.

The blends of PS and PnBMA of different compositions (100 : 0, 90 : 10, . . . , 0 : 100) were prepared by mixing solutions of the polymers in toluene to obtain a 2% solution. The relative viscosities of the blend solutions were measured at 25 ± 0.5°C by using an Ubbelhode suspended level viscometer. The compatibility of binary blend systems was analyzed by using ultrasound technique. The ultrasonic velocity measurements were performed by pulse-echo method by using a MATEC MBS 8000 system (USA). The temperature was maintained at 25°C by circulating water from a thermostat with a thermal stability of ± 0.05°C through the double-wall jacket of the cell. The densities of the solutions were measured by using Hare's apparatus.

Blend solutions were cast on a mercury surface at 65% relative humidity (RH) and 25°C. Films thus obtained were carefully removed without prestretching. They were dried in vacuum and conditioned at 65% RH in a desiccator. Mechanical properties of the films were studied by using an Instron universal tensile testing machine

model 1112 at a temperature of 25°C with a strain rate of 0.5 min^{-1}.

RESULTS AND DISCUSSION

Viscosity Studies

The basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blend lies in the fact that while in solution, the repulsive interaction may cause shrinkage of the polymer coils, resulting in a change in the viscosity of the polymer components, on the assumption of additive law. On the other hand, attractive interactions increase the viscosity of the system.

Huggin's equation[12] expresses the specific viscosity as a function of concentration if one of the components is alone in solution,

$$\eta_{\text{sp}/C} = [\eta] + K^1[\eta]^2 C \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity, $\eta_{\text{sp}/C}$ is the specific viscosity at concentration C, and K^1 is the Huggin's constant.

If $K[\eta]^2 = b$, then eq. (1) becomes

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

where b is the interaction coefficient.

To analyze the viscosity behavior of binary polymer systems, Krigbaum and Wall[13] developed an equation which is used for ideal systems

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

where $\eta_{\text{sp},M}$ is the specific viscosity of the mixed polymer solution, $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of polymer I and II, and b_{11} and b_{22} are the specific interaction coefficients of polymer I and II.

Catsiff and Hewett[14] developed an empirical equation,

$$\eta_{\text{sp},M} = [C_1(\eta_{\text{sp}.1})_c + C_2(\eta_{\text{sp}.2})_c]/C \qquad (4)$$

where $(\eta_{\text{sp}.1})_c$ and $(\eta_{\text{sp}.2})_c$ are the specific viscosities of polymer I and II, respectively, at a concentration of $C = C_1 + C_2$. C_1 and C_2 are the concentrations of polymer I and II. For blend solutions, eq. (2) can be rewritten as

Table I b_{12} Values for PS–PnBMA System

Concn. (%)	Composition PS : PnBMA						
	90	80	70	60	50	40	30
0.1	−19.286	−4.954	0.872	−5.688	1.854	−0.812	2.170
0.2	−13.163	1.207	0.684	0.957	0.115	0.001	1.810
0.3	−2.615	−0.044	−0.693	0.375	0.414	0.064	0.664
0.4	−2.638	0.725	−0.453	0.439	0.206	0.391	0.772
0.5	−1.715	0.496	0.273	0.304	0.220	0.004	0.380

$$\eta_{sp,M} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \tag{5}$$

where

$$b_{12} = \sqrt{b_{11}b_{22}} \tag{6}$$

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

The value of b_{12} obtained according to eq. (6) is not valid for systems that have negative values for b_{11} or b_{22}. Williamson and Wright[15] modified the equation as

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

Compatibility of polymer mixture is characterized by a parameter Δb, which can be expressed as

$$\Delta b = b_{12} - b_{12}^* \tag{8}$$

where b_{12}^* is calculated from eq. (7).

Interaction coefficient (b_{12}) obtained for the mixture of PS and PnBMA for different compositions is presented in Table I. At very low concentrations (0.1%), both b_{12} and Δb (Table II) show negative values at all blend compositions except at 70 : 30 and 50 : 50, suggesting that there is a

change in interactions/phase at these compositions. With the increase of PnBMA in the blend, both b_{12} and Δb follow a specific pattern that is shown in Figures 1 and 2, respectively. Figures 1 and 2 show that the interactions between the PS and PnBMA change with composition specifically at 80 : 20 and 60 : 40, especially at low concentrations. The figures show that at 30 : 70 composition, the interactions are different from the others and take a positive value. The figures also suggest that from 60 : 40 to 40 : 60 compositions, the interactions present in PS–PnBMA are similar (Fig. 2).

Ultrasound Studies

The blend compatibility of PS : PnBMA under various compositions is analyzed on the basis of ultrasound analysis. The relation between composition, ultrasound velocity, and attenuation reflect whether the blend system is compatible, semi-compatible, or incompatible. The variation of velocity as a function of blend composition is presented in Table III. Even a small addition of PnBMA to PS drastically changes the velocity values. With an increase of PnBMA in the blend, the velocity initially decreases and then shows an increase at 60 : 40 composition and levels off. It was reported[16–19] in polymeric liquid blends that

Table II Δb Values for PS–PnBMA System

| Concn. (%)	Composition PS : PnBMA						
	90	80	70	60	50	40	30
0.1	−19.892	−5.560	0.267	−6.294	−1.249	−1.417	1.564
0.2	−13.769	0.601	0.079	0.352	−0.049	−0.605	1.204
0.3	−3.221	−0.649	−1.299	−0.231	−0.192	−0.542	0.059
0.4	−3.224	0.120	−1.059	−0.167	−0.400	−0.214	0.166
0.5	−2.321	0.110	−0.332	−0.302	−0.285	−0.602	−0.225
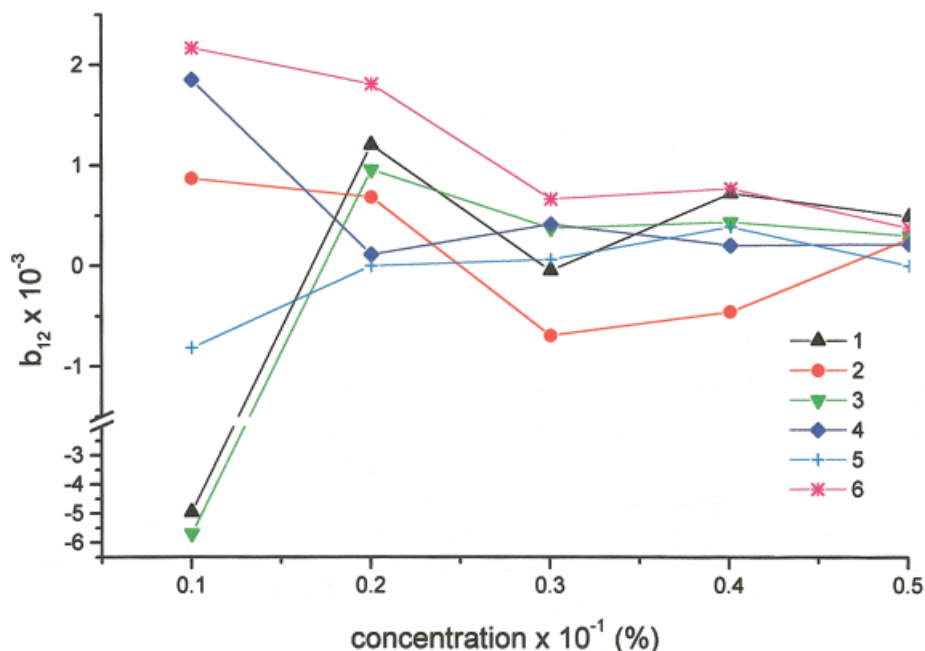
Figure 1 Effect of concentration of blend composition on b_{12}. 1, 80 : 20; 2, 70 : 30; 3, 60 : 40; 4, 50 : 50; 5, 40 : 60; 6, 30 : 70. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ultrasound velocity varies linearly with composition in compatible blends. In the case of incompatible systems, the nature of the curve is S type, and for semicompatible blends, the nature of curve is in between a straight line and an S type of curve.

The average attenuation for all combinations was related to blend composition and is presented
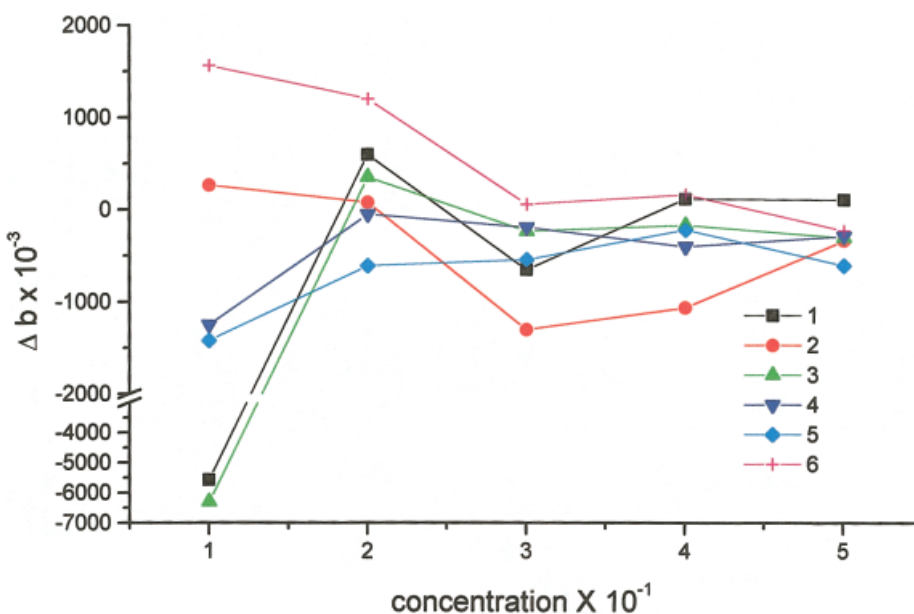
Figure 2 Effect of concentration of blend composition on Δb. 1, 80 : 20; 2, 70 : 30; 3, 60 : 40; 4, 50 : 50; 5, 40 : 60; 6, 30 : 70. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table III   Different Calculated Parameters from Ultrasound Studies

Composition PS : PnBMA	Ultrasound Velocity (m/s)	Viscosity (Poise $\times 10^{-2}$)	Density (g/cm^3)	Adiabatic Compressibility (cm^2/dyn $\times 10^{-11}$)	Intermolecular Free Length (cm $\times 10^{-9}$)
100 : 0	1328.8	3.405	0.9422	6.0108	4.8456
90 : 10	1300.1	3.367	0.9202	6.4293	5.0144
80 : 20	1308.4	3.189	0.9269	6.3021	4.9616
70 : 30	1299.4	3.037	0.9189	6.4453	5.0176
60 : 40	1313.8	2.822	0.8952	6.4717	5.0279
50 : 50	1300.8	2.607	0.8954	6.6002	5.0776
40 : 60	1306.4	2.265	0.9091	6.4451	5.0176
30 : 70	1307.2	2.088	0.9014	6.4923	5.0359
20 : 80	1304.2	1.924	0.9159	6.4189	5.0073
10 : 90	1306.7	1.772	0.9262	6.3232	4.9699
0 : 100	1300.2	1.632	0.9413	6.2842	4.9545

Composition PS : PnBMA	Acoustic Impedance ($\times 10^5$ rayls)	Molar Sound Velocity ($\times 10^3$)	Apparent Molal Compressibility ($\times 10^{-5}$)	Internal Pressure ($\times 10^{-14}$ atm)	Free Volume (ml mol^{-1} $\times 10^{-7}$)
100 : 0	1.252	4.906	15.296	3.570	7.692
90 : 10	1.196	4.987	13.377	3.687	7.837
80 : 20	1.214	4.962	13.004	3.654	8.583
70 : 30	1.194	4.993	9.645	3.689	9.140
60 : 40	1.176	5.144	8.757	3.561	10.374
50 : 50	1.165	5.126	7.948	3.633	11.511
40 : 60	1.188	5.056	6.874	3.630	14.306
30 : 70	1.178	5.101	6.360	3.610	16.178
20 : 80	1.195	5.016	5.671	3.656	18.227
10 : 90	1.210	4.963	5.095	3.662	20.681
0 : 100	1.224	4.875	4.628	3.729	23.224

in Figure 3. According to Singh et al.[19,20] and Sidkey et al.,[3,4] the presence of one maximum reflects the mutual solubility of components and the fact that they are compatible. The presence of more than one maximum indicates phase inversion, and consequently, the blend formed is incompatible. Arman et al.[21,22] have pointed out that bad adhesion between the matrix and the dispersed phase in the blends lead to high values of attenuation coefficient. The excess attenuation may be due to scattering of the waves by particles or by the presence of voids in the blends. In the case of PS–PnBMA blends, this may be the reason for a sudden increase in attenuation after 80 : 20 composition.

To understand more about the system, parameters such as free volume and internal pressure can be calculated by relating density, viscosity, and velocity of the blend solution. The results obtained on density and viscosity for different blend compositions are presented in Table III.

Viscosity decreases with the increase of PnBMA in the blend. Initially, the slope was higher (viscosity versus composition) and between 50 : 50 and 40 : 60 compositions, there is a sudden variation in property with a drastic decrease in viscosity values; the slope values are low after that composition. Density decreases with the increase of PnBMA, takes a minimum value at 60 : 40 and 50 : 50 compositions, and then increases when the PnBMA content is increased in the blend.

Adiabatic Compressibility

Adiabatic compressibility of the blend solution was calculated by using the formula

$$\beta_{ad} = 1/U^2\rho$$

where β_{ad} is the adiabatic compressibility, ρ is density, and U is the ultrasound velocity.
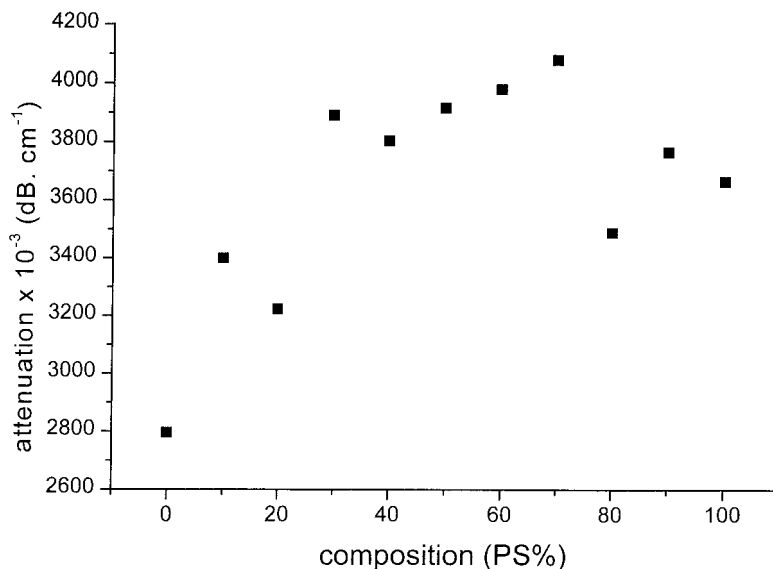
Figure 3 Effect of blend composition on attenuation.

In general, the trend followed with composition is similar to that of ultrasound velocity. The values increase until 50 : 50 composition and then decrease. The change in adiabatic compressibility with composition shows a sudden variation at 80 : 20 and 40 : 60 compositions. After 30 : 70 composition, the change in this property is less.

Intermolecular Free Length

Intermolecular free length was calculated by using the formula

$$L_f = K \sqrt{\beta_{ad}}$$

where β_{ad} is the adiabatic compressibility, and K is the Jacobson's constant (625×10^{-6} at 25°C).

With the increase of PnBMA, the intermolecular free length increases up to a composition of 50 : 50 and starts decreasing. This suggests that after 50 : 50 composition, there is a characteristic change occurring in the interactions between the polymers. The change in intermolecular free length with change in composition follows a trend similar to that of a change in adiabatic compressibility. It is interesting to note that, in general, the variation in magnitude of free length to adiabatic compressibility shows a change by a factor of 2.5. Both adiabatic compressibility and free length show a sudden variation in property at 60 : 40 and 40 : 60 compositions (Fig. 4).

Acoustic Impedance

The acoustic impedance is given by the relation

$$Z = U\rho$$

Acoustic impedance also follows a trend similar to the relation of adiabatic compressibility. Parameters, such as molar sound velocity, free volume, and internal pressure, of the blend solutions were calculated by using the interrelations between effective molecular weight, viscosity, density, and ultrasound velocity. The effective molecular weight of binary solution was calculated by using the theory of additive law.

Molar Sound Velocity

Molar sound velocity was determined by using the formula

$$R = (MU^{1/3})/\rho$$

where R is the molar sound velocity and M is the effective molecular weight.

Molar sound velocity was found invariable for unassociated liquids. For associated liquids, it depends on temperature. The results (Table III) show that with the increase of PnBMA in the blend, the value initially decreases up to 80 : 20 composition and then increases. Molar sound velocity show a higher change at 60 : 40 composition (change in molar sound velocity with change in composition), suggesting that there is an interchange of phases around this composition.

Apparent Molal Compressibility

Apparent molar compressibility was calculated by using the formula
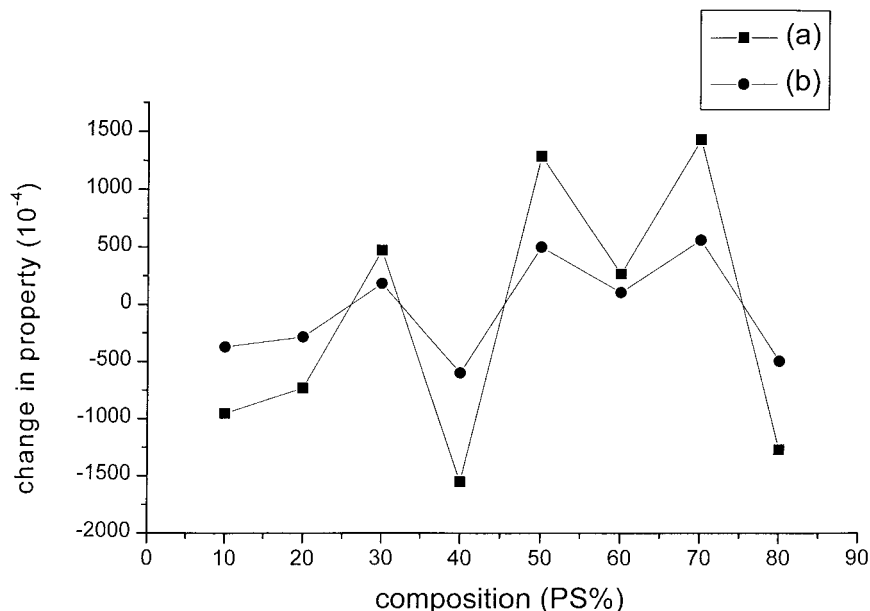
Figure 4   Effect of blend composition on the change in property (a) adiabatic compressibility and (b) intermolecular free length.

$$\phi_k = [1000(\beta\rho_0 - \beta_0\rho)]/\rho\rho_0 + (\beta M/\rho)$$

where β_0 is the adiabatic compressibility of solvent, ρ is the density of blend solution, ρ_0 is the density of the solvent, M is the effective molecular weight of solute, and β is the adiabatic compressibility of blend solution.

Apparent molal compressibility decreases with the increase of flexible polymer (PnBMA) whose T_g is less than room temperature. From 100 : 0 PS to 70 : 30, there is a gradual decrease in the value which shows that up to 70 : 30 PS forms a continuous phase. Apparent molal compressibility shows a very high change in value around 70 : 30 composition. After 70 : 30, possibly phase inversion takes place, showing a trend toward pnBMA which is evident from the values.

Free Volume and Internal Pressure

Free volume refers to the void space between the molecules (i.e., the volume present as holes of monomeric size) due to irregular packing of molecules. It may be defined as the average volume in which the central molecule can move inside the hypothetical cell because of repulsion of surrounding molecules. Free volume increases or decreases according to the packing of the molecules and the values reflect the variation in interactions between the polymers in a blend. Free volume and internal pressure can be calculated by using the formula,

$$V_f = (MU/K\eta)$$

$$\pi = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6})$$

where V_f is the free volume, π is the internal pressure, U is the ultrasound velocity, η is the viscosity of the blend solution, K is a constant (4.28×10^9) which is independent of the nature of the liquid, M is the effective molecular weight, b is the packing factor assumed as 2 in liquid systems and 1.76 for polymer solutions, R is the universal gas constant, ρ is the density of blend solution, and T is the temperature in Kelvin.

The obtained values of free volume and internal pressure are presented in Table III. In general, the internal pressure has an inverse relation when compared to change in free volume. From Table III, it is evident that the free volume initially decreases until 70 : 30 and after that there is a sudden change and the values increase, probably indicating phase inversion after 70 : 30. The free volume for 60 : 40 and 50 : 50 compositions show similar values which suggest that the spatial arrangements of the molecules is comparable at these compositions with increasing PnBMA content. The relation between change in free vol-

Table IV   Effect of Composition on Mechanical Properties of Blend Films

Composition PS : PnBMA	Stress at Break (σ_b) (Mpa)	Stress at Yield (σ_y) (Mpa)	Strain at Break (ε_b) (%)	Strain at Yield (ε_y) (%)	σ_y/σ_b	$\varepsilon_y/\varepsilon_b$
100 : 0	22.74	—	1.82	—	—	—
90 : 10	16.16	—	2.01	—	—	—
80 : 20	15.82	—	1.98	—	—	—
70 : 30	14.70	15.57	2.67	2.17	1.06	0.813
60 : 40	8.19	13.63	4.34	2.55	1.66	0.588
50 : 50	6.36	12.72	4.43	3.17	2.00	0.715
40 : 60	8.08	5.85	3.56	2.17	0.72	0.609
30 : 70	1.67	1.36	143.25	11.25	0.81	0.078
20 : 80	1.31	0.83	193.89	10.56	0.63	0.054
10 : 90	2.07	0.93	189.58	13.33	0.46	0.070
0 : 100	1.41	0.75	236.25	13.33	0.53	0.056

ume with change in composition clearly shows that after 50 : 50 composition there is a change taking place in the phases, and the free volume continued to show very high change above 40 : 60 composition. The variation of internal pressure with composition shows a trend similar to ultrasonic velocity. The internal pressure values between 50 : 50 and 40 : 60 are almost equal, suggesting that the molecular cohesion at these levels are the same, so also are the packing of the polymer chains.

It is possible that the attractive interactions are from the dipole-induced dipole interactions from carbonyl groups of the PnBMA and the phenyl ring. The studies suggest that the repulsion is more pronounced when PnBMA forms into continuous phase, as seen from free-volume values which are the reflection of voids present between the molecules.

Mechanical Properties

Mechanical properties of polymers largely depend on the molecular mobility of the polymer chains. The effect of composition on stress at break and strain at break of the films are presented in Table IV. The stress at break changes from 20.74 to 16.16 MPa by an addition of 10 wt % PnBMA. Between 90 : 10 and 70 : 30 compositions, the variation is minimal (Phase I). After 70 : 30 composition, the value drastically reduces from 14.2. to 8.2 MPa by the addition of 10% PnBMA. Between 60 : 40 and 40 : 60 compositions, the variation in stress at break is minimal (Phase II). In a similar manner, the value again reduces after 40 : 60 and is almost unaffected by the addition of PnBMA (Phase III). The effect of stress at break

and strain at break shows a behavior similar to that of the ultrasonic parameters, which was discussed earlier. The relation between stress at yield/stress at break and strain at yield/strain at break with composition is presented in Table IV. With the increase of PnBMA, (σ_y/σ_b) increases to a maximum and then decreases, whereas $(\varepsilon_y/\varepsilon_b)$ shows a slight decrease initially and then drastically changes after 40 : 60 composition. Comparison of these results with ultrasonic parameters clearly shows the starting and ending of the second phase on the basis of (σ_y/σ_b) and $(\varepsilon_y/\varepsilon_b)$.

Poor elongation and the strength properties are related to poor stress transfer between the phases of the immiscible blend. Better adhesion between ductile and brittle components normally improves ductility. Table IV shows that failure takes place by brittle mechanism in the blends up to 80 : 20 PS : PnBMA composition. In the phase transformation region, the failure takes place after the formation of neck and the (σ_y/σ_b) ratio increases because of variation in interface thickness and the influence of attractive interactions, which affect the mechanical properties.

The overall studies using interaction coefficient, ultrasound, and mechanical properties suggest that the PS–PnBMA system under different compositions show three stages of packing. Initially, PS acts as a continuous phase in which the PnBMA molecules are dispersed. The interactions between the polymer chains are not much modified with the addition of PnBMA in this region. In the second stage, the blends show similar results for parameters calculated on the basis of ultra-

sound technique. It suggests that in this region a uniform interpenetrating of the two polymers takes place.

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