Compatibility Studies of Solution-Blended Poly(acrylonitrile)/Poly(n-butyl methacrylate)

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SYNOPSIS

Poly(acrylonitrile) (PAN) was solution blended with poly(n-butyl methacrylate) (PnBMA) in various proportions. Compatibility in these blend systems was analyzed using ultrasound. The ultrasound velocity and attenuation results show that the two polymers formed a compatible blend. Viscosity and other derived parameters like free volume and internal pressure of the blends show that PAN form into an ideal blend with PnBMA in the compositions of 60 : 40 and 40 : 60. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer–polymer compatibility has received much attention because many polymer blends perform well in attractive new applications for which the individual polymer components are unsuited. Polymer blends refer to intimate mixtures of two or more structurally different polymers which interact through secondary forces.[1] The blends may be homogeneous or heterogeneous on a microscopic scale, but should not exhibit any obvious inhomogeneity on a macroscopic scale. The manifestation of superior properties depends on compatibility or miscibility of homopolymers at molecular levels. To be miscible, some attractions between the two polymers must be present to partially overcome the intramolecular cohesive forces of the individual polymer. The specific interactions capable of inducing polymer miscibility include dipole–dipole interaction, ion–dipole interaction, hydrogen bonding, acid-base reaction, charge transfer, etc.[2,3]

Compatibility of polymer blends can be examined with sophisticated experimental techniques.[4] Such techniques include studies of viscosities,[5] heat of mixing,[6–8] glass transition temperature,[2,9] mechanical properties,[10] and morphological studies.[11] More

recently, many workers[12–16] reported that the ultrasonic velocity measurements may reveal the extent of compatibility in highly viscous or solid-state polyblends. Ultrasonic attenuation was also used to predict the compatibility of polymers.[8,17,18] Schneider reported[8] that compatible polymer blends exhibit specific glass transition/composition behavior. Sidkey et al.[19,20] studied the degree of compatibility of the rubber blend solutions using ultrasonic methods. In this study, compatibility and other interactions in poly(acrylonitrile) (PAN) and poly(n-butyl methacrylate) (PnBMA) blends were studied in detail using ultrasound studies.

EXPERIMENTAL

The monomers AN and nBMA (BDH) were freed from inhibitors and dried over anhydrous sodium sulphate. The monomers were finally vacuum distilled, and the middle fraction of the distilled monomers was used for the experiments.

POLYMERIZATION

Polymerization was done using emulsion polymerization technique in nitrogen atmosphere. The reaction was performed at 60°C with potassium persulphate as the initiator. The reaction was allowed to continue for 6 h. The polymer was precipitated

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using saturated sodium chloride solution, filtered, washed with water, and dried in vacuum.

Molecular Weight Determination of the Polymers

Viscosity average molecular weight of the polymers was determined from the viscosity measurements using Ubbeholde viscometer. DMF was used as a solvent for PAN and acetone for PnBMA. From the flow time of solvent and polymer solution, the molecular weight was calculated using the Mark–Howunik equation[21]

$$[\eta] = KM^a$$

where $[\eta]$ = intrinsic viscosity of the solution, and K and a are constants for the polymer/solvent system.

Solvent Blending

This process involves dissolving of homopolymers in a mutual solvent. A single-solvent blending system was not possible in the blending of PAN–PnBMA; therefore, a mixture of two solvents was used. The solvents[22] used were DMF and butyl methyl ketone (BMK) for PAN and PnBMA, respectively. Known quantities (by weight) of the two polymers were dissolved using 8 : 2 mixture of DMF and BMK. The prepared solutions were of 2% concentration. Pure PAN and pure PnBMA were prepared by dissolving the polymers in DMF and BMK, respectively.

Analysis of PAN–PnBMA Blends

The compatibility of the PAN–PnBMA blend system was analyzed using ultrasound. Compressional ultrasonic velocity measurements were performed on blend solutions using an echo-pulse technique with the MATEC MBS-8000 measurement system. Measurements were carried out at 2 MHz; velocity measurements were accurate to ±0.5%.

Density and Viscosity Measurements

The densities of the blend solutions (2%) were measured using a pyknometer. All density measurements were measured accurately to four decimal places. Viscosity of the blend solutions was determined using a Ubbelhode viscometer. The flow times of the blend solution and DMF : BMK (8 : 2) mixture were determined, and from these data, the relative viscosity of the system was calculated.

RESULTS AND DISCUSSION

The manifestation of superior properties depends on compatibility or miscibility of homopolymer at molecular levels. Depending on the degree of molecular mixing, the blends may be categorized as totally miscible (compatible), semimiscible (semicompatible), or immiscible (incompatible). The compatibility of the polymers in a polyblend is important because it decides the microdomain structure of the blends, which in turn decides the properties, especially the mechanical properties.

The molecular weight of PAN and PnBMA homopolymer was determined using viscometry. From the flow time, the specific viscosity was calculated. The relationship between η_{sp}/C vs concentration for PAN and PnBMA were shown in Figures 1 and 2, respectively. The intercept gave the intrinsic viscosity at infinite dilution, and the molecular weight was determined for both polymers (Table I).

Ultrasound Testing

Ultrasound velocity and attenuation show whether the blend system is compatible or not. Therefore, a thorough study was made in which the ultrasonic velocity and attenuation for different compositions were measured. The variation of velocity and attenuation as a function of composition is presented in
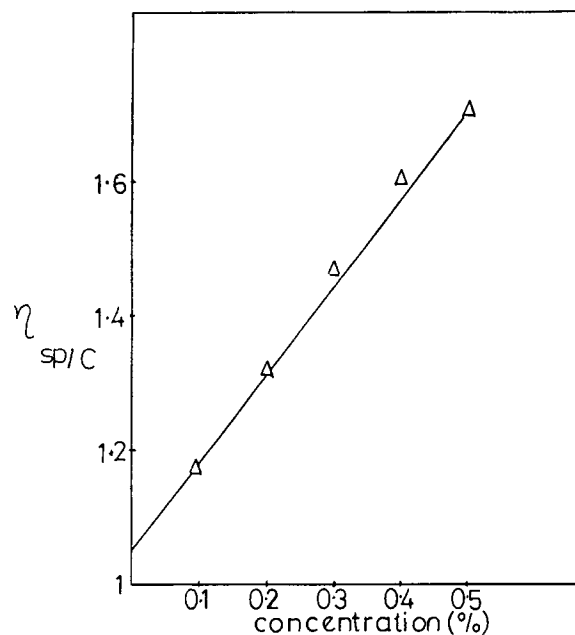

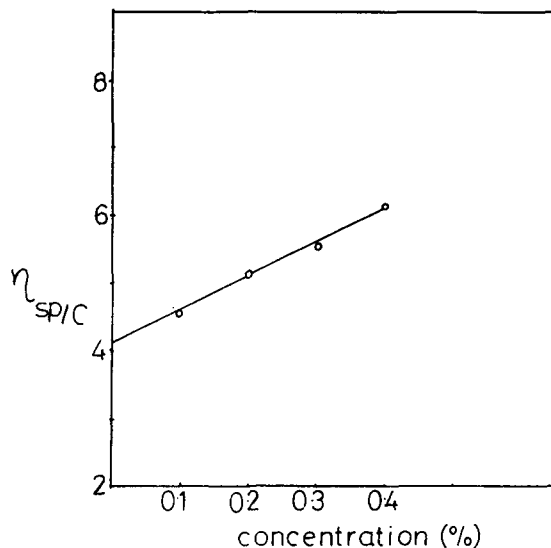**Figure 1** Relation between η_{sp}/C vs. concentration of PAN in dimethyl foramide.

Figure 2 Relation between η_{sp}/C vs. concentration of PnBMA in acetone.

Table I Molecular Parameters of the Polymers

	PAN	PnBMA
Intrinsic viscosity	4.10	1.05
Constants		
$K \times 10^{-5}$	20.90	18.40
a	0.75	0.62
Molecular weight $\times 10^{-5}$	5.30	11.43

position curve is the "S" type. For the semicompatible systems, the nature of curves is in between the straight line and "S" type of curve. The same behavior has been shown by the solution viscosities of the blends.[29] The linear and nonlinear relation of velocity with composition may be attributed to the voids present in the systems, which play a role in deciding the viscosity of the solution. The linear variation of velocity with composition depicts a single-phase morphology due to polymer–polymer miscibility or compatibility.

The average attenuations for all the combinations are given in Table II. Similar to ultrasonic velocity, there is a drastic decrease in attenuation due to the addition of PnBMA. The variation of ultrasonic attenuation/unit length with composition is shown in Figure 4. Figure 4 shows that with the increase of PnBMA content, the attenuation value decreases to a level of 3.0/unit thickness. It can be seen that after 60 : 40 (PAN–PnBMA) composition, the value suddenly increases to a maximum and then levels off. According to Singh et al.[13] and Sidkey et al.,[19,20] the presence of one maximum reflects the mutual solubility of components, and they are compatible.

Table II. The ultrasonic velocity values for pure PAN and pure PnBMA homopolymers were 1527 and 1222 m/sec, respectively. Even a small addition of PnBMA to the system changes the velocity drastically. On the other hand, the velocity increases when a small quantity of PAN is added to pure PnBMA and the value changes from 1222 to 1413 m/sec for 2 : 8 polymer (PAN : PnBMA).

The ultrasound velocity varies linearly with PAN–PnBMA composition (except 70 : 30), as is shown in Figure 3. It was reported[19,20,23–28] that ultrasonic velocity varies linearly with composition in *compatible* blend systems, but in cases of *incompatible* blend systems, the nature of velocity vs composition

Table II Velocity, Attenuation, Density, and Viscosity Data Obtained for PAN/PnBMA Blends

| Composition		Velocity cm/sec 10^5	Attenuation (dB)	Density	Viscosity (Poise)	Adiabatic Compressibility (dB $\times 10^{-11}$)
PAN (%)	PnBMA (%)					
100	0	1.5274	11.533	1.1265	86.9	3.8047
90	10	1.4233	9.867	0.9034	44.2	5.4638
80	20	1.4200	9.617	0.9318	30.5	5.3219
70	30	1.4132	8.915	0.9169	27.4	5.4605
60	40	1.4177	8.889	0.9077	21.6	5.4809
50	50	1.4161	9.865	0.9047	19.9	5.5116
40	60	1.4156	8.872	0.9091	19.2	5.4881
30	70	1.4167	9.114	0.8974	10.7	5.5511
20	80	1.4137	12.495	0.9083	4.3	5.5079
0	100	1.2223	13.363	1.1231	1.9	5.9588
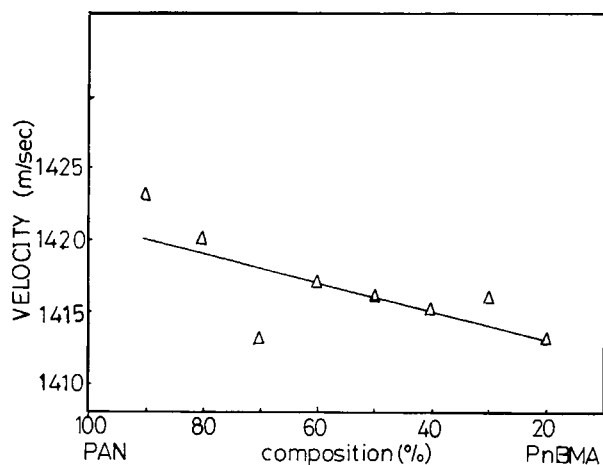
Figure 3   Effect of blend composition on ultrasonic velocity.

They also reported that the presence of more than one maximum indicates phase inversion and, consequently, an incompatible blend system. Arman et al.[17,30] have pointed out that bad adhesion between the matrix and dispersed phase in blends leads to high values of attenuation coefficient. Therefore, the excess attenuation values obtained after 60 : 40 composition may be attributed to a scattering of the waves by particles or by the presence of voids in the blends. Arman[30] theoretically calculated the excess attenuation over the linear dependence on the basis of the presence of voids at the interface between the two phases of blends, which was in turn evaluated in terms of measured decrease of average density of the blend samples.[31] Figure 4 also suggests that the PAN-PnBMA form into a compatible blend, and the blend structure (morphology) is probably the same in 60 : 40 and 50 : 50 combinations.

To have more insights into the system, parameters such as free volume, internal pressure, etc., were calculated by relating density, viscosity, and velocity of the blend solutions. The variation of viscosity with blend composition is presented in Table II. The results show that at room temperature, an increase of PnBMA content in blend composition decreases the viscosity; after 60 : 40 composition, there is no characteristic change in the viscosity values. After that point, the rate of decrease is very high, from 40 : 60 composition. The viscosity results reveal that it is highly probable that between 60 : 40 and 40 : 60 compositions, the interactions between the polymers are similar and, therefore, similar packing. The variation of density with blend composition is similar to that of viscosity change.

Viscometry becomes an attractive method for studying the compatibility of polymers in solution.[32-34] These studies also provide useful information regarding stereocomplex formation between the two polymers.[35-37] The theoretical consideration starts from the derivation by Krigbaum and Wall.[38] The specific viscosity, $\eta_{sp,m}$, of the mixed-polymer solution can be expressed as follows

$$\eta_{sp,m} = [\eta_1] C_1 + [\eta_2] C_2 + b_{11} C_1^2$$
$$+ b_{22} C_2^2 + 2b_{12} C_1 C_2 \quad (1)$$

where $[\eta_1]$ is the intrinsic viscosity of component 1 (PAN) alone in solution and $[\eta_2]$ is the intrinsic viscosity of component 2 (PnBMA) in solution. C_1 and C_2 are the concentrations of component 1 and 2 in mixed polymer solution, respectively, and b_{12} is the interaction coefficient for the mixture of components 1 and 2.

Polymer blends with different PAN and PnBMA compositions were prepared in a solvent mixture containing DMF and BMK in the combinations of 8 : 2 (v/v). The specific viscosity of the blend solutions was determined (Fig. 5). The intrinsic viscosity at infinite dilution was determined for PAN and PnBMA solutions (PAN and PnBMA in 8 : 2 DMF and BMK). From viscosity data, the interaction parameter b_{12} of PAN and PnBMA was calculated. The variation of b_{12} values with blend concentration was presented in Figure 6. Figure 6 shows that the interaction between PAN and PnBMA at 60 : 40 and 40 : 60 compositions is similar, and forms
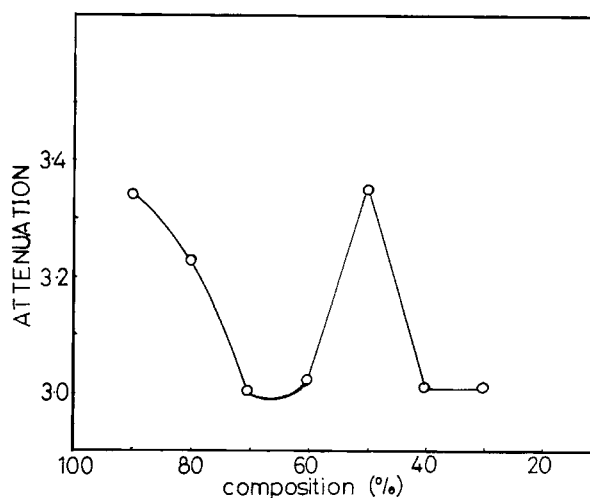

Figure 4   Effect of blend composition on attenuation per unit thickness.
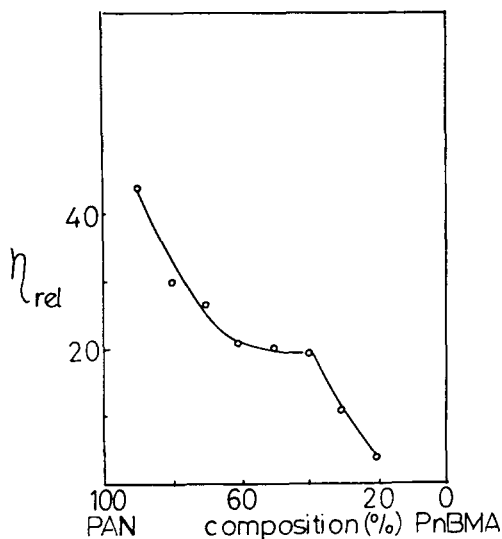
Figure 5 Effect of blend composition on viscosity of the blend solutions.

a group. In the case of 80 : 20 and 70 : 30, b_{12} values are higher and the relation between concentrations is different from the relation obtained for 60 : 40 and 40 : 60 compositions.

Adiabatic Compressibility

The adiabatic compressibility was calculated using the equation of Newton and Laplace[39]

$$\beta_{ad} = 1/U^2d \qquad (2)$$

where

β = adiabatic compressibility
U = ultrasound velocity of the blend
d = density of the blend

Adiabatic compressibility data follows (Table II) a trend similar to that of velocity data, and the results suggest that the system is compatible as reported by Sidkey et al.[20]

Intermolecular Free Length

The intermolecular free length which was calculated using the formula

$$L_f = K\beta_{ad} \qquad (3)$$

Intermolecular freelength shows a linear relationship with composition (Table III) of the blend. In

this equation, K is the Jacobson's constant,[40] having a value of 625×10^{-6} at 25°C.

Acoustic Impedence

The acoustic impedance is given by the relation

$$Z = Ud, \qquad (4)$$

where

Z = acoustic impedance
U = velocity
d = density

The results obtained are presented in Table III. The values decrease because of the addition of PnBMA. The addition of PnBMA does not alter the acoustic impedance much between 60 : 40 and 40 : 60 compositions, suggesting that the material does not undergo any significant change in structure in this range.

Molar Sound Velocity

Molar sound velocity was determined using the formula
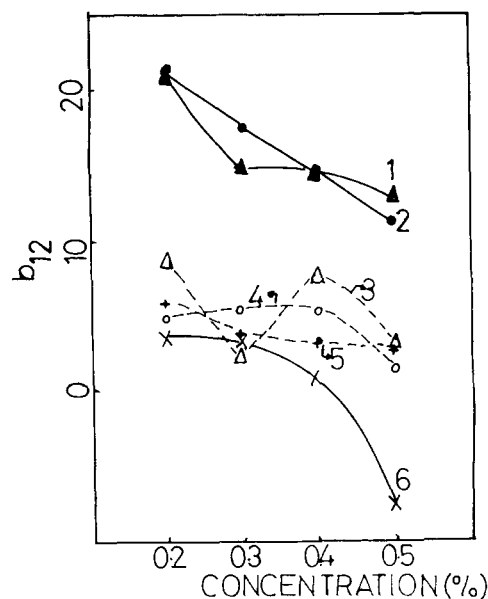
$$R' = MU^{1/3}/d \qquad (5)$$

Figure 6 Effect of concentration on polymer interaction parameter (b_{12}) (PAN : PnBMA). (1 = 80 : 20; 2 = 70 : 30; 3 = 60 : 40; 4 = 50 : 50; 5 = 40 : 60; 6 = 30 : 70.)

Table III   Parameters Calculated Using Velocity, Density, Molecular Weight, and Viscosity of Blend Solutions

Composition		Acoustic Impedance $\times 10^5$	Free Length $\times 10^{-9}$	Molar Sound Velocity $\times 10^3$	Free Volume (mL/mol) $\times 10^{-8}$	Internal Pressure $\times 10^5$
PAN (%)	PnBMA (%)					
100	0	1.7206	3.8551	3.5696	0.5767	4.6261
90	10	1.2858	4.6198	4.3485	1.4315	2.9491
80	20	1.3232	4.5595	4.2129	2.4867	2.5048
70	30	1.2958	4.6184	4.2743	2.8946	2.3558
60	40	1.2869	4.6271	4.3222	4.1476	2.0756
50	50	1.2811	4.6400	4.3352	4.9700	1.9871
40	60	1.2871	4.6301	4.3133	4.9700	1.9562
30	70	1.2715	4.6566	4.3706	11.9088	1.4493
20	80	1.2842	4.6384	4.3152	45.9871	93.0187
0	100	1.3728	4.8246	3.2660	126.6400	76.5253

where M = effective molecular weight and R' = molar sound velocity, also known as Rao's constant.

For calculating the effective molecular weight of blend solution, the theory of additivity (which is used in binary mixtures) was used.

$$M_{eff} = (X_3 \times M_{eff}(\text{solute})) + (X_4 \times M_{eff}(\text{solvent}))$$

where X_3 — mol fraction of solute; X_4 — mol fraction of solvent

$$X_3 = N_3/(N_3 + N_4)$$
$$X_4 = N_4/(N_3 + N_4)$$
$$N_3 = \text{weight of polymer (PAN} + \text{PnBMA)}/M_{eff} \text{ (solute)}$$
$$N_4 = \text{weight of solvent}/M_{eff} \text{ (solvent)}$$
$$M_{eff} \text{ (solute)} = (X_1 \times M. \text{ weight of PAN}) + (X_2 \times M. \text{ weight of PnBMA})$$

Mol fraction of PAN $(X_1) = N_1/(N_1 + N_2)$
Mol fraction of PnBMA $(X_2) = N_2/(N_1 + N_2)$

where N_1 and N_2 are the weight fractions of PAN and PnBMA, respectively. Weight fraction of PAN = weight of PAN/M. weight of PAN. In a similar way, M_{eff} of solvents were also calculated for DMF + BMK (8 : 2) mixtures.

From molar sound velocity results (Table III), one can see that there is an increase in Rao's constant with the increase of PnBMA. As in other parameters, there is no characteristic change between 60 : 40 and 50 : 50 PAN–PnBMA combinations.

Free Volume

Free volume refers to the void space between the molecules, i.e., the volume present as holes because of irregular packing of the molecules. It may be defined as the average volume in which the central molecule can move inside the hypothetical cell due to repulsion of surrounding molecules. The free volume[25] was determined by using the formula

$$V_f = M_{eff}U/K\eta \qquad (6)$$

M = effective molecular weight
η = viscosity of the blend solution in poise
K = a constant (4.28×10^9) which is independent of the nature of the liquid
U = ultrasound velocity

The free volume data (Table III) suggest that with increasing PnBMA content, the free volume increases; this suggests that the blend–solvent interactions increase with an increase in composition. In this study, the concentration of the solution for all the blends was kept constant (2%). Therefore, the changes that can be seen in this property can possibly be attributed to the interaction of blends. This suggests that the complex formation results in a more compact structure, leading to greater free space between the molecules. Like other properties, the rate of change of free volume is less between 60 : 40 and 40 : 60 (PAN–PnBMA) combinations. The dependence of free volume from the average values probably comes mostly from the viscosity term, since

the M_{eff} and velocity are almost linear with blend composition. The interaction parameter b_{12}, discussed earlier, has shown that the interactions between the polymers are drastically changed after 70 : 30 composition. This will be mainly reflected in viscosity and density values of the solution. Although the variation of velocity with composition is linear, the value gradually decreases, and there is a sudden change in velocity, around 70 : 30 composition. The velocity of the solution depends on viscosity and density to a great extent. Therefore, free volume values obtained for blend solutions primarily depend on the viscosity of the solution. The morphological and mechanical strength studies[41] have confirmed that the structure formed by blends between 60 : 40 and 40 : 60 compositions have similar packing. Between these combinations, the blend films show agglomerate structure. The interspacing between the agglomers increases between 60 : 40 and 40 : 60 (increasing PnBMA). At 70 : 30 composition, the blend films show maximum strength and extension at break.

The free volume of pure PnBMA is 1.26×10^{-6} mL/mol, and that of pure PAN is 5.67×10^{-9} mL/mol. The higher value of PnBMA shows that it has good interactions with the solvent. Because of the interaction, there is a marked increase in the free volume from the 60 : 40 combination PnBMA.

Internal Pressure

Suryanarayana[42] introduced a new general formulation based on dimensional analysis to evaluate internal pressure using ultrasound velocity:

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

where

b = the packing factor is assumed as 2 in liquid systems and 1.76 for polymer solutions
R = universal gas constant
T = absolute temperature
K = a constant of value 4.28×10^9
η = viscosity in poise
M_{eff} = effective molecular weight of the blend solution
d = density of the blend solution

The internal pressure values obtained are presented in Table III. The results show a reverse trend of free volume as expected, which suggests that the components prevent the close packing of the polymer chains, reducing the molecular cohesion (polymer–polymer interactions and polymer–solvent interactions).

When PnBMA is added to PAN, the internal pressure shows a decreasing trend toward PnBMA. The possible reason for this is that the interaction in PnBMA is high, which increases the free volume, and this in turn reduces internal pressure. The results also show minimal variation in 60 : 40, 50 : 50, and 40 : 60 (PAN–PnBMA), suggesting that there is little variation in interactions in these combinations. This also shows that these combinations form into blends having a similar structure, when compared to other combinations.

CONCLUSIONS

The interactions and miscibility between PAN and PnBMA were studied using ultrasound techniques. The polymers were solvent-blended. The velocity and attenuation results of the blend solutions suggest that the two polymers form a miscible structure. Viscosity, density, and other parameters also show that the system forms a structure having similar packing of polymers between 60 : 40 and 40 : 60 compositions.

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