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# New Method of Determining Miscibility in Binary Polymer Blends Through Hydrodynamic Interaction: The Free Volume Approach

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Received 4 July 2007; accepted 6 June 2008

DOI 10.1002/app.29046

Published online 10 October 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new method has been developed to determine the probability of miscibility in binary polymer blends through hydrodynamic interaction. This is achieved by the measurement of the free volume content in blends of carefully selected systems—styrene acrylonitrile (SAN)/poly(methyl methacrylate) (PMMA), PMMA/poly(vinyl chloride) (PVC), and PVC/polystyrene (PS)—with positron annihilation lifetime spectroscopy. The free volume content can predict the miscible/immiscible nature of the blends but provides no information on the extent of miscibility for different compositions of the blends. We have generalized a model used to understand the viscometric behavior of polymer/solvent systems to polymer/polymer systems through the free volume approach. This model provides two important parameters: a geometric factor ( $\gamma$ ) and a hydrodynamic interaction parameter ( $\alpha$ ).  $\gamma$  depends on the molecular architecture, whereas  $\alpha$  accounts for the

excess friction at the interface between the constituents of the blend, and we propose that  $\alpha$  can serve as a precursor to miscibility in a system and indicate which composition produces a high probability of miscibility. The efficacy of this proposition has been checked with measured free volume data for the three blend systems. The SAN/PMMA system produces a maximum  $\alpha$  value of  $-209$  at 20% PMMA; PVC/PMMA produces a maximum  $\alpha$  value of  $-57$  at 10% PMMA. Interestingly, for the PS/PVC system,  $\alpha$  is close to zero throughout the entire concentration range. Therefore, we infer that  $\alpha$  is perhaps an appropriate parameter for determining the composition-dependent probability of miscibility in binary blend systems. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 577–588, 2009

**Key words:** blends; interfaces; microstructure; miscibility; voids

## INTRODUCTION

Complete miscibility is a rare phenomenon when a mixture of two or more systems is made. This is particularly true in the case of polymers because of their complex structures and relatively small entropy of mixing. Therefore, the study of miscibility in polymer blends has been pursued with great interest both theoretically and experimentally in the last few decades.<sup>1,2</sup> A number of thermodynamic theories have been proposed to study the miscibility in polymer blends, but to date, they have had limited success in predicting miscibility behavior in detail at the microscopic level.<sup>3</sup> This is mainly due to the fact that miscibility is governed by several factors, including intermolecular interactions such as dipole–

dipole interactions, hydrogen bonding, charge-transfer interactions, and intramolecular repulsive forces. In addition to these factors, the molecular weights and viscosities of the component polymers also influence the mixing to a large extent. Therefore, it is difficult for any model to take into account all these factors to predict miscibility. Also, in certain cases, more than one interaction is involved in driving the system to miscibility. In such situations, understanding the resultant interaction becomes difficult. However, it is clear that whatever the nature and number of the interactions may be, they certainly contribute to the mixing process and final equilibrium state of the attained mixture.

The glass transitions of polymers and polymer blends are expected to depend on well-known factors such as the chain structure, conformation, degree of crystallinity, and dispersion.<sup>4</sup> The glass transition is not a true phase transition, but above this transition, frozen chain segments are unfrozen. Hence, in the case of miscible blends, a single composition-dependent glass-transition temperature is expected to reflect the mixed environment of the blend, whereas immiscible blends generally exhibit two glass transitions characteristic of each phase in the

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Contract grant sponsor: Department of Science and Technology, Government of India (through a junior research fellowship to G.N.K.); contract grant number: SP/S2/M-18/2000.

binary mixture. However, this method is of limited use when the glass transitions of the component polymers of the blend are close to one another, with the result that they cannot be adequately resolved.<sup>2</sup>

Viscosity is considered an important property in understanding the viscoelastic behavior of polymers under stress and strain.<sup>5</sup> The flow behavior of polymer mixtures, mainly polymer/solvent systems, has been studied with various theories in the past. Two such theories dealing with the flow behavior of polymer mixtures have been proposed, one by Rouse<sup>6</sup> based on the works of Kargin and Slonimsky and called the Kargin–Slonimsky–Rouse (KSR) model and the other by Zimm<sup>7</sup> based on the works of Kirkwood and Risemann and called the Kirkwood–Risemann–Zimm (KRZ) model.

The KSR model assumes polymer molecules as a set of identical elements (segments) connected in series, each of which is deformed independently of the others, and the condition of continuity of the chain is provided by the connectivity of the segments. Furthermore, it assumes that the viscoelastic properties of all segments are identical. Moreover, each segment in the polymer chain is considered a bead connected linearly, and the macromolecular coil does not disturb the flow rate. This means that the coil is absolutely permeable to the stream and does not introduce perturbation to the motion of the medium. The KRZ model is the next step in theoretical conceptions of the KSR model. The substantial new point in the KRZ theory is the consideration of the hydrodynamic interaction between separate segments in the polymeric chain. The calculations of the KRZ model account for the perturbation of the flow field rates caused by the presence of foreign bodies. In principle, two extreme cases are possible. In the first, the polymeric chain does not give rise to perturbations to the flow rate; that is, no hydrodynamic interaction is present. This limiting case is the KSR model itself. In the other case, the space occupied by macromolecules is found to be impermeable to the solvent, and this corresponds to the maximum possible hydrodynamic interaction.

Recently, Schnell and Wolf<sup>8,9</sup> provided an elaborate discussion on the effect of the hydrodynamic interaction in various polymer/solvent systems based on these two theories. This theory introduces two parameters, a hydrodynamic interaction parameter ( $\alpha$ ) and a geometric factor ( $\gamma$ ), both of which are evaluated with viscometric data to understand the role of this interaction in the system of their study. The  $\gamma$  parameter is expected to depend on the molecular surfaces and volumes in the system, whereas  $\alpha$  is a measure of friction between the constituents of the blend. Experimentally, they showed that  $\alpha$  varies as the friction between the constituents changes. Therefore,  $\alpha$  is a measure of the deviation of friction

between the surfaces of the components from ideality. Schnell and Wolf advocated that the preference of contacts between molecules of component 1 (solvent) and component 2 (polymer) leads to a reduction of intermolecular friction due to an increased tendency of the unlike molecules to move conjointly. In other words, if there exists an interaction between the solvent molecules and polymer segments, the friction between them is less as they move cooperatively, leading to smaller negative values of  $\alpha$  and vice versa. If this concept is extended to polymer/polymer mixtures, a different situation arises. The flow mechanism of such systems may change from nondraining (nondeformation state) behavior at a low composition of one polymer (say 1) to a fully draining state (deformation state) at a high composition of the same polymer component. Entanglements between chains of a high-molecular-weight polymer modify the flow behavior, which might lead to additional friction. The intermolecular interaction adheres one polymer chain to a number of chains of the other polymer at the segmental level, and this corresponds to a three-dimensional network picture. The number of contacts being greater, the energy dissipation at the interfaces also becomes high, with the result that each chain experiences a greater amount of friction resulting in large negative values for  $\alpha$ , which is especially the situation for miscible blends.

In this study, we have made an attempt to generalize Schnell and Wolf's theory to polymer/polymer blend systems with a particular emphasis on understanding the miscibility level of binary polymer blends through  $\alpha$ . The idea is that this interaction could be used to understand the changes at the interface in both miscible and phase-separated blends. In doing so, we have used free volume data of the studied systems in place of viscometric data, unlike Schnell and Wolf, to evaluate  $\alpha$ . Positron lifetime measurements have been carried out at room temperature, which is below the glass-transition temperature of all the systems under study, to measure the free volume. This means that we are dealing with a nonequilibrium situation. This fact does not necessarily devalue our discussion in terms of the free volume of the systems. In a recent work,<sup>9</sup> Schnell and Wolf clearly demonstrated that this theory works equally well for temperatures below and above the glass-transition temperature, thus validating our approach. To check the efficacy of this generalization, we have carefully selected three blend systems; each one is an example of the three known varieties of blends: miscible blends, partially miscible blends, and immiscible blends. The three selected blend systems are styrene acrylonitrile (SAN)/poly(methyl methacrylate) (PMMA), PMMA/poly(vinyl chloride) (PVC), and PVC/polystyrene

(PS), of which the first one is miscible,<sup>10,11</sup> the second is partially miscible,<sup>12,13</sup> and the third is immiscible.<sup>2</sup> Because of its conceptual simplicity, free volume theory is widely used in polymer science for understanding many polymer properties at the molecular level. In the case of miscible blends, usually a reduction in the free volume is observed versus that predicted by a simple additivity rule, which corresponds to a negative change in volume due to favorable interactions between the blend components.<sup>1,14,15</sup> A positive deviation from the additivity rule corresponds to an immiscible blend. Therefore, studies on microscopic free volume holes have been successfully used in recent times for determining whether blends are miscible or immiscible at the molecular level. This work extends the free volume data measured from positron annihilation lifetime spectroscopy to determine the hydrodynamic interaction for the first time to understand the composition-dependent miscibility level in polymer blend systems. Positron annihilation lifetime spectroscopy has been a versatile tool for free volume studies in polymers for decades<sup>16–19</sup> and recently has been used for polymer blends<sup>20–24</sup> as well. A brief description of positron annihilation and the lifetime technique used is provided in the Experimental section. We have also used differential scanning calorimetry (DSC) to measure the glass-transition temperatures of the blends and constituent polymers to supplement the positron data.

## EXPERIMENTAL

### Blend preparation

Samples of SAN (with 25 wt % acrylonitrile), PMMA, and PS, which had densities of 1.08, 1.20, and 1.04 g/cc and weight-average molecular weights of 165,000, 15,000, and 190,000 g/mol, respectively, were procured from M/s Sigma–Aldrich Chemicals, Ltd. (Bangalore Branch, India) With these samples in their as-received condition, the blends were prepared by the conventional solution-casting method. The weighed fractions of SAN and PMMA were dissolved in tetrahydrofuran at 60°C in different proportions (90/10, 80/20, 70/30, ... 10/90), and the solution was cast onto a clean and flat glass plate. After the solvent was allowed to evaporate at room temperature, the films were lifted from the glass plate. The neat films so obtained were approximately 1 mm thick. Similarly different proportions of PMMA and PVC (molecular weight = 43,000 g/mol and density = 1.34 g/cc; also obtained from M/s Sigma–Aldrich Chemicals) and PVC and PS were dissolved in tetrahydrofuran and methyl ethyl ketone, respectively, and blends of different weight concentrations were prepared by the casting of the solution onto a clean glass plate as stated previously.

The SAN/PMMA and PMMA/PVC blend samples were observed to be optically transparent at all concentrations, but the PVC/PS samples were opaque throughout the concentration range. The blend samples so prepared were vacuum-dried at 70°C for about 10 h to remove the residual solvent. All the samples were stored in a desiccator before actual use in experiments.

### DSC measurements

The glass-transition temperature of the homopolymers and blends were measured with a Universal V3.0G TA Instrument DSC 2010 (Wisconsin, USA) connected to a liquid nitrogen cooling accessory with a nitrogen purge. Each experiment began with cooling from room temperature to 0°C at the rate of 10°C/min. Then, the samples were allowed to equilibrate for 10 min at 0°C before the measurements were started. The glass-transition temperatures of the homopolymers and 50/50 w/w blends of SAN/PMMA, PMMA/PVC, and PVC/PS were determined. Roughly 10-mg samples were used with a heating rate of 10°C/min from 0 to 150°C.

### FTIR measurements

FTIR spectra were recorded on a Jasco FT/IR-460 (Maryland, USA) Plus instrument in the range of 4000–400 cm<sup>–1</sup> at room temperature. The samples were prepared by the mixing of a fine powder of the blend sample with KBr powder for the FTIR measurements.

### Positron annihilation lifetime measurements

#### Positron annihilation process

A positron from a radioactive source (commonly Na-22), when injected into a molecular medium such as a polymer, interacts with the medium and loses its kinetic energy in a very short time (ca. 1 ps), and it reaches thermal energy. The thermalized positron may pick up an electron from the medium and annihilate as a free positron, be trapped into defects present in the crystalline and crystalline–amorphous interface regions of the system and then annihilate, or form a bound state with an electron of the medium ( $e^+e^-$ ) called the positronium (Ps) atom. Ps exists in two allowed spin states: *para*-positronium (*p*-Ps), in which the spins of  $e^+$  and  $e^-$  are antiparallel, annihilates into two  $\gamma$  photons with a lifetime of 0.125 ns, and *ortho*-Positronium (*o*-Ps), in which spins are parallel, annihilates with a lifetime of 140 ns in free space. However, in molecular media such as polymers, the positron of *o*-Ps picks up an electron from the surrounding medium and annihilates through a fast channel called pick-off annihilation, and its lifetime is shortened to a few

nanoseconds. The fact that o-Ps preferentially localizes in the free volume holes of polymers from which it annihilates<sup>25</sup> makes it the microprobe of free volume holes because its lifetime and intensity are related to the free volume size and number of cavities in the system. As such, o-Ps lifetime measurements have been widely used over the last few decades in the study of the microstructural behavior of polymers and recently blends. Generally, positron researchers correlate the free volume hole size and content to the viscoelastic properties of the polymer system under investigation. Therefore, the study of the free volume in polymer blends certainly provides an avenue for understanding the molecular-level mixing in blends.

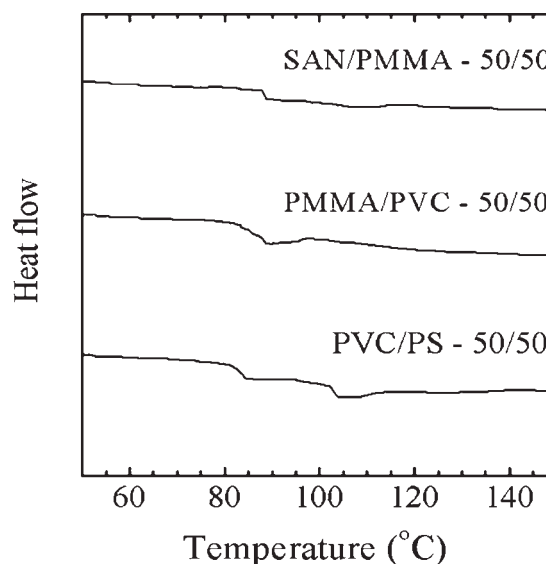
#### Lifetime measurements and free volume determination

Positron annihilation lifetime spectra were recorded for the pure polymers and their blends with a positron lifetime spectrometer. The spectrometer consisted of a fast-fast coincidence system with BaF<sub>2</sub> scintillators (Scionix, Holland) coupled to photomultiplier tubes (type XP2020/Q) with quartz windows as detectors. The BaF<sub>2</sub> scintillators were conically shaped to achieve better time resolution. Two identical pieces of the sample were placed on either side of a 17- $\mu$ Ci <sup>22</sup>Na positron source, which was deposited onto pure kapton foil 12.7  $\mu$ m thick. This sample-source sandwich was placed between the two detectors of the spectrometer to acquire the lifetime spectrum. The prompt time spectrum was obtained by the acquisition of the time spectrum with a <sup>60</sup>Co source, which gave 180 ps as the resolution of the spectrometer. However, to reduce the acquisition time and increase the count rate, the spectrometer was operated at 220 ps. All lifetime measurements were performed at room temperature with more than a million counts under each spectrum recorded in a time of 1–2 h. The source correction term and resolution functions were estimated from the lifetime of well-annealed aluminum with the program RESOLUTION.<sup>26</sup> Therefore, three Gaussian resolution functions were used in this analysis of the positron lifetime spectra for all the blends and pure polymer samples. All spectra were analyzed into three lifetime components with the help of the computer program PATFIT-88<sup>26</sup> with proper source and background correction.

## RESULTS AND DISCUSSION

### DSC results

The characterization of the glass-transition temperatures of polymer blends is widely used to study



**Figure 1** DSC thermograms of 50/50 blends of SAN/PMMA, PMMA/PVC, and PVC/PS.

their miscibility. Generally, a blend with a single composition-dependent glass transition is termed a miscible or single-phase system. A binary mixture with two glass transitions is called immiscible. Over the past 5 decades, a number of theoretical models have been proposed to predict the composition dependence of glass-transition temperatures for miscible blends. The relations most frequently used for this were proposed by Gordon and Taylor,<sup>27</sup> Fox,<sup>28</sup> and Couchman.<sup>29</sup> In practice, positive and negative deviations from the prediction of the Fox relation have frequently been observed. These deviations have been interpreted as due to specific interactions such as hydrogen bonding, dipole–dipole interactions, and charge-transfer interactions between the blend components. Therefore, the measurement of the glass-transition temperature helps to distinguish a blend as a phase-separated or single-phase system.<sup>2</sup> However, this method is of limited use when the glass transitions of the component polymers of the blend are close to each other, with the result that they cannot be adequately resolved. Generally, DSC or differential mechanical analysis is used to determine the glass-transition temperature, but these techniques are sensitive only to heterogeneities with domain sizes larger than 15 nm. Second, the results will not provide the level of miscibility.<sup>1,2</sup>

Measured DSC thermograms (Fig. 1) indicate that the glass-transition temperatures of SAN, PMMA, PVC, and PS are 100, 84, 80, and 98°C, respectively. In the same figure, the DSC scans of 50/50 blends of SAN/PMMA, PMMA/PVC, and PVC/PS are presented. For the PVC/PS system, two clear glass transitions can be observed. The two glass-transition temperatures correspond to the constituents of the



blend, suggesting the immiscible nature of the system. In the case of the SAN/PMMA and PMMA/PVC systems, we can observe single broad transitions around 85 and 80°C, respectively. However, on the basis of these observations, it is difficult to conclude that these blends are miscible because the difference in the glass-transition temperatures of the constituent polymers is small (<20°C) and the two glass-transition temperatures cannot be adequately resolved. It looks like an overlapping of the transitions appearing as a single transition. Therefore, DSC, although widely used to determine the miscibility of polymer blends, is not reliable in the case of constituent polymers for which there is only a small difference in the glass-transition temperatures.

### IR spectroscopy results

We have carried out IR absorption measurements to detect possible interactions between SAN and PMMA groups. The expected interactions involve the carbonyl group (C=O) of PMMA and phenyl group or hydrogen of SAN. From the measurements of the IR spectra, we observed no significant changes in the stretching frequencies of the carbonyl group of PMMA in the blend because the C=O band in pure PMMA occurred at 1736, and in 30/70 and 50/50 blends, it occurred at 1735 cm<sup>-1</sup>. It is known that strong intermolecular interactions such as hydrogen bonding and dipole interactions lead to the miscibility of polymer blends, and in such cases, a significant shift in the absorption bands of the groups involved in the interactions has been observed.<sup>30</sup> Therefore, we conclude that for SAN/PMMA blends, the intermolecular interactions are not responsible for the miscibility.

FTIR spectra of PMMA and selected blends of PMMA and PVC (70/30 and 50/50 blends) were taken. The carbonyl group of PMMA, being polar, has the possibility of being involved in dipolar or hydrogen interactions with other polymers. The  $\alpha$ -hydrogen of PVC is also slightly polar. Therefore, we expected an interaction between the carbonyl group of PMMA and  $\alpha$ -hydrogen of PVC. In the spectra, we clearly observed a shift in the carbonyl group band from 1742 cm<sup>-1</sup> in pure PMMA to 1730 cm<sup>-1</sup> in its blends. The shift in the carbonyl absorption band frequency to the lower side is considered an indicator of a negative heat of mixing,<sup>31</sup> which results from the attractive interactions between the carbonyl group of PMMA and  $\alpha$ -hydrogen of PVC.<sup>32,33</sup> Therefore, the observed shift in the absorption band is attributable to the miscibility of PMMA/PVC blends. For both blends (70/30 and 50/50), the shift is the same, suggesting that the strength of the interaction is of the same order in both compositions. Because of space limitations, we

have not given the spectra but have given only the results.

### Free volume data

All the measured lifetime spectra were resolved into three lifetime components ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ) with corresponding intensities ( $I_1$ ,  $I_2$ , and  $I_3$ ), with the variance of fit around unity. Therefore, the results of three-component analysis are described in this work. The general description of the three lifetime components is as follows.<sup>25</sup> The shortest lifetime component,  $\tau_1$ , with intensity  $I_1$  can be attributed to annihilations from p-Ps and free positron annihilations. The intermediate lifetime component,  $\tau_2$ , with intensity  $I_2$  is mainly due to annihilation of positrons trapped at the defects present in the crystalline regions or in the crystalline–amorphous interface regions. The longest lived component,  $\tau_3$ , with intensity  $I_3$  is due to pick-off annihilation of o-Ps in the free volume sites present mainly in the amorphous regions as well as the interface regions of the polymer matrix or in the blends.<sup>34</sup> Of these lifetime components, only o-Ps lifetime  $\tau_3$  is related to the free volume hole size according to the relation of Nakanishi et al.<sup>35</sup> This relation was developed on the basis of theoretical models originally proposed by Tao<sup>36</sup> for molecular liquids and later by Eldrup et al.<sup>37</sup> for molecular solids. In this model, Ps is assumed to be localized in a spherical potential well having an infinite potential barrier of radius  $R_0$  with an electron layer in the region of  $R < r < R_0$ , where  $R$  is the free volume cavity radius. The relation between  $\tau_3$  and  $R$  from which o-Ps annihilates is given as follows:

$$(\tau_3)^{-1} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right] \text{ns}^{-1} \quad (1)$$

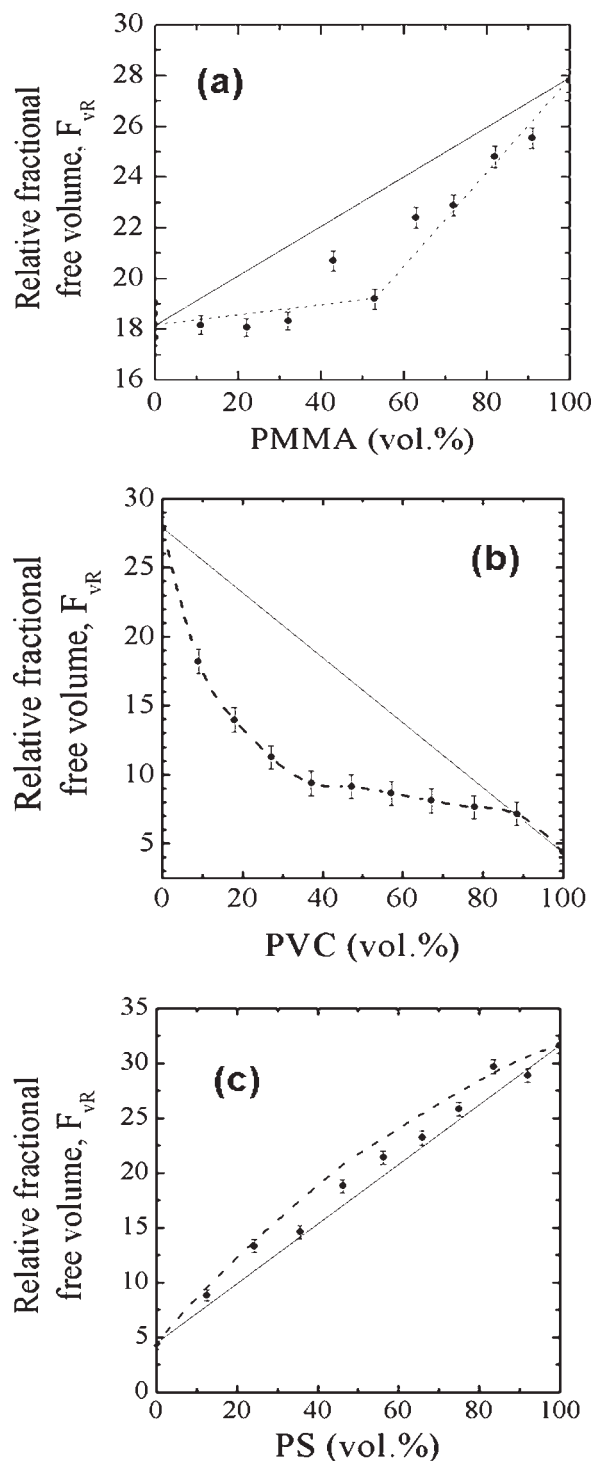
where  $R_0$  is equal to  $R + \delta R$  and  $\delta R$  is an adjustable parameter. Through the fitting of eq. (1) with  $\tau_3$  values for known hole sizes in porous materials such as zeolites, a value of  $\delta R = 0.166$  nm was obtained.<sup>31</sup> We verified that this value of  $\delta R$  is true for the systems of our study. With this value of  $\delta R$ , the free volume radius ( $R$ ) is evaluated with eq. (1), and the average size of free volume holes ( $V_f$ ) is calculated as  $V_f = (4/3)\pi R^3$ . The fractional free volume or free volume content ( $F_v$ ) of the system can then be estimated as follows:

$$F_v = C \times V_f \times I_3 \quad (2)$$

where  $C$  is a constant and  $I_3$  is the o-Ps intensity.  $I_3$  is considered a relative measure of the number of free volume cavities present in the system. Parameter  $C$  can be found from an independent experiment. In the absence of a measured value of  $C$ , the relative

fractional free volume ( $F_{vR}$ ), defined as  $F_{vR} = V_f \times I_3$ , is generally used to understand the changes in the free volume content of the system under study.<sup>16,17,20,22,23</sup>  $I_3$  is usually meant to represent the number of free volume sites (hole density) in the material. However, there are arguments that  $I_3$  could be influenced by other mechanisms such as quenching and inhibition as well, so one cannot directly use this to represent the number density of free volume holes. The presence of organic species such as NO, NO<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub> will influence the changes in  $I_3$  to a considerable extent.<sup>38</sup> The effect of radiation could influence the changes in  $I_3$ .<sup>39</sup> However, in this study, we understand that no such influence of the previously described mechanisms exists, and hence to predict the blend miscibility, consideration of  $F_{vR}$  seems to be justified.

The free volume in polymeric systems evolves because of the empty spaces between and along the polymer chains. Therefore, the free volume hole size and the free volume fraction depend on the chain structure, spacing, and molecular orientations. Polymeric systems, having an ordered arrangement of chains with close packing, give rise to a smaller free volume. When two polymers are blended and the blending process results in some specific interactions between the chains of the component polymers, the orientation of chains in a particular direction results in close packing. If this occurs, it results in reduced free volume of the system. This change in the free volume of the blend can be observed by a comparison of the measured free volume of the blend with that calculated according to the simple linear additivity rule.<sup>40,41</sup> We have plotted in Figure 2(a)  $F_{vR}$  as a function of the PMMA volume percentage in the SAN/PMMA blend system. The solid line represents values predicted by the additivity rule. The  $F_{vR}$  value for pure SAN is 17.7, and that for pure PMMA is 27.8. Therefore, it is expected that the addition of PMMA to SAN will result in an increase in  $F_{vR}$ . From the figure, we observe that as the PMMA volume percentage in SAN increases,  $F_{vR}$  increases from 17.7 to 27.8 but with a negative deviation from the linear additivity rule throughout the composition range. These changes in  $F_{vR}$  can be explained as follows: with up to 50 vol % PMMA, SAN is the matrix and PMMA is the dispersed phase, and because there is repulsion between the SAN chains, they give way to PMMA chains to slide between them; this results in good mixing. However, after 50 vol %, PMMA becomes the matrix, and SAN becomes the dispersed phase; therefore, PMMA chains prefer to associate with the SAN chains. That is, mixing between them is not as good as that in the earlier situation, which could be considered loose packing and a different kind of molecular orientation. For the PMMA/PVC system, the positron



**Figure 2** Plot of  $F_{vR}$  as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.

results are shown in Figure 2(b). In this, we observe a decrease in the  $F_{vR}$  value with an increase in the PVC concentration in the blend system and a negative deviation from the linear additivity relation, but it is less beyond 50 vol % PVC, which could be seen as an indicator of less miscibility of the system at higher PVC concentrations. For the PVC/PS system,

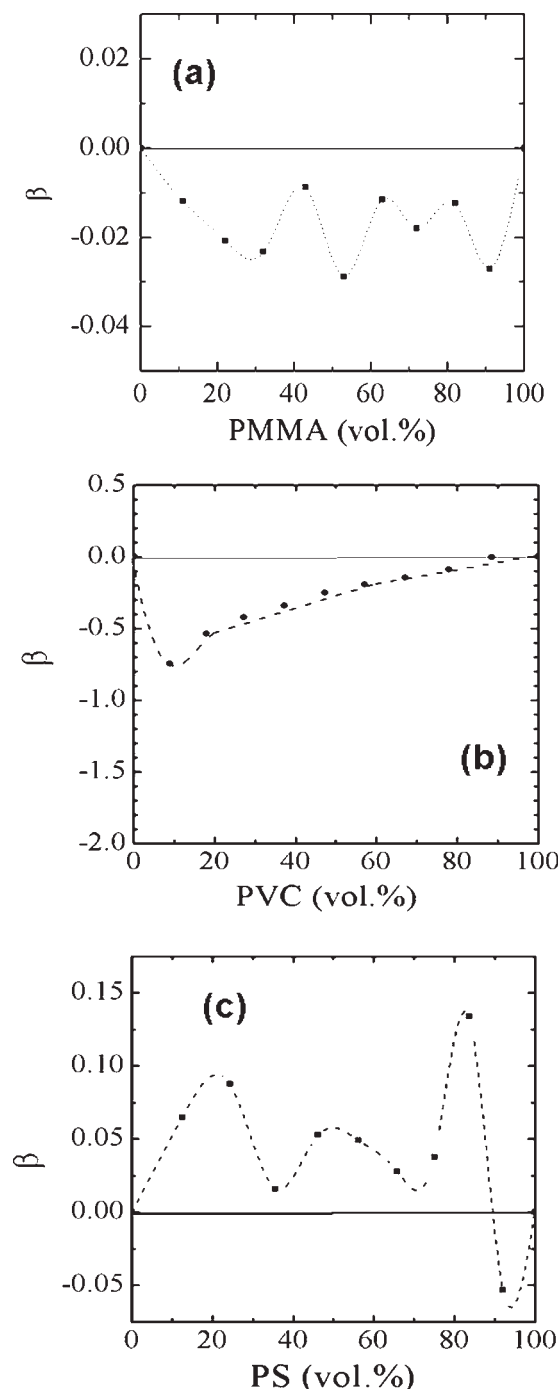
the results are presented in Figure 2(c). It is clear that the addition of PS to PVC results in a continuous increase in the value of  $F_{vR}$ , and at the same time, it deviates positively from the additivity rule throughout the concentration range. This suggests the evolution of additional free volume possibly due to the incompatibility between PVC and PS components. Therefore, in this case, the variation of  $F_{vR}$  reveals the immiscible nature of the system.

It is known that only the occupied volume of the blend components is additive; the free volume is nonadditive.<sup>5</sup> When two polymers are mixed, it is obvious that their occupied volumes add up, but generally we observe a decrease or increase in their resultant total volume. This behavior of the mixtures can be explained if we take into account the free volumes of the independent components and that of the mixture. If we take the free volume as non-additive, depending on the molecular arrangement, interaction, and orientation, it may decrease, or additional free volume may evolve. This results in the deviation of the total volume from the linear additivity. Therefore, on the basis of the theory of Wu<sup>42</sup> and Liu et al.,<sup>15</sup> we have a relation to estimate the relative free volume fraction in a blend:

$$F_{vR} = F_{vR1}\phi_1 + F_{vR2}\phi_2 + \beta F_{vR1}F_{vR2}\phi_1\phi_2 \quad (3)$$

where  $\phi_1$  and  $\phi_2$  correspond to the volume fractions of constituent polymers 1 and 2, respectively.  $\beta$  is considered the interchain interaction parameter. Using the  $F_{vR}$  values of the blends and the constituent polymers, we have evaluated parameter  $\beta$  from eq. (3) for different compositions of the blend systems of our study. According to the literature,  $\beta$  has been observed to be negative<sup>15</sup> in the case of miscible blends and positive or zero for immiscible blends.<sup>15,20</sup>

The  $\beta$  parameter so calculated is presented in Figure 3(a–c) for the SAN/PMMA, PMMA/PVC, and PVC/PS systems, respectively. For the SAN/PMMA system,  $\beta$  is negative throughout the concentration range, and according to the earlier description, we conclude that this behavior is an indication of miscibility, which is also indicated by the behavior of  $F_{vR}$  in Figure 2(a). Because the miscibility varies with the composition, in comparison with the results of Figure 2(a),  $\beta$  as a parameter fails to suggest which composition produces good miscibility as it exhibits complex behavior. From Figure 3(b), we see that for the PMMA/PVC system,  $\beta$  is negative throughout the concentration range, suggesting that the blends are miscible. Additionally, we observe an interesting behavior in this system:  $\beta$  shows a systematic variation. It has a large negative value with 10% PVC and then gradually decreases with an increase in the PVC content. It could be concluded that 10% PVC



**Figure 3** Plot of  $\beta$  as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.

produces good miscibility.  $\beta$  for the PVC/PS system in Figure 3(c) exhibits oscillatory behavior but is positive up to 80% PS and becomes negative only at 90%. A comparison of the behavior of  $\beta$  in all three systems suggests that, although it could be taken as an indicator of miscibility, its behavior is not systematic enough to determine which composition provides higher miscibility. Therefore, it is concluded



that  $\beta$  is not the right parameter to determine the level of miscibility.

### New model for miscibility determination

The previously described limitation of  $F_{vR}$  or  $\beta$  in predicting the concentration-dependent degree of miscibility or probability of miscibility motivated us to look for other alternatives. As outlined in the introduction of this article, we thought Schnell and Wolf's<sup>9</sup> theory might provide an answer to this through  $\alpha$ . This theory supposes that the points of contact between the polymer segments and solvent molecules, that is, interfaces, act as energy dissipation centers. Assuming that energy dissipation occurs at the interfaces between like molecules and excluding specific interactions such as hydrogen bonding and dipole-dipole interactions between the components, we can formulate an ideal mixing law (thermodynamically, the free energy of mixing is negative) for the viscosity ( $\eta$ ) of a binary polymer mixture in terms of the surface fractions ( $\Omega$ ) of its components (1 and 2) as follows:

$$\ln \eta = \Omega_1^2 \ln \eta_{11} + 2\Omega_1 \Omega_2 \ln \eta_{12} + \Omega_2^2 \ln \eta_{22} \quad (4)$$

where  $\eta_{11} = \eta_1$  and  $\eta_{22} = \eta_2$  represent the friction between like molecules and  $\eta_{12}$  measures the mutual friction between the different components. To render this relation comparable with experimental results,  $\Omega$  values are converted to volume fraction ( $\phi$ ) values, and they are related through  $\gamma$ :

$$\Omega = \frac{(1 + \gamma)\phi}{(1 + \gamma)\phi} \quad (5)$$

$\gamma$  is defined as

$$\gamma = \frac{F_2/V_2}{F_1/V_1} - 1$$

where  $F_1$  and  $F_2$  and  $V_1$  and  $V_2$  are the van der Waals surfaces and volumes of the component polymers, respectively.

Invoking the concept that free volume and viscosity are inversely related,<sup>43</sup> we have modified the equations given by Schnell and Wolf<sup>9</sup> in terms of free volume instead of viscosities, and the final form of the equation is

$$\Delta F_{vR} = \left\{ \delta [\gamma(1 + \gamma\phi_2)^2 - \phi_1(1 + \gamma)] + 2\alpha(1 + \gamma)^2 \phi_2^2 + e^{\frac{1}{F_{vR}}} \rho \phi_1 \right\}^{-1} \frac{(1 + \gamma\phi_2)^3}{\phi_1 \phi_2} \quad (6)$$

In eq. (6), the left-hand-side quantity  $\Delta F_{vR}$  is calculated as follows:

$$\Delta F_{vR} = \left[ \frac{1}{F_{vR}} - \frac{\phi_1}{F_{vR1}} - \frac{\phi_2}{F_{vR2}} \right]^{-1}$$

where the right-hand-side parameters are known from the positron data.  $\delta$  in eq. (6) is defined as

$$\delta = \frac{1}{F_{vR2}} - \frac{1}{F_{vR1}},$$

which is the difference in the reciprocal of the free volumes of the homopolymers. Here  $\rho$  is the density of the blend, and  $\phi_1$  and  $\phi_2$  are the volume fractions of the blend constituents. It has been observed that  $\alpha$  attains large negative values in the case of miscible blends, which are indicative of good thermodynamic mixing, and it decreases to small values (close to zero) with a decrease in the miscibility level or increases with positive values in phase-separated systems.

$\gamma$  in eq. (6) can be evaluated from the following relation<sup>44</sup> because we know  $\phi_1$ ,  $\phi_2$ ,  $F_{vR}$ ,  $F_{vR1}$ , and  $F_{vR2}$ :

$$F_{vR} = \left[ \frac{\phi_1}{F_{vR1}} + \frac{\phi_2}{F_{vR2}} + \delta \left( \frac{\gamma \phi_1 \phi_2}{1 + \gamma \phi_2} \right) \right]^{-1} \quad (7)$$

In the original theory,  $\gamma$  was considered to be constant (i.e., composition-independent) and was expressed as

$$\gamma = \frac{N_2}{N_1} - 1 \quad (8)$$

where  $N_i$  is the ratio of the surface fraction to the volume fraction of component polymers 1 and 2. According to Mertsch and Wolf,<sup>46</sup>  $\gamma$  can also be expressed as the ratio of the surface fraction to the volume fraction of the constituent polymers because the surface fractions, not the volume fractions, quantify the geometrical effects in the molecular architecture, particularly those involving changes in the conformation and the resulting close packing. Let us recall the definition of  $\gamma$ :

$$\gamma = 1 - \left[ \frac{F_2}{V_2} / \frac{F_1}{V_1} \right] \quad (9)$$

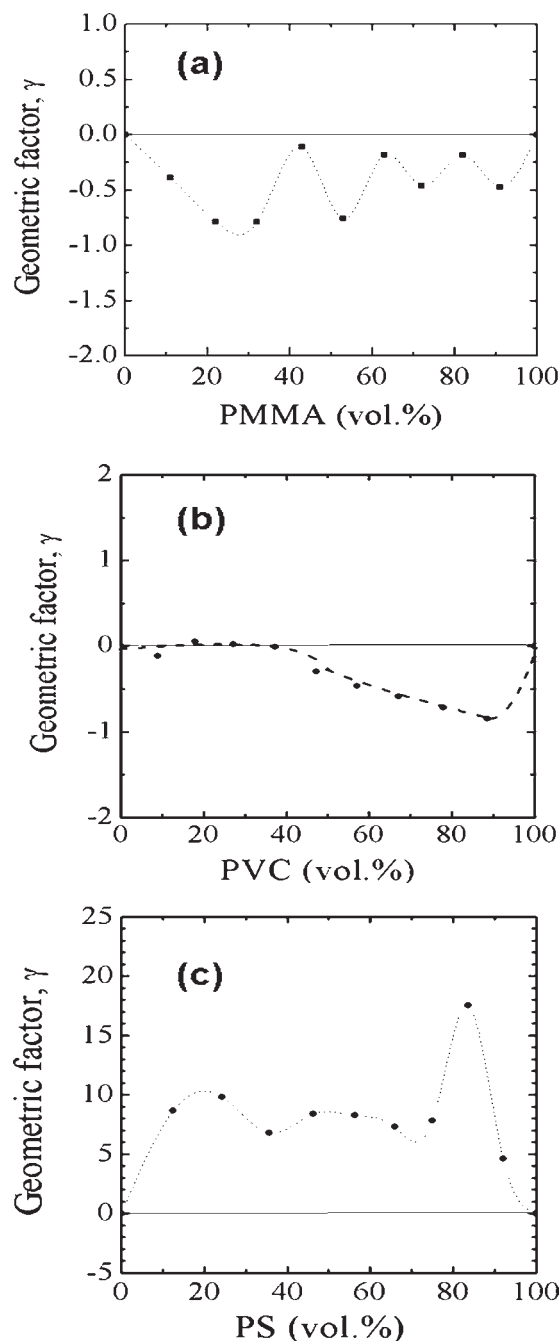
where  $F_1$  and  $F_2$  and  $V_1$  and  $V_2$  are the van der Waals surfaces and volumes of the component polymers, respectively. From eq. (9), it is clear that  $\gamma$  is a constant for a given pair of polymers used in making a blend and is independent of the composition of the mixture. We have calculated the  $\gamma$  value from

eq. (9) by replacing the molar surface and molar volume by the free volume surface area ( $S$ ) and  $F_{vR}$ .  $S$  was calculated with the empirical relation  $I_3 = 3.0 + 0.033S$ , where  $I_3$  is the o-Ps intensity.<sup>46</sup> The value of  $\gamma$  so calculated turns out to be  $-0.256$ . The parameter  $\gamma$  can also be obtained if we make use of Bondi's data<sup>47</sup> for van der Waals surfaces and van der Waals volumes for the two component polymers SAN and PMMA, using the following relation:

$$\gamma_B = \frac{N_2}{N_1} - 1 \quad (10)$$

where  $N_1$  and  $N_2$  are the ratios of the molar surfaces to the molar volumes of component polymers 1 and 2, respectively. The Bondi method is based on a group contribution for the molecular architecture. For this studied system,  $\gamma_B$  turns out to be  $-0.183$ . This value is in reasonable agreement with the free volume data obtained above  $-0.256$ . Kapnistos et al.<sup>44</sup> performed a similar calculation and compared their experimental viscosity data. For the PS/poly(vinyl methyl ether) miscible system, Bondi's method gave them  $\gamma_B = -0.15$ , whereas their experimental  $\gamma$  value was  $-0.35$ . Considering the large discrepancy between the viscosity measurements and theoretical values, we argue that free volume measurement is a better technique because the molecular architecture has a direct bearing on the free volume. This is the first positron measurement to evaluate  $\gamma$  for polymer blends, and we are of the opinion that free volume measurement seems to be better than viscosity measurement. Furthermore, eq. (8) suggests that  $\gamma$  may vary with the composition, and Schnell and Wolf<sup>45</sup> have expressed the same opinion. To explore this, we have used eq. (7) and evaluated the values of  $\gamma$  at different compositions for the three systems, and they are shown in Figure 4(a–c) as a function of the blend composition.

In Figure 4(a), we see that  $\gamma$  as a function of the PMMA concentration in the SAN/PMMA blend does not show any systematic behavior. However, one interesting aspect that we notice here is that the behavior of  $\gamma$  is similar to that of  $\beta$  [Fig. 3(a)]. On the other hand, the behavior of  $\gamma$  in the PMMA/PVC system [Fig. 4(b)] shows a minimum at 90 vol % PVC, which is quite the opposite of what we observe for  $\beta$  [Fig. 3(b)]. This is somewhat intriguing, in the sense that the free volume depends on the molecular architecture of the system, and by definition,  $\gamma$  depends on the geometry of the molecular arrangement and equilibrium orientation, which also reflect more or less the same aspect. Finally, in Figure 4(c), we observe that  $\gamma$  in this system does not exhibit any systematic variation, but the important point is that it has positive values like  $\beta$  and its



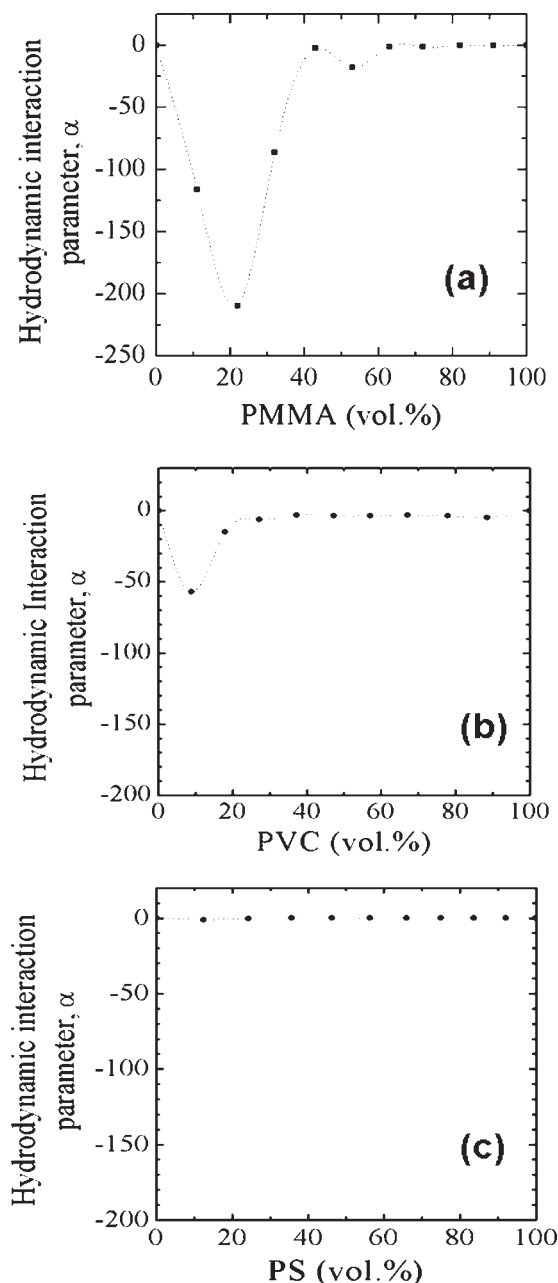
**Figure 4** Plot of  $\gamma$  as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.

trend is very similar to that of  $\beta$  [Fig. 3(c)]. Therefore, if we consider the forces that influence the molecular arrangement and orientation, we may be able to understand the behavior of  $\gamma$  in comparison with  $\beta$ . Of course,  $\beta$  is still not well described. For the systems SAN/PMMA and PVC/PS, in which  $\gamma$  and  $\beta$  show similar trends, there are no intermolecular interactions between the chains of the constituent polymers of the blends as reported earlier.<sup>10</sup> In such

cases, the free volume generated in the system is solely due to the molecular arrangements and orientations, whereas in the case of the PMMA/PVC system, there exists an intermolecular interaction between the carbonyl group of PMMA and  $\alpha$ -hydrogen of PVC,<sup>12,13</sup> and this interaction governs the molecular arrangement in the system. Therefore, in this system, both the free volume and  $\gamma$  are influenced by the interaction. The changes in  $\gamma$  and  $\beta$ , however, occur at exactly the opposite compositions of the blend. That is,  $\beta$  is minimum (negative) at 10% PVC, whereas  $\gamma$  is minimum (negative) at 10% PMMA. At the moment, it is not clear to us how to correlate these two parameters in a system in which intermolecular interactions drive the blends to miscibility. We feel that a few more investigations are necessary for different blend systems in which intermolecular interactions are involved to draw meaningful conclusions for  $\gamma$  and  $\beta$ .

The clear failure of the two parameters  $\beta$  and  $\gamma$  to indicate the degree of miscibility for a given system necessitated the introduction of the new model described earlier. We have carried out calculations of the hydrodynamic interaction parameter of Wolf's theory with the previously determined  $\gamma$  values in eq. (5).  $\alpha$  by definition quantifies the deviation of friction from ideality between components 1 and 2 of the blend, especially unlike components, and measures the excess friction that has developed in the system because of the interactions between the constituent polymer chains. Therefore, the changes at the interface influence the  $\alpha$  parameter. Let us see how this parameter varies for the three blends.

For a miscible blend, the chains of polymer 1 are evenly distributed in polymer 2, and hence the interaction sites are large; thus, when a chain tries to move, several other chains with which it has segmental level interactions pull it. This implies that a good amount of friction is generated in the system for which  $\alpha$  attains large negative values. In Figure 5(a), we show a plot of  $\alpha$  as a function of the PMMA percentage in the SAN/PMMA blend. The SAN/PMMA blend systems are known to be miscible, not because of the intermolecular interactions but because of the intramolecular repulsion between the SAN chains.<sup>10,11</sup> It is important to note that several techniques have shown this blend to be miscible throughout the concentration range, but none of them have indicated the extent or degree of miscibility for different compositions. We can see from Figures 2(a) and 3(a) that this system exhibits miscibility throughout the range of concentrations, but there is no indication of maximum miscibility at any composition. In contrast, a large negative value ( $-209$ ) at 20% PMMA, observed in Figure 5(a), can be considered to indicate that the degree of miscibil-



**Figure 5** Plot of  $\alpha$  as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.

ity is maximum because  $\alpha$  shows only smaller values at a higher concentration of PMMA. This behavior of  $\alpha$  can be understood in the following way: At lower concentrations of PMMA, SAN is the matrix, and PMMA is the dispersed phase. Because SAN has a large molecular weight (1,65,000 g/mol) compared to PMMA (15,000 g/mol), the repulsive forces between SAN chains make it easy for PMMA chains to slide fast between chains of the matrix, and hence a fine dispersion may result. As the SAN content decreases, the net repulsive force also decreases, and

hence the dispersion also decreases. Therefore, 20% PMMA might be the optimum value to produce a good dispersion in the SAN matrix, resulting in excess friction and a high degree of miscibility in the SAN/PMMA blend.

Another possible explanation for the fine dispersion comes from free energy considerations. A lower molecular weight of PMMA results in a higher degree of freedom, which results in increased entropy and reduced free energy for PMMA molecules to diffuse to form miscible blends.

In the case of PMMA/PVC blends, the interaction between the carbonyl group ( $\text{C}=\text{O}\cdots$ ) of PMMA and  $\alpha$ -hydrogen ( $\cdots\text{H}-\text{C}-\text{Cl}$ ) of PVC drives the system to miscibility. However, this system is known to be partially miscible, and at some compositions, it becomes immiscible.<sup>11</sup>  $\alpha$  for this system [Fig. 5(b)] is negative and maximum at 10% PVC ( $-57$ ) and decreases as the PVC content increases. Beyond 30% PVC,  $\alpha$  attains smaller values closer to zero. Compared to that of the SAN/PMMA system ( $\alpha = -209$ ),  $\alpha$  for this system at 10% PVC is still a good value. This composition could produce considerable interactions at the molecular level cited previously. The increase in the PVC concentration reduces interactions, and this results in smaller  $\alpha$  values.

In the case of immiscible blends with a lack of interactions between polymer components, they form their own domains in the system, thereby reducing the possible contacts between the chains. In other words, the friction between the chains of the constituent polymers is diminished. For such systems, we expect the  $\alpha$  values to be smaller. The  $\alpha$  values obtained for the PVC/PS blend system shown in Figure 5(c) are a clear indication that the  $\alpha$  values are not zero but are close to zero. This indicates that the system is immiscible throughout the concentration range and that the friction at the interface is very negligible. This is truly supported by the other three parameters, namely,  $F_{vR}$ ,  $\beta$ , and  $\gamma$ .

In comparison, we see that  $\alpha$  for the three different binary polymer blends studied here clearly indicates the level of miscibility, in the sense that it is maximum at a given composition of a blend. It attains very low values closer to zero, suggesting that there is no hydrodynamic interaction in immiscible blends. However, small values of  $\alpha$  should not be construed as an indication of immiscibility in the case of miscible blends with a higher concentration of the second polymer. That is no friction or much less friction between the chains of the constituent polymers, particularly at the interface, for low values of  $\alpha$ . Therefore, we can conclude that to find a composition that produces maximum miscibility for a given system,  $\alpha$  is a suitable parameter if it assumes larger values.

## CONCLUSIONS

This investigation has led to the following conclusions:

- Although DSC is a technique widely used to study miscibility in polymer blends, an ambiguity arises when the blend constituents' glass-transition temperatures are narrowly separated ( $<20^\circ\text{C}$ ). It fails to indicate the level or degree of mixing.
- $\beta$  can be taken as an indicator of miscibility only, but this also fails to reveal clearly the composition-dependent miscibility level.
- For blend systems with weak intermolecular interactions (SAN/PMMA and PVC/PS),  $\gamma$  follows the same trend as that of  $\beta$ , but for blends with strong intermolecular interactions (PMMA/PVC), it behaves completely different from  $\beta$ . This needs to be investigated further.
- From the behavior of  $\alpha$ , we conclude that perhaps this is an excellent parameter for determining the composition of a binary mixture that produces maximum homogeneity or a high degree of miscibility. The SAN/PMMA system produces a maximum  $\alpha$  value of  $-209$  at 20% PMMA; PVC/PMMA produces a maximum  $\alpha$  value of  $-57$  at 10% PMMA. The immiscible blend PS/PVC exhibits very low values closer to zero, which suggest very little friction at the interface throughout the entire concentration range.

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