
VOLUME 53 ISSUE 3, 2 FEBRUARY 2012
ELSEVIER
polymer
Agglomerated
Intermediate
Dispersed
Steady Shear
Steady State
σDC (S/cm)
Time (s)
Carbon Nanotubes in a Polymer Melt
Available online at www.sciencedirect.com
SciVerse ScienceDirect

Polymer 53 (2012) 842–850

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Characterization of interfaces in Poly (styrene-*co*-acrylonitrile) (SAN) based ternary polymer blends: A new approach from positron lifetime spectroscopy

D. Meghala, C. Ranganathaiah*

Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore-570 006, India

ARTICLE INFO

Article history:
Received 23 August 2011
Received in revised form
12 December 2011
Accepted 18 December 2011
Available online 29 December 2011

Keywords:
Free volume
Interface
Hydrodynamic interaction

ABSTRACT

Positron lifetime spectroscopy is used to develop a new approach to characterize the individual interfaces in ternary polymer blends and hence determine composition dependent miscibility level. This approach has its genesis in KSR and KRZ models for the evaluation of hydrodynamic interaction parameters (α_{ij}). The method successfully applied for binary blends (single interface) earlier is theoretically modified for ternary blends and experimentally verified by measuring free volume content in blends and their constituents. We have tested the efficacy of this method in two ternary blends namely SAN/PVC/PMMA and SAN/EVA/PVC at different compositions. The effective hydrodynamic parameter α_{eff} evaluated using individual α values turns out to be handy in predicting the overall miscibility level of a ternary blend. Results show that SAN/PVC/PMMA exhibits maximum α_{eff} of −9.67 at composition 75/5/20 and SAN/EVA/PVC shows −3.18 at 50/35/15 indicating that miscibility level is high at these compositions for these two blends. DSC and SEM studies have also been used to supplement positron results.

1. Introduction

When a polymer blend is produced by mixing, mostly the blend phase separates into domains, in which one of the components is enriched and the other is depleted. These spatially segregated regions are separated by interfaces. On a larger length scale, one can envisage the material as an ensemble of interfaces. The structure and thermodynamics of these interfaces determine many practically important properties of the blend [1,2]. From the practical perspective, 'interface' means the region between two phases for example in a binary blend which is important and expected to change with composition.

It is well known that most of the binary polymer blends are found to be thermodynamically demixed due to the minuscule repulsion between monomeric units of the long macromolecules and this leads to a gain in entropy of mixing [2]. As a result, the practical applications of such blends are limited due to the weak interfacial adhesion. To improve the adhesion, another properly chosen polymer is generally added which preferentially locates itself at the interface between the two immiscible phases thereby reduces the interfacial energy between phases. This is generally termed as chemical compatibilization. A "ternary polymer blend" results, if the compatibilizer is in good amount in the blend. Now, the degree of complexity has increased in an already complex system of binary blend [3]. There have been few studies reported on ternary blends so far [4–16]. In these studies, miscibility of the pairs was considered as an important property of blend system. However, rarely 100% miscibility is achieved and this becomes detrimental to the successful application of the blend. Therefore, one needs to understand in greater detail miscibility particularly at the molecular level. There have been several attempts to study miscibility of a large number of blends, binary or ternary and these studies were mainly relying on techniques such as Differential Scanning Calorimetric measurements [4–6,8,14], Viscometric measurements [11], SEM [8], TEM [4], Turbidity measurements [8] and so on. On the theoretical front, a number of thermodynamic theories have been developed to explain the miscibility in polymer blends, with limited success in predicting miscibility behavior in detail at the microscopic level [17]. Added to this misery, none of the techniques used in the study of blends so far is proficient enough to endow a way to gaze at all the interfaces in blends like ternary, their composition dependence etc. Additionally, it is evident from literature that for understanding miscibility levels in ternary blends, separate experiments were conducted in which the individual interfaces were characterized by constructing the respective binary blends [11,18]. The inferences on ternary blends drawn from such experiments however are indirect due to the fact

---

* Corresponding author. Tel.: +91 821 2419604; fax: +91 821 2419301.
E-mail addresses: cr@physics.uni-mysore.ac.in, crang1@rediffmail.com (C. Ranganathaiah).

0032-3861/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2011.12.041

that the characteristics of three interfaces in a real ternary blend is certainly different and more complicated than assessing from three separate interfaces of constructed binary blends.

The compatibilization is known to enhance dispersion, decrease interfacial tension, and strengthen the interface adhesion either through increased specific interactions [1] or through increased frictional forces at the interface. All these results to increased miscibility level of the blend. As the number of interfaces becomes more than one like in ternary blends (binary blend-one, ternary blend-three), the complexity of the problem is compounded. Suppose one of the interfaces shows that the respective two components are compatible or miscible, other interfaces might show that the respective components are incompatible or immiscible, the net result is that the blend system exhibits poor physical properties. To be able to address these issues i.e., to understand the interfaces at the microscopic level in a better way, which will help to device methods to improve the compatibility between immiscible components through a suitable compatibilizer or some other route. As of now, information on individual interfaces in ternary polymer blends is not available.

To this end, we find a novel approach to explain the miscibility level in polymer blends using free volume results. The existence of free volume in polymers was postulated by Doolittle [19]. There is whole lot of data available on free volume in polymers [20–24] and in few binary polymer blends as well [25–34]. To date, Positron Lifetime Spectroscopy (PLS) has been proved to be a versatile and accurate method of measuring the nanometer sized free volume sites and their relative concentration because of its sensitivity and selectivity. However, in polymer blends the information on the interfacial properties could not be obtained by mere measurement of free volume, since the fractional free volume (F_v) obtained from PLS provides free volume of the entire blend and the changes occurring in one of the phases of an immiscible blend or at the interface, is not revealed. Therefore, it is imperative that a new method for assessing the interfacial properties of polymer blends is to be found. In this regard, a new method was developed by exploiting the usefulness of hydrodynamic interaction between the constituents of binary blends particularly at the interface [31]. This method owes its success to Wolf et al. [35,36] work who used the concept of Kirkwood–Risemann–Zimm (KRZ) model [37] which was an extension of the Kargin–Slonimsky–Rouse (KSR) model [38] for polymer/solvent systems. This formalism introduces two parameters measured from viscosity data: They are geometric factor (γ), which depends on the molecular arrangement and architecture of the blend, and the second parameter hydrodynamic interaction parameter (α) considered as a measure of excess friction generated between the blend constituents at the interface. These two parameters can be deduced using the viscometric data of blend and its constituents. The extension of KSR model by Zimm is a significant advancement that ‘hydrodynamic interaction’ is taken into account that influences the viscoelastic behavior of the system in liquid phase or solid phase which excludes specific interactions. That means it is due to the mechanical interactions between polymeric chains at the segmental level [39]. This treatment is equal to the assumption that each monomer is a point source of friction in the solvent [40] and α accounts for the friction at the interface. Furthermore, due to friction associated with the viscoelastic flow, energy dissipation occurs at the interface which also depends on the composition of the polymer and solvent in the system. Using these basic ideas, this method of Wolf et al. [35,36] was later modified by Ranganathaiah et al. [31] for polymer/polymer binary mixtures in solid phase characterized by single interface, using the concept that free volume and viscosity are inversely related [41]. It is also known that for the solid polymer blend, it is free volume that is easily measurable not the viscosity. It shall be noted that even in the solid phase, the polymer or the polymer blend exhibits viscoelastic properties and as far as the flow dynamics of polymer/solvent system is considered it is justifiable for the solid phase as well. However the level of hydrodynamic interactions will be on a smaller scale compared to polymer/solvent system. The efficacy of the method had been checked by Ranganathaiah's group for few binary blend systems [30–34] by calculating the hydrodynamic interaction parameter in terms of free volume data obtained from positron lifetime spectroscopy. However, the same approach is not directly applicable to ternary systems as the number of interfaces involved between the constituents is three and hence needed modification. For ternary polymer blends, because of three distinct interfaces, three hydrodynamic interaction parameters, one for each interface, are to be associated to characterize such a system. So, the required mathematical formulations for three α's (α_{12}, α_{23} and α_{31}) have been derived and put to experimental test in this work. Using this method, we have investigated two ternary blend systems namely (1) SAN/PVC/PMMA and (2) SAN/EVA/PVC for different compositions. The individual α's so derived are used to compute an effective α_{eff}, using simple additive rule so that present results could be easily compared with literature results. We find this value is very handy in deciding the given ternary blend as miscible or immiscible and is in good agreement with literature reports.

2. Experimental

2.1. Sample preparation

Polymer samples used in the preparation of ternary blends and some relevant information on them is given in Table 1. Blends of SAN/PVC/PMMA and SAN/EVA/PVC of different compositions were prepared by conventional solution casting technique. The weighed fractions of SAN, PVC and PMMA were dissolved in tetrahydrofuran at 60 °C in four combinations (a) 20/65/15, (b) 75/5/20, (c) 15/50/35 and (d) 5/50/45, and each solution was cast onto a clean and flat glass plate. The solvent was allowed to evaporate at room temperature for 4 days and then the samples were dried in an oven at 60 °C to remove any traces of the solvent left in the sample. The

Table 1
Characteristics of materials used in the present study.

Sample	Supplier	Specifications			
			Molecular Weight (g/mol)	Density (g/cc)	T_g (°C)
Poly(styrene-*co*-acrylonitrile) (SAN)	Sigma–Aldrich Chemicals Ltd, Bangalore, India.	AN content - 25%	1,65,000	1.08	106
Poly(vinyl chloride) (PVC)	Sigma–Aldrich Chemicals Ltd, Bangalore, India.		43,000	1.34	74
Poly(methyl methacrylate) (PMMA)	Sigma–Aldrich Chemicals Ltd, Bangalore, India.		15,000	1.2	84
Poly(ethylene-*co*-vinyl acetate) (EVA)	Lanxess India Private Limited, New Delhi	VA content - 45%	2,00,000	0.99	−20

neat films so obtained were approximately 1 mm thick. Similarly, blend samples of SAN/EVA/PVC of two combinations (a) 50/35/15 and (b) 70/15/15 were dissolved in tetrahydrofuran and prepared in the same way described above and dried at 60 °C. All the samples were stored in a desiccator before actual use in experiments.

2.2. *Measurements*

2.2.1. *Differential scanning calorimetry (DSC)*

The glass-transition temperature of the homopolymers and their blends of different compositions were measured using a Universal VA.7A TA Instruments DSC Q 200 connected to a liquid nitrogen cooling accessory with a nitrogen purge. For the DSC scan, roughly 10 mg samples were used at a heating rate 10 °C/min, in the temperature range 30 °C–120 °C for SAN/PVC/PMMA blends and from −40 °C to 120 °C for the blend samples of SAN/EVA/PVC.

2.2.2. *Scanning electron microscopy (SEM)*

The morphological studies of the blend samples have been carried out using the LEICA S 4401 scanning electron microscope operated at 10 kV with magnification of 1000× by coating the samples with gold alloy. This is just to check the surface morphology of the samples and positron results on the other hand provide information on the bulk of the samples.

2.2.3. *Positron lifetime spectroscopy (PLS)*

A brief description of positron lifetime spectroscopy is provided in the following paragraph. Positron, the antiparticle of electron, when injected from a radioactive source into a material medium like polymers, loses its kinetic energy through inelastic collisions within 1-2 ps time and gets thermalized. The thermalized positron will then annihilate with an electron of the medium either through free annihilation with a lifetime of about 200 ps or from trapped site like defects or voids and annihilate with a lifetime of about 200–500 ps or form a bound state with an electron called positronium (Ps) atom. Positronium comes with two spin states: para-positronium (*p*-Ps), with anti-parallel spins of $e^+ e^-$ pair and ortho-Positronium (*o*-Ps), with parallel spins. The *p*-Ps annihilates into two γ photons with a lifetime of 125 ps and *o*-Ps annihilates into three γ photons with a lifetime of 140 ns in free space. However, in molecular media such as polymers, the positron of *o*-Ps may pick up an electron of opposite spin from the surrounding medium and annihilates through a quick channel called pick-off annihilation, and its lifetime gets reduced to a few nanoseconds from 140 ns. The *o*-Ps localizes in free volume holes of polymers [42] and annihilates from these sites, and as such makes it the microprobe of free volume holes. The *o*-Ps pick-off lifetime (τ_3) and its intensity (I_3) are a measure of the free-volume size and their relative concentration respectively [42] since lifetime of *o*-Ps depends on the overlap of the Ps wave function with the electron wave function of the free-volume cavity and its intensity on the probability of o-Ps formation in the medium of study.

2.2.3.1. *Lifetime measurements.*

In the present study, Positron Lifetime Spectrometer (PLS) consisting of a fast–fast coincidence system with conically shaped BaF_2 scintillators (Scionix, Holland) coupled to photomultiplier tubes of type XP2020/Q having quartz window as detectors were used to record the lifetime spectra. The lifetime spectrometer had a time resolution of 220 ps. Two identical pieces of the sample were placed on either side of a 17-μCi ^{22}Na positron source, which was deposited onto a pure kapton foil of 12.7 μm thick. This source-sample sandwich was placed between the two detectors to record the spectra. Each spectrum with more than a million counts was recorded in a period of 1–2 h at room temperature. The source correction term and instrumental time resolution were estimated from the lifetime spectrum of a well-annealed aluminum using the program RESOLUTION [43]. All the acquired lifetime spectra were analyzed into three lifetime components using the computer program PATFIT-88 [43]. The samples were prepared in the same way twice and all the measurements (DSC, SEM and PLS) were done twice to check the reproducibility.

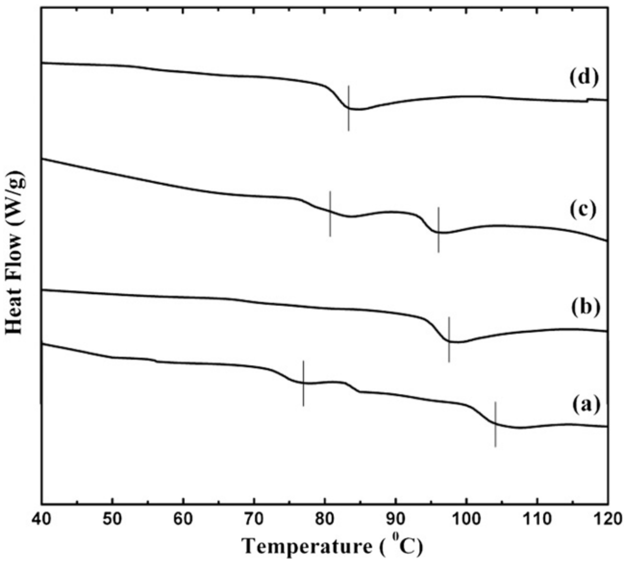


Fig. 1. DSC scans of SAN/PVC/PMMA blends for compositions (a) (20/65/15), (b) (75/5/20), (c) (15/50/35) and (d) (5/50/45).

3. Results & discussion

3.1. *DSC results*

Characterization of the glass-transition temperature (T_g) of a blend is a commonly used method in the study of polymer blend miscibility. A miscible blend normally exhibits single T_g characteristic of a single phase of the system whereas, phase-separated blend

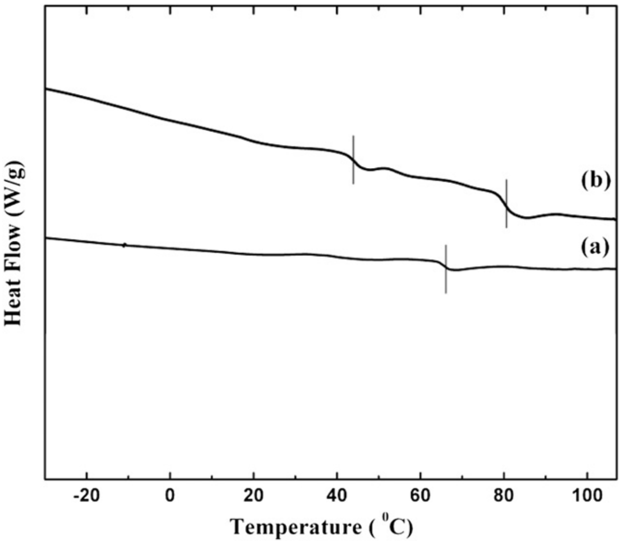


Fig. 2. DSC scans of SAN/EVA/PVC blends for compositions (a) (50/35/15) and (b) (70/15/15).

exhibits multiple glass transitions. The measured DSC thermo grams of the blends SAN/PVC/PMMA and SAN/EVA/PVC are shown in Fig. 1 and Fig. 2 respectively. For the blend SAN/PVC/PMMA, the DSC traces show a single T_g for the composition (75/5/20) and (5/50/45) at around 95 °C and 81 °C respectively indicating single phase nature of the blend. On the other hand, composition (20/65/15) shows three distinct T_gs around 74 °C, 84 °C and 102 °C which correspond to the T_gs of blend constituents and for (15/50/35) composition, two T_gs at around 78 °C and 94 °C are observed suggesting phase separated nature and the blend is immiscible. Similarly for the blend SAN/EVA/PVC, the composition (50/35/15) exhibits single T_g at about 81 °C suggestive of single phase and the blend is miscible whereas composition (70/15/15) exhibits two T_gs at around 44 °C and 81 °C indicating the blend is immiscible. However, this method is of limited use when the glass-transition temperatures of the component polymers of the blend are close to each other (within 20 °C) in which case inference might be misleading sometimes due to overlap of the T_gs of the components. Another point to be noted of this technique is its sensitivity. It is sensitive only to heterogeneities with domain sizes larger than 15 nm [17,44] and below this it is not accurate, and thirdly this method fails to differentiate composition dependent miscibility level [31,44].

3.2. SEM Photomicrographs

Scanning electron micrographs of the blend systems SAN/PVC/PMMA and SAN/EVA/PVC are shown in Fig. 3a–d and Fig. 4a and b respectively. From Fig. 3a and c it can be seen that the compositions (20/65/15) and (15/50/35) of SAN/PVC/PMMA, display phase separated morphology which is possibly due to agglomeration of like polymer domains (dispersed phases) whereas the compositions (75/5/20) (3c) and (5/50/45) (3d) show no signs of phase separation. This can be attributed to homogenous dispersion of the dispersed phases in the matrix. These results are in support of DSC scan results. From Fig. 4a and b, it can be seen that the composition (50/35/15) (4a) of the blend SAN/EVA/PVC, shows no phase separation whereas the composition (70/15/15) (4b) exhibits phase separated morphology. Again these results are in support of the respective DSC scan results discussed above. The phase separations are due to interfacial boundaries and the possible reasons for observed phase morphology will be described along with free volume results.

3.3. Free volume results

3.3.1. Analysis of positron lifetime spectra

The acquired spectra of both pure polymers and ternary polymer blend samples were resolved into three lifetime components τ_1, τ_2, and τ_3 with intensities I_1, I_2 and I_3 respectively, with the variance of fit around unity. These resolved components of the positron lifetimes are generally attributed to three states of positron annihilation: The shortest lifetime component, τ_1, with intensity I_1 can be attributed to *p*-Ps annihilations and free positron annihilations. The second lifetime component, τ_2, with intensity I_2 is due to annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline–amorphous boundaries. The longest lived component, τ_3, with intensity I_3 is due to the pick-off annihilation of *o*-Ps in the free volume sites present mainly in the amorphous regions as well as in the interface regions of the

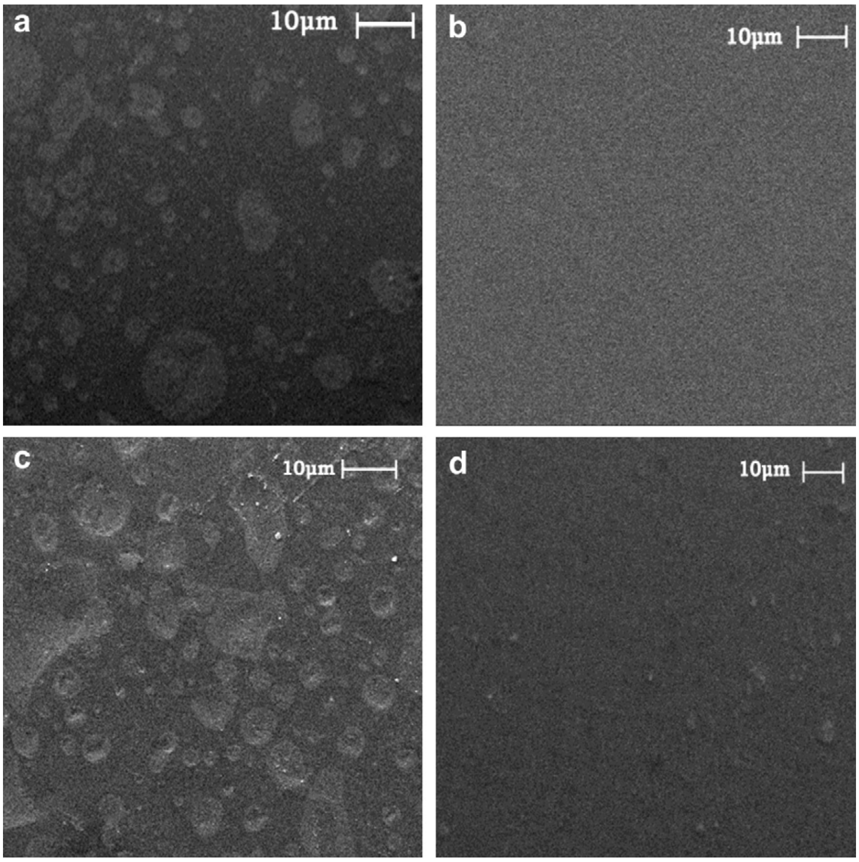


Fig. 3. (a) The scanning electron microscopy image of SAN/PVC/PMMA (20/65/15) blend. (b) The scanning electron microscopy image of SAN/PVC/PMMA (75/5/20) blend. (c) The scanning electron microscopy image of SAN/PVC/PMMA (15/50/35) blend. (d) The scanning electron microscopy image of SAN/PVC/PMMA (5/50/45) blend.

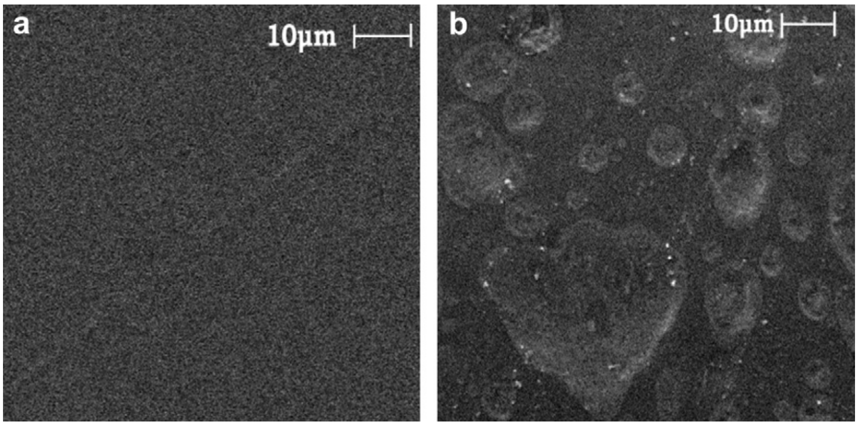


Fig. 4. (a) The scanning electron microscopy image of SAN/EVA/PVC (50/35/15) blend. (b) The scanning electron microscopy image of SAN/EVA/PVC (70/15/15) blend.

polymer blends. In polymers, among the three lifetime components, the *o*-Ps pick-off lifetime τ_3 with intensity I_3 is important because τ_3 is related to the average free volume hole size and I_3 is considered as a measure of the relative concentration of free volume holes. I_3 also represents the probability of *o*-Ps formation in polymers and their blends [45]. We have used Nakanishi et al. [46] simple relation connecting *o*-Ps lifetime τ_3 and free volume hole is as given below

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

where, $R_o = R + \Delta R$ and ΔR is a fitting parameter. The best-fitted value of ΔR for all known data is 1.656 Å. The average free volume holes size V_f is then evaluated as $V_f = (4/3)\,\pi R^3$ and the fractional free volume as $F_V = CI_3V_f$ where C is a constant and its value is taken as 0.0018Å^{-3} [42].

The obtained τ_3 values of the respective pure polymers and the blends (from the analysis of the Positron lifetime spectra) are used to calculate the free volume hole radius R, free volume V_f and fractional free volume F_v as per equation (1) and the following expressions. The fractional free volumes are labeled as F_{V1}, F_{V2} and F_{V3} respectively for pure polymers and F_{VB} for the respective blends. The values so derived are tabulated in Table 2 for the pure polymers SAN, PVC, PMMA and EVA and their blends SAN/PVC/PMMA and SAN/EVA/PVC. Also, a plot of fractional free volume F_V of the pure polymers SAN, PVC, PMMA and their blends is shown in Fig. 5. As can be seen from this figure, PVC has the least fractional free volume (F_V) due to the presence of Cl which inhibits Ps formation in the system resulting in o-Ps intensity drastically reduced and this is true for other halogen containing polymers. The polymer PMMA has the highest F_V. For blends, we observe the F_{VB} of a particular composition is closer to the F_V of its matrix.

Table 2
Ortho positronium lifetime results in SAN/PVC/PMMA and SAN/EVA/PVC ternary blends.

Sample	*o*-Ps lifetime $\tau_3 \pm 0.01$ (ns)	*o*-Ps intensity $I_3 \pm 0.14$ (%)	Free volume hole size $V_f \pm 0.8$ (Å^3)	Fractional free volume $F_V \pm 0.03$ (%)
SAN	2.10	16.96	107.09	3.27
PVC	1.97	5.32	94.74	0.91
PMMA	2.19	23.99	115.83	5.00
EVA	2.32	21.56	128.68	4.99
SAN/PVC/PMMA				
(20/65/15)	2.06	6.72	103.34	1.25
(75/5/20)	2.09	17.45	106.12	3.33
(15/50/35)	2.10	8.22	107.46	1.59
(5/50/45)	2.11	10.05	107.79	1.95
SAN/EVA/PVC				
(50/35/15)	2.11	13.04	108.41	2.54
(70/15/15)	2.05	14.15	102.26	2.61

As pointed out in earlier works [30–34], F_v has limitations and it will not reveal what is the situation at the interface since it represents the average fractional free volume of the blend as a whole. This led to the development of a new method of characterizing the interfaces in polymer blends from free volume data [31–34]. In this accomplishment the theory given by Wolf et al. [35,36] for polymer/solvent system is the basis. According to this the excess viscosities in a ternary system ($\Delta\ln\eta$) can be defined as

$$\Delta\ln\eta = \ln\eta - \phi_1\ln\eta_{11} - \phi_2\ln\eta_{22} - \phi_3\ln\eta_{33} \qquad (2)$$

where, η is the viscosity of the ternary polymer mixture, $\eta_{11} = \eta_1$, $\eta_{22} = \eta_2$, $\eta_{33} = \eta_3$ are the viscosities of the components 1, 2 and 3 respectively with volume fractions ϕ_1, ϕ_2 and ϕ_3.

Then, the viscosity of the mixture η can be expressed with the assumption of additivity of frictions between like molecules ($\eta_{11} = \eta_1$; $\eta_{22} = \eta_2$; $\eta_{33} = \eta_3$) and between those of unlike molecules (η_{12}, η_{23}, η_{31}) in terms of respective surface fractions Ω as:

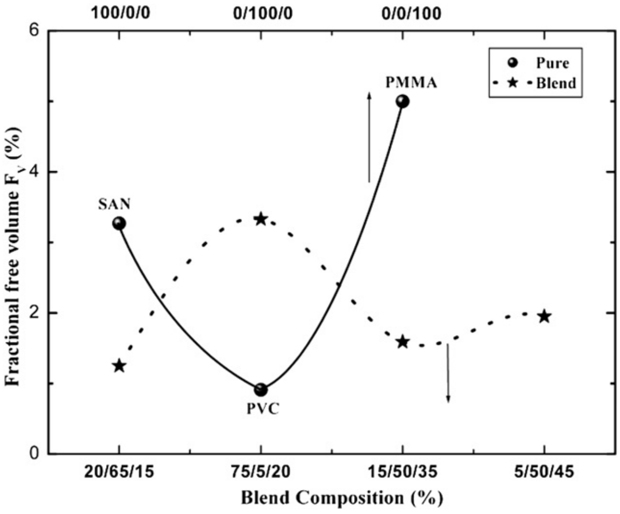


Fig. 5. Plot of fractional free volume F_V as a function of blend composition; Upper *X*-axis for pure polymers and lower *X*-axis for ternary polymer blends.

$$\begin{aligned}\ln\eta &= \Omega_1^2\ln\eta_{11}+\Omega_2^2\ln\eta_{22}+\Omega_3^2\ln\eta_{33}+2\Omega_1\Omega_2\ln\eta_{12}\\ &\quad+2\Omega_2\Omega_3\ln\eta_{23}+2\Omega_3\Omega_1\ln\eta_{31}\end{aligned}\tag{3}$$

where Ω_1, Ω_2 and Ω_3 are the surface fractions and they are related to volume fractions (ϕ_1, ϕ_2 and ϕ_3) through,

$$\begin{aligned}\Omega_1 &= \frac{(1+\gamma_{12})(1+\gamma_{31})\phi_1}{(1+\gamma_{12})(1+\gamma_{31})\phi_1+(1+\gamma_{31})\phi_2+(1+\gamma_{12})\phi_3};\\ \Omega_2 &= \frac{(1+\gamma_{23})\phi_2}{(1+\gamma_{12})\phi_1+(1+\gamma_{23})\phi_2+\phi_3}\\ \Omega_3 &= \frac{\phi_3}{(1+\gamma_{31})\phi_1+(1+\gamma_{23})\phi_2+\phi_3}\end{aligned}\tag{4}$$

Here, γ quantifies the differences in the surface to volume ratios of the components and is defined as [47]

$$\gamma = \frac{F_j/V_j}{F_i/V_i}-1\tag{5}$$

where, F_i, F_j and V_i, V_j are the molecular surfaces and volumes of monomers. Wolf et.al., address γ as the geometric parameter.

Now, we establish realistic expressions that allow calculation of η_{12}, η_{23}, η_{31} from η_{11}, η_{22}, η_{33}. By analogy with the relations for binary system [35], we construct the expressions for the calculation of viscosity between unlike molecules (η_{12}, η_{23}, η_{31}) in terms of like molecules (η_{11}, η_{22}, η_{33}) (in the absence of specific thermodynamic interactions), for ternary blend system as,

$$\begin{aligned}\eta_{12} &= \exp[\alpha_{12}+\beta_{12}(1-\Omega_2-\Omega_3)](\eta_1\eta_2)^{0.5}\\ \eta_{23} &= \exp[\alpha_{23}+\beta_{23}(1-\Omega_3-\Omega_1)](\eta_2\eta_3)^{0.5}\\ \eta_{31} &= \exp[\alpha_{31}+\beta_{31}(1-\Omega_1-\Omega_2)](\eta_3\eta_1)^{0.5}\end{aligned}$$

Here, α_{12}, α_{23}, α_{31} are the hydrodynamic interaction parameters for respective interfaces and measures the excess friction developed at the interface (for instance from the changes in entanglement density) in the limit of vanishing solvent concentration. β_{ij} quantifies the alteration in the flow mechanism with composition which is given by,

$$\sum_{\substack{i,j=1\\ j=i+1}}^{3}\beta_{ij} = \frac{[\eta]\rho}{2\left(1+\gamma_{ij}\right)}-\frac{\delta_{ij}}{2}-\alpha_{ij}$$

where ρ is the density of the blend.

Here, the parameter δ_{ij} is determined by the viscosities of the pure components according to the relation [35]

$$\sum_{\substack{i,j=1\\ j=i+1}}^{3}\delta_{ij} = \ln\eta_j-\ln\eta_i$$

Substituting the expressions for friction between unlike molecules (η_{12}, η_{23}, η_{31}) in equation (3), we get,

$$\begin{aligned}\ln\eta &= \Omega_1^2\ln\eta_1+\Omega_2^2\ln\eta_2+\Omega_3^2\ln\eta_3+2\Omega_1\Omega_2\\ &\quad\times[\alpha_{12}+\beta_{12}(1-\Omega_2-\Omega_3)]+\Omega_1\Omega_2(\ln\eta_1+\ln\eta_2)\\ &\quad+2\Omega_2\Omega_3\ [\alpha_{23}+\beta_{23}(1-\Omega_3-\Omega_1)]+\Omega_2\Omega_3(\ln\eta_2+\ln\eta_3)\\ &\quad+2\Omega_3\Omega_1[\alpha_{31}+\beta_{31}(1-\Omega_1-\Omega_2)]\\ &\quad+\Omega_3\Omega_1(\ln\eta_3+\ln\eta_1)\end{aligned}\tag{6}$$

By substituting the expressions for β_{ij} and δ_{ij} into equation (6), rearranging different terms, and using the concept that free volume and viscosity are inversely related [19] yields the following equation:

$$\begin{aligned}\frac{1}{\Delta F_V} &= \delta_1[\phi_1-\Omega_1(1+\Omega_1\Omega_2)]+\delta_2\left[\Omega_3\left(1-\Omega_2^2\right)-\phi_3\right]-\delta_3\Omega_3^2\Omega_1\\ &\quad+\sum_{\substack{i,j=1\\ j=i+1}}^{3}\left[\frac{e^{1/F_{VB}}\rho\Omega_i^2\Omega_j}{1+\gamma_{ij}}+2\alpha_{ij}(1-\Omega_i)\Omega_i\Omega_j\right]\end{aligned}\tag{7}$$

Here, the term on the left hand side is given by

$$\frac{1}{\Delta F_V} = \frac{1}{F_{VB}}-\frac{\phi_1}{F_{V1}}-\frac{\phi_2}{F_{V2}}-\frac{\phi_3}{F_{V3}}\tag{8}$$

where F_{VB}, F_{V1}, F_{V2}, F_{V3} are the experimentally measured fractional free volumes of the ternary blend, pure polymers (blend constituents) 1, 2 and 3 respectively and ϕ_1, ϕ_2 and ϕ_3 are the volume fractions of the blend components 1, 2 and 3 respectively.

For a ternary blend, an effective hydrodynamic parameter (α_{eff}) in terms of the individual α's and volume fractions of the component polymers can be evaluated for the purpose of comparison of the existing literature data. This is evaluated using the relation

$$\alpha_{eff} = (\phi_1+\phi_2)\alpha_{12}+(\phi_2+\phi_3)\alpha_{23}+(\phi_3+\phi_1)\alpha_{31}\tag{9}$$

where ϕ_1, ϕ_2, ϕ_3 have the same meaning as described earlier and α_{12}, α_{23}, α_{31} are the hydrodynamic interaction parameters corresponding to interfaces between polymer1-2, 2-3 and 3-1 respectively.

According to the definition of γ, which can be evaluated from the group contribution method [47] for the molecular architecture, it was considered to be constant for a given pair of polymers (i.e., composition-independent). Since the free volume depends on the molecular architecture of the system, and this definition of γ needs to be re-looked i.e., it has to be considered as a composition dependent parameter. In case of binary polymer blends, it has already been reported that γ is not a composition-independent parameter [31], and Wolf et al. [48] also had expressed the same view and the relation given by Kapnistos et al. [49] was modified by Ranganathaiah et al. [31] in terms of F_V to determine the geometric factor. Now for a mixture of three polymers, we modified the expression to calculate parameter γ_{ij} and this is written as

$$\frac{1}{F_{VB}}=\frac{\phi_1}{F_{V1}}+\frac{\phi_2}{F_{V2}}+\frac{\phi_3}{F_{V3}}+\sum_{\substack{i,j=1\\ j=i+1}}^{3}\left[\left(\frac{1}{F_{Vj}}-\frac{1}{F_{Vi}}\right)\left(\frac{\gamma_{ij}\phi_j\phi_i}{1+\gamma_{ij}\phi_j}\right)\right]\tag{10}$$

where the parameters carry the same meaning as defined earlier.

In case of miscible binary blends, the entanglements of polymer chains generate additional friction at the interface, which results in an increase of energy dissipation accompanied by reduction in interfacial tension. This situation corresponds to good dispersion of the dispersed phase in the matrix which leads to increased sites of interaction between the constituent polymer chains. In terms of the present model parameter α, it acquires larger negative values indicating energy dissipation at the interface. In case of immiscible blends, each polymer forms its own domain in the system results to fewer contacts between chains of polymer 1 and 2. This situation corresponds to less or no friction at the interface between the chains of constituent polymers. For such systems α acquires values equal to or greater than zero. Further, for a given pair of polymers, α may become negative for some compositions and positive for some compositions. Such systems are termed as partially miscible systems. This is the general interpretation of the interfaces in terms of α value and its sign.

Using the obtained F_V(s) and the respective volume fractions ϕ_1, ϕ_2, ϕ_3, the geometric factor γ_{ij} are obtained by using equation (10).

Using these γ_{ij}, the surface fractions Ω_1, Ω_2 and Ω_3 are calculated using the equation (4). As per our calculation, the errors on $F_V(s)$, ϕ_1, ϕ_2, ϕ_3, γ_{ij}, Ω_1, Ω_2, Ω_3, and the density of the blend ρ turns out to be 0.035% on $F_V(s)$, 0.002% on volume fractions, 5% on γ_{ij}, 0.6% on surface fractions, and 0.001% on density of the blend ρ.

We have used equation (7) to obtain the hydrodynamic interaction parameters α_{ij} for different blend systems and for different composition. The calculation of error on α_{ij} turned out to be 7%. Using these α_{ij} values and volume fractions of the blend constituents, an effective alpha (α_{eff}) for a particular composition of the ternary blend has been calculated according to equation (9). The uncertainty on this α_{eff} turns out to be 8%. These data are tabulated in Table 3. In Fig. 6, we show the plot of hydrodynamic interaction parameters α_{ij} for the ternary blend SAN/PVC/PMMA as a function of PMMA wt. %. Here, the three hydrodynamic interaction parameters for the interfaces formed among the blend constituents are designated as α_{12} for SAN/PVC, α_{23} for PVC/PMMA and α_{31} for PMMA/SAN. As can be seen from Fig. 6 and data in Table 3, we observe that the interface between SAN/PVC characterized by the hydrodynamic interaction parameter α_{12} of the ternary blend SAN/PVC/PMMA, exhibits positive values at the compositions (20/65/15), (75/5/20), (15/50/35). The magnitude and sign of α parameter is used to explain interface characteristics as said above which is exactly identical to that described in ref 31. Accordingly, positive values of α_{12} means that the friction at the interface is negligibly small and hence interfacial tension is high, so the adhesion at the interface is weak. This also means SAN and PVC components are incompatible at these compositions and the corresponding interfaces are that of an immiscible blend. At composition (75/5/20), in which the concentration of PVC is only 5% and is the dispersed phase, the α_{12} is 13.48 and this is highest positive value of all the compositions of the two blends studied. This means for this composition of SAN/PVC, interface is very weak due to high interfacial tension. Interestingly, we observe a negative value for α_{12} of -1.85 at composition (5/50/45) in which SAN becomes the dispersed phase and PVC is the matrix. This suggest that the repulsion between styrene and acrylonitrile groups of the SAN copolymer provides PVC chains to slide in between them since PVC is the matrix [50,51]. This in terms of friction, this means there is some friction and the tension at the interface eases due to dispersion. The nature of the interface between SAN/PVC can be understood from that in the binary blend SAN/PVC and it corresponds to partially miscible means miscible over few compositions only [11,52,53]. The second interface α_{23} between PVC/PMMA shows positive values (3.56 and 0.27) for the compositions (20/65/15) and (15/50/35) respectively and the inference of immiscible nature holds good as derived from PVC/PMMA interface observed in binary blend of this and is an immiscible blend. However, the compositions (75/5/20) and (5/50/45) produce small negative values of -0.31 and -1.48 for α_{23} respectively. This may be due to limited favorable interactions between the carbonyl group of PMMA and α- hydrogen of PVC (see Scheme 1) [54–57]. For (75/5/20), PVC content is less compared to 20% of PMMA which is probably the reason for small value of α_{23} while for (5/50/45) composition, PVC and PMMA are almost of the same amount resulting to considerable number of interactions and hence a slightly higher value of -1.48 for α_{23}. This suggests that miscibility level at this composition is still low and hence poor adhesion at the interface, a fact in agreement with earlier experimental inferences [56]. However, it is interesting to note that the third interface characterized by α_{31} between PMMA/SAN of this ternary blend exhibits negative values of -6.65, -21.48, -2.82 and -7.09 respectively at all the four compositions (20/65/15), (75/5/20), (15/50/35) and (5/50/45) studied. Further (75/5/20) composition produces the highest α_{31} value which for this blend could be considered as the stronger interface ($\alpha_{31} = -21.48$) by comparison and the two polymer components involved are highly miscible. As per our prescription, this suggests increased friction at the interface (highest negative value of α_{31}) since it is well known mechanism producing the binary blend of PMMA/SAN highly miscible due to repulsive interaction between the styrene and acrylonitrile segments of the SAN chains (see Scheme 1), and in the process SAN chains are pushed apart and PMMA chains easily slide in between them [31,58–61]. This observation agrees very well with literature assertion that SAN/PMMA blend is miscible at all compositions [58–61].

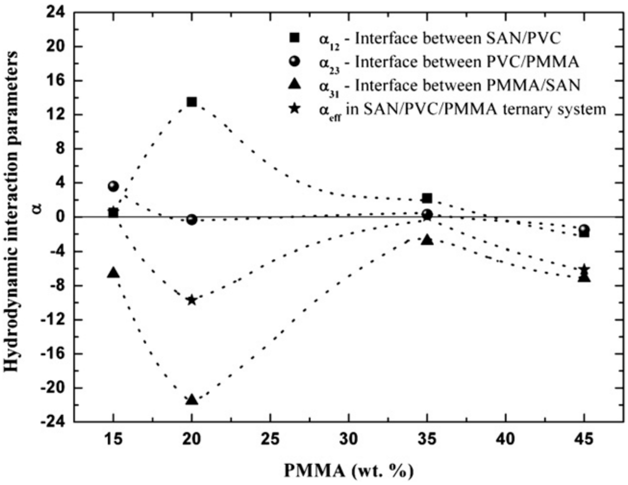
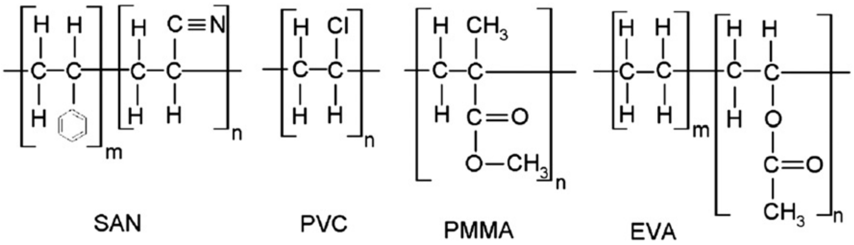


Fig. 6. Plot of hydrodynamic interaction parameters α as a function of PMMA wt. (%) for the ternary polymer blend SAN/PVC/PMMA.

Now having understood on the individual interfaces characterized by α_{12}, α_{23} and α_{31} of the ternary blend SAN/PVC/PMMA, let us look at the observations made by other workers on this ternary blend (8). From the present study we have the effective alpha values deduced for each composition and these are plotted in Fig. 6 and also given in Table 3. It can be seen that at the compositions (20/65/15) and (15/50/35), α_{eff} become positive inferring that the ternary blend SAN/PVC/PMMA is a phase separated and immiscible

Table 3
Hydrodynamic interaction parameters (α) for SAN/PVC/PMMA and SAN/EVA/PVC ternary polymer blends (in the last column numbers in the parenthesis indicate references of works referred to).

Blend	Composition	γ_{12}	γ_{23}	γ_{31}	α_{12}	α_{23}	α_{31}	α_{eff}	Inference from literature
SAN/PVC/PMMA	(20/65/15)	0.76	3.74	−6.14	0.49	3.56	−6.65	0.55	Immiscible (8)
	(75/5/20)	0.73	−4.60	−1.32	13.48	−0.31	−21.48	−9.67	Miscible (8)
	(15/50/35)	1.99	0.35	−2.66	2.21	0.27	−2.82	0.12	Immiscible (8)
	(5/50/45)	−0.67	−0.40	−2.07	−1.85	−1.48	−7.09	−6.13	Miscible (8)
SAN/EVA/PVC	(50/35/15)	−1.97	−1.65	3.08	−0.74	−4.28	−0.61	−3.18	Miscible (11,53)
	(70/15/15)	−3.85	−3.98	0.48	1.35	0.09	−0.28	0.98	Immiscible (53)



Scheme 1. Illustration of chemical structures of polymers used in the preparation of ternary blends.

system at these compositions. Table 3 also provides the inferences drawn for these compositions from available literature [8]. However, for the other two compositions i.e., (75/5/20) and (5/50/45), the α_{eff} parameter is negative suggesting that at these two compositions the blends are miscible with varying level of miscibility. Table 3, provides comparison between present conclusions with those from literature for these compositions [8] and we find good agreement with these results.

Now it becomes very clear that the information on individual interfaces in the ternary blends is not evident from any of the earlier works and hence the present results are first of their kind in this context. Another important point to be noted is that inferences like phase separated, single phase, immiscible, miscible, fine dispersion and coarse dispersion derived from DSC and SEM results, could only help to infer for example the compositions (75/5/20) and (5/50/45) of SAN/PVC/PMMA are miscible while compositions (20/65/15) and (15/30/45) are immiscible: But one cannot arrive at the result that the individual interfaces are stronger, strong or weak which is an essential input for a researcher to device methods to improve the properties of the ternary blends through compatibilization by any of the suitable methods. If we learn that one of the interfaces is very weak, only that interface can be stabilized or compatibilized and such useful information comes from the exploitation of hydrodynamic interactions resulting from viscoelastic behavior of the blends even in solid phase. Furthermore, this method also provides a useful parameter like α_{eff}, through which level of miscibility for each composition can be evaluated.

Let us now understand the results for the other ternary blend namely SAN/EVA/PVC studied in this work. Characterization of the interfaces in this system is same as the one described previously and the results obtained are also tabulated in Table 3. Here the three interfaces formed between the blend constituents are assigned as α_{12} for SAN/EVA, α_{23} for EVA/PVC and α_{31} for PVC/SAN. From Table 3, it can be seen that the interface between SAN/EVA characterized by α_{12} is negative with a value of −0.74 at (50/35/15) and positive with a value of 1.35 at (70/15/15). Similar arguments can be used for SAN/PVC/PMMA ternary blend case also. For the composition (50/35/15) the friction generated at the interface seems to be very small as indicated by α_{12} with a negative value of −0.74 which further suggest the compatibility between the components SAN and EVA is not high. However, literature results indicate that at 70/30 of SAN/EVA is immiscible based on viscosity shear rate measurement [11]. Since the compositions are different, we cannot compare our results with data. The second interface i.e. between EVA/PVC characterized by α_{23} of the ternary blend is negative with a value of −4.28 for the same composition (50/35/15) whereas slightly positive 0.09 at (70/15/15). In analogy with our earlier description, the negative α_{23} (−4.28) indicates good compatibility of the pair and increased friction at the interface and reduced interface tension. Therefore, for this blend this is the strong interface. The reason for this is as per literature, physical cross-linking between EVA and PVC chains is possible and this appears to be more for this composition [11]. However, for the composition (70/15/15), a situation like a co-continuous phase in binary blend (equal amounts of PVC and EVA) exists and the probability of the above mentioned physical cross links may be very small and therefore α_{23} becomes positive [11,18]. The interface between SAN/PVC components characterized by α_{31} are negative with values of −0.61 and −0.28 at both the compositions (50/35/15) and (70/15/15) respectively. The small values of α_{31} is due to the repulsive interaction among the SAN segments and this might make way for PVC chains to slide in [50,51]. The difference in magnitude of α_{31} is attributed to the variation in SAN and PVC content. Earlier work on the binary blend SAN/PVC concluded that the pair produces partial miscible blend due to the reduction in physical cross links between the pairs [11].

The calculated values of α_{eff} for the ternary blend SAN/EVA/PVC are shown in Table 3 and the inference is that this blend at (50/35/15) composition is miscible [11,53]. The miscibility of the blend at this composition is attributed to the physical cross links between EVA and PVC chains [11] and the present results show that the interface between responsible for this is characterized by α_{23}. The other composition (70/15/15), however, remains phase separated system since α_{eff} is positive. By comparison, our results agree with those reported in literature [53] for this ternary blend. It is clear from literature that for understanding of the ternary blends miscibility levels, indirect experiments were carried out like for the individual interfaces respective binary blends were constructed and inferred based on this that a given ternary blend as miscible or immiscible. Further such inferences are not correct since the situation of simultaneous presence of three interfaces in a real ternary blend is different and more complicated due to three dimensional microstructure compared to an individual interface that one finds in binary blend. This laborious route is simplified remarkably by the present method which provides information on the in situ individual interfaces formed in ternary blends.

4. Conclusions

Based on the results discussed above, the following conclusions are made:

1. It is evident that techniques like DSC and SEM widely used in the study of miscibility in ternary polymer blends, fail to provide information on individual interfaces. Therefore, we could say they had limited success in predicting the composition dependent miscibility level of the system of study.
2. The fractional free volume (F_V) obtained from PLS cannot by itself capable of providing information on the individual interfaces formed in ternary polymer blends.
3. Newly found hydrodynamic interaction approach using the same F_V obtained from PLS is found to serve as a method of choice to characterize interfaces in ternary blends.

4. As of now, we believe this is the only method which provides individual interface characteristics to infer that component polymer 1 is miscible in polymer 2 but immiscible in polymer 3 which serves as a precursor to device methods to improve final properties of the blend in question.
5. The ternary blend SAN/PVC/PMMA produces a maximum α_{eff} value of -9.67 at the composition (75/5/20) suggesting high miscibility with strong interfaces. The second ternary blend SAN/EVA/PVC at (50/35/15) composition has α_{eff} value of -3.18 and by comparison with SAN/PVC/PMMA is less miscible and EVA/PVC interface is responsible for this.

Acknowledgements

The first author (DM) thanks the UGC, New Delhi and University of Mysore for providing financial support in the form of UGC Junior fellowship for carrying out this work.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.12.041.

References

[1] Ajji Abdellah. In: Utracki LA, editor. Polymer blends Handbook, vol. 1. London: Kluwer academic publishers; 1999. p. 295–338.
[2] Stamm M. Polymer surfaces and interfaces – Characterization, modification and applications. Springer, Verlag Berlin Heidelberg; 2008.
[3] Le Menesterl Christophe, Bhagwagar Dorab E, Painter Paul C, Coleman Michael M. Macromolecules 1992;25:7101–6.
[4] Kwei TK, Frisch HL, Radigan W, Vogel S. Macromolecules 1977;10:157–60.
[5] Wang YY, Chen SA. Polym Eng Sci 1981;21:47–52.
[6] Shah VS, Keitz JO, Paul DR, Barlow JW. J Appl Polym Sci 1986;32:3863–79.
[7] Nishi T, Suzuki T, Matsuzawa N, Michizono S, Tanaka H. Polym Prepr (Am Chem Soc Div Polym Chem) 1987;28:110–1.
[8] Hurang JC, Min Kyonsuku, White James L. Polym Eng Sci 1988;28:1085–94.
[9] Brannock GR, Paul DR. Macromolecules 1990;23:5240–50.
[10] Pomposo JA, Calahorra E, Eguiazabal I, Cortazar' M. Macromolecules 1993;26:2104–10.
[11] Lizymol PP, Thomas Sabu. Eur Polym J 1997;33:1397–9.
[12] Goh SH, Ni X. Polymer 1999;40:5733–5.
[13] Pinoit Dominique, Prud' homme Robert E. Polymer 2002;43:2321–8.
[14] Hsu Wen-Ping. J Appl Polym Sci 2005;96:2064–70.
[15] Liu Hung-Ling, Li Shu-Hsien, Woo Eamor M. J Polym Science Part B Polym Phys 2006;44:1147–60.
[16] Abolhasani MM, Arefazar A, Mozdianfard M. J Polym Science Part B Polym Phys 2010;48:251–9.
[17] Utracki LA. In: Utracki LA, editor. Polymer blends handbook, vol. 1. London: Kluwer academic publishers; 1999. p. 123.
[18] Lizymol PP, Thomas Sabu. J Mater Sci Lett 1998;17:507–10.
[19] Doolittle AK. J Appl Phys 1951;22:1471–5.
[20] Ramani R, Ramachandra P, Ravichandran TSG, Ramagopal G, Gopal S, Ranganathaiah C. Appl Phys A 1995;60:481–6.
[21] McGonigle EA, Liggat JJ, Pethrick RA, Jenkins SD, Daly JH, Hayward D. Polymer 2001;42:2413–26.
[22] Ashalatha MB, Sathyanarayana PM, Shariff G, Thimmegowda MC, Ramani R, Ranganathaiah C. Appl Phys A 2003;76:1–9.
[23] Thimmegowda MC, Ravikumar HB, Ranganathaiah C. J Appl Polym Sci 2004;92:1355–66.
[24] Dlubek G, Bondarenko V, al-Qaradawi Y, Kilburn D, Krause-Rehberg R. Macromol Chem Phys 2004;205:512–22.
[25] Wastlund C, Maurer HJ. Macromolecules 1997;30:5870–6.
[26] Peng ZL, Olson BG, Srithawatpong R, McGervey JD, Jamieson AM, Ishida H, et al. J Polym Sci Part B Polym Phys 1998;36:861–71.
[27] Aravind I, Albert P, Ranganathaiah C, Kurian JV, Thomas S. Polymer 2004;45:4925–37.
[28] Ravikumar HB, Ranganathaiah C, Kumarswamy GN, Thomas S. Polymer 2005;46:2372–80.
[29] Ravikumar HB, Ranganathaiah C, Kumaraswamy GN, Deepa Urs MV, Jagannath JH, Bawa AS, et al. J Appl Polym Sci 2006;100:740–7.
[30] Raj JM, Ranganathaiah C, Ganesh S. Polym Eng Sci 2008;48:1495–503.
[31] Ranganathaiah C, Kumarswamy GN. J Appl Polym Sci 2009;111:577–88.
[32] Raj JM, Ranganathaiah C. J Polym Sci Part B Polym Phys 2009;47:619–32.
[33] Raj JM, Ranganathaiah C. J Polym Degrad Stab 2009;94:397–403.
[34] Kumaraswamy GN, Ranganathaiah C, Deepa Urs MV, Ravikumar HB. Euro Polym J 2006;42:2655–66.
[35] Schnell M, Wolf BA. J Rheol 2000;44:617–28.
[36] Schnell M, Wolf BA. Polymer 2001;42:8599–605.
[37] Zimm BJ. Chem Phys 1956;24:269–78.
[38] Rouse PJ. J Chem Phys 1953;21:1272–80.
[39] Riande E, Diaz-Calleja R, Prolongo MG, Masegosa RM, Salom C. Polymer viscoelasticity: stress and strain in practice. New York: Marcel Dekker; 2000. p.583.
[40] Zwanzig Robert, Kiefer James, Weiss George H. Proc Natl Acad Sci U S A 1968;60:381–6.
[41] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1955;77:3701–7.
[42] Jean YC. Microchem J 1990;42:72–102.
[43] Kirkegaard P, Pedersen NJ, Eldrup M. Riso Nat Lab Rep; 1989:M-2740.
[44] Utracki LA. Polymer alloys and blends-thermodynamics and Rheology. New York: Hanser; 1990.
[45] Hsieh TT, Tiu C, Simon GP. Polymer 2000;41:4737–42.
[46] Nakanishi H, Wang SJ, Jean YC. In: Sharma SC, editor. Positron annihilation in fluids. Singapore: World Scientific; 1988.
[47] Bondi A. J Phys Chem 1964;68:441–51.
[48] Mertsch R, Wolf BA, Bunsenges Ber. Phys Chem 1994;98:1275–80.
[49] Kapnistos M, Hinrichs A, Vlassopoulos D, Anastasiadis SH, Stammer A, Wolf BA. Macromolecules 1996;29:7155–63.
[50] Kim JH, Barlow JW, Paul DR. Polym Eng Sci 1989;29:581–5.
[51] Chul-Wan Kim, Jung-Ki Park, Taek-Sung Hwang. Polym Eng Sci 1996;36:535–40.
[52] Hurang JC, Min Kyonsuku, White James L. Polym Eng Sci 1988;28:1590–9.
[53] Lizymol PP, Thomas Sabu. Thermochimica Acta 1994;233:283–95.
[54] Schurer JW, Deboer A, Challa G. Polymer 1975;16:201–4.
[55] Khan Mohammad Saleem, Qazi Raina Aman, Wahid Mian Said. Afr J Pure Appl Chem 2008;2:41–5.
[56] Deshpande VD, Singh Umesh. J Appl Polym Sci 2006;101:624–30.
[57] Sato Takanori, Tsujita Yoshiharu, Takizawa Akira, Kinoshita Takatoshi. Macromolecules 1991;24:158–60.
[58] Robertson CG, Wilkes GL. Polymer 2001;42:1581–9.
[59] Fowler ME, Barlow JW, Paul DR. Polymer 1987;28:1177–84.
[60] Janarthanan V, Kressler J, Karasz FE, MacKnight WJJ. Polym Sci Phys 1993;31:1013–7.
[61] Pfennig JLG, Keskkula H, Barlow JW, Paul DR. Macromolecules 1985;18:1937–40.