

Free Volume as an Internal Material Parameter to Probe Interfaces in Ternary Polymer Blends: A Positron Lifetime Study

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ABSTRACT: A new method to characterize individual interfaces in ternary polymer blends from experimentally measured fractional free volume from Positron Annihilation Lifetime Spectroscopy (PALS) has been developed. By this, we derive the composition dependent miscibility level in ternary polymer blends. This method has its genesis in KRZ (Kirkwood–Risemann–Zimm) theory which introduces hydrodynamic interaction parameter as a measure of excess friction generated at the interface between dissimilar polymer chains resulting in energy dissipation. The method successfully applied for binary blends has been theoretically modified to suit ternary blends in the present work. The efficacy of this method has been tested for two ternary blends namely polycaprolactone/poly(styrene-co-acrylonitrile)/poly(vinyl chloride) (PCL/SAN/PVC) and polycaprolactone/poly(vinyl chloride)/poly(vinyl acetate) (PCL/PVC/PVAc) in different compositions. We obtained a maximum effective hydrodynamic interaction (α_{eff}) of -12.60 at composition 80/10/10 of PCL/PVC/PVAc while PCL/SAN/PVC showed -1.60 at 68/16/16 composition. These results suggest that these compositions produce high miscibility level as compared to other compositions. DSC measurements have also been used to supplement positron results. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3335–3344, 2013

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INTRODUCTION

Interfaces in polymeric systems are ubiquitous. “Interface” is the region formed between two phases which is important and is expected to change with composition. The composition, structure, and behavior of these interfaces play a pivotal role in dictating the overall strength of polymer blends. For instance, miscibility, adhesion, compatibilization, blend morphology, mechanical strength, etc, are all controlled by the interfacial behavior.^{1–3} Owing to this, miscibility and phase-separation phenomena, in polymer blends, have received significant attention in recent times due to wide applications of polymer blends.^{4–7} The manifestation of superior properties of blends is in their constituents and on the thermodynamic miscibility at the molecular scale. Therefore, this needs to be understood in greater detail at the molecular level. Thermodynamic miscibility means the system exhibits single phase down to the molecular level. Miscibility of polymer blends is a result of specific interactions that exists between the blend constituents which leads to negative free energy of mixing.⁸ Many experimental and theoretical methods have been used to investigate polymer-polymer

miscibility in solution and in solid phase. Thermal analysis, electron microscopy, turbidity and viscometry are some of the methods extensively reported in literature.^{9–12} Unfortunately, none of these techniques reveal the important information on the nature of interfaces in a blend and compatibility of the chains involved in particular compositions. That is, the composition dependant miscibility level is not derivable from these methods. More often, lack of compatibility and hence weaker interfaces render such blends unsuitable for their intended applications. Therefore, it is essential that the weak interface in such blends be identified.

Moreover, the most popular techniques commonly used to characterize polymer blends suffer from limitations. For example, viscometric technique; the viscosity measurement no doubt is the simplest and inexpensive method. There are many criteria proposed by various researchers to determine polymer–polymer miscibility through viscosity method, to mention a few: intrinsic viscosity-composition plots,¹³ reduced specific viscosity - concentration plots,¹⁴ interaction parameter “ μ ” proposed by Chee¹⁵ and thermodynamic parameter approach proposed by Sun et al.¹⁶ These methods use intrinsic viscosity to ascertain

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that a blend is miscible or immiscible; and, to obtain the intrinsic viscosity, viscosities of the solutions at various concentrations are determined and extrapolation to zero concentration is used. In doing so, a considerable amount of time, effort, and materials are lost in conducting a series of experiments and moreover, this graphical method do not provide very accurate estimation of intrinsic viscosities. To be more precise, determination of intrinsic viscosity is an indirect method. Also, it is reported that the level of mixing of polymers in solid phase is more important than in liquid phase.¹⁷ This is very important because blending of polymers is necessitated by the fact that individual polymers do not deliver what is demanded by commercial or scientific applications. Further, the era of ternary blends started when binary blends also failed to fulfil some such demands⁷ and in this context it shall not be considered that study of ternary blends is purely for academic interest but for technological point of view as well. Literature reveals that for viscometric studies, ternary blends are invariably considered as two polymers and the third component is a solvent or simply they are polymer/polymer/solvent systems. It is to be noted that any new material synthesized or fabricated in the laboratory finds its use in the commercial world generally as a solid material. Further, the compatibility between polymers in the presence of a solvent, as measured by viscosity depends on the solvent used^{18,19} and hence cannot be considered as accurate. Furthermore, these methods help to infer that a blend is miscible or immiscible only but never reveal information on the level of miscibility (what composition of constituents produce highest homogeneity) in the blend and the nature of interfaces that exists in the blend. As far as the final utility of the blend is concerned, interfaces in the blends play an important role since the final properties are manifested in the interfaces. To this end, the method described in this article certainly turns out to be unique in the sense that information on the individual interfaces formed in a three-dimensional ternary blend is readily forthcoming. This helps to recognize the weakest interface that leads to poor mechanical properties of the blend. With such information in hand, methods to stabilize/improve the weak interface and improve the overall quality and strength of the blend can be devised.

With this view point, we found that the hydrodynamic interaction approach is a powerful method to understand the interfaces although specific interactions prescription is not directly attached to it. The experimental method we adopted here to evaluate hydrodynamic interaction is a novel nondestructive tool namely Positron Annihilation Lifetime Spectroscopy (PALS). Direct experimental measurement of fractional free volume (F_V) of the blends and their pure components in the solid phase is used to extract hydrodynamic interaction. In this context, free volume which has been in use for a long time is considered as an internal material parameter of the polymer material. The efficacy of the method is tested by studying the nature of interfaces and the overall miscibility in two ternary polymer blends namely PCL/SAN/PVC and PCL/PVC/PVAc in different compositions.

THEORY

The hydrodynamic interaction concept owes its origin to KRZ model,²⁰ proposed by Zimm based on the works of Kirkwood

and Risemann, which is an extension of the (Kargin–Slonimsky–Rouse) KSR model.²¹ These models deal with the flow behavior of polymer mixtures. KRZ model can be considered as the next step in theoretical conceptions of the KSR model. The significant new point in KRZ theory is the consideration of hydrodynamic interaction that exists between segments of the polymeric chains, due to the mechanical interactions at the segmental level.²² This flow influences the visco-elastic behavior of the system both in liquid and in solid phase but to different levels. Hydrodynamic interaction excludes specific interactions between the components of the mixture but it deals with the friction generated at the interface due to motion of the chains involved. As friction is associated with the visco-elastic flow, energy dissipation occurs at the interface which depends on the composition of the polymer and the solvent in the system. Schnell and Wolf^{23,24} used the concepts of the KRZ model for polymer/solvent system by parameterizing the hydrodynamic interaction namely: the geometric factor (γ) related to the molecular architecture and geometrical arrangement of the segments in the blend and the hydrodynamic interaction parameter (α) which is a measure of the excess friction generated at the interface. As all materials exhibit viscoelastic response, and more so by polymers, Ranganathaiah et al.^{2,25} modified Schnell and Wolf^{23,24} theory for polymer/solvent system to polymer/polymer system in solid phase on the basis of inverse relation between free volume and viscosity.²⁶ However, the strength of hydrodynamic interaction will be generally small in polymer/polymer system in solid phase as compared to polymer/solvent system. Ranganathaiah's method has been successfully applied for few binary polymer blends, characterized by single interface^{25,27–30} and was shown to be sensitive to the changes at the interface brought in through e-beam and microwave irradiation.^{27–29} The hydrodynamic interaction parameter α has been derived in terms of the fractional free volume (F_V) directly measured by Positron Annihilation Lifetime Spectroscopy. The composition dependent miscibility level is clearly indicated by this method in terms of the magnitude and sign of the parameter α . This method however, cannot be simply extended to ternary polymer blends which are characterized by three interfaces. To characterize such a system, three discrete hydrodynamic interaction parameters α 's (α_{12} , α_{23} , and α_{31}), one for each interface are to be associated. The necessary mathematical formulations have been carried out in the present work keeping in mind the simple additivity relations (with regard to volume fractions, etc.). To check the efficacy of the method, two ternary blends poly(styrene-*co*-acrylonitrile)/poly(vinyl chloride)/poly(methyl methacrylate) (SAN/PVC/PMMA) and poly(styrene-*co*-acrylonitrile)/poly(ethylene-*co*-vinyl acetate)/poly(vinyl chloride) (SAN/EVA/PVC) in different compositions have been studied and found to be very satisfactory.³¹ Encouraged by the initial success of this method³¹ and realizing that the information derivable from this method is unique which is not derivable from any of the other existing methods employed in such studies, we tested the efficacy and reliability of this method by studying two other ternary blends. The individual α 's derived for the corresponding interfaces are used to obtain an effective alpha (α_{eff}) for the ternary blend by employing simple additivity

rule. This is very handy to compare our results with the existing literature reports. The versatility of α_{eff} in depicting the blend's miscibility level has been found to be in good agreement with the available literature data for the blends reported here.

Here we give a brief outline to connect the measured fractional free volume from PALS to the hydrodynamic interaction parameter α . We start from Schnell and Wolf^{23,24} relation for excess viscosity in a blend wherein, for ternary polymer blends, it is assumed that the excess viscosity is contributed by the excess viscosity generated from the three constituent polymers. By analogy, we define the excess viscosities in a ternary blend ($\Delta \ln \eta$) as

$$\Delta \ln \eta = \ln \eta - \phi_1 \ln \eta_{11} - \phi_2 \ln \eta_{22} - \phi_3 \ln \eta_{33} \quad (1)$$

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

Assuming that the energy dissipation takes place at the interfaces between like molecules ($\eta_{11} = \eta_1$; $\eta_{22} = \eta_2$; $\eta_{33} = \eta_3$) and unlike molecules (η_{12} , η_{23} , η_{31}), and excluding specific interactions, for an ideal mixing law for viscosity η of the mixture in terms of the surface fractions Ω of the constituents may be written as:

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

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

$$\begin{aligned} \Omega_1 = & \frac{(1+\gamma_{12})(1+\gamma_{31})\phi_1}{(1+\gamma_{12})(1+\gamma_{31})\phi_1 + (1+\gamma_{31})\phi_2 + (1+\gamma_{12})\phi_3}; \\ \Omega_2 = & \frac{(1+\gamma_{23})\phi_2}{(1+\gamma_{12})\phi_1 + (1+\gamma_{23})\phi_2 + \phi_3} \\ \Omega_3 = & \frac{\phi_3}{(1+\gamma_{31})\phi_1 + (1+\gamma_{23})\phi_2 + \phi_3} \end{aligned} \quad (3)$$

Here, γ is the geometric factor given by

$$\frac{1}{F_{VB}} = \frac{\phi_1}{F_{V1}} + \frac{\phi_2}{F_{V2}} + \frac{\phi_3}{F_{V3}} + \sum_{\substack{i,j=1 \\ j=i+1}}^3 \left[\left(\frac{1}{F_{Vj}} - \frac{1}{F_{Vi}} \right) \left(\frac{\gamma_{ij}\phi_j\phi_i}{1+\gamma_{ij}\phi_j} \right) \right] \quad (4)$$

Now, we establish realistic expressions that allow us to calculate η_{12} , η_{23} , η_{31} from η_{11} , η_{22} , η_{33} . Again by analogy with the binary system,²³ we construct the expressions for 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 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. As described earlier, α 's are considered to be a measure of excess friction developed at the interface (for

instance when the entanglement density changes) in the limit of vanishing solvent concentration. β_{ij} quantifies the alteration in the flow mechanism with composition which is given by,

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

where ρ is the density of the blend and δ_{ij} is given by,

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

By substituting the appropriate expressions into eq. (1), by rearranging different terms, and using the concept that free volume and viscosity are inversely related, we arrive at the following equation:

$$\begin{aligned} \frac{1}{\Delta F_v} = & \delta_1 [\phi_1 - \Omega_1(1 + \Omega_1\Omega_2)] + \delta_2 [\Omega_3(1 - \Omega_2^2) - \phi_3] - \delta_3 \Omega_3^2 \Omega_1 \\ & + \sum_{\substack{i,j=1 \\ j=i+1}}^3 \left[\frac{e^{1/F_{VB}} \rho \Omega_i^2 \Omega_j}{1 + \gamma_{ij}} + 2\alpha_{ij}(1 - \Omega_i)\Omega_i\Omega_j \right] \end{aligned} \quad (5)$$

Here, the term on left hand side is written as

$$\frac{1}{\Delta F_v} = \frac{1}{F_{VB}} - \frac{\phi_1}{F_{V1}} - \frac{\phi_2}{F_{V2}} - \frac{\phi_3}{F_{V3}} \quad (6)$$

Here, F_{VB} , F_{V1} , F_{V2} , and F_{V3} , are the measured fractional free volumes of the blend and its constituents respectively from PALS.

We found from literature that the work reported so far describes ternary blends as either miscible or immiscible and no description on the individual interfaces is provided. The effective α in terms of the individual α 's and volume fractions of the component polymers of the ternary blend are computed as given below:

$$\alpha_{\text{eff}} = (\phi_1 + \phi_2)\alpha_{12} + (\phi_2 + \phi_3)\alpha_{23} + (\phi_3 + \phi_1)\alpha_{31} \quad (7)$$

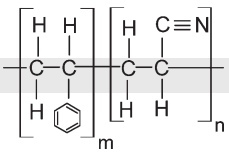
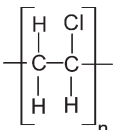
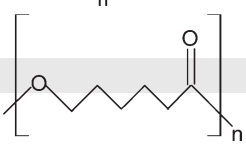
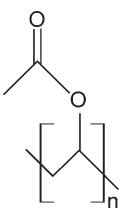
where ϕ_1 , ϕ_2 , ϕ_3 are the volume fractions of component polymers 1, 2, and 3 of the blend and α_{12} , α_{23} , α_{31} are the hydrodynamic interaction parameters corresponding to interfaces between polymers 1-2, 2-3, and 3-1 respectively.

EXPERIMENTAL

Sample Preparation

The polymer samples used in the preparation of the ternary blends and their properties are given in Table I. These were prepared from M/s Sigma-Aldrich Chemicals, Bangalore, India. Ternary blends of PCL/SAN/PVC and PCL/PVC/PVAc of different compositions were prepared by the conventional solution casting technique. The weighed proportions of PCL, SAN, and PVC were dissolved in a common solvent namely tetrahydrofuran (THF) at 60°C in four different compositions (a) 20/40/40, (b) 34/33/33, (c) 68/16/16, and (d) 70/25/5 respectively and the uniform solution was cast onto a clean and flat glass plate. The solvent was allowed to evaporate at room temperature for 4

Table I. Characteristics of Materials Used in this Study

Sample	Chemical structure	Specifications		
		Molecular weight (g/mol)	Density (g/cm ³)	<i>T_g</i> (°C)
Poly(styrene-co-acrylonitrile) (SAN)		AN content ~25% 1,65,000	1.080	106
Poly(vinyl chloride) (PVC)		43,000	1.340	74
Polycaprolactone		<i>M_n</i> : 90,000	1.145	-60
Poly(vinyl acetate) (PVAc)		1,00,000	1.180	45

days and the samples were then dried in an oven at 60°C to remove any traces of the solvent left in the sample. The neat and nice films (air bubble free) so obtained were approximately 1-mm thick. Similarly, ternary blend samples of PCL/PVC/PVAc of four compositions (a) 10/45/45, (b) 50/10/40, (c) 50/40/10, and (d) 80/10/10 respectively were dissolved in THF and prepared in the same way as described above and dried at 60°C. All the samples were stored in a vacuum desiccator before the actual use in experiments.

Measurements

Differential Scanning Calorimetry. The glass transition temperatures of the pure polymers and their blends of different compositions were measured using Universal VA.7A TA Instruments DSC Q 200 instrument. The experiments were carried out in an inert atmosphere (N₂). The ternary blend sample weighing roughly 10 mg was used at a heating rate 10°C/min, in the temperature range -80–120°C for both the blends.

Positron Lifetime Measurements. The positron lifetime measurements were carried out using a standard fast-fast coincidence system equipped with conically shaped BaF₂ scintillators (Scionix, Holland), coupled to photomultiplier tubes of type XP2020/Q having quartz window as detectors. The lifetime spectrometer had a time resolution of 220 ps as monitored by using ⁶⁰Co source. A 17-μCi ²²Na positron source was deposited at the center of a pure kapton foil of 12.7 μm thick, and sandwiched between two similar pieces for each sample. This source-sample sandwich was placed between the two detectors of the Positron Lifetime Spectrometer (PLS) to record the lifetime spectra. Typical spectrum accumulation time was around

1–2 h with more than a million counts under the spectrum. All the measurements were carried out in an air-conditioned room with temperature maintained at 24 ± 1°C. The source correction term and instrumental time resolution were estimated from the lifetime spectrum of a well-annealed aluminum using the program RESOLUTION.³² All the acquired lifetime spectra were deconvoluted into three discrete lifetime components using a finite-term lifetime analysis method using PATFIT-88³² computer program. The experimental and procedural details of this technique could be found in our earlier work.²⁵

The samples were prepared in the same way twice and all the measurements (DSC and PALS) were carried out twice. The reproducibility of the results was found to be good and was within the experimental errors.

RESULTS AND DISCUSSION

DSC Results

The common method to study the miscibility or immiscibility of a polymer blend is to measure its glass transition temperature *T_g* from a DSC scan. A miscible blend exhibits single *T_g*, characteristic of a single phase of the system while, a phase-separated blend exhibits multiple glass transitions. The measured DSC thermograms for the ternary blends PCL/SAN/PVC and PCL/PVC/PVAc are shown in Figures 1 and 2, respectively. For the blend PCL/SAN/PVC, the DSC traces show a single *T_g* at around -15 and 10°C for the compositions 68/16/16 and 70/25/5 respectively indicating single phase of the blends. Although the other two compositions of 20/40/40 (around -30 and 10°C) and 34/33/33 exhibit two distinct *T_g*s (around -5 and 30°C) indicating that

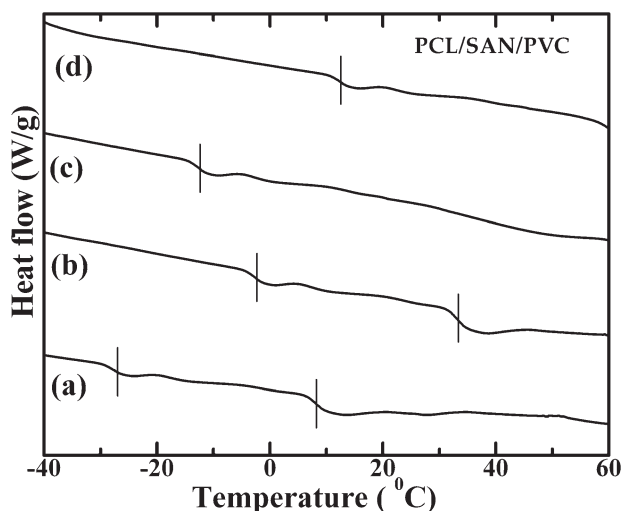


Figure 1. DSC scans of PCL/SAN/PVC blends for compositions (a) (20/40/40), (b) (34/33/33), (c) (68/16/16) and (d) (70/25/5).

they are phase separated. Conversely, the blend PCL/PVC/PVAc shows a single T_g at all the four compositions studied. These are around 25, -10, -20, and -35°C at 10/45/45, 50/10/40, 50/40/10, and 80/10/10, respectively. This implies that all the four compositions studied are miscible.

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 about 20°C) wherein the inference might be misleading sometimes due to overlap of the T_g s of the components. Another point to be noted is that this technique is sensitive only to heterogeneities with domain sizes larger than 15 nm and third and most importantly this method will not provide information on composition dependent miscibility level.^{6,25}

Free Volume Results from PLS

Positrons generally are known to probe the electron density distribution in matter. When a positron is implanted into a

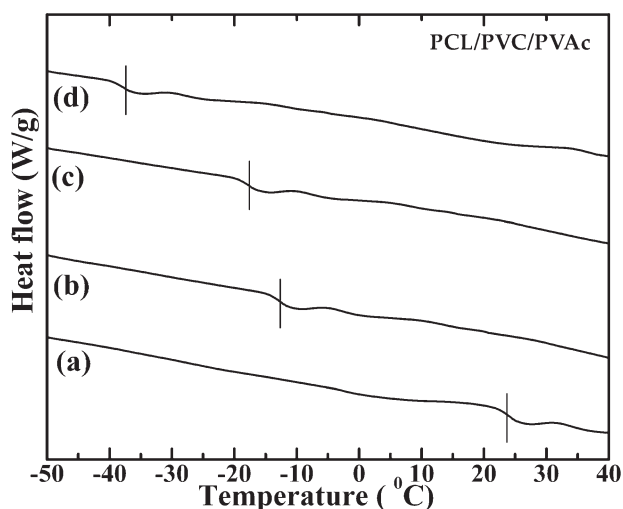


Figure 2. DSC scans of PCL/PVC/PVAc blends for compositions (a) (10/45/45), (b) (50/40/10), (c) (50/10/40) and (d) (80/10/10).

polymeric material from a radioactive source, it has different channels of annihilation: that is positron may annihilate as free positron, trapped positron annihilation or form hydrogen-like positronium atom (Ps) in two spin states and annihilate. The lifetime spectra usually consist of different mean lifetimes τ_1 , τ_2 , and τ_3 with relative intensities I_1 , I_2 , and I_3 respectively. The intensity indicates the relative number of positrons annihilating from that state. The three resolved positron lifetime components are attributed to the three states of positron annihilation. The shortest lifetime (~ 0.2 ns) component τ_1 with intensity I_1 is ascribed to p-Ps and free positron annihilations. The intermediate lifetime (0.2–0.5 ns) component τ_2 , with intensity I_2 , is considered as due to annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline-amorphous interface regions of the medium. The longest-lived component τ_3 , with intensity I_3 , is due to pick-off annihilation of the o-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix. The o-Ps annihilates with a lifetime of 140 ns in free space but in molecular media such as polymers, the lifetime is shortened due to interaction with electrons of the surrounding medium to few nanoseconds (pick-off annihilation). In the free volume model, the ortho-positronium (o-Ps) is assumed to be confined in a spherical potential well (free volume) and the lifetime of this specie (τ_3) is directly related to the free volume radius (R). The lifetime of o-Ps depends on the overlap of the Ps wave function with the electron wave function of the free-volume cavity. Therefore, larger the hole size, smaller is the overlap and hence lifetime is longer.³³ Also, it has been well established that the free volume hole size and concentration correlates to several visco-elastic properties of the polymer under study. Therefore, study of free volumes in polymer blends provide a means of understanding the molecular level of mixing in blends.²⁸

In polymers, the o-Ps pickoff annihilation is of prime importance because it is related to the average free volume hole size and intensity I_3 is considered as a measure of the relative concentration of free volume holes. Further, I_3 also represents the probability of o-Ps formation in polymers and their blends.³⁴

A simple relation developed by Nakanishi et al.³⁵ connects o-Ps lifetime τ_3 to free volume hole radius R given by

$$(\tau_3)^{-1} = 2 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right] \text{ns}^{-1} \quad (8)$$

where, $R_0 = R + \Delta R$ and ΔR is a fitting parameter representing the electron layer thickness. The value of ΔR is determined by fitting eq. (8) for known hole sizes in porous materials like zeolites and other molecular media and is found to be 1.656 Å. The average free volume hole size V_f is then evaluated as $V_f = (4/3) \pi R^3$ and the fractional free volume as $F_v = C I_3 V_f$ where C is a constant and its value is taken as 0.0018 \AA^{-3} .³⁶ A word of caution is in place for the argument that I_3 is influenced by several factors of the microstructure does not hold in this work because our calculations are done in terms of the fractional free volume rather than relative number of free volume cavities. It is important to note that only the occupied volume of the blend components is additive, not the free volume.³⁶ The free volume

is nonadditive because it depends on the molecular architecture, interaction, and orientation of the molecules. It may contract or expand and additional free volume may be generated when two or more polymers are mixed which results in negative or positive deviation from the simple linear additivity rule for volume.

The experimental τ_3 values of the pure polymers and their blends are used to calculate the free volume hole radius (R), free volume hole size (V_f) and fractional free volume (F_V) as per eq. (8) 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 their respective blends. The values so derived are tabulated in Table II and the fractional free volume of the ternary blends and the respective pure polymers are plotted in Figures 3 and 4. We observe from the data that the F_{VB} of a particular composition is closer to the F_V of its matrix (major component).

For ternary blends in the present study, we have used measured $F_V(s)$ and the respective volume fractions ϕ_1 , ϕ_2 , ϕ_3 to calculate the geometric factor γ_{ij} from eq. (4). Then from eq. (5), the hydrodynamic interaction parameters α_{ij} for different compositions of the blend system under study are calculated. Based on these α_{ij} values and volume fractions of the blend constituents, the effective alpha (α_{eff}) for each composition of the ternary blend has been calculated using eq. (7). The calculated values of α_{ij} and α_{eff} are tabulated in Table III.

From the hydrodynamic interaction perspective, although miscibility is due to specific interactions between the components, the component chains (segments) are certainly pulled closer at the interface due to these specific interactions and hence additional friction is expected to be generated at the interface if the blend is miscible and this is further influenced by the entanglements. As a consequence, dissipation of energy due to friction results and hence reduces the interfacial tension at the interface. If the above description holds well, we can expect good dispersion of

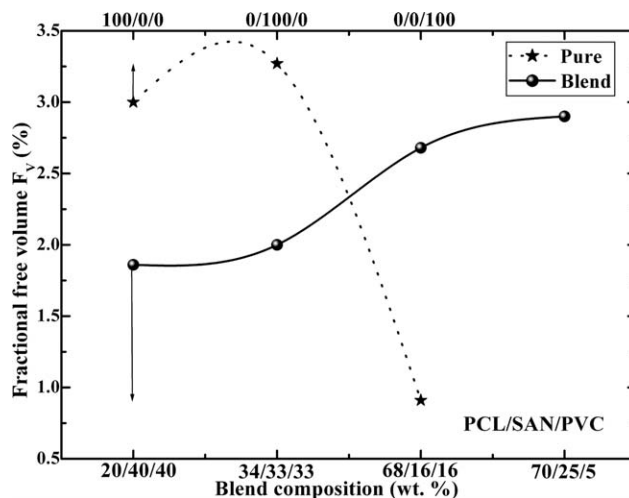


Figure 3. Plot of fractional free volume F_V as a function of blend composition for the ternary blend PCL/SAN/PVC; Upper X-axis for pure polymers and lower X-axis for ternary polymer blends.

the dispersed phase in the matrix. This could also be envisioned as the sites for interaction is increased. As said earlier, dissipation of energy is symbolized by the negative sign for α parameter of the present model in accordance with hydrodynamic theories. Conversely, for immiscible blends, each polymer forms its own domain in the system and hence reduces the possible sites of interaction, and, therefore, we expect less friction at the interface between the constituent polymer chains. This situation results to α acquiring either zero or positive values.

In practice, it has been observed that α takes on both positive and negative values depending on the compositions in conformity with hydrodynamic theories. Such blends are termed as partially miscible systems. This is the simple description of hydrodynamic interaction approach to understand the miscibility level in polymer blends.^{25,27–29,31}

Table II. Ortho-Positronium Lifetime Results in PCL/SAN/PVC and PCL/PVC/PVAc Ternary Polymer Blends

Sample	σ -Ps lifetime $\tau_3 \pm 0.01$ (ns)	σ -Ps intensity $I_3 \pm 0.14$ (%)	Free volume hole size $V_f \pm 0.8$ (\AA^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
PCL	2.24	13.75	121.19	3.00
PVAc	2.11	12.69	107.64	2.46
PCL/SAN/PVC				
(20/40/40)	2.08	9.80	105.14	1.86
(34/33/33)	2.10	9.90	111.96	2.00
(68/16/16)	2.19	12.86	115.83	2.68
(75/5/20)	2.23	13.34	120.40	2.90
PCL/PVC/PVAc				
(10/45/45)	1.89	8.30	87.39	1.30
(50/10/40)	2.11	8.60	108.08	1.67
(50/40/10)	1.70	8.90	70.52	1.12
(80/10/10)	2.22	12.80	118.84	2.74

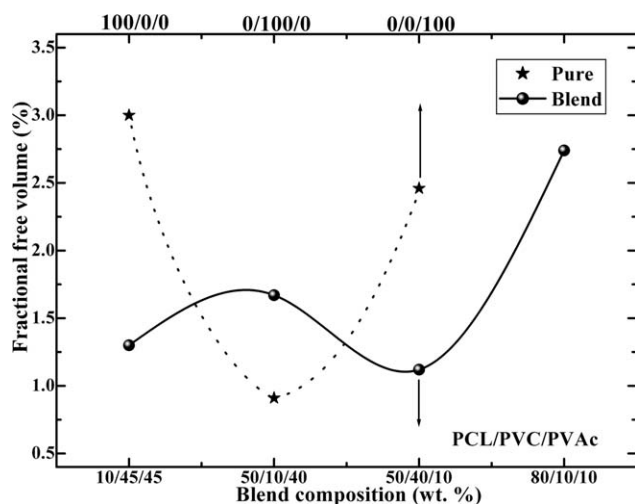


Figure 4. Plot of fractional free volume F_V as a function of blend composition for the ternary blend PCL/PVC/PVAc; Upper X-axis for pure polymers and lower X-axis for ternary polymer blends.

Figure 5 is a plot of hydrodynamic interaction parameters α_{ij} for the ternary blend PCL/SAN/PVC as a function of blend composition. The three α 's corresponds to the three interfaces formed in the blend and are designated as α_{12} for PCL/SAN, α_{23} for SAN/PVC and α_{31} for PVC/PCL. From Table III and Figure 5, we observe that the interface between PCL and SAN of the ternary blend PCL/SAN/PVC, characterized by the hydrodynamic interaction parameter α_{12} , exhibits negative values of -0.55 , -0.4 , and -0.3 for the compositions (34/33/33), (68/16/16), and (70/25/5) respectively and a positive value of 2.97 for the composition (20/40/40). As per the description given above, characterization of this interface is as follows. The negative values of α_{12} indicate compatibility of the polymer pair involved and hence polymer chains are pulled closer which gives rise to excess friction at the interface. This will happen if an interaction is involved. In this case, an interaction between the segments of PCL and SAN may occur due to proton donor–acceptor type interaction that exists between the oxygen atom in the carbonyl group of PCL and the tertiary hydrogen in the

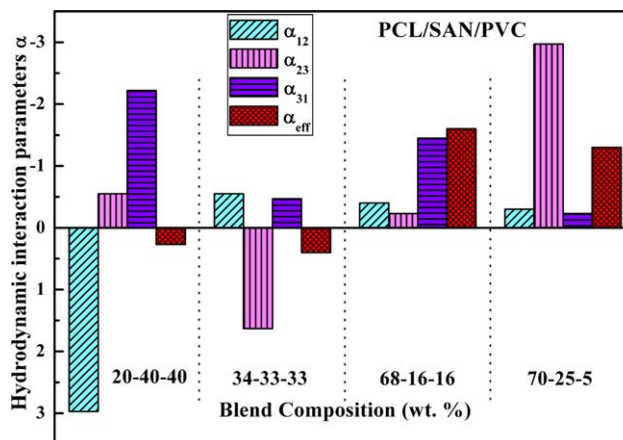


Figure 5. Plot of hydrodynamic interaction parameters α as a function of blend composition for the ternary polymer blend PCL/SAN/PVC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

acrylonitrile unit in SAN, a proton donor.³⁷ But, we observe a positive value of 2.97 at the composition 20/40/40 and this suggests that the friction at this interface is negligibly small. This means interfacial tension is more, adhesion is less and hence the interface formed is weak. It is noticeable that the negative values of α 's observed corresponds to the situation wherever PCL is the matrix and SAN is the dispersed phase. The weak interface for the composition 20/40/40 is because PCL is not the matrix. Therefore, this particular interface could be improved by subjecting the blend to microwave irradiation, as it was suggested that for polymers containing polar groups, interactions can be improved.²⁸ The second interface α_{23} between SAN/PVC takes on negative values of -0.55 , -0.17 , and -2.97 for the compositions 20/40/40, 68/16/16, and 70/25/5 respectively. The composition 70/25/5 produces a good interface due to high negative value of α_{23} and provides good adhesion with reduced tension. But, the interfaces with α_{23} values -0.55 and -0.17 have to be further improved such that the overall strength of the blend should be improved significantly. Further, it can be observed that for the composition at which α_{23} is

Table III. Hydrodynamic Interaction Parameters (α) for PCL/SAN/PVC and PCL/PVC/PVAc Ternary Polymer Blends

Blend	Composition	α_{12}	α_{23}	α_{31}	α_{eff}	Inference	
						Literature	Present
PCL/SAN/PVC	(20/40/40)	2.97	-0.55	-2.22	0.24	Im ⁴²	Im
	(34/33/33)	-0.55	1.63	-0.47	0.36	Im ⁴²	Im
	(68/16/16)	-0.40	-0.17	-1.45	-1.60	M ⁴²	M
	(70/25/5)	-0.30	-2.97	-0.14	-1.30	M ⁴²	M
PCL/PVC/PVAc	(10/45/45)	-7.27	0.15	-2.52	-5.21	M ⁴⁶	M
	(50/10/40)	-0.64	0.09	-2.29	-2.02	M ⁴⁶	M
	(50/40/10)	-1.38	-1.14	-1.34	-2.61	M ⁴⁶	M
	(80/10/10)	-0.15	0.93	-13.84	-12.60	M ⁴⁶	M

In the last column, numbers in the superscript indicate references of works referred to. Note: Im: Immiscible; M: Miscible.

more negative, that is, -2.97 , SAN is the matrix and PVC is the dispersed phase. This compatibility is the effect of the repulsive nature of the acrylonitrile and styrene chains of SAN copolymer which provides pathways for the PVC chains to slide in between SAN chains, a well known concept for SAN/PVC blend.^{38,39} But the positive value of 1.63 for the composition $34/33/33$ suggests that the friction is less at the interface and this agrees well with the results of SAN/PVC binary blend which exhibits partially miscible behavior.^{11,40} Like the previous case, this weak interface can also be improved by employing e-beam irradiation rather than microwave since this interface contains weak polar group.²⁸ Interestingly, the third interface formed between PVC/PCL, characterized by α_{31} , takes negative values of -2.22 , -0.47 , -1.45 , and -0.14 at all the four compositions of $20/40/40$, $34/33/33$, $68/16/16$, and $70/25/5$ respectively. This suggests that due to the aforesaid interactions, the component polymer chains are brought closer, of course to different levels. This interpretation agrees very well with literature that the binary blend of PVC/PCL is miscible at all compositions with varying level of miscibility and the compatibility is attributed to the interaction between polar oxygen of PCL and proton of PVC.^{41,42}

With the information on the individual interfaces formed in the ternary blend PCL/SAN/PVC characterized by α_{12} , α_{23} , and α_{31} , for the purpose of comparing our results with the published data based on DSC and turbidity measurements⁴² the effective alpha (α_{eff}) according to eq. (7) is calculated and given in Table III and plotted in Figure 5. As can be seen that the α_{eff} is positive for the compositions $20/40/40$ and $34/33/33$ suggesting that the ternary blend PCL/SAN/PVC forms a phase separated immiscible blend at these compositions. Table III also provide the inferences drawn by other researchers for this blend⁴² and it is interesting to note that our results agree very well with those in the table. For compositions $68/16/16$ and $70/25/5$, α_{eff} becomes negative suggesting that the ternary system PCL/SAN/PVC is miscible at these compositions with varying level of miscibility. The compositions $20/40/40$ and $34/33/33$ are phase separated blends and the reason for this could be that these compositions have less PCL content ($<50\%$).⁴²

An important aspect of the present method lies in the information it provides on the composition depended miscibility level and also the strength of individual interfaces in terms α_{eff} parameter. That is, whether the component polymer chains are under tension or not as indicated by α_{eff} . This information is very important from the point of finding means to stabilize or strengthen the weak interfaces.

What we learn from the results of the second ternary blend namely PCL/PVC/PVAc studied seems to be very interesting as well. Characterization of the interfaces in this system is same as the one described above and the results obtained for this blend are tabulated in Table III and plotted in Figure 6. Here the three interfaces between the blend constituents are designated as α_{12} for PCL/PVC, α_{23} for PVC/PVAc and α_{31} for PVAc/PCL. From Table III, it can be seen that the interface between PCL/PVC characterized by α_{12} is negative with values of -7.27 , -0.64 , -1.38 , and -0.15 at all the four compositions of $(10/45/45)$, $(50/10/40)$, $(50/40/10)$, and $(80/10/10)$ and this is quite a

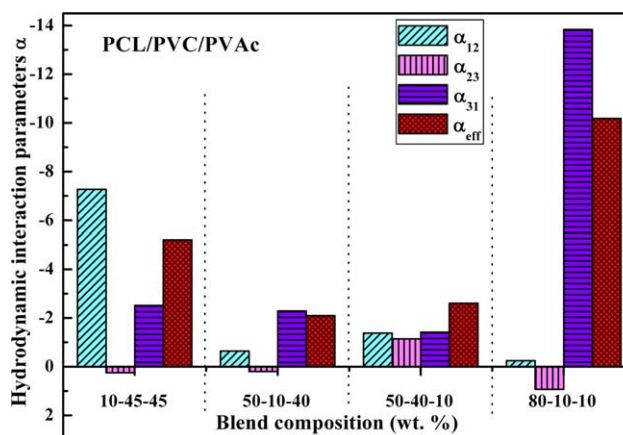


Figure 6. Plot of hydrodynamic interaction parameters α as a function of blend composition for the ternary polymer blend PCL/PVC/PVAc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

unique result. As described in the case of PCL/SAN/PVC ternary blend, a large negative value of the hydrodynamic interaction parameter α is the signature of the formation of a strong interface. This is due to increased or additional friction generated at the interface. It is known that the compatibility between PCL/PVC components arises from the interaction between the oxygen of the polar group in PCL and proton in PVC.^{41,42} However, for the compositions $50/10/40$ and $80/10/10$, α values are less negative and hence it supposes increased tension between the component chains rendering the interfaces weak. The plausible reason for this is the less percentage of PVC. These two interfaces need to be improved by some suitable compatibilizing route. The second interface between PVC/PVAc characterized by α_{23} takes on positive values of 0.15 , 0.09 , and 0.93 at the compositions $(10/45/45)$, $(50/10/40)$, and $(80/10/10)$ suggesting the formation of weak interfaces due to the absence of favorable interactions between the components. Let us consider how this particular interface is understood as reported in literature. We learn from literature that the binary blend PVC/PVAc is as an immiscible blend^{43,44} as revealed by the conventional method DSC. Surprisingly the present study provides the composition $(50/40/10)$ to be miscible as we observe negative value of α_{23} equal to -1.14 which is a new result. The third interface, that is, between PVAc/PCL, characterized by α_{31} , exhibits negative values of -2.52 , -2.29 , -1.34 , and -13.84 for all the compositions studied. Further, it is significant to note that the composition $80/10/10$ results in a maximum value of α_{31} (-13.84) and this interface can be considered as the strongest interface for the blend PCL/PVC/PVAc. From literature, the binary blend PVAc/PCL was reported as highly miscible^{45,46} and our results strongly support this. For the composition $80/10/10$, the chains of PVAc and PCL seem to be very close resulting in high friction and hence large α_{31} . From this, it could be inferred that interactions between the proton-accepting and proton-donating nature of the carbonyl group of PCL and α -hydrogen of PVAc are responsible for this miscibility level.^{45,46}

No investigation reported earlier provide the information on the individual interfaces in ternary polymer blends and their

role with regard to the final properties of the blend. From this point of view, our results are unique and first time reported. We have plotted α_{eff} values from Table III and shown in Figure 6 to arrive at the overall miscibility level. From Figure 6, for PCL/PVC/PVAc, the blend is miscible for all the compositions studied with varying level of miscibility. Further, it can be noted that α_{eff} takes a high negative value of -12.60 for the composition 80/10/10 inferring that this composition produces highest level of miscibility for this blend. This further infers that the formation of stronger interface between PVAc/PCL characterized by α_{31} is well supported from literature.^{45,46} For comparison, the last column of Table III results is to be considered. We find excellent agreement with the literature results which are based on Scanning Electron Microscopy (SEM) and Thermal Gravitimetric Analysis (TGA)⁴⁶ for this ternary blend. Further we suggest that to improve the overall miscibility and final properties of this blend, the weak interface between PVC/PVAc is to be improved. As they contain polar group, microwave irradiation would be a suitable route to improve the interaction between PVC and PVAc. From this point of view we understand that this is a versatile method beyond any ambiguity to characterize individual interfaces in ternary polymer blends.

As a final noting, our calculations show that the error on measured $F_V(s)$ is 0.035%, volume fractions ϕ_1 , ϕ_2 , ϕ_3 have errors of 0.002%, the density of the blend ρ is up to 0.001%. These errors additively propagate in the expressions for γ and α , and hence we get an error on geometric factor γ_{ij} as 5%, on α_{ij} as 7% so that it is about 8% on α_{eff} .

CONCLUSIONS

From the discussions made above, the following conclusions can be derived:

1. The Differential Scanning Calorimetric (DSC) studies do not reveal the composition dependent miscibility level in ternary polymer blends and the nature of the interfaces formed as strong or weak. This is also true with respect to the fractional free volume data obtained from PALS.
2. Use of fractional free volume to extract hydrodynamic interaction facilitates to uncover the miscibility level at each composition of the blend so that it can be labeled as a weak or strong interface in ternary blends.
3. The results of the present method indicate that the ternary blend PCL/SAN/PVC has lower miscibility for the compositions (68/16/16) and (70/25/5) compared to the ternary blend PCL/PVC/PVAc which has a stronger interface at 80/10/10 composition with a maximum effective hydrodynamic interaction parameter value of -12.60 .
4. From the information on the individual interfaces revealed by α 's and knowing the chemistry of the blend constituents, this method serves as a precursor to device routes to improve the compatibility of a particular interface resulting in a ternary blend of improved properties.

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