Characterization of interfaces in Binary and Ternary Polymer Blends by Positron Lifetime Spectroscopy

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Abstract. A miscible blend is a single-phase system with compact packing of the polymeric chains/segments due configuration/conformational changes upon blending. Differential Scanning Calorimetry (DSC) is the most employed method to ascertain whether the blend is miscible or immiscible. Positron Lifetime Spectroscopy (PLS) has been employed in recent times to study miscibility properties of polymer blends by monitoring the ortho-Positronium annihilation lifetimes as function of composition. However, just free volume monitoring and the DSC methods fail to provide the composition dependent miscibility of blends. To overcome this limitation, an alternative approach based on hydrodynamic interactions has been developed to derive this information using the same o-Ps lifetime measurements. This has led to the development of a new method of measuring composition dependent miscibility level in binary and ternary polymer blends. Further, the new method also provides interface characteristics for immiscible blends. The interactions between the blend components has a direct bearing on the strength of adhesion at the interface and hence the hydrodynamic interaction. Understanding the characteristic of interfaces which decides the miscibility level of the blend and their end applications is made easy by the present method. The efficacy of the present method is demonstrated for few binary and ternary blends.

1. Introduction
In the last few decades, it has been realized that many physical and mechanical properties of polymers can be significantly improved by the process of blending. The main objective of blending two or more polymers or copolymers is to produce a product with a set of desired properties for the end use of the material. Blending is a cost effective method to modify properties of polymers such as processability, heat distortion, impact strength etc. Polymer blends have been studied not only for their growing industrial applications but also for scientific and academic interest as well.

Depending on the structure and properties, polymer blends are generally classified into three types, \textit{viz.} miscible polymer blends (M), immiscible polymer blends (IM) and partially miscible blends (PM). Thermodynamically, for miscible blends, the Gibbs free energy of mixing $\Delta G < 0$. Blends of immiscible polymers obtained by simple mixing show a strong separation tendency leading to a coarse structure and low interfacial adhesion. Complete miscibility is a rare phenomenon to occur when a mixture of two or more systems is made. This is particularly so in case of polymers due to their
complex structure and relatively small entropy of mixing. Due to this reason, the miscibility level of a new polymer blend is often the first property to be investigated.

To characterize polymer blends, DSC is the most commonly used thermal analysis technique in which the glass transition temperature \(T_g\) is measured. Here, a single glass transition \(T_g\) is observed for a miscible blend, and evidence of phase separation is inferred from the observation of two or more \(T_g\)s. Microscopic techniques such as SEM, TEM have been also used to study the surface morphology of polymer blends. Scattering techniques such as SAXS and SANS provides information on polymer blend structures. Interactions in polymer blends are studied using the spectroscopic methods like FTIR and NMR. In this study, we have employed Positron Annihilation Lifetime Spectroscopy (PALS).

The interface in a blend is intimately connected to adhesion and interfacial tension, which quantify miscibility, and compatibilization capability. To understand better the nature of interfaces at the microscopic level, we used the novel approach proposed by Schnell and Wolf [1,2] for polymer/solvent systems in terms of the hydrodynamic interaction parameter \(\alpha\) evaluated from viscosity measurements. This method was modified by Ranganathaiah et al [3] for polymer/polymer binary blends in solid phase for the characterization of a single interface by invoking the concept that free volume and viscosity are inversely related. The efficacy of this method has been verified for several binary blend systems under varying conditions [3,4] by determining hydrodynamic interaction parameter from the measured free volume data obtained from positron lifetime spectroscopy. The method is extended to ternary blends as well. However, the same approach is not directly applicable to ternary blends with three interfaces. So, the required mathematical formulations have been modified for the three distinct interfaces characterized three hydrodynamic interaction parameters \(\alpha_{12}, \alpha_{23}\) and \(\alpha_{31}\) and this has been used to test the efficacy in few ternary blends. The results are compared with literature reports and found to be in good agreement.

2. Experiment

The blends of Polystrene-co-acrylonitrile/Polymethyl methacrylate (SAN/PMMA), Polymethyl methacrylate /Polyvinyl chloride (PMMA/PVC) and Polystyrene/ Polyvinyl chloride (PS/PVC) of different compositions were prepared by solution casting method using methyl ethyl ketone as the common solvent. We have also prepared the ternary blends of Polycaprolactone/Polyvinyl chloride /Polyvinyl acetate (PCL/PVC/PVAc) and Polycaprolactone/ Polystrene-co-acrylonitrile /Polyvinyl chloride (PCL/SAN/PVC) by the solvent casting method. The \(T_g\)s of pure polymers are: SAN:106°C, PVAc:-45°C PVC:74°C, PCL:-60°C. For ternary blends, some selected compositions were prepared keeping in mind results for these composition are available from literature so that our method’s efficacy can be easily checked. Lifetime spectra for the blends and their respective individual polymers were acquired using positron annihilation lifetime spectrometer (PALS) with a time resolution of 220 ps. A 17 μCi \(^{22}\)Na positron source on kapton foil was used. All the measurements were done at ambient room conditions. The lifetime spectra have been resolved into three lifetime components using computer program PATFIT-88 with proper source and background corrections. Further details of experimentation can be found from earlier works [4]. The \(\alpha\)-Ps lifetime \(\tau\) and intensity \(I\) are used to obtain the fractional free volume \(F_v\) of the blends as well as individual polymers. DSC studies of pure polymers and their respective blends were carried out as the first step of assessing a given blend as M, PM or IM based on the observation of single glass transition temperature \(T_g\), two \(T_g\)s respectively. The PM blends exhibited a broad single \(T_g\) smearing the two \(T_g\)s of the pure components. The inferences were inconclusive because no composition could be decided as the optimum to produce maximum miscibility for that blend.

3. Results and Discussion

For binary polymer blends, Kelly and Bueche [5] derived the composition dependent free volume additive rules in terms the free volume of blend components. According to them, at constant pressure and temperature, the fractional free volume \(F_v\) of the blend is given by,

\[
F_v = w_1 F_{v1} + w_2 F_{v2}
\]  

... 1
here $w_1$, $w_2$, $F_{v1}$ and $F_{v2}$ are the weight fractions and fractional free volumes of component polymers 1 and 2 respectively. However, it was later realized that free volume is not linearly additive unlike volume due to the complex nature of its formation. Hence, Jean et al. [6] proposed a relation, based on the work of Wu [7], by introducing a parameter called the inter-chain interaction parameter $\beta$ to represent the interaction between dissimilar chains in a binary mixture and this is

$$F_v = F_{v1}\phi_1 + F_{v2}\phi_2 + \beta F_{v1}F_{v2}\phi_1\phi_2 \quad \text{... 2}$$

Here, $\phi_1$, $\phi_2$, are the volume fractions of component polymers 1 and 2. It has been observed that free volume parameters of the blends exhibit negative and positive deviations from the linear additive rule (Equation 1) depending on whether the blend is a single phase or a two phase system. Accordingly, the inter-chain interaction parameter $\beta$ acquires negative and positive values respectively (Equation 2). This implies that, for miscible blends negative values of $\beta$ indicate favorable interactions between the component polymers and positive values of $\beta$ indicate the absence of any interaction between the components and hence the blend is termed as immiscible [6,7].

![Figure 1: Plot of $\beta$ as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.](image)

In Figure 1, we notice that $\beta$ is negative throughout the concentration range for SAN/PMMA blend and hence concluded as miscible. As miscibility varies with composition, figure 1a fails to suggest which composition produces highest miscibility since it exhibits oscillatory behavior. Similarly, the PMMA/PVC blend is miscible. In case of PVC/PS, $\beta$ is negative at 10% of PVC, but for other compositions it is positive hence immiscible. A comparison of the behavior of $\beta$ in all three systems suggests that, although it could be taken as an indicator of miscibility, its behavior is not systematic (i.e., it exhibits complex behavior like oscillation) to infer a composition of highest miscibility [3].

### 3.1. Hydrodynamic Interactions parameter method: (Ranganathaiah’s Method [3,10])

All materials exhibit visco-elastic properties in a given condition. These include amorphous polymers, semi-crystalline polymers, biopolymers etc. To be more specific, visco-elasticity is a molecular rearrangement. Polymers remain as solid materials even when these parts of their chains are rearranging in order to accompany the stress. As this occurs, it creates a back stress in the material. Hence, the adaptation of the theory developed to understand the polymer/solvent system in liquid phase to polymer/polymer blend in solid phase is thus justified. It is well known that free volume and viscosity are inversely related [8]. This concept was well adopted by Ranganathaiah et al. [3,10] to suitably modify the theory of hydrodynamic interactions for polymer/solvent systems formulated by Wolf et al. [1,2] based on the models developed to understand the behaviour of polymer solutions.

Ranganathaiah et al. [3,10] modified Wolf et al. theoretical equations [1,2] and deduced expressions for the hydrodynamic interaction parameter $\alpha$ suitable for polymer/polymer blend in solid phase. Here, the hydrodynamic interaction parameter is calculated by using the fractional free volumes of pure polymers and their respective blends which are experimentally measured from positron lifetime experiment. This approach was successful in revealing the composition dependent miscibility level and further discerns the nature of interfaces formed. The veracity of the method was also tested by bringing in phase modifications through irradiation with energetic electron beam and microwaves.
and found it clearly indicates the changes occurred at the interface/interfaces in binary and ternary blends [4,11].

The parameter $\alpha$ can be defined as the strength of hydrodynamic interaction at the interface. So also $\alpha$ can be viewed as a measure of the strength of adhesion at the interface. The final simple expression derived for the hydrodynamic interaction parameter $\alpha$ is shown to be

$$\Delta F_V = \left\{ \delta \gamma (1 + \gamma \phi_2) - \phi_1 (1 + \gamma) \right\} + 2 \alpha (1 + \gamma)^2 \phi_2 + \frac{e^{2\gamma \phi_2}}{\rho \phi_1} \left( 1 + \gamma \phi_2 \right)^3 \phi_1 \phi_2 \right\}^{-1} \quad \text{...3}$$

here $\gamma$ is the geometric parameter $\varphi_1$ and $\varphi_2$ are volume fractions of polymer 1 and 2, $\rho$ is the density of the blend. Further $\Delta F_V$ is defined as

$$\Delta F_V = \left[ \frac{1}{F_{V1}} - \frac{\phi_1}{F_{V1}} - \frac{\phi_2}{F_{V2}} \right] \quad \text{...4}$$

i.e., difference in the reciprocal fractional free volumes of the constituent polymer 1 and 2 of the binary blends.

For Ternary polymer blend, it is characterized by three interfaces. We define $\varphi_1$, $\varphi_2$, $\varphi_3$ as the volume fractions of component polymers 1, 2 and 3 of the blend and $\alpha_{12}$, $\alpha_{23}$, $\alpha_{31}$ are the hydrodynamic interaction parameters corresponding to interfaces between polymer 1-2, 2-3 and 3-1 respectively, and their relationships are as follows.

$$\frac{1}{\Delta F_V} = \delta_1 [\varphi_1 - \Omega_1 (1 + \Omega_2 \Omega_2)] + \delta_2 [\Omega_2 (1 - \Omega_2^2) - \varphi_3] - \delta_3 \Omega_3^2 \Omega_1$$

$$+ \sum_{i,j=1}^{3} \left[ \frac{e^{\gamma F_{V1}} \rho \Omega_2^2 \Omega_1^2}{1 + \gamma_{ij}} + 2 \alpha_{ij}(1 - \Omega_j \Omega_i) \right] \quad \text{...5}$$

Here, the term on the left hand side is written as

$$\frac{1}{\Delta F_V} = \frac{1}{F_{V1}} - \frac{\phi_1}{F_{V1}} - \frac{\phi_2}{F_{V2}} - \frac{\phi_3}{F_{V3}} \quad \text{...6}$$

where, $F_{V1}$, $F_{V2}$ and $F_{V3}$, are the measured fractional free volumes of the blend and its constituents 1, 2 and 3 respectively. We define an effective hydrodynamic interaction parameter ($\alpha_{eff}$) for the purpose of comparing the present results with published literature results and is expressed in terms of the individual $\alpha_{ij}$ and the respective volume fractions as [10,11]

$$\alpha_{eff} = (\varphi_1 + \varphi_2) \alpha_{12} + (\varphi_2 + \varphi_3) \alpha_{23} + (\varphi_3 + \varphi_1) \alpha_{31} \quad \text{...7}$$

Details of derivation of mathematical equations can be found in our earlier works [3,10].

The friction associated with the visco-elastic flow results in energy dissipation at the interface and is influenced by the composition of the blend. In the case of miscible blends, the polymer chains are brought closer to each other so the friction at the interface increases. As energy dissipation increases the tension at the interface decreases. In Ranganathaiah’s method, the negative sign of the hydrodynamic interaction parameter ($\alpha$) is inferred as dissipation of energy at the interface. If miscibility is high at certain composition of the blend, $\alpha$ takes large negative values [3]. On other hand, for immiscible blends, $\alpha$ is close to zero or positive. Zero or positive value is interpreted as the absence of any favorable interactions between the constituent polymers and hence friction at the interface is very less.

For a miscible blend, when a chain moves, several other chains with which it has segmental level interactions pull it. This generates a good amount of friction in the system for which $\alpha$ attains large negative values. In Figure 2(a), we show a plot of $\alpha$ as a function of the PMMA percentage in the SAN/PMMA blend. The SAN/PMMA blend is known to be miscible, but not because of the intermolecular interactions but because of the intra-molecular repulsion between the SAN chains. It is important to note that several techniques have shown this blend to be miscible throughout the concentration range, but none of them have indicated the extent or degree of miscibility for different compositions. We can see from Figures 1(a) that this system exhibits miscibility from $\beta$ parameter throughout the range of concentrations, but there is no indication of maximum miscibility at any
composition. In contrast, a large negative value (-209) at 20% PMMA, observed in Figure 2(a), can be considered to indicate that the degree of miscibility is maximum because $\alpha$ shows only smaller values at a higher concentration of PMMA. SAN has high molecular weight and repulsion between the SAN chains make it easy for PMMA chains to slide in between. As the SAN content decreases, the repulsion also decreases, thus, PMMA with 20% content has the highest negative value of $\alpha$.

Figure 2 : Plot of $\alpha$ as a function of the volume percentage of the second polymer: (a) PMMA in SAN/PMMA, (b) PVC in PMMA/PVC, and (c) PS in PVC/PS.

In the case of PMMA/PVC blends, the interaction between the carbonyl group (C=O) of PMMA and $\alpha$-hydrogen (H-C-Cl) of PVC drives the system to miscibility. However, this system is known to be partially miscible, and at some compositions, it becomes immiscible. $\alpha$ for this system in figure 2(b) is negative and maximum at 10% PVC (-57) and decreases as the PVC content increases. Beyond 30% PVC content, $\alpha$ attains smaller values closer to zero. The increase in the PVC concentration reduces interactions, and this results in smaller $\alpha$ values. The $\alpha$ values obtained for the PVC/PS blend system shown in Figure 2(c) are a clear indication that the $\alpha$ values are not exactly zero but are close to zero. This indicates that the system is immiscible throughout the concentration range suggesting friction at the interface is very negligible. In such immiscible blends with no specific interactions between polymer components, they form their own domains in the system, thereby reducing the possible contacts between the chains. In other words, the friction between the chains of the constituent polymers is negligible. Above method was verified by Xiaoyu Meng et.al [12] who employed this method to determine miscibility of binary polymer SBS/PS. Interestingly, the mechanical properties showed large improvement for highest miscibility composition.

For the ternary blend PCL/SAN/PVC, the $\alpha_{12}$, $\alpha_{23}$, $\alpha_{31}$ denote the hydrodynamic interaction parameters corresponding to respective interfaces between PCL/SAN, SAN/PVC and PVC/PCL, and evaluated according to equation 5. The interface $\alpha_{12}$ between PCL/SAN takes both positive and negative values depending on composition. Here, negative $\alpha$ indicates increased interfacial friction, observed when PCL is matrix and SAN is dispersed phase. This may be due to the interaction between the carbonyl group of PCL and tertiary hydrogen of SAN [13]. The second interface, $\alpha_{23}$ is positive at 34/33/33 composition while at other compositions it is negative. The negative values of $\alpha$’s is due to the repulsive force among the SAN chains paving way for PVC chains to slide in [14]. Interestingly the third interface in the blend that is between PVC/PCL, produces negative values for all compositions studied, indicating the formation of good interfaces attributable to the interaction between polar oxygen of PCL and proton of PVC [15]. Finally, the $\alpha_{\text{eff}}$, plotted in figure 3, shows positive values at 20/40/40 and 34/33/33 compositions and thus we infer the blends are immiscible at these compositions. On the other hand, the negative values at 68/16/16 and 70/25/5 indicate the blends are miscible at these compositions. Importantly, 68/16/16 composition produces highest miscibility for this blend since $\alpha_{\text{eff}}$ has a high negative value. These results agree with literature data[11].
In case of PCL/PVC/PVAc blend, three interfaces are designated as $\alpha_{12}$ for PCL/PVC, $\alpha_{23}$ for PVC/PVAc and $\alpha_{31}$ for PVAc/PCL. From figure 3, it can be seen that the interface between PCL/PVC is negative for all the four compositions studied. The second interface between PVC/PVAc shows positive values for three compositions suggesting the formation of weak interfaces due to the absence of favorable interactions between the components. The third interface is PVAc/PCL and is known to be miscible and is supported by negative $\alpha$ value for all compositions. The $\alpha_{eff}$, also plotted in figure 3 shows that the blend is miscible at all compositions studied. Further, $\alpha_{eff}$ 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.

![Figure 3: Plot of hydrodynamic interaction parameters $\alpha$ as a function of blend composition for the blend (a) PCL/SAN/PVC and (b) PCL/PVC/PVAc](image)

4. Conclusion

A new method based on hydrodynamic interactions to determine the miscibility level of binary and ternary polymer blends is described. It has also been demonstrated that one can characterize the individual interfaces in ternaries by this method. The efficacy of the present method has been tested for few binary blends namely PS/PMMA, PMMA/PVC and PS/PVC and in ternary blends namely PCL/SAN/PVC and PCL/PVC/PVAc. The experimentally measured fractional free volume of pure polymers and their respective blends form the basis of evaluating the hydrodynamic interaction parameters.

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