Interface profile studies in immiscible and partially miscible binary polymer blends from free volume measurement

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Interface profile studies in immiscible and partially miscible binary polymer blends from free volume measurement

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Abstract. The diffused interface widths in an immiscible and a partially miscible polymer blend namely Polyvinyl chloride/Ethylene vinyl acetate (PVC/EVA) and Polystyrene/Polymethylmethacrylate (PS/PMMA) are experimentally measured and reported here. A new empirical relation found between hydrodynamic interaction parameter α derived from free volume data and the Flory-Huggins interaction parameter χ is used to construct density profile across the interface to derive the interface width in above two binary blends.

1. Introduction

The combination of two or more chemically and structurally different polymers gives raise to materials with a range of properties, not deliverable by any of the constituents. This is called polymer blending. Blending usually results in immiscible or partially miscible blends. Stabilizing interfaces in such blends is essential for the end use of these materials in several applications. In this context the interface width in such blends needs to be understood. Generally, the interface width is considered as the third phase whose width depends on the inter-diffusion between two component polymers [1,2].

Most of the published literature on interface widths deal with welded interfaces between slabs or thin films of the polymers but very few consider the equilibrium interfaces that exist in an immiscible or demixed blends of different morphology [1]. Further, the interfaces in welded polymer thin films are completely different in morphology compared to engineering or disperse polymer blends produced by chemical or physical blending. In the present work, Positron Annihilation Lifetime Spectroscopy (PALS) is used to measure fractional free volume and hence determine hydrodynamic interaction parameter (α) from which the interface widths in two disperse polymer blends are derived by constructing the density profile across the interface.

2. Experimental

The blends of Polyvinyl chloride/Ethylene vinyl acetate (PVC/EVA) and Polystyrene/Polymethyl methacrylate (PS/PMMA) of different compositions were prepared by solution casting method using methyl ethyl ketone as the common solvent. Positron lifetime spectra for the blends and pure polymers were recorded using PALS with a time resolution of 220 ps. A 17 µCi ^{22}Na positron source was used

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in the measurement. The acquired positron lifetime spectra were analyzed into three lifetime components with the help of computer programs PATFIT-88 [3] with proper source and background corrections and program CONTIN PALS-2 [4] for free volume distribution analysis. The PATFIT analysis is made to check the correctness of the CONTIN results. The CONTIN analysis provides the annihilation rate probability density function (PDF). The free volume radius PDF and free volume size PDF are transformed by the method of Gregory [4]. Accordingly, free volume radius PDF: f(R) and free volume size PDF: g(V) are expressed as

$$f(R) = 2\Delta R\{\cos[2\pi R/(R + \Delta R)]-1\}\alpha(\lambda)/(R + \Delta R)^2 \qquad (1)$$

and $g(V)=f(R)/4\pi R^2$ (2)

where $\Delta R= 1.656$ Å [5]. Further details can be obtained from the earlier publication [5].

3. Results and discussion

Figure 1a shows the *o*-Ps lifetime and radius distribution and figure 1b shows the free volume hole size distribution in PS/PMMA with composition 20/80 and PVC/EVA with composition 80/20. The broad distribution in the PVC/EVA blend can be attributed to the formation of interfacial regions between the component polymer chains and hence additional free volume generated [5]. This also indicates a lack of mutual interaction between the component polymers. From figure 1b it can be observed that the curve for PVC/EVA is broader in comparison with PS/PMMA (20/80). The FWHM (full width at half maximum) of the PS/PMMA (20/80) is 30Å^3 while that of PVC/EVA (80/20) is 35Å^3. The small FWHM of PS/PMMA blend suggests close packing of the constituent polymer chains.
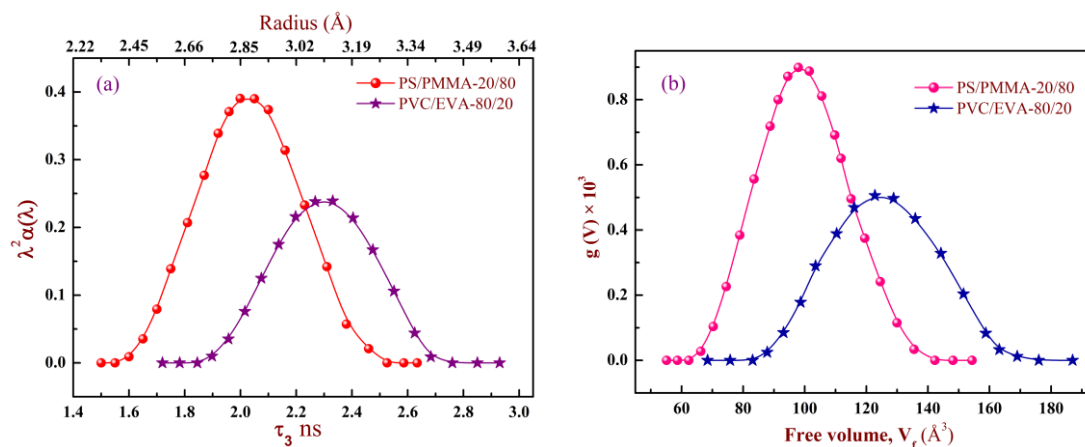

Figure 1. a) *o*-Ps lifetime (τ_3) v/s *o*-Ps probability density function (b) free-volume size (V$_f$) probability density function for PS/PMMA (20/80) and PVC/EVA (80/20) blends.

The hydrodynamic interaction parameter of Schnell and Wolf work [6] for polymer/solvent systems modified by Ranganathaiah and coworkers [7,8] is used here. We derive two parameters namely the geometric factor (γ): which relates to molecular arrangement and architecture of the chains of the blend components and the hydrodynamic interaction parameter (α): which is treated as a measure of excess friction generated at the interface between the blend constituents. For details readers are referred to refs 7 and 8. The efficacy of the method was tested for few binary polymer blends under different conditions and proved to be very successful [8,9]. From the measured free volume results, the hydrodynamic interaction parameter α is evaluated according to the Ranganathaiah method [7-9] using equation (3).

$$\Delta F_V = \left\{ \delta\left[\gamma(1+\gamma\varphi_2)^2 - \varphi_1(1+\gamma)\right] + 2\alpha(1+\gamma)^2\varphi_2 + e^{\frac{1}{F_V}}\rho\varphi_1 \right\}^{-1} \frac{(1+\gamma\varphi_2)^3}{\varphi_1\varphi_2} \qquad (3)$$

where $\quad \Delta F_v = \left[\dfrac{1}{F_{vb}} - \dfrac{\varphi_1}{F_{v1}} - \dfrac{\varphi_2}{F_{v2}}\right] \quad$ and $\quad \delta = \dfrac{1}{F_{v2}} - \dfrac{1}{F_{v1}}$ $\qquad$ (4)

F_{V1} and F_{V2}, are the fractional free volume of the pure polymers, ρ is the density of the blend, φ_1 and φ_2 are volume fraction of the blend constituents. The parameter γ is related to fractional free volume [7]

$$F_V = \left[\frac{\varphi_1}{F_{V1}} + \frac{\varphi_2}{F_{V2}} + \delta\left(\frac{\gamma\,\varphi_1\,\varphi_2}{1+\gamma\,\varphi_2}\right)\right]^{-1} \qquad (5)$$

To determine interface width, use of the Flory–Huggins interaction parameter χ is made. Chain orientation and entanglements influence the χ parameter similar to the repulsion between unlike monomeric units in addition to other properties of the constituent polymers [1]. Since α is the result of friction at the interface due to mobility of chains is thought to be related to χ. This is used to determine the interface width as both parameters predict miscibility of polymer blends. The χ parameter has been extensively used in the study of interface width based on a mean field theory approach and is well established irrespective of its unrealistic assumptions. We have adopted a similar approach based on α. To meet this requirement a correlation between χ and α parameter is essential and is obtained as follows. A plot of ln α against χ shown in figure 2 is constructed from the α and χ data (from literature) for ten polymer blends which include both partially miscible and immiscible blends.
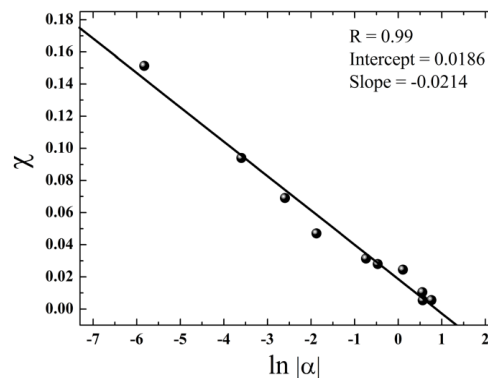

Figure 2 plot of χ against ln $|\alpha|$

It is clear from figure 2 that for the range of α and χ considered a linear relation fits the data given below:

$\chi = 0.0186 - 0.0214 \ln|\alpha|$ $\qquad$ (6)

This result is an additional support for the inverse relation between viscosity and free volume. Then the well known Helfand-Tagami theory [10] approach is used to construct a composition density profile across the interface. According to this the composition density profile is given as

$\rho_i = \rho_{i,0}\, y^2 / \left(1 + y^2\right)$ $\qquad$ (7)

where $\rho_i \rightarrow$ density ; i= polymer A or B and $y \equiv \exp\{(6\chi)^{1/2}\,(x/b)\}$ with x/b designated as the reduced distance across the interface. In the present case, the expression for y is modified to the form

$y \equiv \exp\{(6H)^{1/2}\,(x/b)\}$ $\qquad$ (8)

where $H = 0.0186 - 0.0214 \ln|\alpha|$

Using equation 7, composition density profile across the interface of PS/PMMA and PVC/EVA binary blends are constructed and shown in the figure 3a and figure 3b respectively.

In this calculation, the α distribution values obtained from CONTIN analysis are used. From figure 3a and b, the interface is centered at x=0; the positive x region is rich in one polymer while the negative x region is rich with the other. The solid curve is for the first polymer of the blend and the dotted curve is for the second polymer. A tangent is drawn at the point (x/b)=0 and this intersects the

x-axis at $(\rho/\rho_0) = 0$ and $(\rho/\rho_0) = 1$ meaning the volume fraction of the constituents corresponds to $\varphi = 0$ and 1 respectively [2,10]. The interface width Δl is read between these two points of intersection.
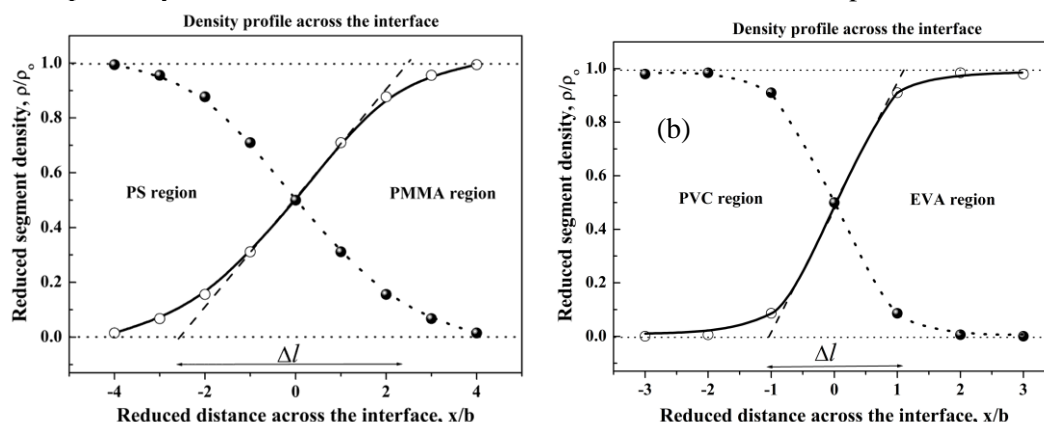

Figure 3. Composition density profile of (a) PS/PMMA-20/80 composition blend (b) PVC/EVA-80/20 composition blend.

The interface width value determined in this way for PS/PMMA blend is 5.04 nm. For this partially miscible blend the possible interaction is between $O-CH_3$ of PMMA and hydrogen of PS [8]. Depending on the strength of this interaction, it is expected that inter-diffusion of PMMA into the PS chains across the interface will be higher and hence wider interface width. The interface width for the immiscible PVC/EVA is determined to be 2.17 nm. An immiscible blend lacks any kind of interaction between the components and so is similar for the PVC/EVA blend. This suggests very little inter-diffusion of PVC into EVA or vice versa and hence a narrow interface width.

4. Conclusion

An empirical relation between the hydrodynamic interaction parameter α and the Flory-Huggins interaction parameter χ has been established for a limited range of α and χ values. The composition density profile of the constituent polymers across the interface of the blends is constructed for the two polymer blends PVC/EVA and PS/PMMA. From density profiles, the diffused interface width values so obtained are 2.17 and 5.04 nm respectively for the immiscible (PVC/EVA-80/20) and the partially miscible (PS/PMMA-20/80) blend. For other compositions studied, these values are lower than the values reported here.

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