Abstract
This chapter outlines introduction to the thesis work beginning from polymers, polymer blends, their processing techniques, various aspects of polymer-polymer interfaces and their importance, free volume concept, basis of hydrodynamic interaction and current state of Positron Lifetime Spectroscopic studies on the afore mentioned topics. Details of the literature survey undertaken by the author and motivation for the present study are specified. The structure of the thesis is highlighted at the end.
Introduction

Polymer science has had a major impact on the way we live. It is difficult to find an aspect of our lives that is not without polymers. Just 5 decades ago, materials we now take for granted were non-existent. With advances in the understanding of polymers, and with new applications being researched, there is no reason to believe that the revolution will stop any time soon. The polymers have been replacing metals and ceramics in a wide range of applications because of their low density and good process abilities.

An extensive study made on polymer research field revealed that synthesis of specialized polymers is always a time consuming and also a complicated process. Therefore, the alternative thought against the synthesis of new specialized polymers was the modification of existing polymers so as to suit the desired requirement. This was done by mixing two polymers A and B where it is expected that the resulting product C possess some properties of Polymer A and some properties of Polymer B. In this method of preparation, the modification was rather easy and scientists tried this through various means and ended up with different class of polymers namely co-polymers, polymer blends and interpenetrating polymer networks.

Among the above three class of polymer mixtures, Polymer blends are the most attractive ones due to the ease of designing and production compared to the other two types.

1.1 Polymer Blends

Developing a new polymer with a new chemical structure that fits the needs of the market is difficult; blending of polymers is an indispensable method for developing new polymeric materials. Blending of polymers is an established method in which, mixing together of two or more polymers is used to arrive at new property combinations without having to synthesize new structures with the desired characteristics. Especially in the area of engineering thermoplastics, this approach has created a significant number of large volume products like PS/PBT, PPE/HIPS, PC/ABS, PC/PBT, PA/PBT, PA/PPE, PA/ABS, etc., [Utracki, 1990;
A prominent example is polystyrene (PS), which is a stiff material, but relatively brittle, what makes it inappropriate for many applications. However, a blend of it with rubbers, e.g. polybutadiene (PBT), meets the criterion of a tough material with a still large stiffness. The commercial success of these materials is mainly related to their combination of properties that enable their use in a multitude of applications.

Despite the large scale increase in the sales of materials based on blending by industry, a fundamental understanding of blend morphology and properties is still required. To do this, several experimental methods have been used on numerous processing techniques to understand the different aspects of phase morphology development and properties in polymer blends.

1.2 Blending Techniques

Polymer mixing is carried out by a variety of techniques which include physical mixture of two or more polymers through melt blending, solution blending, latex blending or synthesis of co-polymers and inter penetrating networks (IPN). Very briefly these methods are described below

(i) Melt Blending: Melt blending is a dispersive technique that involves the intimate mixing of an additive into the polymeric matrix. It requires the polymer to be in the molten or rubbery state during mixing, and it necessitates high shear forces to bring about the mixing. Obtaining the proper viscosity is the key to the successful operation of the Bar bender and fabrication of a uniformly dispersed composite. However, it requires high energy of mixing and since the temperature of the mixer should be maintained above the melting temperatures of both the constituents, it may influence to some extent degradation, chain scission and chemical decomposition of the blend.

(ii) Solution blending: Solution blending or solution casting is the simplest mixing method available and widely used by researchers. In this technique both the polymers are dissolved in a common solvent, mixed well and the solution is casted on a neat, clean and uniform glass plate. The solvent is allowed to evaporate so as to get the blend films of almost uniform thickness and air bubble free. This method allows easy and rapid mixing of the components. However, this
technique cannot be used for all the polymer pairs because of the difficulty in finding a common solvent and also it cannot be used in producing bulk quantities of the materials. This is rather the first choice of the researchers to prepare the blend samples for study. This is the method used by the author to make the blends investigated in this study.

(iii) **Latex blending**: Mixing of two low viscous lattices is also in practice to obtain a blend without involving any organic solvent. The limitation of this method is that the components should be free from impurities and should be miscible.

(iv) **Freeze drying**: This method is very similar to solution casting except for the fact that instead of casting the solution, it is driven to very low temperature so that all the three components in the blend i.e., two polymers and solvent attains solid phase and the solvent is removed by sublimation process. In this method since the components do not get enough time and energy for phase separation, the mixture generally exhibits homogeneous phase.

### 1.3 Classification of Polymer blends

Polymer blends depending on their phase behaviour are widely classified into miscible, partially miscible and immiscible blends as shown in Figure 1.1.

(i) **Miscible blend**: It is a homogeneous system with chain segments of the different polymers miscible down to the molecular level and hence result in negative heat of mixing i.e., exothermic heat of mixing ($\Delta G < 0$). These blends show single glass transition temperature which depends on the composition of the blend.

(ii) **Partially miscible blend**: Some blends are neither completely miscible nor immiscible. These blends show limited mutual interactions, but small amounts of one polymer is miscible in the other. The best properties of each polymer may be combined often without the need of developing a compatibilization mechanism.
(iii) **Immiscible blend:** Among the binary mixtures, majority of them are immiscible blends, having a completely phase separated structure. Therefore, the glass transition temperatures of the components of the blends are exactly the same as for the pure components. In such polymer blends, one component form its own distinguishable domains in the matrix of other and vice versa. The interfacial strength in the immiscible blends is very poor, leading to adhesive failure and poor mechanical properties.

### 1.4 Factors influencing miscibility

The miscibility in polymer blends is a complex phenomenon and is controlled by several factors as discussed below.

**Polarity:** Polarity refers to separation of electric charge of a molecule or its chemical groups having an electric dipole or multipole moment. The unequal sharing of electrons between two bonding atoms results in one atom exerting more force on the electron cloud than the other. This drag is termed electronegativity and measures the attraction for electrons a particular atom has. The unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charge. For example; water molecule. Here oxygen is slightly negatively charged and hydrogen is slightly positively charged and therefore the water molecule acquires polar character. Therefore, polymers that are similar in structure or generally similar in polarity are less likely to repel each other and more likely to form miscible blends.
(ii) **Specific group influence:** Many experimental results have indicated that the presence of special interactions in a blend including hydrogen bonding, ion-ion pairing, acid-base interaction, charge transfer etc. favours the enthalpy of mixing, and allows the components to mix completely. Among all these interaction, hydrogen bonding is quite common and efficiently improves the miscibility without accompanying much change of the component polymers [Zhang et al., 2000].

(iii) **Molecular Weight:** Compared to higher molecular weight, the low molecular weight permits greater randomization of polymer chains on mixing and therefore greater gain of entropy, which favors miscibility. More surprisingly, polymers of similar molecular weights are more miscible, while polymers of very different molecular weights may be immiscible even if both have the same compositions.

(iv) **Composition:** It has been observed that two polymers appear immiscible at a fairly equal composition but it is quite possible that a small amount of one polymer may be soluble in a large amount of the other polymer resulting in moderate miscibility. Thus by varying the composition of one of the constituent polymers a blend can result in partial miscibility.

1.5 **Role of interfacial phenomena in polymer blends**

Another important aspect of polymer blend miscibility is related to phase behavior and interfaces in the polymer blends [Sanchez, 1992; Binder, 1999; Holys and Vilgis, 1996]. The interface is defined as a surface forming a common boundary between two different phases. These features have attracted a great deal of attention because of intriguing physical properties and an essential role in polymer technology. The practical importance arises from the many industrial applications of these materials and scientific importance arises from the complex behavior they display and the molecular description of this is a challenging problem in statistical mechanics. Therefore, the study of interfaces in polymer blends or alloys is very important for the design of new multiphase materials as well as to understand their complex behavior.
An important feature of the interfaces in polymer blends is that they are often characterized by structure and correlations on scales significantly larger than the monomer size [Sanchez, 1992], this results to a degree of universality of interfacial properties. Correlations between interfacial and bulk properties exist on various length scales. For example the mechanical stability of a polymer blend depends upon the local interfacial structure - the interface width, the conformation of polymer chains, enrichment of chain ends or the solvent at the interface.

Therefore it becomes imperative that without the knowledge of interfaces which in turn depends on the compatibility of polymers, it is difficult to combine the advantages of different polymers in a blend. In this direction, knowledge about the degree of phase separation is also important.

Although the polymer–polymer interfaces of blend materials of interest to industry are often very complicated, nevertheless there are several attempts to understand the physics of polymer–polymer interfaces through several experimental investigations carried out and all of these deals with inter-diffusion at the interface [Anastasiadis, 1988; Bucknall et al., 1998; Jain and Pablo, 2003; Careli et al., (2005,2006)] interfacial tension [Schnell, 1998; Dlubek et al., (2002,2003(a,b)); Patra and Yethiraj, 2003; Stamm, 2008]. The important point to be noted in these studies is that inter-diffusion and interfacial tension at the interface characteristics have been studied in bilayer polymer blends. On the other hand the large number of blends made by blending technology is different from the bilayer blends. So, studies pertaining to the interface structure in terms chain separation, width etc for these blends are still missing which exhibit three dimensional (3D) morphology.

1.5.1 Interface characteristics

Of the several characteristics of the interface, we consider two important ones namely (i) The chain proximity distance ($\Delta s$) which arises due to the parting or separation of the adjacent chains of unlike polymers in a polymer mixture [Anastasiadis et al., 1988]. The separation is a consequence of minuscule repulsion between segmental/chain units of the long macromolecules in
thermodynamically unmixed binary polymer blends which may lead to a gain in entropy by mixing [Stamm, 2008]. Secondly, (ii) the diffused interface width ($\Delta l$); this arises due to inter-diffusion of one of the constituent polymer chains into the domain of another constituent polymer of the blend and vice versa. This forms the third region in the blend, whose properties are different from either of the two constituents. This region is called “interface region” and its thickness range is called “diffused interface width” [Utracki, 2002].

There have been several attempts in the past to understand the actual mechanism working at the unlike polymer chains in polymer-solvent and polymer-polymer-solvent systems leading to separation at the interface of these systems. [Kirkwood and Riseman, 1948; Riseman and Kirkwood, (1949,1956); Zimm, 1956; Zwanzig et al., 1968]. From these studies it is evident that the polymer properties like viscosity and hydrodynamic effects in relation to flow dynamics control the interface properties in such systems. It is also true that a very large number of studies carried out in the past [Helfand and Tagami, 1972(a,b)] on the diffused interface width have not made any attempts to differentiate and highlight the importance of chain proximity distance and diffused interface width.

Now let us have a look at the studies on theoretical aspects of diffused interface width so far. Morse and Fredrickson [1994] have studied interfaces in polymers using the self-consistent field theory. They considered asymmetric systems of semi flexible polymers and derived analytic expressions for the interface width and interface tension. It was observed that both these parameters decrease with the increase in rigidity of the semi flexible polymers. Mueller has studied [Mueller, (1995, 1999)] the phase behavior of polymer mixture of flexible and semi flexible polymers by computer simulation for very low stiffness and disparity. The author has shown that the critical temperature, at which two components phase separate, increases with the increase in stiffness of semi flexible components of inflexible-semi flexible polymer blend.

In the later work, Mueller and Werner [1997] observed the effect of stiffness disparity on the interfacial properties of the well segregated phases using the
Monte Carlo simulations and compared their data with self-consistent field theory [Carmesin and Kremer, 1988]. Due to limitations of the lattice based approach, their work was restricted to rather small bending rigidities of the semi flexible components.

Literature survey done by the author showed that theoretical descriptions do vary with regard to interfaces between two unmixed domains of polymer blends [Helfand and Tagami, 1972(a,b); Helfand, 1975; Noolandi and Hong, 1981; Shull, 1993; Matsen and Schick, 1995; Muller and MacDowell, 2000; Patra and Yethiraj, 2003; Muller and Schmid, 2005].

Experimental investigations of the interface between incompatible polymers has been performed by many researchers using different techniques such as Small Angle Neutron Scattering (SANS), Neutron Reflectometry (NR) [Broseta et al., 1990; Bucknall, 1999; Careli et al., (2005,2006); Beziel et al., 2008], Small Angle X-ray Scattering (SAXS) [Flaris et al., 1995], Differential Scanning Calorimetry (DSC) [Dlubek et al., 2003b], Transmission Electron Microscopy (TEM) [Liao et al., 2007], Rutherford backscattering spectrometry (RBS), [Composto and Kramer, 1992], Ellipsometry [Sauer and Walsh, 1991; Kressler et al., 1993], X-ray reflectometry (XR), [Huttenbach et al., 1991; Harton et al., 2005], Positron Annihilation Lifetime Spectroscopy (PALS), [Dlubek et al., (2002,2003a)] nuclear magnetic resonance spectroscopy (NMR), [Lodge, 1999; Price et al., 2006], Raman spectroscopy, [Tomba et al., 2004; Arzondo et al., 2005], secondary ion mass spectroscopy (SIMS) [Harton et al., 2005] and Scanning Transmission Electron Microscopy (STEM), [Siangchaew and Libera, 1999] in polymer blends with varying success.

It shall be noted that many of the above mentioned experimental methods such as, RBS and NR cannot measure concentration profiles directly, in spite of the fact that these techniques have high resolution on the scale of angstroms because a special pre-processing of the samples is necessary for their evaluation. On the other hand, to derive the concentration profiles which are essential to evaluate the interface width, some assumptions have to be made in Ellipsometry, XR, and PALS. Raman spectroscopy is limited by the depth resolution of 0.1-1μm,
though it can provide useful information at large inter-diffusion depths. SIMS can directly measure the concentration profile with high resolution of 10 nm, but it is required that the top layer be planar and of uniform thickness. The conventional TEM and STEM techniques usually require specimens to be stained with heavy metals for profiling the concentration. This staining process, however, may also lead to distortion of the original structure. Hence, a technique with advantages of high spatial resolution, real space observation, and nontoxic pre-processing is needed. Besides a technique with no special requirement regarding specimen geometry could be quite promising for the study of interfaces in real blends or the engineering blend systems. A technique that meets the above mentioned requirements undoubtedly is Positron Annihilation Lifetime Spectroscopy (PALS) \cite{Stamm, 2008} from which one can directly measure the free volume and its concentration in a polymer or polymer based material. Dlubek et al., \cite{2002, 2003a} are the only group to test the efficacy of PALS in investigating inter-diffusion in disperse blends moulded by a particle-matrix system through free volume parameters.

1.6 Free volume concept in polymers and polymer blends

Studies on the microstructure of polymers have great significance from the point of view of their technological applicability. The free volume theory developed by Doolittle to explain the molecular motions and physical behaviour of glassy and liquid state of the molecular systems has accelerated the polymer research \cite{Doolittle, 1951}. Naively, free volume cavities are the open spaces with low electron density, existing mainly in the amorphous domains of the polymer \cite{Jean et al., 1986}. The free volume refers to disorder in molecular arrangement and evolves due to molecular architecture such as chain folding, conformations, cross-links, and chain relaxation. Below the glass transition temperature (T_g), the free volume behave like frozen state with respect to temperature. Above T_g, free volume expands and molecular segments have considerable long range chain mobility and resulting in appreciable free volume in the polymer.

Free volume permits segmental motion (translational or rotational) of polymeric chains under applied stress (which may be mechanical, thermal,
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radiation, chemical, etc.). Therefore, it is closely related to visco-elastic, diffusion, weathering, aging and impact properties of polymers. Varieties of structural changes like first order phase transitions, second order transitions like glass transition and relaxation processes in polymers are well described by considering the free volume as an internal material parameter [Jean, 1990; Pethrick, 1997; Ramani and Ranganathaiah, 2001; Ranganathaiah et al., 2003]. Thus, the free volume concept has great intuitive appeal and owing to its conceptual simplicity, this theory is widely used in polymer science for understanding many polymer properties at molecular level [Huang and Rhim, 1990; Rueda and Varkalis, 1995; Pethrick, 1997; Ramgopal et al., 1998; GaniShariff et al., 2002(a,b); Ranganathaiah et al., 2003; Thimmegowda et al., 2004; Budd et al., 2005; Raj and Ranganathaiah, (2008, 2009(a,b))].

A simple definition of the free volume ($V_f$) is the total volume ($V_t$) minus the occupied volume ($V_o$) [Doolittle, 1951; Ferry, 1980]

$$V_f = V_t - V_o$$

(1.1)

The occupied volume represents volume occupied by the atoms or molecules of the material. The free volume corresponds to the unoccupied spaces such as vacancies or voids within the material. In the Figure 1.2 various forms of voids, gaps or empty spaces in material medium with their approximate size domain are shown.

It has been well established now that the temperature dependence of viscosity is associated with the free volume. The idea behind this is the fluidity in liquid which is due to the presence of free volume. Keeping in view of these aspects, Batchinski [1913], proposed a remarkable but simple formula in which the viscosity ($\eta$) is inversely proportional to the free volume $V_f$

Based on his experimental data of the viscosity of n-alkanes, Doolittle proposed a semi-logarithmic dependence of viscosity on free volume is given by

$$\eta = A \exp \left[ B \left( \frac{V_o}{V_f} \right) \right]$$

(1.2)

where A and B are constants.
The free volume approach has been effectively used by our laboratory and other researchers world over to understand the miscibility of polymer blends [Mayo et al., 1988; Naslund and Jones, 1992; Tino et al., 1993; Zipper et al., 1995; Flaris et al., 1995; Liu et al., 1995; Maurer and Wastlund, 1995; McCullagh et al., 1995; Hill et al., 1996; Peng et al., 1998; Machado et al., 2000; Ravikumar et al., 2005; Jamieson et al., 2010]. These studies have firmly established that free volume approach provides useful and meaningful information in understanding the miscibility properties of polymer blends.

**Figure 1.2:** Schematic representation of free space/voids in different materials.

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>Size</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Vacancies</td>
<td>0.1 nm</td>
<td>Metals</td>
</tr>
<tr>
<td>Dislocations</td>
<td>1 nm - 10 μm</td>
<td>Metals</td>
</tr>
<tr>
<td>Voids</td>
<td>0.1 nm - 1 μm</td>
<td>Metals</td>
</tr>
<tr>
<td>Free volume cavities/ cavities</td>
<td>0.1 nm - 10 nm</td>
<td>Polymers</td>
</tr>
</tbody>
</table>
1.6.1 Blend Miscibility and role of interface from free volume perspective

As mentioned earlier, free volume is known to influence the properties of polymers/polymer blends; like transport properties, mechanical properties and rheological properties. Therefore, the study of change in free volume provides insight into the final physical and mechanical properties of the blend system [Mayo et al., 1988; Naslund and Jones, 1992; Tino et al., 1993; Zipper et al., 1995; Flaris, 1995; Liu et al., 1995; Maurer and Wastlund, 1995; McCullagh et al., 1995; Hill et al., 1996; Pethrick, 1997; Peng et al., 1998; Machado et al., 2000; Ravikumar et al., 2005]. One of the most important properties of the polymer blends is miscibility. Generally, the formation of miscible blends depends on the type and strength of the forces acting between the chains of constituent polymers. The specific interactions such as hydrogen bonding, dipole interactions drive the mixture to homogeneous phase leading to miscibility. Due to these specific interactions, the chains of the constituent polymer chains are pulled towards each other and good mixing results. As a result the distance of separation between the monomer units or in other words the chains decreases suggesting increased diffusion of the one polymer chains into other polymer domain and vice versa. In such cases, a decrease in free volume that is fractional free volume is expected and observed [Puska and Niemen, 1994]. A polymer chain with two different functional groups in its side chains with similar polarity exhibit intramolecular repulsive forces [Kleintjens, 1985; Kumaraswamy and Ranganathaiah, 2006; Kumaraswamy et al., 2006] may aid miscibility. Blending of such polymers with other polymers of low molecular weight, the repelling polymer chains make way for the chains of the other polymer to slide in, leading to close packing of the two polymers resulting in miscible blend. Such polymer blends exhibit narrow separation at the interface. An example of such a system is SAN/PMMA [Robertson and Wilkes, 1987, 2001; Kumaraswamy and Ranganathaiah, 2006]. Here the system exhibits reduced free volume and miscibility even in the absence of intermolecular interactions.

Absence of the above mentioned specific interactions generally leads to immiscibility. In immiscible systems, one polymer forms its own domains in the
matrix of the other polymer and hence increased separation between the unlike polymer chains (chain proximity distance). This leads to lesser diffusion of the dissimilar polymer chains into one another and the net result is the generation of additional free volume in the system. Therefore, the free volume in such polymer blends is more than that of a miscible blend.

Stabilization of the interface in phase separated blends is commonly made by compatibilization process. Compatibilization results in interfacial modification of the blend which enhances the mutual diffusion of the constituent polymers at the interface. If the inter-diffusion is more (possible by specific interactions), this results to improvement in physical, mechanical and optical properties of the blends. The specific interactions like hydrogen bonding, dipole interactions etc. will have a direct effect on the free volume of the system. That is, the free volume content of the blend system can decrease (if cross linking occurs) or increase (if chain scission occurs) which aids inter-diffusion. Therefore, by monitoring free volume changes, one can understand the interaction among the constituent polymers.

Several techniques have been employed to probe the free volume cavities in polymers and polymer based materials; like Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Small Angle X-Ray Scattering (SAXS) [Flaris et al., 1995], Neutron Diffraction [Naslund et al., 1994], Photo-chromic and Fluorescence Spectroscopy [Fox and Flory, 1951] etc. However, these techniques can measure the free volume cavities of dimension 10 Å and larger, but not below 10 Å sizes of free volume hole sizes. For cavities of size less than 10 Å, the technique widely used world over is Positron Lifetime Spectroscopy (PLS) particularly in polymers and blends. In this technique ortho-positronium lifetimes (τ) are measured and used to derive the information on the free volume cavities of dimensions from 1-10 Å of the material. Its exceptional features like non-destructive technique, very high defect sensitivity and no special preparation of the sample has made it a novel and sophisticated technique for the experimental measurement of nanometre sized free volume cavities in polymers and also in blends [Jean, 1990; Williams et al., 1955; Ranganathaiah et al., 2002;
Kumaraswamy and Ranganathaiah, 2006; Raj and Ranganathaiah, [2008,2009(a,b)]). In Figure 1.3 a comparison is made to show the sensitivity of PLS with various other analytical methods. The author has used this method in the present work, to study the microstructure, chain proximity distance and diffused interface width in polymer blends.

**Figure 1.3:** Estimated ranges depicting the sensitivity of different experimental techniques employed in the study of microstructure of molecular materials.

1.7 Positron Annihilation Spectroscopy (PAS): An overview

1.7.1 The positron and its annihilation

Now a brief introduction to positron annihilation process is given in the following paragraphs. Prediction of positron ($e^+$), an anti-particle of electron ($e^-$) by Dirac in 1930 [Dirac, 1930] and its subsequent discovery by Anderson in 1932 in the cloud chamber photographs of cosmic ray showers [Anderson, 1932] is one of the greatest success of the theory of relativistic quantum mechanics. The annihilation of positron with electrons in matter was first studied in 1940s. It was discovered early that the energy and momentum conservation during the annihilation process could be utilized to study the properties of solids. In 1934, Mohorovicic [1934] predicted the formation of the bound state of a positron with an electron. This $e^+e^-$ bound state is called *Positronium (Ps)*, which was later discovered by Deutsch [1951(a,b)].
Positron, a successful unique scientific probe to study matter, has been realised through a number of studies carried out on the interaction of positron with matter. When an energetic positron (emitted with energy of 545 keV from a radioactive source $^{22}$Na) is injected into a material medium, it slows down due to the inelastic collisions with the electrons of the medium and gets thermalized in a very short time of few pico seconds ($10^{-12}$) [Garwin, 1953; Lee-Whiting, 1955]. The thermalised positron diffuses through the medium with a thermal energy ($\sim kT$, where $k$ is Boltzmann constant and $T$ is absolute temperature) until it finds an electron, mostly a conduction electron, it undergoes annihilation. Upon annihilation, the total energy of the annihilating pair ($\approx 2m_0c^2 = 1.02$ MeV, the sum total of rest mass energies of electron and positron) is converted into one, two, three or more gamma rays. The annihilation gamma ray energy depends on the number of gamma rays emitted. In comparison with the magnitude of gamma ray energy, the linear momentum of the positron and electron pair is quite small. Hence, the decay into one gamma ray can take place only in the presence of a third body to absorb the recoil momentum and its relative probability is negligibly small. The common modes of annihilation are found to be either two or three gamma rays. The three-gamma ray annihilation occurs to a much lesser extent than two-gamma ray annihilation. When the spins of the particles are parallel (triplet - $^3S_1$ state) the ortho-Positronium, in which case the total energy $2m_0c^2 = 1.02$ MeV of the annihilating pair is shared by the three gamma rays and these are emitted in one plane with the restriction that no two gamma rays will lie in the same half plane. In two gamma ray emission, they go out from the annihilation site in nearly opposite directions carrying energy of 0.51 MeV each. This process of positron annihilation is shown schematically in Figure 1.4.
1.7.2 Positron Annihilation Experimental Techniques

Positron annihilation spectroscopy (PAS) is a sensitive and non-destructive tool for studying the electronic structure of defects in solids (free volumes in polymers). The method relies on the tendency of positrons to become localized at open-volume regions of a solid and the emission of annihilation gamma rays escape the system carrying the information of the site of annihilation \cite{Puska1994}.

Generally the following three measurements are performed to study positron annihilation in matter \cite{Hautojarvi1979}

1. Positron Lifetime Technique (PLT)
2. Doppler Broadening of Annihilation Radiation (DBAR)
3. Angular Correlation of Annihilation Radiation (ACAR)

In Positron Lifetime Technique (also called as Positron Lifetime spectroscopy (PLS) or Positron Annihilation Lifetime Spectroscopy (PALS)) the survival time of positron in a medium is measured which provides information on the local electron density present at the annihilation site. The latter two methods yield information on the momentum of the annihilating positron-electron pair. In DBAR experiment, Doppler shift in the energy of the annihilation gamma rays is studied through a line shape parameter. This is a measure of the parallel component of momentum of the annihilating pair. Since the positron is thermalised before annihilation, the shift in energy of the annihilation gamma rays

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**Figure 1.4**: Illustration of positron annihilation process.
rays is due to the motion of the pair and the momentum of the pair is that of the electron of the medium, so that, the momentum component information from DBAR is that of the electron itself. In ACAR experiment, the deviation from collinearity of the two annihilation gamma rays, emitted almost in opposite directions when viewed in laboratory frame of reference, is measured. This provides information on the perpendicular component of momentum of the annihilating pair to the direction of emission of gamma rays. By correlating the results of the above three techniques, more information on the electron density distribution, defects/voids, etc., and their influence on the properties of the material in which positron undergoes annihilation can be derived.

The early experiments with positrons were used mainly to study the electronic structure, e.g. the Fermi surface in metals and alloys [Behringer and Montgomery, 1942; de Benedetti et al., 1950]. It was realized by the end of the 1960s, that the annihilation parameters are sensitive to lattice imperfections as well. It was also discovered that positrons might be trapped in crystal defects, i.e. positron is localized at the defect site until annihilation. As a consequence of these developments, the number of research papers has increased enormously. Up to the mid-1980s, defect studies in solids were mainly carried out in metals and alloys. The experience obtained was useful in exploring the utility of the techniques to semiconductors. The study of defects in compound and elemental semiconductors has become so large it amounts to about half of the total number of papers on defect studies with positrons [Schrader and Jean, 1988; Mogensen, 1995] which lead to naming the positron techniques as defect spectroscopy tools.

In the present scenario, the field of positron spectroscopy extends from advanced problems in solid-state physics to industrial applications in the area of characterization of high-tech materials like semiconductors [Puska and Nieminen, 1990], Carbon fullerenes [Ranganathaiah, 2000], zeolites [Nakanishi and Ujihira, 1982], polymers [Krištiak, et al., 1994; Jean, 1995(a,b)] and polymer blends [Liu et al., 1995; Raj and Ranganathaiah, 2008,2009(a,b)], superconductors [Briscoe and Beardsley, 1966], biomaterials [Deepa Urs, 2008; Sen et al., 2009], and recently nanomaterials [Mukherjee et al., 1996; Murakami and Mizuka Sano,
Natural polymers are the new class of materials that have been probed by the positron method [Akiyama et al., 2007; Roudaut and Duplatre, 2009, Chandrashekara and Ranganathaiah, (2009, 2010)] demonstrating such efforts, specifically, using PALS, the most versatile and useful of the three PAS methods. Figure 1.5 shows the positron lifetimes in various materials.

1.7.3 Positronium and its decay in polymers

In polymers, the thermalized positrons annihilate with electrons of the medium through different states viz. free state, trapped state and bound state. In free positron annihilation, the positron annihilates with an electron of the medium, without getting trapped into defects present in the medium. The free annihilation lifetime is of the order of ~200 ps. Some of the free positrons get trapped into the defects like vacancies/voids present in the medium and annihilate in a time range of 200 - 500 ps. The thermalized positron can also form a bound state called positronium in molecular materials and exists in two allowed spin states.
Because of statistical nature of Positronium formation from two fermions, the ground state of Positronium (Ps) is an admixture of singlet ($^1S_0$ : spins antiparallel) and triplet ($^3S_1$ : spins parallel) states respectively called para - Positronium (p-Ps) and ortho - Positronium (o-Ps). Therefore the ground state admixture of ortho and para states are in the ratio of 3:1 i.e.,

$$\text{Ps} = \frac{3}{4} (o-\text{Ps}) + \frac{1}{4} (p-\text{Ps})$$  \hspace{1cm} (1.3)

Various states from which positron and positronium can annihilate with characteristic lifetimes are given in Figure 1.6.

![Figure 1.6: Characteristic time scales of different positron annihilation states in matter.](image)

The characteristic lifetime of $p$-Ps is 0.125 ns and $o$-Ps is 140 ns in free space. However in polymers, the positron of $o$-Ps annihilates in a fast channel predominantly with an electron from the surrounding medium possessing opposite spin and suffers two-gamma annihilation. This process is called pick off annihilation process for which the mean lifetime of $o$-Ps reduces from 140 ns to few ns [Brandt et al., 1960]. Extensive reviews are available on PLS studies [Tao, 1974; Goldanskii, 1982; Schrader and Jean, 1988; Mogensen, 1995] in molecular solids.

1.7.4 Positron Lifetime Spectroscopy (PLS) study in polymers and polymer blends

Benedetti and Riching [1952] were the first to use the positron lifetime technique to study metals and solid materials. Later, Bell and Graham discovered
the long-lived lifetime component namely $o$-Ps lifetime [Bell and Graham, 1953], in their work which is regarded as revolutionary work on positron annihilation. With the advancement in timing spectroscopy, the positron lifetime technique is now capable of detecting very small lifetimes of the order 100-200 ps. Therefore, the Positron Lifetime Spectroscopy (PLS) has emerged as a highly sensitive and sophisticated technique for characterizing defects, micro voids or free volume cavities of smaller dimensions. Presence of free volumes in molecular media like polymers aid the motion of the polymer chain segments. From the early days scientists were searching for a relationship between the movement of atoms and empty space in condensed matter which had been a topic of immense importance. In recent years, PLS has been widely used by polymer scientists to probe free volume cavities in polymers to understand their microstructure and its connection to various properties by measuring the $o$-Ps lifetime in polymer. The $o$-Ps lifetime measures the nanometre size free volume cavities and $o$-Ps intensity provides information on relative number density of such free volume cavities in the material and this distinct nature makes this special technique for the understanding of microstructure of the polymer blends compared to any other available analytical tools. The review articles by Stevens [1980] and Jean [1990] provide a good introduction to the application of PLS in the study of polymers. The literature survey on the study of polymers and polymer blends using PLS clearly showcases the fact that free volume measured from PLS studies correlated well with physical, mechanical and transport properties of amorphous and semi crystalline polymers [Eldrup et al., 1981; Jean et al., 1986; Hill et al., 1990; Singh and Efterkhari, 1992]. These studies include the effect of temperature, pressure [Deng et al., 1992], sorption studies [Aithal et al., 1990; Macqueen and Granata, 1993; Ramani and Ranganathaiah, 2001]; Gani Shariff et al., 2002(a,b)], polymerization [Suzuki et al., 1993], physical ageing [Ranganathaiah et al., 2002; Sathyanarayana et al., 2002(a,b)], electric field effects [Bisi et al., 1961] etc. In recent years, it has been shown that PLS can as well be effectively used to study the microstructure of biopolymers like contact lens materials, human hair etc., [Singh, 1990; Thimmegowda et al., 2004; Ramani
et al., 2005; Deepa Urs, 2008; Chandrashekar and Ranganathaiah, (2009, 2010) and miscibility studies in binary and ternary polymer blends [Raj and Ranganathaiah, (2008, 2009(a,b)); Ranganathaiah and Kumaraswamy, 2009; Meghala and Ranganathaiah, 2012]

1.7.5. Positronium lifetime and free volume size

A schematic sketch of Ps localization in a free volume cavity is shown in Figure 1.7. The lifetime of $o$-Ps depends on overlap of the Ps wave function with the electron wave function within the free volume cavity from where it annihilates. This in turn depends on the size of the free volume cavity. Greater is the size of the cavity, smaller is the overlap of the wave functions and longer is the $o$-Ps pick-off lifetime.

Figure 1.7: Cross-sectional view of in-situ nature of Ps as a probe of free volume cavities in a polymeric material. Ps is preferentially localized in free volume cavities before annihilation.

Consequently, the $o$-Ps pick-off lifetime ($\tau_3$) and its intensity ($I_3$) are a direct measure of free-volume cavity size and their number density respectively within a polymer.

Nakanishi et al. [1988] developed a simple relation connecting $o$-Ps lifetime $\tau_3$ to the average free volume hole radius $R$ and this relation has been extensively used by polymer researchers all over the world to evaluate free volume size. Since the free volume in a polymer microstructure evolves with a variety of
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dimensions, $\alpha$-Ps lifetime is not of one value but has a distribution in a given polymer. By measuring the distribution of $\alpha$-Ps lifetimes, and deriving free volume hole size distribution using computer program CONTIN-PALS2 [Provencher, 1984; Gregory (1991,1995)] free volume information of the polymer understudy will be close to actual situation.

The challenges

From the literature survey it was found that, a good number of polymer blend systems have been studied so far using free volume measurements [Tino et al., 1993; Zipper et al., 1995; Liu et al., 1995; Flaris et al., 1995; Maurer et al., 1995; Machado et al., 2000; Ranganathaiah and Kumaraswamy, 2009; Raj and Ranganathaiah (2008, 2009 (a,b))]. From a careful analysis of these results it is observed that free volume parameters namely free volume size, ($V_f$), $\alpha$-Ps intensity ($I_3$) and fractional free volume ($F_V$) have been used to understand the miscibility and phase morphology of the blends. In the above referred studies for miscible blends, the free volume size $V_f$ was observed to show a negative deviation from the simple linear additivity relation. However the $\alpha$-Ps intensity $I_3$ and fractional free volume $F_V$ showed complex oscillatory behavior making inferences like the blends as either miscible or immiscible difficult. Later, Liu and Jean [Liu et al., 1995], based on Wu's theory [Wu, 1987] suggested free volume will not be additive when two or more polymers are mixed and hence the linear additivity rule was modified with the introduction of interaction parameter $\beta$ between dissimilar chains. This parameter $\beta$ is appropriately called interchain interaction parameter. This parameter was used to infer that if $\beta$ is negative then the blend is miscible and in case of immiscible systems it is positive. But in several binary polymer immiscible blends it was observed that the $\beta$ exhibited complex oscillatory behavior between positive and negative values making inferences difficult. Further, for miscible systems $\beta$, could not reveal information about the composition dependency of the miscibility or the miscibility level. As mentioned in the beginning of this chapter that, most of the polymer blends produced are immiscible and to make them useable in some applications, understanding of their phase behavior and compatibilization to improve their
performance, prior knowledge of the nature of interface in such blends is of topmost importance.

So the interfaces and their characteristics in polymer blends assume great significance. From the literature survey outlined above it becomes very clear that PALS has been widely used to probe polymers and blends in the pursuit of gaining knowledge of their properties but we distinctly noticed that it has not been exploited for the study of interface characteristics in real polymer blends. It is true that PLS is the most effective tool to study the nano-sized interface domains in the three dimensional polymer blends as the $o$-Ps lifetime measures the nanometer size free volume cavities, and its intensity provides information on relative number density of the free volume cavities.

From this perspective, let us consider the work of Dlubek et al. (2002, 2003a). They studied the interfaces in polymer blends in terms of inter-diffusion of component polymers at interface using the Positron Annihilation Technique. They assumed a core shell model for the description of the $o$-Ps response to the local chemical in homogeneity which makes use of a calculated concentration distance profile, the interface width and kinetic parameters such as the exponent of the time dependence of the interface width. They found that PALS parameters ($\tau_3, I_3$) are inadequate in the determination of the concentration dependence of the mutual diffusion co-efficient which lead to the difficulty in understanding the obtained results.

Further there were no attempts to overcome the difficulties in the use of PALS data for the study of interface characteristics. The real problem in the measurements was the lifetime parameters ($\tau_3, I_3$) of the blend will only show an overall increment or decrement in free volume depending on the level of thermodynamic mixing. These changes might be in one of the component polymers or both and as well at the interface. This cannot be revealed by free volume data alone. From this ascertaining the changes taking place at interface was difficult. If by some means this change is monitored or the changes at the interface could be connected to total free volume of the blend, then the effect of the interface on the free volume could be understood. This limitation of lifetime
parameters leads to other alternatives to look at the interface. A better and an alternative came from the new method developed by our group for measuring the miscibility properties in polymer blends by exploiting the usefulness of hydrodynamic interaction between blend constituents, particularly at the interface through a parameter called hydrodynamic interaction parameter (\(\alpha\)) [Ranganathaiah and Kumaraswamy, 2009; Jamieson et al., 2010]. Its efficacy has been tested on a number of miscible, partially miscible, immiscible and compatibilized blends [Raj and Ranganathaiah, (2008, 2009(a,b)); Meghala and Ranganathaiah, 2012; Ramya and Ranganathaiah, (2012,2013)].

1.8 Hydrodynamic Interactions in Polymer Blends

1.8.1 Hydrodynamic interaction and interface

![Figure 1.8: Models used to study polymers. (a) two dimensional lattice model, (b) perl necklace, off-lattice model and (c) the bead spring, off-lattice model.](image)

For polymers, viscosity is considered as an important property in understanding the viscoelastic behavior of polymers under stress and strain [Riande et al., 2000] using a wide range of theoretical models. Pictorial representation of few of the models is shown in Figure 1.8.

Of the several theories, we consider two main and important theories dealing with the flow behavior of polymer mixtures one by Rouse [1953] based on the works of Kargin and Slonimsky called KSR model and the other by Zimm [1956] based on the works of Kirkwood and Riseman called KRZ model. Figure 1.9 is the pictorial representation of these models. The KSR model assumes bead-spring model i.e. polymer molecules as a set of identical elements (segments) connected in series through covalent bond. Further, each segment in the polymer chain is
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considered as a bead connected linearly and that the macromolecular coil does not disturb the flow rate and does not introduce perturbation to the motion of the medium.

Figure 1.9: Schematic representation of KSR and KRZ Model.

The KRZ model is the next step in theoretical conceptions of the KSR model. The substantial new point in the KRZ theory is the consideration of the hydrodynamic interaction between separate segments in the polymeric chain. The calculations of KRZ model accounts for the perturbation of the flow field rates caused by the presence of foreign bodies. In principle, two extreme cases are possible; the first is the case where the polymeric chain does not give rise to perturbations to the flow rate, that is no hydrodynamic interaction is present; this limiting case is the KSR model itself and in the other case, the space occupied by macromolecules is found to be impermeable to the solvent and this corresponds to the maximum possible hydrodynamic interaction (KRZ Model). The presumption of KRZ model is that the specific interactions between component polymers of the blend are excluded since it deals with only the flow characteristics of the medium. However, we will see later that the presence of specific interactions do influence the hydrodynamic interaction in an indirect way.

The monomer units considered as beads get closer to each other in the presence of interaction between the component polymers which results to an increase in the friction at the interface. This might eventually result in energy dissipation at the interfaces. Recently, Wolf and co-workers [Schnell and Wolf, (2000,2001)] have experimentally explored the possible influence of
hydrodynamic interactions on the viscometric behaviour of polymer solutions. The above said effects have been prominently observed in their work through hydrodynamic interaction parameter ($\alpha$). Hydrodynamic interaction parameter $\alpha$ is considered as a measure of excess friction generated between the constituents of the blend system. In miscible blends there exists specific interactions between the constituent polymeric chains; therefore it is expected that high friction between them exists (see Figure 1.10). The excess friction is determined by the value of $\alpha$. Another parameter introduced in the theory of Wolf et.al [Schnell and Wolf, (2000, 2001)] is the geometric factor ($\gamma$) which has a direct bearing on the arrangement and orientation of the molecules in the system. These two parameters have been successfully calculated by Wolf et al. [Schnell and Wolf, (2000, 2001)] by measuring the viscosity. Since the relations developed by Wolf et al. are applicable to polymer solvent systems in terms of viscosity, for free volume parameters of the blend system in the solid phase Wolf et al. relations have been modified by Ranganathaiah and Kumaraswamy [2009] making use of the basic relation that free volume is inversely proportional to viscosity. The new method developed by these authors was shown to be effective in experimentally measuring the hydrodynamic interactions through free volume measurement [Ranganathaiah and Kumaraswamy, 2009; Jamieson et al., 2010].

![Figure 1.10](image)

**Figure 1.10:** Schematic illustration of friction and hydrodynamic interaction parameter, $\alpha$.

The above figure (Figure 1.10) is the visualization of friction generated at the interface when the monomer units in the blend of two different polymers move. The hydrodynamic interaction can be described in its simplest way as: "In dilute solutions there exists a long range interaction between segments mediated by the flow of the solvent called the hydrodynamic interaction. When a segment moves in a
solvent, it draws the surrounding solvent molecules towards it, and induces local flow field. Such a local flow propagates in the solvent induces a flow field at a distant point, which imposes a force on the segment at that point. As a result long range force is produced between the two segments in question.”

The concept of hydrodynamic interaction in polymer/polymer mixtures is slightly different. The flow mechanism in such systems may change from non-draining behavior at low composition of one polymer (say polymer A) to a fully drained behavior at high composition of the same polymer (that is polymer A). Entanglements between the chains of high molecular weight polymer modify the flow behavior leading to additional friction generated at the interface. The intermolecular interactions would push the chains of one polymer to other polymer chains. This would result in higher value of $\alpha$, and according to this model large values of $\alpha$ corresponds to miscible blends and near zero or positive values of $\alpha$ corresponds to immiscible blends.

The new method just described is very helpful in determining the miscibility level in binary and ternary polymer blends through hydrodynamic approach [Ranganathaiah and Kumaraswamy, 2009; Jamieson et al., 2010; Meghala and Ranganathaiah, 2012]. The basic premise of this approach is the friction generated at the interface of unlike polymer chains. The friction at the interface in binary blends is an indicator of how close the surfaces of the polymer chains/segments or how far apart are they. This also results to close packing if the chains/segments are closer. This in turn depends on the type of force/interaction at the interface. Therefore separation between the chains/segments at the interface that is chain proximity distance ($\Delta s$) is also important like the diffused interface width ($\Delta l$). From the hydrodynamic interaction point of view, miscible blends show high values for $\alpha$ suggesting high friction at the interface and hence we can expect narrow separation between the chains of unlike polymers at the interface leading to lower values of $\Delta s$. On the other hand an immiscible blend is expected to produce wide separation between the chains of unlike polymers hence larger values of $\Delta s$. Generally the diffused interface width ($\Delta l$) is defined as the third phase in a binary polymer blend.
enhanced by “inter-diffusion or compatibilization” [Utracki, 1990] and this is measured in several investigations based on Flory-Higgins parameter ($\chi$) measurement. So we exploited the usefulness of $\alpha$ in this work to extract the chain proximity distance ($\Delta s$) in binary blends as well as the diffused interface width ($\Delta I$) which is reported for the first time making use of positron lifetime measurements.

1.8.2 Hydrodynamic interaction parameter and its connection to Stokes-Einstein Relation

Based on Kirkwood and Riseman work [Kirkwood and Riseman, 1948; Riseman and Kirkwood, 1956] several theories on transport phenomena in polymer solutions incorporating the hydrodynamic interaction between segments of the polymer chains have been developed. The theories assumed each monomer to be a point source of friction in the solvent.

One of the steps in the calculation of the transport coefficients is the solution of a set of equations of the form

$$G_{km} = \delta_{km} - \alpha \sum_{l=0}^{N} \frac{1}{|k-l|} G_{ln}$$

(1.4)

where $N$ is the number of monomer units in the polymer and the parameter $\alpha$ is a measure of the strength of the hydrodynamic interaction given by the following equation.

$$\alpha = \zeta/8\pi\eta\Delta s$$

(1.5)

where $\eta$ is the viscosity of the solvent, $\Delta s$ is the distance between adjacent monomers, and $\zeta$ is the friction coefficient easily described by the following Stokes’ law (Stokes-Einstein relation)

$$\zeta = 6\pi\eta r$$

(1.6)

where $r$ is the radius of a monomer; then $\alpha$ takes the form

$$\alpha = \left(\frac{3}{4}\right) \left(\frac{r}{\Delta s}\right)$$

(1.7)
Equation (1.7) connects monomer-monomer interface separation (chain proximity distance) to hydrodynamic interaction through Stokes-Einstein relation. And this concept is entirely different to the diffused interface width discussed in the next section.

1.8.3 Diffused interface width and Flory-Huggins interaction parameter ($\chi$)

The diffused interface width is extensively studied in the bilayer polymer thin films are based on the Flory-Huggins interaction parameter ($\chi$). The parameter $\chi$ is a dimensionless quantity. This parameter gives a theoretical description of the phase separation curves for polymers of different chain lengths and compositions. Negative values for $\chi$ results in homogenous or miscible blends whereas positive value indicates immiscibility. From the literature review it was also found that Flory–Huggins theory, through the interaction parameter $\chi$, has been the basis of many investigations on polymer-solvent and polymer-polymer systems and has provided information on diffused interface widths [Stamm, 2008]. In a binary polymer blend this parameter quantifies the repulsion between unlike monomeric units. Depending on the magnitude of the interaction parameter, incompatible polymers form an equilibrium interface region (see Figure 1.11) in the blend and the interface width depends on the parameter $\chi$.

![Figure 1.11: Schematic of the interface between two immiscible polymers.](image)

Let us look in to different theories which relate the interfacial properties of two phase immiscible polymer blends to the microscopic interactions in terms of F-H interaction parameter $\chi$. In the early 1970s, Helfand and co-workers
constructed a self-consistent field theory of polymer interfaces [Helfand and Tagami, 1972(a,b)]. It was found that in the limit of infinite molecular weight very simple expressions were derived relating the interfacial thickness $\Delta l$ and interfacial tension $\gamma$. The characteristic interface thickness $\Delta l$ goes as $\chi^{-1/2}$ for small $\chi$ values and interfacial tension $\gamma$ (surface free energy) goes as $\chi^{1/2}$. This standard method evolved from the Helfand and Tagami self-consistent field theory [Helfand and Tagami, 1972(a,b); Utracki, 2002] determines the configurational statistics of the macromolecules in the interface region. At the interface, the interactions between statistical segments of constituent polymers are determined by the Flory-Huggins interaction parameter, $\chi$. So far the Flory-Huggins interaction parameter ($\chi$) along with the Helfand-Tagami theory of self consistent field (SCF) theory has been widely used in deriving interface widths in bilayer polymer blends. On the contrary the hydrodynamic interaction parameter ($\alpha$) which is a direct measure of interfacial friction has not been attempted to derive diffused interface widths. The present work reports such an effort and found that it works quite well for the binary polymer blends of three dimensional morphology.

1.9 Motivation

The phase morphology is an important aspect in understanding the properties of immiscible polymer blends. Through its size and shape, the interface between the two phases determines final properties of the blends. Most of the published work so far addresses the interfaces that exist between immiscible polymers welded between slabs (bilayer polymer blends) of the same or different polymers. The process of welding, i.e., short time inter-diffusion is believed to occur by reptation in which first a chain end crosses the interface and then the rest of the chain follows. Hence a partly joined interface formed by reptation with a given width may refer to quite different chain topography from that of an equilibrium interface of the same width formed in dispersed polymer blends of three dimensional morphology derived by blending process.
To characterize the interfaces in blends, several experimental techniques are available like Small Angle Neutron Scattering (SANS), Neutron reflectometry, Small Angle X-ray Scattering (SAXS), Differential Scanning Calorimetry (DSC), Transmission Electron Microscopy (TEM) \cite{Anastasiadis et al., 1988; Broseta et al., 1990; Careli et al., 2005, 2006; Beziel et al., 2008; Dlubek et al., 2003b; Liao et al., 2007]. However, none of these analytical tools are capable of probing the interface widths formed in real blends which are the diffused interfaces due to diffusion of one component polymer into the other with a greater accuracy and precision. Therefore, a method different from the conventional $\chi$ parameter based is required. For this, in this work the method developed by Ranganathaiah and Kumaraswamy is employed \cite{Ranganathaiah and Kumaraswamy, 2009; Jamieson et al., 2010}. The advantage of this method is that the same positron lifetime spectrum is used to derive $\alpha$ value. The free volume data derived from lifetime spectra itself will not indicate what happens at the interface. But according to the new method the hydrodynamic interaction parameter ($\alpha$), measure of excess friction at the interface, characterizes the miscibility level of binary blends. These results are further used to obtain the chain proximity distance ($\Delta s$) and the diffused interface width ($\Delta l$) in selected binary polymer blends.

To achieve the objectives set out above, we have carried out positron lifetime measurements in selected blends namely SAN/PMMA, PS/PMMA, PVC/SAN, PVC/EVA, PVC/PS, SAN/EVA, and PP/HDPE. The method of Ranganathaiah and Kumaraswamy has been employed to evaluate the hydrodynamic interaction parameter $\alpha$ for these blends. Making use of these $\alpha$ values the chain proximity distance between the chains of unlike polymers of the blends have been derived following the Stokes-Einstein relation (equation 1.6). Further, we have constructed density profiles across the interface, following the standard SCF theory, for all the blends studied to determine the diffused interface widths. The determined chain proximity distance and diffused interface width cover the different aspects of interface in the binary polymer blends under study which
comprises of miscible, partially miscible and immiscible blends for the
comparison purpose.

**Thesis organisation**

The thesis is divided into seven chapters. First chapter gives an introduction
to the present study. It outlines the literature survey on the polymer blends,
interface phenomenon and the current state of PLS study in the afore-mentioned
topics together with the motivation for the present study. Chapter 2 provides the
relevant theoretical background for the present study. Chapter 3 details the
experimental details of the present study such as data acquisition from PLS setup,
analysis of positron lifetime spectra using computer programs PATFIT-88 and
CONTIN-PALS2, the DSC and SEM experiments as supplementary techniques to
support positron results. Chapter 4 presents the results obtained by PLS, DSC,
SEM and hydrodynamic interaction parameter $\alpha$. In chapter 5 the author outlines
how the chain proximity distance in seven polymer blends is derived. Chapter 6
discusses the diffused interface width in partially miscible and immiscible blends
(PVC/SAN, PS/PMMA, PP/HDPE, PVC/EVA, PVC/PS and SAN/EVA)
Chapter 7 summarizes the results of the present investigation and conclusions
drawn.

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