CHAPTER 1

Introduction
Introduction

In the last few decades, the continuous need for materials of high technological properties has stimulated scientists to develop new classes of polymers with special properties, for applications where the usual materials fail. One of the most exciting and rapidly expanding branches of materials science is the area of polymers and polymer blends.

There are a variety of polymers available in the market. However, a single polymer often cannot achieve the desired properties for industrial or technical applications. Developing a new polymer with a new chemical structure that fits the needs of the market is very difficult and is not cost effective. So blending of polymers is an indispensable method for developing new polymeric materials.

Many new multi component polymeric materials have been developed during the past few decades. The large number of scientific papers, meetings and exhibitions devoted to this class of materials is sufficient to exhibit the strategic importance of the field.

1.1 Polymer blends

Mixing two or more different polymers together makes it possible to achieve property combinations of the individual components in the final material—usually in a more cost-effective way than synthesis of new polymers [1]. Therefore, polymer blends have played a significant role in revolutionizing polymer technology, leading to important and useful applications. The term polymer blend may be defined as a combination of two or more structurally different polymers or copolymers giving rise to materials with a range of properties, not delivered by any of the constituents.
For blending, polymers are generally selected to complement each other in one or more of the following properties: cost, processability, mechanical properties, chemical resistance, thermal performance and a variety of other properties [2,3]. Blending is typically viewed as a cost-saving method, in a sense an expensive polymer may be combined with a less costly polymer to provide improved or adequate performance at a significantly reduced price to the customer. The versatility of matching the price/performance requirements of specific application allows for a myriad of different products from the combination of the polymers. By simply varying the concentration of the constituent polymers, a variety of materials, each with a unique set of properties can be obtained. Most pairs of polymers are thermodynamically immiscible, but some polymer pairs are compatible and their blends exhibit excellent physical properties that offer advantages over either of the individual polymers. Sometimes a third component is added as a compatibiliser, which allows the improvement in the blending level of two immiscible polymers.

1.2 Methods of Blending

There are several methods available for blending which are well described in literature. Few important blending methods are briefly outlined below.

Melt Blending:
Blends can be prepared by melt mixing the individual polymers in an internal mixture. In this process, one polymer is heated to molten state and then the temperature is held above the melting temperatures of both the polymers and the second polymer is then added. Due to high temperature, the second polymer also melts eventually and they are mixed thoroughly in the melt state. The melted blend was passed through a two roll mill and made into sheets of samples. The
advantage of this technique is that the product is pure, uncontaminated and is useful for preparing bulk quantities of the material. The primary disadvantage of melt mixing is the possibility of degradation and high cost of equipments.

**Solution blending:**
This is the simplest mixing method available and widely used by many researchers. In this technique both the polymers are dissolved in a common solvent, mixed thoroughly and then the solution is cast on a neat, clean and uniform glass plate. The solvent is allowed to evaporate completely so as to get the blend films of almost uniform thickness. 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 the method used by the author to prepare the blends for the present study.

**Latex blending:**
Mixing of two low viscous lattices (polymers) 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 be miscible.

**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, the components do not get enough time and energy for phase separation and hence the mixture generally exhibits homogeneous phase. However, as the temperature of the system
increases (process of sublimation), phase separation results if the blend components are incompatible.

**Mill mixing technique:**
Very small amount of polymer can be mixed in electrically heated two-roll mixing mill. The efficiency of a two roll mixing method can vary from good to poor depending upon the rheology of the components and the skill of the operator.

**1.3 Types of Polymer blends**
Polymer blends can be broadly classified in to three groups depending on their phase behaviour and a schematic sketch is given below:

![Types of Polymer blends](image)

*Figure 1.1: Types of Polymer blends*
**Miscible blends:**

A miscible blend is produced in the blending process when the change in enthalpy, $\Delta H_m < 0$ which results in negative heat of mixing ($\Delta G < 0$) due to specific interactions. Homogeneity is observed at least on a nanometer scale, if not on the molecular level. This type of blends exhibit a single glass transition temperature ($T_g$), whose value lies in between the glass transition temperatures of the blend components. A well known example of a blend, which is miscible over a very wide temperature range and in all compositions, is Polystyrene (PS)/Polyphenylene Oxide (PPO).

**Partially Miscible blends:**

Some blends are labelled as partially miscible which are neither completely miscible nor immiscible. These blends show limited specific interactions, but small amounts of one polymer is miscible in the other. More clearly, we can describe this in the following way: Few polymer pairs that sometimes mix and sometimes don't. The variables that control this are usually temperature and composition. A lot of polymer pairs are only miscible when there is more of one polymer than of the other. This is shown schematically for two polymers A and B which demonstrates that for few compositions the resulting blend is miscible but for other compositions it is immiscible.

![Miscible blends diagram](image)

Examples for this type of blends are PC/ABS and PBT/PC blends [1].
**Immiscible blends:**

Immiscible blends are completely phase separated systems. In these blends, one component forms its own domains in the matrix of the other and vice versa. In such cases the domains size is usually larger of the order 5-10 µm [4-6]. Immiscible blends exhibit $T_g$'s corresponding to the $T_g$ of the component polymers. That is, for a binary blend, two $T_g$'s will be generally observed. For such phase separated systems, the interfacial strength will be very poor, leading to adhesive failure and poor mechanical properties. So these blends are not of much use without compatibilization or phase stabilization. Examples of fully immiscible blends are PA/ABS, PA/PPO, PA/PP etc. However, the above blends have become commercially successful only after being efficiently compatibilised using suitable compatibilisers and are termed as polymer alloys [1].

**1.4 Polymer/Polymer Miscibility**


The formation of a homogeneous and thermodynamically stable blend under given temperature and pressure conditions is controlled by the change in Gibbs free energy of mixing i.e. $\Delta G_m$. Based on the thermodynamic viewpoint, miscibility refers to the molecular level homogeneity that requires the free energy
of mixing be negative i.e. \( \Delta G_m < 0 \). Figure 1.2 shows the three possible ways in which the \( \Delta G_m \) of a binary mixture may vary with composition. Curve B corresponds to a system of two totally miscible polymers. Curve A is that corresponding to a totally immiscible polymer mixture and curve C represents a partially miscible system. In addition, curve C exhibits a gap in miscibility where conditions laid down by equation (2) are not fulfilled.

Figure 1.2: Schematic diagram for the variation of free energy change with composition in binary polymer mixture: A) Immiscible B) Miscible C) Partially miscible

Thermodynamic miscibility of polymers requires two criteria to be satisfied at constant temperature and pressure [13]. These are:

\[
\Delta G_m = (\Delta H_m - T \Delta S_m) < 0 \quad \text{and} \quad \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right]_{T,P} = \left\{ RT \left[ \frac{\rho A}{\phi_i M_A} + \frac{\rho B}{\phi_i M_B} \right] - 2B \right\} > 0
\]

in order to ensure stability against phase separation. In above equations, \( \Delta H_m \) and \( \Delta S_m \) indicate the change in enthalpy and entropy respectively on mixing, \( T \) is
the absolute temperature, $\phi$, $\rho$ and $M$ represents the volume fraction, density and molecular weight of the components respectively.

Equation (1) suggests that for spontaneous mixing to occur, $\Delta G_m$ must be negative. However, if two high molecular weight polymers are blended, the gain in entropy, $\Delta S_m$ is negligible and the free energy of mixing can only be negative if the heat of mixing $\Delta H_m$ is negative. In other words, the mixing must be exothermic, which requires specific interactions between the blend components. These interactions may range from strong ionic to weak and non-bonding interactions, such as hydrogen bonding, charge transfer forces, dipole-dipole interactions etc. Usually, Van der Waals interactions occur, which explains why polymer miscibility is an exception rather a rule.

The second thermodynamic requirement given in equation (2) is applicable to partially miscible-systems. This suggests that the second derivative of $\Delta G_m$ with respect to volume fraction of one of the components at constant temperature and pressure should be greater than zero to ensure stability against phase separation. However, in these systems, the composition fluctuation may lead to phase separation.

Based on above description, we can infer that in majority cases, macromolecular components in the polymer blends are found to be immiscible (phase-separated) due to the small contribution from the entropy to the free energy of mixing and therefore, miscibility (single phase) is rare and an exception that exists only for very few polymer combinations and this schematically shown in following chart.
1.4.1 Factors influencing Miscibility

The miscibility in polymer blends is a complex phenomenon and is controlled by several factors as discussed below [4].

(i) Polarity: When the atoms bond together to form a monomeric molecule of a polymer, the lower coordination number atom may attain slight positive charge and other atoms become slightly negative. For example, we can consider water molecule. Here oxygen is slightly negatively charged and hydrogen is slightly positively charged. Therefore, polymers that are similar in structure are generally similar in polarity and are less likely to repel each other and more likely to form miscible blends.

(ii) Specific group attraction (Specific interactions): Polymers that are drawn to each other by hydrogen bonding, acid-base, charge transfer, ion-dipole, donor-acceptor adducts or transition metal complexes which are less common, but when such attractive forces exist, they are likely to produce miscibility.

(iii) Molecular Weight: Low molecular weight permits greater randomization on mixing and therefore greater gain of entropy, which favours miscibility. More surprisingly, polymers of similar molecular weights are more miscible, while
polymers of very different molecular weights show immiscible nature, even if both have the same compositions.

**Composition:** Even though two polymers appear immiscible, at a fairly equal composition, 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.

**Crystallinity:** When a polymer crystallizes, it readily forms a two phase system, with important consequences for practical compatibility. In a polymer blend, when one polymer crystallizes, it adds another phase to the system. If both polymers in a blend crystallize, they will usually form two separate crystalline phases since it is quite rare for two polymers to crystallize into a single phase.

### 1.4.2 Determination of Polymer/Polymer Miscibility

Thermodynamic miscibility in polymer mixtures means the homogeneity down to the molecular level. In a more practical sense, we may define it as the appearance of homogenous system when characterized by a particular type of test. However, it has been reported that a blend system observed to be miscible by one test may turn out to be immiscible system when tested by a different technique [1-6]. This is because of the sensitivity of the technique. Miscibility, though generally defined as existence of single phase, one has to take into account the size of the dispersed particles. However, the methods used in the study of blend miscibility can be broadly classified into three groups.

- Phase equilibria methods
- Flory-Huggins interaction parameter approach ($\chi$)
- Indirect compatibility tests
**Phase Equilibria methods:**

High molecular weight blends have small combinatorial entropy of mixing and the free volume contribution further increases the free energy of mixing. As a result, the miscibility depends on specific interactions or intramolecular repulsions. Various types of specific interactions are responsible for miscibility as discussed before and they all contribute for the negative heat of mixing:

\[
\frac{\Delta H_m}{\Phi_1 \Phi_2} = B < 0
\]

Where \(\Delta H_m\) is the enthalpy of mixing, \(\Phi_1\) and \(\Phi_2\) are the fractions of polymer 1 and 2 respectively in the blend and \(B\) is the binary interaction parameter. The value of \(B\) determined from analogue Calorimetry is taken for judging the miscibility [1]. If the parameter \(B\) takes negative values (attractive interaction), this is taken as an indicator for a miscible blend and if \(B\) takes positive values (repulsive interaction), it is taken as an indicator of immiscibility.

**Flory-Huggins interaction parameter \((\chi_{ij})\):**

 Miscibility in polymer blends is judged by the determination of Flory-Huggins interaction parameter, \(\chi_{ij}\). Negative \(\chi_{ij}\) results in homogenous or miscible system.

The three major factors influencing \(\chi_{ij}\) are,

- Specific interactions
- Dispersion forces
- Free volume
Small Angle Neutron Scattering (SANS), Small Angle X-rays Scattering (SAXS) and melting point ($M_p$) depression (DSC) can be employed to determine the interaction parameter $\chi_{ij}$ [1-6].

**Indirect compatibility tests:**

A well known and widely used indirect method to study miscibility is the measurement of glass transition temperature ($T_g$). It has been observed that a binary miscible blend exhibits single glass transition temperature, whereas an immiscible blend shows two glass transition temperatures characteristic of each component of the blend.

Study of optical properties of the blends also can provide primary information about the miscibility of the system. A homogeneous blend will have a refractive index in between those of the blend components. For a heterogeneous system, one polymer appears as dispersed phase embedded in other polymer and it scatters the incident light according to its domain size and hence the system usually lacks optical transparency.

Spectroscopy techniques such as NMR and IR, and microscopic techniques such as SEM, TEM are also used to study the miscibility of the blend systems. It has been reported that from these techniques, one can derive information on the nature of interaction and phase behaviour in polymer blends [1-6]. A recent entry to this characterization is Positron Annihilation Spectroscopy (PAS) for miscibility and phase separation study of binary polymer blends [31,32,37,39,50-51,79-82]

From thermodynamics point of view, the blends of immiscible polymers obtained by simple mixing show a strong separation tendency, leading to a coarse structure and low interfacial adhesion [1]. The final material then shows poor
mechanical properties. The above discussions do not mean to say that immiscible polymer blends are of little use and hence the only solution is to search for miscible ones. In fact, immiscible polymer blends are much more interesting for commercial development and some properties can be achieved only through immiscible blends [1-6]. The immiscibility or limited miscibility of polymers enables formation of wide range structures, some of which, if stabilized, can impart excellent end-use properties to the final material [1-6,12]. Therefore, the challenge is to develop processes or techniques that allow control of both the morphology and interface of phase separated blends [1-6,12].

1.5 Compatibilization of Polymer blends

Compatibilization is defined as a process of interface modification of phase separated polymer blends, leading to improved interface properties and/or morphology. When two immiscible polymers are blended without compatibilisation, generally a coarse and unstable morphology coupled with poor interfacial adhesion between the phases is obtained. As a result, the blend exhibits inferior physical properties to those of individual polymers coupled with poor structural integrity and heat stability. Even their performance will be irreproducible. Therefore, compatibilization is an essential treatment in the case of partially miscible and immiscible blends so as to get improved properties of the blends.

1.5.1 Role of interfacial properties in Polymer blends

The structure and morphology of partially miscible and immiscible blends depends on many factors among which the interfacial properties are the most important. When analyzing the linear dimension ($l$) as a function of composition in immiscible blends, one finds that between a domain of polymer A and that of
polymer B, there exist an interfacial layer of thickness $\Delta l$. The value of $\Delta l$ as determined by Small Angle X ray Scattering can be as large as 4nm [1]. This inter domain region is considered as interface and this region is different from both (polymer A and polymer B) the phases in its structural properties. It has been observed that in several polymer alloys, stabilization of the interface (via chemical means, selective radiation cross-linking, or by thermal means) results in reproducibility of performance, processability and recyclability. However, in the melt, the interface is not a mathematical plane separating the two phases, but a region of inter-diffusion of the two types of polymers. The concentration gradient $g$ of micro and macro heterogeneities at the interface is given by,

$$ g = \frac{\delta C}{\delta l} = \frac{l}{\Delta l} \quad (4) $$

where $\delta C$ is the concentration gradient across the interphase.

In general, the segmental mobility within the interface is lower as evidenced by increased $T_g$. The relation between $T_g$ and $\Delta l$ is non monotonic as are the packing density, surface tension and the free energy of mixing. The thickness of the interface layer depends on the thermodynamic interactions, macromolecular segment size, concentrations and phase conditions. As a result, the interface is not a homogeneous diffused layer but a complex entity with micro and macro-heterogeneities. The two important parameters that characterize the interface are interfacial tension and domain adhesion. Almost all the final properties of blend materials are decided by their interfacial properties. As mentioned earlier that, in partially miscible and immiscible blends, the interfacial adhesion is not strong and hence their applications are limited. Therefore, in order to make these types of blends to be used for end user applications
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successfully, interfacial modification is required which can be achieved by compatibilization through different means.

1.5.2 Strategies for Compatibilization

The important compatibilization routes adopted by the researchers for partially miscible and immiscible blends are:

(i) Addition of functional polymers:
Usually a polymer, chemically identical to one of the blend components is modified to contain functional units; which have some affinity for second blend component. The functional modification may be achieved in an extrusion modification process. Examples include the grafting of maleic anhydride or similar compounds to polyolefins, the resulting pendant carboxyl group having the ability to form chemical linkages with polyamides via their terminal amino groups [2].

(ii) Reactive blending:
This is one of the new methods employed in producing compatible thermoplastic blends. This differs from other compatibilization routes. Here blend components themselves are either chosen or modified; so that reaction occurs
during melt blending process. Important advantage of this method is that there is no need of using a third component (Compatibilizer).

(iii) Addition of block and graft copolymers:
The addition of block or graft copolymers represents the most extensively researched approach to compatibilization of blends. The block and graft copolymers containing segments chemically identical to the blend components are the obvious choice as compatibilizer, given that miscibility between the copolymer segments and the corresponding blend component is assured, provided that the copolymer meets certain structural and molecular weight requirements and that the copolymer locates preferentially at the blend interfaces. Copolymer structure and molecular weight have important influences on their effectiveness as compatibilizers. As far as the molecular weight is concerned, the solubilisation of a discretely dispersed homopolymer into its corresponding domain of a block copolymer compatibilizer occur only when the homopolymer molecular weight is equal to or less than that of the corresponding block copolymer. However, stabilization of a matrix homopolymer into its corresponding domain of a block copolymer compatibilizer will occur even if the molecular weights are mismatched. But generally, balanced molecular weight is needed for copolymer compatibilizer. The requirement that the copolymer should locate preferentially at the interfaces also has implications for the molecular weight of the compatibilizer since the thermodynamic driving force to interface and the kinetic resistive force to diffusion increases with molecular weight. Therefore, low molecular weight copolymers having short diffusion times are the better materials as compatibilizers. Copolymers with blocks of chemical composition identical to those of the two homopolymers represent the best technical option for compatibilization.
(iv) **Radiation induced modification:**

This is relatively a new technique used to modify the interfacial properties in partially miscible and immiscible blends. When a polymer is exposed to high-energy radiation, such as high-energy electron beam, γ-rays, X-rays, UV rays and light ion beams, its structure undergoes some changes [14-17], which leads to changes in physical and chemical properties of the polymers. The changes caused by high-energy radiation are complicated and so far, have not been fully understood. A great deal of effort has been devoted to studies in this area and some advances have been made, especially in the mechanisms at the initial stage of irradiation [14,15,18-22]. At the initial stage, the high-energy radiation is less selective to the nature of the primary bonds of a polymer owing to the extreme high energy of the radiation compared to the dissociation energy of the primary bonds. When a high-energy photon or electron is sufficiently close to an organic molecule, it will cause local polarization (even ionization) of the atoms and, therefore, create a highly excited state. The excitation energy can be dissipated in a number of ways - the excited molecules may decompose into free radicals or ion radicals and then initiate various chemical reactions. The exact reaction process, reaction rate, and resultant products are different for different polymers.

The net effect of irradiation depends on the chemical structure of the polymers, their morphology and irradiation conditions like – dose rate, atmosphere and temperature [23]. The irradiation provokes two main processes – *crosslinking* and *chain scission* that can affect the microstructure and in blends, structure of the interface, which in turn affect the mechanical, optical and electrical properties of the materials. The crosslinking promotes the interfacial bonding between components [23,24] and the chain scission leads to lowering of molecular weight and creation of chain ends. The low molecular weight chains
on the surface induce a decrease in free energy of mixing and interfacial tension, leading to improved interfacial properties.

Recently, e-beam irradiation of polymer blends have attracted considerable attention due to its capability in bringing out some improved phase morphology through crosslinking reactions [25-30]. It is expected that this is a promising route to stabilize or even fix morphology of the immiscible blends, provided that the constituent polymers are selected with appropriate beam response [20]. However, there are only few investigations reported in literature on this useful aspect of electron beam irradiation in particular polymer blends. Some of the important studies in this area are mentioned below: The effect of electron irradiation on the micro rheological behaviour of PP/EPDM and PS/LDPE system studied by Van Gisbergen and his co-workers [25-27], the radiation induced crosslinking and degradation mechanism in LDPE/EVA studied by Dalai et. al. using Thermo Gravimetric Analysis [28], Thermal degradation study of PP/HDPE done by Hassanpour et. al. [29], Crosslinking study of PVC studied by Ratnam et. al. [30], study of diffusion kinetics in electron irradiated polycarbonate by Ranganathaiah et.al. [19] etc. Compared to other compatibilization methods such as chemical compatibilization, radiation induced interfacial modification is found to have many distinct advantages in many ways such as:

- Radiation cross-linking is carried out without the addition of initiator and it is solvent free process.
- The process is very fast, clean and can be controlled precisely.
- The irradiation is carried out at lower temperature and sometimes can be controlled in comparison with chemical operation.
However, the success rate of e-beam irradiation modification of polymer blends is limited due to following reasons: Suppose the dose rate exceeds the required amount, due to increase in temperature (if not controlled), the color of the blend sample changes which is not desirable. Secondly, irradiation time is not short to achieve few hundred K Gy dosage. If high dosage is needed, the time for irradiation will be certainly longer. Owing to the above reasons, that in many cases, improved phase modifications could not be achieved to the desired extent [31,32]. So, we report in this work, a new method of interface stabilization in partially miscible and immiscible blend systems in which adhesion at the interface is poor. Although this method is commonly used in synthetic chemistry as synthesizer, catalytic agent in organic chemistry [33], we use this simple and efficient route for improving the interface adhesion in binary polymer blends which need phase stabilization. The route is microwave irradiation and compares that with e-beam irradiation. The microwave-irradiation is an alternative to conventional heating but this brings out far reaching effects for the interfacial modification in polymer blends [31,32].

The acceleration of reactions by microwave exposure results from material-wave interactions leading to thermal effects and specific effects. Clearly, a combination of these two contributions could be responsible for the observed effects.

**Thermal effects** (dielectric heating) can result from dipolar polarization as a consequence of dipole-dipole interactions between the polar molecules and the electromagnetic field. This is illustrated in figure 1.4. The microwave effect originate in the dissipation of energy into heat as an outcome of agitation and intermolecular friction when dipoles change their mutual orientation at each alternation of the electric field at a very high frequency (ν = 2450 MHz) [34].
This energy dissipation in the core of materials allows a much more regular repartition in temperature when compared to classical heating. Classical thermal phenomena (conduction, convection, radiation etc) only play a secondary role in the posterior equilibrium of temperature.

Specific microwave effect can be expected for the polar mechanism i.e. due to dipolar polarization; the greater the polarity of a molecule, more pronounced is the microwave effect with the rise in temperature [33,34]. In other words, polar molecules present in the system absorbs microwave energy very effectively thereby increases its reactivity which results in initiating large number of interactions with surrounding molecules.

Taking this concept of microwave mechanism into our system of interest i.e. polymer blends, in which the component polymers may contain polar groups in them, we felt some interactions can be induced through microwave irradiation between blend constituents thereby interfacial properties gets modified. Also, the process is found to be pure i.e. before and after irradiation the sample shows no sign of physical changes like color, brittleness etc. by visual inspection and the
time and power required for irradiation is very small (few tenths of seconds and just 30 watts) unlike in other irradiation techniques.

Therefore, in this thesis we have made use of e-beam and for the first time microwave irradiation on some of the selected partially miscible and immiscible blends for interfacial modification and a comparison is made as to which type of irradiation is a better route for interfacial modification.

1.6 The Free volume concept

We may consider two types of volumes in matter, namely occupied volume and free volume. The occupied volume represents volume occupied by the atoms or molecules of the material. The free volume corresponds to the free unoccupied spaces such as vacancies or voids within the material. Free volume $V_f$ is generally represented as $V_f = V - V_o$, where $V$ is the total volume of the material and $V_o$ is the volume occupied by the molecules [35,36,37]. Figure 1.5 is a schematic representation of existence of free volume in different materials. This ranges from single-atom vacancies through bigger voids or holes. More precisely the free volume holes or cavities are the open spaces evolved due to molecular architecture and chain arrangement (like chain folding) and are characterized as low electron density regions, existing mainly in the amorphous domains of the polymer system.
Polymers consist of long chains of monomeric units. Due to the long range of polymeric chains, they undergo twisting and bending to give highly disordered amorphous structures. The bending and twisting of these long range chains gives rise to a lot of free space along and between the chains. This free space is generally referred to as free volume.

In the following figure various forms of voids, gaps or empty spaces in material medium with their approximate size domain are provided.

<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 holes/ cavities</td>
<td>0.1 nm - 10 μm</td>
<td>Polymers</td>
</tr>
</tbody>
</table>

*Figure 1.5:* Schematic representation of free space/voids in different materials
We can find the literary meaning to free volume which comes from the 1st century BC, wherein, poet Lucretius wrote down the thoughts of Epicurus (341-271 BC) on empty space which reads as:

“Therefore there is intangible space, voids, emptiness. But if there were none, things could not in any way move; for that which is the province of body, to prevent and obstruct, would at all times be present to all things; therefore nothing would be able to move forward, since nothing could begin to give place.”

These words were probably the first clear statement about the free volume. Though this statement has been made in keeping view of the macroscopic free volume or space, it is interesting that link between free volume and mobility was so clearly understood.

The free volume permits the segmental motion (may be translational or rotational) of the polymeric chains under applied stress. Therefore it is closely related to the visco-elastic, diffusion, ageing and impact properties of a polymer.

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 [18-22,37,39]. The derived macroscopic properties from the approach of free volume are fruitful with the assistance of Quantum and Statistical calculations.

It has been well established 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 [40], proposed a remarkable but simple formula in which the viscosity \( \eta \) is inversely proportional to the free volume \( V_f \). In the year 1951, Doolittle proposed the free volume theory to explain the molecular motions and physical behaviour of glassy and liquid state of the molecular systems [38]. Based on his
experimental investigations of the viscosity of n-alkanes, Doolittle proposed a semi-logarithmic dependence of viscosity over free volume, which is given by the following equation,

\[ \eta = A \exp \left( B \left( \frac{V_o}{V_f} \right) \right) \tag{5} \]

where \( A \) and \( B \) are constants.

Owing to its conceptual simplicity, this theory is widely used in polymer science for understanding many polymer properties at molecular level. Williams, Landel and Ferry \[41\] in 1952 suggested a simple relation for the temperature dependence of free volume popularly known as WLF equation in which it is assumed that for \( T < T_g \), the free volume is frozen and the free volume at \( T_g \) has been shown to have a universal value of 0.025 or 2.5\%. Further, the WLF equation is valid for temperatures from \( T_g \) to \( (T_g + 100 \, ^\circ C) \). Fulcher \[42\] for molten inorganic glasses and Tammann and Hesse \[43\] for super cooled organic liquids, modified the Doolittle equation (equation 5) by using the temperature dependence of free volume. This modified equation is called Fulcher – Tammann formula.

The free volume provides qualitative explanations for the dependence of \( T_g \) on the molecular weight, diluents, pressure and dependence of visco-elastic relaxation times on temperature, pressure \[44\], static tensile strain \[45\] and anti-plasticization \[46\]. Therefore, the free volume can now be considered as an important internal material parameter for polymer blends as well, which needs to be investigated fully for a better understanding of the microstructure and other properties of blends which find multitude of applications.

Worth mentioning is that, recently the free volume approach has been effectively used by this laboratory and few other researchers to understand the
miscibility of polymer blends [47-62]. These studies have shown that free volume approach seems to provide useful and meaningful information in understanding the miscibility properties of polymer blends.

### 1.6.1 Free volume and miscibility

Generally, the formation of miscible blends depends on the type and strength of the forces acting between the chains of constituent polymers. The attractive interactions such as hydrogen bonding, dipole interactions drive the mixture to homogeneous phase leading to miscibility. Due to the attractive interactions and good mixing, the chains of the constituent polymers are pulled towards each other. In such cases, a decrease in free volume occurs [63]. In few cases miscibility may happen due to the intra-molecular repulsive forces [64, 65]. This usually happens in case of polymeric chains which have two different functional groups in its side chains with similar polarity. When such polymers are blended with other polymers, the repelling polymer chains try to associate with the chains of the other polymer rather than its own leading to miscibility. An example of such a system is SAN/PMMA [65,66]. Here the system exhibits miscibility even in the absence of any inter molecular interactions. This also marks reduction in the overall free volume of the system.

The absence of any of the above said interactions generally leads to immiscibility. In immiscible systems, one polymer forms its own domains in the matrix of the other polymer. This generates additional free volume in the system. Therefore, the free volume in such polymer blends is expected to increase.

Free volume is also known to control other characteristics such as transport properties, mechanical properties and rheological behavior of the system. Therefore the study of change in free volume also provides insight into
the ultimate physical and mechanical properties exhibited by the blend system [39,47-62].

The free volume holes can be probed using many techniques such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Techniques like Small Angle X-Ray Scattering (SAXS) [61], Neutron Diffraction [67], Photo-chromic and Fluorescence Spectroscopy [68] etc. However, these techniques are more sensitive to free volume holes of dimension 10 Å and larger. If the free volume holes size is less than 10 Å, these techniques are not sensitive. In such cases, the technique widely used to probe free volume holes in polymers and blends is Positron Lifetime Spectroscopy (PLS). In this technique ortho-positronium lifetimes are used to obtain the information about the free volume holes of the material and this detects free volume holes of dimensions from 1-10 Å. Its exceptional features such as non-destructiveness and very high defect sensitivity has made it to emerge as a novel and sophisticated technique for the experimental measurement of nanometre sized free volume holes in polymers and also blends [18-22,37,41,47-49]. The author uses this technique in this work to study the phase modification brought out by e-beam and microwave irradiation.

1.7 Positron Annihilation Spectroscopy (PAS)

1.7.1 Historical Background
The ‘Positron’ the antiparticle of the electron was predicted by Dirac ("On the quantum theory of electron":1928). First experimental indications of an unknown particle were found in cloud-chamber photographs of cosmic rays (Anderson 1932). This particle was identified later as the positron, which was thus the first antiparticle discovered. The annihilation of positron with electrons
in matter was first studied in the 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 predicted the formation of bound state of a positron with an electron. This $e^+ - e^-$ bound state is called ‘Positronium (Ps)’, which was later discovered by Deutsch (1951).

### 1.7.2 Principle of Positron annihilation

The electromagnetic interaction between electrons and positrons results in the annihilation of $e^+ - e^-$ pairs in which the total energy of the annihilating pair is transferred to quanta of the electromagnetic field - photons ($\gamma$ rays).

The principal channel of this reaction can be written as,

$$e^+ + e^- \rightarrow \gamma_1 + \gamma_2$$  \hspace{1cm} (6)

This process is called ‘Positron annihilation’ in a material medium. In the centre-of-mass system of the $e^+ - e^-$ pair, the energy of each annihilation photons is equal to the rest energy of the electron (positron), $E_0 = mc^2$, and the two photons are emitted in opposite directions to conserve linear momentum. The positron lifetime in a material medium is defined as the survival time of positron in the medium before it annihilates. Therefore, the lifetime of a positron is directly related to the electron density it will run into and annihilates. The electron density of the material governs positron lifetimes in materials; higher the electron density, shorter is the lifetime \[^{[69]}\]. Measurement of positron lifetime constitutes what is known as **Positron Lifetime Spectroscopy (PLS)**. Due to finite momentum of the annihilating $e^+ - e^-$ pair, the emission directions of the two photons deviate from collinearity and if this deviation is measured experimentally, it provides the transverse component of the electron momentum.
with which positron annihilated. This constitutes the *Angular Correlation of Annihilation Radiation (ACAR)* experiment. The motion of $e^+ - e^-$ pair in the medium before annihilation also produces a Doppler shift in the energy of annihilation photon and if measured accurately using a high-resolution detector provides longitudinal component of electron momentum. This is known as *Doppler Broadening measurement (DB)* through a line shape parameter. The conglomeration of these three techniques is what we call now “*Positron Annihilation Spectroscopy (PAS)*”.

PLS is widely used to measure the positron and positronium lifetimes in condensed matter. DB and ACAR, although quite different from each other experimentally, are related in that they both provide a measure of the electron momentum distribution in a material of study. Neither technique, however, has found much application to polymers, probably because the information generated could not be easily applied to assess the structural state of a polymer directly.

The early experiments with positrons were dedicated to the study of the electronic structure, e.g. the Fermi surface in metals and alloys (Behringer and Montgomery 1942; de Benedetti et al. 1950). The above three experimental techniques of positron annihilation were developed based upon the equipment of nuclear spectroscopy, particularly in the two decades after 1945. It was realized by the end of the 1960s, that the annihilation parameters are sensitive to lattice imperfections. 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 continuously. Up to the mid-1980s, defect studies in solids were mainly carried out in metals and alloys. The experience obtained in this field was applied to semiconductors. The study of defects in compound and elemental
semiconductors amounts to about the half of the total number of papers on defect studies with positrons [70,71].

Today, the field of positron annihilation spectroscopy extends from advanced problems in solid-state physics to industrial applications in the area of characterization of high-tech materials like semiconductors, zeolites [39], polymers [18-22,39], polymer blends [47-62], superconductors [39], biomaterials [39,72,73] and recently nanomaterials etc [39,74,75]. In recent years, we are witnessing an increasing number of applications of the Positron Annihilation Spectroscopy (PAS) in industrial laboratories; indeed, a large amount of data gathered in practical situations is giving full evidence of the usefulness of the method.

1.7.3 Positronium and its decay in Polymers

In molecular media like polymers, positrons annihilate from three different states viz. free state, trapped state and bound state. The free positron annihilation is the one in which 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 voids present in the medium and annihilate in a time range of 200 to 500 ps. However, during the slowing down process of the positron in losing energy and at nearly thermalized state, it can form the bound state called Positronium (Ps) (figure 1.6) and annihilates as described above. 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). The characteristic lifetime of $p$-Ps is 0.125 ns and $o$-Ps is 140 ns in free space.

Therefore the ground state admixture of ortho and para states are in the ratio of 3:1 i.e.,

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

(7)

In polymers, the positron of $o$-Ps annihilates in a fast channel predominantly with an outside 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 [76]. Extensive reviews [77,78,70,71] are available on PLS studies in molecular solids. Various states from which positron and Positronium can annihilate with characteristic lifetimes are given in table 1.1.

<table>
<thead>
<tr>
<th>Positron (e$^+$) State</th>
<th>Annihilation Process</th>
<th>Characteristic lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘free’ e$^+$</td>
<td>$2\gamma$</td>
<td>$\sim 0.2$ ns</td>
</tr>
<tr>
<td>‘trapped’ e$^+$</td>
<td>$2\gamma$</td>
<td>$\sim 0.5$ ns</td>
</tr>
<tr>
<td>$p$-Ps</td>
<td>$2\gamma$, self-annihilation</td>
<td>0.125 ns</td>
</tr>
<tr>
<td></td>
<td>$2\gamma$, pick-off process</td>
<td>$\sim 1$ ns</td>
</tr>
<tr>
<td>$o$-Ps</td>
<td>$3\gamma$, self-annihilation</td>
<td>140 ns</td>
</tr>
<tr>
<td></td>
<td>$2\gamma$, pick-off process</td>
<td>$1-5$ ns</td>
</tr>
</tbody>
</table>

Table 1.1: Characteristic time scales of various positron annihilation Processes in matter
1.7.4 PLS study in Polymer blends

Nearly two decades after the discovery of positron, DeBenedetti and Riching [79] used the positron lifetime technique in the study of solids. In the pioneering work on positron annihilation, Bell and Graham discovered the long-lived lifetime component namely o-Ps lifetime [80]. With the advancement in timing spectroscopy, the positron lifetime technique is now capable of detecting very small lifetimes of the order 100-200ps. Therefore, the Positron Lifetime Spectroscopy (PLS) has emerged as a highly sensitive and sophisticated technique for characterizing defects, micro voids or free volume holes of smaller dimensions. In molecular media like polymers, the motion of the polymer chain segments may take place due to the existence of the free space. The search for a relationship between the movement of atoms and empty space in condensed matter has been an imperious topic for scientists. Even though, a great deal of efforts have been spent on the theoretical development of free volume concept, the experimental investigations in polymers and in particular polymer blends are not very extensive and in some cases non-existent.

However, in recent years, PLS has been extensively used by polymer scientists to probe free volume holes in polymers [81-83, 18-22] and polymer blends [47-62, 65, 84, 85]. Since, ortho-Positronium lifetime measures the nanometre size free volume holes and its intensity provides information on relative number density of such free volume holes, this technique is a better technique for understanding of the microstructure of the polymer blends compared to any other available techniques.
1.7.5 Free volume study on compatibilized polymer blends

Earlier discussions showed that, in most of the cases, phase separated system results due to thermodynamic conditions and hence a need for compatibilization to stabilize their interface for better end uses applications. Compatibilization results in interfacial modification thereby, enhancing many physical, optical properties of the blends through specific interactions etc. As mentioned before, we are interested in radiation induced phase modification, the most probable reactions are crosslinking and chain scission. These interactions will have an effect on the free volume properties of the system. The free volume content in the system can decrease or increase based on bond formation (crosslinking) or bond breaking (chain scission). Therefore, through free volume monitoring, we can judge whether any improved interaction has taken place or not between blend constituents upon irradiation and importantly to what extent.

The Limitation...

From the literature survey it becomes clear that the free volume data derived from positron lifetime measurements provides the average values of the free volume size and overall free volume content of the system. Careful analysis of these results reveals another important feature that they do not reveal the actual site of changes if introduced to the system like phase modification. This becomes very important with partially miscible or immiscible blends which can be compatibilized or phase stabilized. Since, we are looking at the interfacial modification through irradiation, knowledge about the interfacial changes and how to monitor these changes becomes important. The free volume will only show an overall increase or decrease depending upon microstructural changes. 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 by itself. This limitation of free volume prompted us to find some other alternatives to look at the interface and our group has recently developed a new method for measuring the miscibility properties in polymer blends by exploiting the usefulness of *hydrodynamic interaction* between blend constituents, particularly at the interface [85].

### 1.8 Hydrodynamic Interactions

Viscosity is considered as an important property in understanding the viscoelastic behavior of polymers under stress and strain [86]. The flow behavior of polymer mixtures, mainly polymer/solvent systems, has been studied in various theories in the past. Two such theories dealing with the flow behavior of polymer mixtures had been proposed, one by Rouse [87] based on the works of Kargin and Slonimsky and is known as the *Kargin–Slonimsky–Rouse* (KSR) model and the other by Zimm [88] based on the works of Kirkwood and Risemann known as the *Kirkwood–Risemann–Zimm* (KRZ) model. The KSR model assumes polymer molecules as a set of identical elements (segments) connected in series, each of which is deformed independently of the others, and the condition of continuity of the chain is provided by the connectivity of the segments. Furthermore, it assumes that the viscoelastic properties of all segments are identical. Moreover, each segment in the polymer chain is considered a bead connected linearly, and the macromolecular coil does not disturb the flow rate. This means that the coil is absolutely permeable to the stream and does not introduce perturbation to the motion of the medium. The concept of this model is shown schematically in figure I.6
The KRZ model is the next step in theoretical conceptions of the KSR model. The KRZ model concept is schematically shown in figure 1.7. 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 the KRZ model account for the perturbation of the flow field rates caused by the presence of foreign bodies. In principle, two extreme cases are possible in these models. In the first, 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. 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.

Recently, Schnell and Wolf [89-92] provided an elaborate discussion on the effect of the hydrodynamic interactions in various polymer/solvent systems based on these two theories. In the theory, it is supposed that the point of contacts between the polymer segments and solvent molecules acts as energy dissipation centers at the interface. These energy dissipation centers are generated due to the interaction between the solvent molecules and polymer chain segments and also due to their molecular arrangement and orientations. The friction generated at these junctions is considered as due to hydrodynamic effect. This theory introduces two parameters, a hydrodynamic interaction parameter (\( \alpha \)) and a geometric factor (\( \gamma \)), both of which are evaluated with viscometric data to understand the role of this interaction in the system of their study. The \( \gamma \) parameter is expected to depend on the molecular surfaces and volumes in the system, whereas \( \alpha \) is a measure of excess friction generated between the constituents of the blend at the interface excluding specific interactions. Experimentally, they showed that \( \alpha \) varies as the friction between the constituents changes. Therefore, \( \alpha \) is a measure of the deviation of friction between the surfaces of the components from ideality.

Schnell and Wolf [89-92] advocated that the preference of contacts between molecules of component 1 (solvent) and component 2 (polymer) leads to a reduction in intermolecular friction due to an increased tendency of the unlike molecules move conjointly. In other words, if there exists an interaction between the solvent molecules and polymer segments, the friction between them
is less as they move cooperatively, leading to smaller negative values of $\alpha$ and vice versa. If this concept is extended to polymer/polymer mixtures, a different situation arises. The flow mechanism of such systems may change from non-draining (non-deformed state) behaviour at a low composition of one polymer (say I) to a fully draining state (deformed state) at a high composition of the same polymer component. Entanglements between chains of a high-molecular-weight polymer modify the flow behaviour, which might lead to additional friction being generated at the interface. The intermolecular interaction adheres one polymer chain to a number of chains of the other polymer at the segmental level, and this corresponds to a three-dimensional network picture. If the contacts between the blend constituents is more (the case of miscible blend), the excess friction generated will be more as a result of which the temperature increases. Due to rise in temperature, there will be an increased dissipation of energy at the interface and therefore interfacial tension decreases. This can be viewed as fine dispersion of the two blend constituents at the interface. In such a situation, $\alpha$ the hydrodynamic interaction parameter takes large negative values. The negative sign is to indicate the energy dissipation at the interface. In the case of partially miscible and immiscible blends, the contacts between the blend constituents will be weak and hence friction generated will also be small thereby $\alpha$ takes lesser values. This is schematically illustrated in figure 1.8. The theoretical equations of Wolf et. al. [89,90] were developed for the viscosity of the systems involved. We, in our study adapted these to free volume with necessary modifications exploiting the inverse proportionality between viscosity and the free volume. Therefore, the parameter $\alpha$ can be easily derived from the same free volume data from PLS measurements.
Introduction

Figure 1.8: Schematic illustration of friction and hence the parameter \( \alpha \)

Based on above discussion, we understand that \( \alpha \) seems to be a good parameter to characterize the changes at the interface, one way looking at it is it represents the adhesion strength of the constituent polymer chains at the interface. Also, the composition dependent miscibility level in polymer blends can also be understood.

1.9 Motivation

Blending of two polymers of choice generally produces immiscible or partially miscible blends with poor adhesion at the interface making the blend not suitable for end use applications for which it was intended [1]. So, in recent times a focused attention to understand the phase behaviour of such blend systems is on the rise aiming to improve the structural properties [1-6]. The interface stabilization in immiscible and partially miscible blends requires some form of compatibilization. The compatibilization is to accomplish three important tasks: 1. Reduce the interfacial tension, which is the result of fine dispersion, 2. Stabilize the interface morphology, 3. Increase the interfacial adhesion [1-6,12]. The most common compatibilization strategies adopted are chemical and physical compatibilization. Since the former has been in use for a long time because of its advantages, it still contains some practical disadvantages. As such
researches are pursuing different approaches which come under physical compatibilization and realized compatibilization through radiation induced phase modification. Irradiation by high-energy radiation like electrons and gamma rays has been tried in the past but with little success. Irradiation leads to chain scission, cross-linking, free radical formation, dangling pair production etc., causing modification in the structure of polymeric system. If cross linking results through covalent bonds between the blend constituents, blend properties like optical, mechanical, electrical etc. gets improved [23-27]. It is expected that this is a promising route to stabilize or even fix morphology of the immiscible blends, provided that the constituent polymers are selected with appropriate beam response [25-27]. However, the success rate of e-beam irradiated modification of polymer blends is limited due to reasons discussed earlier.

On the other hand, use of microwave irradiation, which is an alternative to conventional heating, seems to be a useful approach for the above-mentioned purpose but so far it has not been exploited. The microwave effect results from the material–wave interactions and, due to the dipolar polarisation phenomenon, the greater the polarity of the molecule, the more pronounced will be the microwave effect [33,34]. Therefore, one expects that a polar group present in the blend component systems may absorb the microwave energy and thus become reactive, thereby initiating improved interaction between the blend components resulting to some interfacial modification.

The characterization of polymer blends is generally done by the Differential Scanning Calorimeter (DSC) but recently our group has illustrated its limitation and alternatively developed a new method [85] based on free volume measurement from positron lifetime technique for the said purpose. Further, even the free volume data has its limitation since it fails to reveal
composition dependent miscibility [65]. Even though the free volume data derived from positron lifetime measurements provides the average values of the free volume size and overall free volume content, it does not reveal the actual site of modification occurred in partially miscible or immiscible blends. What occurs at the interface could not be directly obtained from this. To overcome this hurdle, the new method developed for characterizing the miscibility level of binary blends could be exploited through the usefulness of hydrodynamic interaction between the constituents of a polymer blend particularly at the interface [85]. Therefore, through the parameter $\alpha$ one can study effectively the interfacial properties of binary polymer blends before and after phase stabilization/modifications which is very important from the point of view of blends final application.

Motivated by the above facts, in the present study, we have employed the positron lifetime method to monitor the free volume of the blend constituents and the blend systems and evaluated hydrodynamic interaction $\alpha$ and for the first time. This is used to understand interfacial changes brought about by e-beam and microwave irradiation in five suitably selected polymer blend systems. To check the efficacy of the method, blend components with polar groups, non-polar and weak polar groups have been selected for comparison to infer which route of interface stabilization/modification namely e-beam or microwave brings about appreciable changes/improvements in the blends. The blends selected for this study are PS/PMMA, PVC/EVA, PP/NBR, PP/LDPE and PVC/SAN.

The thesis is divided into six chapters. First chapter gives an introduction to the present study. It outlines the literature survey on the polymer blends and the current state of PLS study in the afore-mentioned topics and the motivation
for the present study. Chapter 2 provides the relevant theoretical background for the present study. Chapter 3 details the experimental part of the study such as data acquisition and analysis of positron lifetime spectra using computer program PATFIT-88, the DSC experiments and analysis. Chapter 4 presents the results obtained by PLS, DSC and hydrodynamic interaction parameter $\alpha$ of two polar blend systems namely PS/PMMA and PVC/EVA before and after irradiation. Chapter 5A discusses the results on PP/NBR blend (Polar system) and PP/LDPE blend (non-polar system) before and after irradiation and a comparison study is made. Chapter 5B discusses the results of the weakly polar system namely PVC/SAN blend before and after irradiation. Chapter 6 summarizes the results of the present investigation and conclusions drawn.

References


Introduction


