Chapter 1

INTRODUCTION
1 Introduction

Polymer science and technology has undergone an enormous growth over the last several decades primarily through innovations in polymer chemistry and polymer processing. First, several new homopolymers were developed from a variety of monomers. Random copolymerization was then used as an effective technique for tailoring or modifying polymers to achieve a desired property profile. The introduction of block and graft copolymerization techniques afforded more precise control over the composition and properties of the polymer. However, it is evident that innovations in polymer chemistry is not the only strategy to meet new requirements or to solve old problems. Desired properties can also be achieved by incorporating a second component such as low molecular weight additives to the polymer. The concept of physically blending two or more existing polymers to obtain new products has also attracted widespread interest and commercial utilization.

Two component systems are now widely used to achieve desired combinations of mechanical, electrical or thermal properties which are not possible with either component alone. The physical as well as mechanical properties of the composite differ drastically when two or more polymers are blended with each other, as compared to when both monomers are copolymerized with each other. There are many ways by which two or more components are combined to form a new material with different properties such as blends, alloys, block or graft copolymers, and inter-penetrating polymer networks. The fact that two phase systems can be tailor made as per the desired application, makes them important from a commercial point of view.

1.1 Types of two phase systems

The various types of two-phase polymeric systems can be broadly divided into the following categories; copolymers, blends, alloys, and interpenetrating polymer networks (IPN). These categories are defined below:
i) Copolymers can be considered as a two phase system wherein the second phase is polymeric and chemically linked to the first polymeric phase. While there are several types of copolymers like block, graft or random copolymers, random copolymers do not form two macroscopically distinct phases.

ii) Blends are two or more component systems in which the various components are immiscible with each other. Here, we consider blends in which an immiscible second phase of either an organic compound, inorganic compound, or polymer is dispersed in the first polymer which forms the continuous phase.

iii) Alloys can be considered as blends where the additive (second polymer or low molecular weight compound) is miscible with the first polymeric phase. Some blends also exhibit partial miscibility i.e. the blend components are miscible with each other only over a limited temperature or composition range.

iv) An IPN can be considered as a special case of a blend where both the polymeric phases form continuous networks which interpenetrate each other and may also be crosslinked with each other.

This thesis examines the transport properties of two phase systems based on blends, alloys and IPNs. These type of systems are described in more detail below:

(a) **Blends** :-

Blends are comparatively easy to form and less time consuming to develop. It is possible to obtain desired properties such as impact strength, Tg etc. by blending polymers which are easily and cheaply available.

The compatibility of the two phases in a blend plays a major role in determining the system properties. Generally, the better the compatibility between the two immiscible phases of the blend, the smaller is the dispersed phase domain. It is known that properties such as viscosity of the polyblend are related to the compatibility and composition of the two phases in the blend. Many other properties and subsequent uses of a blend depend on the arrangement of the two phases. For example, when one phase is dispersed in a matrix of the other; the matrix phase will dominate properties such as tensile strength. In the case of transport properties also, the continuous matrix will be dominant; however, it is possible to modify the transport properties by controlling the nature,
amount, and method of addition of the dispersed phase. If the second phase is present as a parallel arrangement, both phases contribute to many transport properties such as permeability, conductivity etc. in direct proportion to their composition in the blend. However, perpendicular to this parallel direction, the system represents a series arrangement with transport properties such as permselectivity which disproportionately favor one phase.

(b) Alloys:

An alloy is a type of blend in which the individual components are miscible and together behave as a single component system for the physical properties of interest. In the case of metallic alloys, miscibility extends to the level of co-crystallization. In the case of polymers, blends with two co-crystallizable semi-crystalline polymers are very rare. Polymeric alloys are defined as miscible blends or those blends which are homogeneous at a molecular level. Polymer alloys show one glass transition temperature. Blends that are homogeneous at some temperature and phase separate in other accessible temperature regions are referred to as partially or nearly miscible blends.

Blends and alloys may be either synergistic or nonsynergistic with respective to their characteristics. If $P_1$ and $P_2$ represent the values of a given polymeric property for the respective pure polymers, and $C_1$ and $C_2$ are their corresponding concentrations in the blend, the value of that property for the blend, $P$, can be frequently be correlated by a simple equation:

$$P = C_1 P_1 + C_2 P_2 + I P_1 P_2$$

When $I > 0$, a synergistic enhancement in that property is seen beyond that predicted by simple additivity rules ($I=0$). Nonsynergistic blend are characterized by $I < 0$ i.e. there is a loss of the property. As an example, the glass transition temperature in blends of miscible polymers exhibits a dependence of $1/T_g$ on composition given by the following relationship:

$$1 / T_{g,b} = w_1 / T_{g,1} + w_2 / T_{g,2}$$

where $w_{1,2}$ are the mass fraction of the respective components, $T_{g,b}$ is the $T_g$ of the blend, and $T_{g,1}$, and $T_{g,2}$ are the $T_g$'s of polymer 1 and 2, respectively.
(c) **Interpenetrating polymer network (IPNs)**

In this concept, both polymer phases are continuous and simultaneously form a interpenetrating network (IPN). IPNs are defined as a material containing two polymers, each in network form, which have been synthesized or cross-linked in presence of each other. A related but different concept is the idealized interpenetration of two molecular networks called as simultaneous interpenetrating network (SINs). Formation of an SIN begins with a solution of both monomers and cross-linkers which are then polymerized by noninterfering modes, such as addition and condensation reactions.

The guidelines concerning phase continuity which are applied to IPNs, and more broadly, to many two phase polymer systems are as follows:

1. For simple melt blends, the polymer with the higher concentration or the lower viscosity tends to form the continuous phase.
2. For bulk or solution graft copolymerizations, the polymer synthesized first forms the more continuous phase. Polymer II usually forms cellular domains within polymer I.
3. Crosslinking of either polymer I or II tends to promote phase continuity. Materials with both polymers crosslinked (IPNs) tend to develop two continuous phases.

### 1.2 Transport properties

The permeability of a single polymer can be expressed as:

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P = D S
\]

where \(D\) is the diffusivity coefficient and \(S\) is the solubility coefficient of the polymer. The diffusivity is affected by polymer-penetrant dynamics while the solubility is affected by polymer-penetrant interactions. Diffusivity is affected to a large extent by the amount of free volume available in the polymer matrix for the penetrant molecule to pass through. If the available free volume of the polymer is reduced, there is usually an increase in the selectivity of the polymer for small molecules over larger ones. There is a large amount of data as well as theoretical developments regarding permeation in amorphous polymers.

While it is possible to design polymer blends so as to achieve desired mechanical or thermal characteristics, the effect of blending on transport properties is not as well
understood. However, literature shows that additives in the form of either a second polymer, organic compounds or, inorganic fillers can significantly alter the transport properties of the first polymer. The transport properties of the composite are sensitive not only to the choice of components being blended but also to the blending method.

Polymer blending can be achieved by melt, solution or emulsion blending techniques. In the case of melt blending, the permeability of the blend depends mainly on whether the two blended polymers are crystalline or amorphous in nature, as well as the way these two components have been mixed together. In the case of solution blending, the evaporation of solvent and crystallization kinetics of the polymer(s) and additive plays a major role in determining the morphology of the blend, which in turn affects the permeability. In case of emulsion blending, the rate of stirring of one component, viscosity and the rate of mixing of second component and the amount of emulsifying agent determines the compatibility and miscibility of the two.

Polymer permeability is an important parameter in applications such as gas separation, packaging etc. Differing permeabilities towards different gases can be exploited for selective separation of a particular gas from the mixture. Polymeric membranes are being used for gas separations in many commercial processes such as recovery of hydrogen from the purge stream of ammonia reactors, nitrogen separation from air, and oxygen enrichment of air. In the case of hydrogen recovery, hydrogen, being smaller in molecular diameter, permeates faster and can be separated from nitrogen. Similarly, membranes which have a higher selectivity for oxygen over nitrogen are used in air separation applications. When air is passed through these membranes, the permeating mixture contains a higher amount of oxygen.

Polymeric films are widely used for packaging of various materials such as fruits, vegetables, cereals, electric goods, etc. If the packaging material retains the moisture content, the packaged fruits or vegetables remain fresh for a longer time. For cereals, absorption of moisture from the atmosphere is a major problem, thus a packaging material which restricts the passage of moisture is useful. Nitrogen gas is sometimes used in
packaging fruits and vegetables in order to restrict oxidative damage. Thus polymer films with low permeability for water vapor and nitrogen are useful for packaging applications.

It may be possible to prepare suitable membranes and/or packaging materials by combining components in two phase systems. Encouraging results toward this have been reported by several investigators. These results and the theoretical basis of permeation in two phase systems are described in the following chapter.

1.3 Organization of the thesis

This First Chapter gives an overview of the thesis and defines the type of two phase systems studied. The rationale for the study of the transport properties of two phase polymeric systems is given.

Chapter Two reviews the literature on transport through two phase systems with emphasis on permeability studies with blends, alloys, and IPNs.

Chapter Three lists the scope, rationale and objectives of this thesis.

Chapter Four describes the experimental techniques used for the preparation of the blends and IPNs. The methodology used for the characterization of the two phase system films, and for their permeation studies are also given in this chapter.

Chapter Five summarizes the results and discusses the effect of film morphology on permeability of each of the three types of systems investigated.

Chapter Six summarizes the conclusions for each two phase system based on the discussion in Chapter Five.

1.4 Terminology

Some common terminologies / abbreviations which are used frequently in this thesis are defined as follows:

PS - polystyrene
PA - polyarylate
BMA - 2,3 dimethyl-4-n-butyl-4- (4’’-methoxybenzoyloxy) azobenzene
HDPE - high density polyethylene
VLDPE - very low density polyethylene
PU - polyurethane
VP - vinyl pyridine
PVP - polyvinyl pyridine
TMP - trimethaloyl propane
TDI - toluene diisocynate
BP - benzoyl peroxide
PUP - pre polymer of maleic anhydride and polyethylene glycol 200 (PEG-200)
IPN - interpenetrating polymer network
Tg - the glass transition temperature of the polymer
T_m - the melting temperature of the polymer
T_C-N - the crystalline to nematic transition temperature
T_N-I - the nematic to isotropic transition temperature
δsp - the intersegmental distance in the polymer chains
LM - polarized light microscopy
DSC - differential scanning calorimetry
WAXD - wide angle x-ray diffraction
SEM - scanning electron microscopy
Perm-selectivity - the ratio of the permeability of two gases
Tortuosity - the ratio of actual diffusion path to effective thickness of membrane
Wiggles - resistance due to tortuous diffusion path because of the impermeable phase