Chapter 1

INTRODUCTION
INTRODUCTION

Development of new molecules and chemical modifications of existing ones have been the most common ways of facing new challenges for polymeric materials. These routes have become increasingly complex and expensive over the years and thus alternative ones have become more interesting and attractive. Polymer blending is one such approach that is presently in a state of rapid scientific and commercial development. The reduced probability of finding new, inexpensive and wide utility homopolymers led to the blending technology as one of the fastest growing segments of polymer technology. The increasing range of application makes polymer blending more attractive. The rapid development and commercialisation of polymer blends is due to their

quick modification of performance,

higher performance at reasonable price,

ability to extend the performance of expensive resins

and potential for recycling of plastic wastes.

BASIC THEORY OF BLENDING

A successful polymer blend is a cost effective mixture of two or more polymers with a better combination
of different properties. Depending upon the polymer miscibility, the blends can be classified as miscible, partially miscible and immiscible, or in a technological sense as compatible, semicompatible and incompatible. An ideal blend is one which is homogeneous and behaves like a single component system. A large number of compatible polymer blends and alloys have been investigated and successfully commercialised.\textsuperscript{5-9} Alloys are a class of polymer blends in which a large interpenetration of domains is secured by physical and/or chemical means. Although the terms alloys and blends are often used synonymously, they differ in the level of thermodynamic compatibilities and resulting properties. On the high end of the compatibility spectrum are the alloys. Alloys give a tighter, denser molecular structure than blends.

The structure and stability of polymer blends depends primarily on the miscibility of polymers used in its preparation. Miscibility is governed by the Gibbs free energy of mixing ($\Delta G_m$). The thermodynamic condition for obtaining miscible blend is that the free energy of mixing must be negative

$$\Delta G_m = \Delta H_m - T \Delta S_m$$
where $\Delta H_m$ is the change in enthalpy, $\Delta S_m$ the change in entropy upon mixing and $T$, the absolute temperature. Since the entropy term is negligible for polymers, the heat of mixing $\Delta H_m$ is the key factor deciding the polymer-polymer miscibility. In the case of purely dispersive forces $\Delta H_m$ is always positive. Consequently, high molecular weight systems with this type of interaction are rarely miscible. Miscibility drops significantly with growing chain length. If however, there exist so called specific interactions (ion-dipole interactions, hydrogen bonds) between the components, then $\Delta H_m$ can be negative and the polymers can become miscible. Or, in other words, miscibility depends upon the degrees of interaction among the polymer components. From the standpoint of selecting polymer blends, a quantitative means of predicting the affinities of polymer pairs in terms of easily measured properties of the components would be desirable. One possibility is through the use of solubility parameter $\delta$, which has proved useful in the study of the dissolution and swelling of polymers in low molecular weight liquids. Compilation of the solubility parameters of the polymers is available. For nonpolar liquids the internal energy change upon solution is given by $\Delta E = \phi_1\phi_2(\delta_1-\delta_2)^2$(cal/cc of solution) where $\phi$s are
volume fractions of the components. Realising that amorphous polymers are essentially liquids and assuming that the volume change upon mixing is negligible this is an expression for the change in enthalpy on solution since $\Delta E = \Delta H$ for constant volume, constant pressure process. This equation always results in a positive $\Delta H$, indicating that for nonpolar high polymers, where the $\Delta S$ term is small, true solution will not occur unless the $\delta$s are almost perfectly matched.

Most of the polymer pairs are thermodynamically unfavourable to form homogeneous mixtures and mixing them leads to multiphase systems. In order to achieve a homogeneous or a compatible blend, it is necessary to choose polymer components capable of specific interactions among them leading to negative heats of mixing.

The usual miscibility criterion is the measurement of glass transition temperature $T_g$. Miscible polymers are considered to be those which give a blend with a single glass transition temperature dependent on the composition of the blend. Polymers, which in a blend, exhibit two or more $T_g$s, corresponding to the glass transition temperatures of the individual components are considered to be immiscible.
METHODS OF PRODUCING POLYMER BLENDS

The simplest and most direct method is mechanical blending. This may be accomplished on two roll mill or in internal mixers, eg., Banbury. The nature of the resulting dispersion depends on the length of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Also there is a possibility of chemical effects produced by the milling operation.

When the individual components can be obtained in latex form, they may be conveniently combined by blending the latices. The polymer is then recovered by coagulation or spray drying. This method results in an intimate, uniform dispersion. However, one drawback is the difficulty in completely removing the nonpolymer material (emulsifier etc.) present in the latices.

Mixing of polymer solutions is in practice mainly used for coatings, because it allows rapid and easy mixing of the components at low energy costs, leads to simple applications at normal temperatures and neither causes degradative colour changes nor premature
crosslinking reactions. But, for the preparation of the solid polymer blends, this method requires removal of the solvent, which usually leads to phase separation. Furthermore, the use of solvents implies problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually only laboratory samples of solid polymer blends are prepared by this method.

Blends may also be prepared by dissolving a polymer in the monomer of the other component and then polymerising the second component. This may result in appreciable grafting of the polymer in addition to good dispersion.

PROPERTIES OF POLYMER BLENDS

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property deciding the practical utility of a polymer blend.\textsuperscript{1,11,18} Polymer blends can be described by the following equation:

\[ P = P_1 C_1 + P_2 C_2 + I P_1 P_2 \]
where $P$ is the property value of the blend, $P_1$ and $P_2$ the properties of the isolated components and $C_1$ and $C_2$ the respective concentrations of the constituents. $I$ is a term for the system which defines the level of synergism created by the combination of the two components.

For $I > 0$ the property is synergistic

$I = 0$ the property is additive

$I < 0$ the property is nonsynergistic.

The most important factor governing the ultimate properties of a polymer blend is the intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor adhesion between the molecules at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialised, the applicability of polymer blends is limited because of the inferior macroscopic properties. Modification of incompatible polymer systems for developing useful materials has become an active field of research both in the industrial and academic level.
INTERFACE MODIFICATION IN POLYMER BLENDS

The performance of a polymer blend is dependent upon the strength of the interface. It is possible to make a polymer blend compatible so that the resultant properties may be more synergistic and the blend becomes more homogeneous. Modification of polymer blend can be achieved by a variety of ways.\textsuperscript{18,19}

By Addition of a Polymeric Compatibiliser

The incorporation of block, graft or random copolymers whose chemical structures are identical with the blend components is found to promote miscibility. Such compatibilisers are able to make specific interactions with each of the blend components.\textsuperscript{20-24} Di or triblock copolymers of styrene and butadiene have been found to be more useful in this way to act as interfacial agents in blends of polyolefine/polystyrene (PS) mixtures. Diblocks are more efficient interfacial agents than triblock or graft copolymers.\textsuperscript{25-27} Ethylene-propylene-diene rubber (EPDM) and poly (methyl methacrylate) (PMMA) can be made more or less compatible by adding EPDM-g-MMA copolymer.\textsuperscript{28} The compatibilising or emulsifying action of certain solid phase dispersants in poly (vinyl chloride) (PVC)/Polyethylene (PE) and PVC/PS blends has been
reported earlier.\textsuperscript{29-34} Boutevin et al.\textsuperscript{35} investigated P(E-g-MMA) copolymers as a compatibiliser to low density polyethylene (LDPE)/PVC blends. They found values of tensile strength to be almost double compared to those of homopolymer mixtures. Statistical copolymers have also been found to be useful to a limited extent as in the case of ethylene-propylene rubber compatibilising polypropylene (PP) and high density polyethylene (HDPE).\textsuperscript{36-39} The compatibilisers can be either added separately or may be formed in situ during blending.

Compatibilising action of a block or graft copolymer
By Blending Functionalised Polymers

Chemical modification of polymers is a common means of improving properties of the polymer blends. Blending of polymers containing carboxyl and epoxy groups has been reported as a promising way to promote interfacial strength.\textsuperscript{18,40-42} The reactive blending of such functionalised polymers is followed by the in situ formation of compatibilising interchain polymers. Carboxyl terminated butadiene/acrylonitrile rubber (NBR) has been utilised for the successful blending with epoxies. Polypropylene can be functionalised to link with functionalised NBR during melt mixing.\textsuperscript{21} As a result, improved ultimate properties are achieved by making the polymer blend less incompatible.

By Addition of Low Molecular Weight Materials

A variety of low molecular weight chemicals can also act as modifiers or compatibilisers through reactions such as grafting, crosslinking, co-crosslinking etc. Recently, grafting of maleic anhydride on LDPE followed by blending with PS was investigated by Liu et al.\textsuperscript{41} as a possible means for improving the compatibility. The addition of some polyfunctional monomers in presence of peroxide was reported to be effective in blends of PVC
with polyethylene.\textsuperscript{43,44} Mori and Nakamura studied the effect of co-crosslinking by triazine trithiols on the property modification for a series of blends.\textsuperscript{45-47} Examples of the class include PVC/NBR, PVC/CR and PVC/EPDM.

The continuous nature of the phases as a result of such interface modifications leads to efficient force/stress transfer between the component phases.

**PVC BASED POLYMER BLENDS**

Poly(vinyl chloride) (PVC) is a versatile polymer, used in flexible, semirigid and rigid forms. In world wide plastic production it is second only to polyolefines. The rapid expansion and consumption of PVC is due to lower cost, greater availability, good mechanical properties and diversity of its properties.\textsuperscript{48-50} It is mainly produced by the polymerisation of vinyl chloride by suspension method. The structure of PVC is,

\[
\left[ \begin{array}{c} \text{CH}_2 - \\ \text{Cl} \end{array} \right]_n
\]
Although PVC has many desirable properties, it has two shortcomings in commercial applications: poor processability and poor impact strength. Common ways of overcoming poor processability are to mix with plasticizers or to increase the processing temperature. There are associated disadvantages since by the former method, it is not possible to obtain high impact strength because of antiplasticizing effect and by the latter method there is a risk of thermal degradation. Also low molecular weight plasticizers of PVC have a tendency to leach out on ageing. These problems can be solved successfully by the addition of small amounts of polymeric modifiers/plasticizers to yield polymer blends.\textsuperscript{51-53} Hence polymeric plasticizers like chlorinated polyethylene (CPE), ethylene-vinyl acetate (EVA), acrylonitrile-butadiene rubber (NBR), polyether-ester block copolymer (Hytrel) etc. are being used.\textsuperscript{54-57} PVC behaves generally as an electron acceptor and thus should interact strongly with electron donors. In fact, it is said that of all polymers studied to date, PVC is the most miscible with structurally different homopolymers and copolymers. A lot of work has been done on the compatibility of PVC with various polymeric plasticizers.\textsuperscript{58,59} Combining nonpolar elastomers with PVC is one of the promising methods of
increasing the oil, petrol and fire resistance of the vulcanizates based on them. Majority of the PVC systems show multiphase behaviour. Yet, they are used in several applications. The mechanical properties of such blends are far inferior to those expected. This is probably due to the low level of compatibility between the polymers and also the insufficient fusion characteristics of PVC particles. Deak et al. studied the effect of small quantities of additives on the properties of rigid PVC and PVC modified with other polymers.

**BLENDS OF ELASTOMERS WITH PVC**

One of the most prominent needs for PVC in application end use is permanent plasticization. A very important and commercially significant blend is that of NBR and PVC. NBR acts as a permanent plasticizer for PVC and at the same time PVC improves the ozone, thermal ageing and chemical resistance of NBR. PVC/NBR blends are used in applications such as wire and cable insulation, O-rings and oil seals, printing roll covers, gaskets, fuel hose covers, shoe soles, anti static floor tiles etc. The amount and type of vulcanising system has a great effect on the properties of the blends. The effect of non-conventional vulcanising system for property modification
of PVC/NBR blends was investigated. P-nitrosophenyl amine plays the role of a modifier and aids the vulcanisa-
tion of the blend in presence of sulphur (S) and TMTD.66 More recently modification of NBR/PVC blends was studied using natural rubber (NR), polybutadiene rubber (BR) and styrene-butadiene rubber (SBR).67 Co-crosslinking is found to be an effective means of improving the mechanical properties of the blends. Triazine trithiols can be used effectively as a co-crosslinking agent for PVC/CR, PVC/NBR and PVC/EPDM blends.45-47 Blending of SBR with PVC results in a marked improvement in the impact strength of PVC.68 The effect of addition of a third component on the mechanical properties, compatibility and morphologies of the PVC blends with SBR and BR was investigated.69 NBR is found to be a good compatibiliser for PVC/SBR and PVC/BR blends. Properties of PVC/EPDM blends modified with CPE were also investigated.70 The mechanical, rheological and morphological studies of PVC/Epoxidised natural rubber (ENR) have shown that higher levels of epoxidation makes NR to be more compatible with PVC.71,72 Mixing with PVC is found to be an effective method for the property modification and cost reduction of high priced speciality rubbers like polysulphide and chloroprene rubber (CR).73,74
BLENDS OF OTHER PLASTICS WITH PVC

The impact resistance of PVC can also be improved by introduction of polymeric modifiers in particular acrylonitrile-butadiene-styrene (ABS) or methyl methacrylate-butadiene-styrene (MBS) plastics. The toughness and processability of ABS combines with the flame resistance of PVC in PVC/ABS blends. The miscibility of the system depends upon the acrylonitrile content in ABS. PVC/ABS and PVC/MBS blends are noted for their good dimensional stability. PVC/ABS blends have been utilised for interior truck panels, communication relays, electrical housings, appliance housings, television housings etc. The impact modification of PVC by CPE has been reported earlier. CPE also acts as a permanent plasticizer for PVC. Recently, compatibilisation of PVC/CPE blends with epoxidised NR has been studied by Stathis and coworkers. The effectiveness of epoxidised hydrocarbons to produce compatible polymers were reported by several research groups. Epoxidised SBS was found to be a typical example for improving the compatibility of PVC/PS systems. PVC/PMMA blends combine the heat resistance of PMMA with chemical and flame resistance of PVC in some applications. The main
application of this blend is in mass transit vehicles. Paul and Barlow\textsuperscript{79} studied the miscibility behaviour of PVC/styrene-acrylonitrile (SAN) copolymers. NBR is found to be useful for the compatibilisation of poly vinylidene-fluoride co-vinyl chloride/PVC blends. The effect of some solid phase dispersants on the mechanical performance of the immiscible PVC/PE blends was studied as a means for reutilisation of these plastic wastes.\textsuperscript{29,32,80} Function-alised polyolefine/PVC blends are used for the development of low halogen and non-halogen, fire resistant, low smoke cable sheathing compound.\textsuperscript{81} PVC/PE combinations are also used for the preparation of thermofoamable blisters.\textsuperscript{82} Mixtures of acrylic terpolymer with PVC are used for preparing adhesive sealent compositions with improved properties and enhanced outdoor resistance.\textsuperscript{83} The processability of PVC can be improved by the addition of EVA, CPE, Hytrel etc.\textsuperscript{54-57,84}

COMMERCIAL PVC BLENDS

Mixing of PVC with various types of polar and non-polar polymers changes the properties of PVC, so significantly that the application spectrum of this polymer is continuously increasing. The commercially important blends of PVC and their properties are given in Table 1.1.
<table>
<thead>
<tr>
<th>No.</th>
<th>Additive</th>
<th>Improved property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ABS; MBS</td>
<td>Impact resistance, hardness, tensile strength, distortion temperature.</td>
</tr>
<tr>
<td>4.</td>
<td>SAN</td>
<td>Low temperature toughness, processability, dimensional stability.</td>
</tr>
<tr>
<td>5.</td>
<td>Poly(imide)</td>
<td>Transparency, high distortion temperature, impact resistance.</td>
</tr>
<tr>
<td>7.</td>
<td>Nitrile rubber</td>
<td>Plasticization, toughness.</td>
</tr>
<tr>
<td>8.</td>
<td>EVA</td>
<td>Plasticization, toughness, adhesiveness.</td>
</tr>
</tbody>
</table>

11. PE + CPE  Ductility, elongation, low temperature toughness

12. PB  Toughness, weatherability.

13. Hytrel  Low temperature toughness, plasticization.

14. PVC/EVA copolymer  Processability, mechanical properties.

15. Chlorinated POM  Processability, plasticization.

FUSION OF RIGID PVC

PVC differs from other widely used plastics like PE, PS, PP in that the polymer has a distinct structure. Suspension PVC consists of grains of about 100 μm size. Inside these grains, smaller primary particles of about 1 μm size are found partly agglomerated to larger units. This hierarchial structure of PVC has to be destroyed in order to get a thermoplastic melt necessary for processing rigid PVC. Fusion involves the loss of identity of grains and primary particles of PVC which is highly dependant upon both shear and thermal history of PVC.
Fusion mechanism of PVC

The processing behaviour and end use properties of PVC are strongly influenced by the degree of fusion.\textsuperscript{85-89}

**RHEOLOGY OF PVC BLENDS**

The rheological properties of polymer melts have been studied extensively over the past decade. These studies have concentrated on pure polymer systems. Recently rheological properties of polymer mixtures are also being studied due to the great practical use of such mixtures. Investigation of the rheological properties of
the mixtures will make it possible to assess their behaviour during manufacture into article. Moreover, the rheological properties of mixtures help gaining insight into the structure of polymer melts. In regard to two phase flow of molten polymers, rheology should clearly be known to rationally design processing devices and to smoothly operate equipments which handle two phase systems. One of the most fundamental requirements is to determine the rheological properties of a given two phase system in terms of viscosities and elasticities of individual components, composition ratio and melt temperature. Rheology of PVC blends is particularly important due to the fusion behaviour of PVC. The mechanical strength of PVC blends is critically dependant upon the fusion state of PVC and hence study of the processing characteristics of PVC blends is of great importance.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

The present investigation is mainly on PVC blends. PVC resins surpass every class of polymers in world wide commercial importance, both in diversity of applications and in total tonnage of finished products. The factors responsible for PVC's number one position are low cost and ability to be compounded into various
flexible and rigid forms with good physical, chemical and weathering properties. In addition, PVC has broad processability including calendering, extrusion, moulding (injection, compression, rotational, blow) fluid (solution, latex, organosol, plastisol) coating and impregnation.

PVC formulations contain varying amounts of the following ingredients in order to give the polymer the desired processing and end use characteristics.

- Plasticizers
- Polymeric modifiers
- Fillers
- Heat stabilisers
- Lubricants
- Colourants
- Light stabilisers
- Blowing agents
- Flame retardants.

The present study is mainly in the area of solid polymeric modifiers for PVC. The first part of the study is on PVC/Elastomer blends. Polymeric modifiers can be classified into four categories: those that plasticize, increase impact strength, increase heat distortion temperature and improve processability. The property modification is highly dependent upon the miscibility of
the modifying polymer with PVC. By far the wide range of polymeric modifiers for PVC fall into the broad category that can be classified as partially miscible. A broad range of properties may be obtained depending upon the degree of miscibility. These polymers can increase the rate of fusion of PVC powder leading to a more rapid formation of a homogeneous melt having higher melt strength. The present study on the blends of PVC with elastomers was undertaken with a dual purpose of improving the fusion behaviour and melt strength of PVC along with imparting special properties to the elastomers. Effect of compatibilizers in improving the mechanical and processing behaviour of PVC/Elastomer blends is a major part of the study.

The second part of the study is on PVC/Linear low density polyethylene (LLDPE) blends. The study was selected mainly as a possible means of reprocessing mixed scrap or waste plastics, since PVC and polyethylene form a sizable fraction of such wastes. Their lack of biodegradability is generating new problems owing to their large space requirements and the possible damage to the environment by the various materials contained in them. The best solution to reducing waste, according to many
scientists, is a combination that includes bio-degradable plastics and plastic recycling. However, by 2002 bio-degradable plastics are expected to account for only three per cent of all plastic packaging waste and hence there is very good scope for polymer recycling in the years to come.

Recycling by reprocessing of plastic waste is a major solution to the problem. However, blends of mixed scrap or waste plastics usually have very poor ductility and toughness, a situation which renders their practical use difficult. This problem generally exists because the ingredients of most polymer blends are grossly incompatible and separate into individual phases. Application of mechanical stress usually results in interfacial failure. It has been shown that mechanical properties of the blends of incompatible polymers can be significantly improved by addition of agents which improve interfacial adhesion. The most common compatibilisers are block, graft or random copolymers, co-solubilisers enhancing interpenetration of resin domains, co-reactants or catalysts enhancing chemical reaction between the resins and modifiers or additives enhancing the specific interactions.
Co-crosslinking of the polymers is also a special means of achieving miscibility.\cite{43,44} Several of these methods are investigated as possible means of improving the mechanical behaviour of PVC/LLDPE blends.

This thesis is divided into five chapters.

Chapter 1: Introduction

Chapter 2: Experimental Techniques

Chapter 3: Studies on Poly(Vinyl Chloride)/Elastomer Blends

Chapter 4: Studies on Poly(Vinyl Chloride)/Linear Low Density Polyethylene Blends

Chapter 5: Summary and Conclusions
REFERENCES


