Chapter 1

INTRODUCTION
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A considerable amount of research has been done over the last several years with a view to obtaining new polymeric materials with enhanced properties for specific applications or a better combination of different properties. After the syntheses of polymers from new monomers had been largely explored, efforts were focussed on multiphase polymeric systems that have two or more distinct phases such as block or graft copolymers, composites, polymer blends and interpenetrating networks.\(^1\)\(^-\)\(^5\) Much attention is currently being devoted to the simplest route for combining outstanding properties of different existing polymers, that is, the formation of polymer blends.\(^6\)\(^-\)\(^28\) Although an increasing number of miscible blends is reported in the literature,\(^29\) most polymer pairs are nonetheless immiscible, thus leading to heterophase polymer blends.\(^30\),\(^31\)

Polymer Blends

The following definitions are assigned to the commonly used terms.\(^32\)
- Polymer Blends (PB): the all inclusive term for any mixture of homopolymers or copolymers.

- Homologous Polymer Blends: a sub-class of PB limited to mixtures of chemically identical polymers differing in molar mass.

- Polymer Alloys: a sub-class of PB reserved for polymer mixtures with stabilised morphologies.

- Miscible Polymer Blends: a class of PB referring to those blends which exhibit single phase behaviour.

- Immiscible Polymer Blends: a sub-class of PB referring to those blends that exhibit two or more phases at all compositions and temperatures.

- Partially Miscible Polymer Blends: a sub-class of PB including those blends that exhibit a 'window' of miscibility, i.e., are miscible only at some concentrations and temperatures.

- Compatible Polymer Blends: a utilitarian term, indicating commercially useful materials, a mixture of polymers without strong repulsive forces that is homogeneous to the eye.
- Interpenetrating Polymer Network (IPN): a sub-class of PB reserved for mixtures of two polymers where both components form continuous phases and at least one is synthesised or crosslinked in the presence of the other.

Miscibility in Polymer Blends

The most basic question when considering a polymer blend concerns the miscibility as governed by the law of thermodynamics. According to this law, for two polymers to be miscible the free energy of mixing $\Delta G_m$ must be negative, i.e.,

$$\Delta G_m = \Delta H_m - T \Delta S_m$$ (1.1)

where $\Delta H_m$ is the heat of mixing and $\Delta S_m$ is the entropy of mixing.

The combinatorial entropy of mixing $\Delta S_m$ of two polymers is dramatically smaller than that for two low molecular weight compounds. The enthalpy of mixing $\Delta H_m$, on the other hand, is often a positive quantity or at best zero. In such cases immiscibility results when polymers are mixed. Consequently the number of known miscible blends
is relatively small. If however, there exist specific interactions (ion-dipole interactions, H-bonds) between the components, the heat of mixing $\Delta H_m$ becomes negative and the resulting system is miscible. In other words, miscibility depends on the degree of interaction between polymer components.

The concept of solubility parameter, a measure of the attractive forces between molecules, is used as an aid in comparing the relative compatibility of polymers. It is based on the principle that molecules of two different species will be able to coexist if the force of attraction between different molecules is greater than the force of attraction between like molecules of either species.

The energy of vaporisation per unit weight is a measure of the forces of attraction holding molecules together. The energy of vaporisation per unit volume is known as the cohesive energy density and its square root is known as the solubility parameter.

$$
\sqrt{\gamma} = \left( \frac{\Delta E}{V} \right)^{\frac{1}{2}}
$$

$$
= \left( \frac{H - RT}{Mw/D} \right)^{\frac{1}{2}}
$$

(1.2)
where, $E$ is the energy of vaporisation

$V$ is the molar volume

$R$ is the gas constant

$T$ is the temperature

$M_w$ is the molecular weight and

$D$ is the density.

Solubility parameter $\delta$ can also be calculated from a list of molar attraction constant, $G$ for various parts of the molecule, which on addition gives $\delta$ from the relation,

$$\delta = \frac{D \times G}{M_w}$$  \hspace{1cm} (1.3)

where, $D$ is the density

$M_w$ is the molecular weight

$\delta$ values calculated in this way help in predicting compatibility.

Methods of Preparation

Polyblends are mixtures of structurally different homopolymers, copolymers, terpolymers and the like. The copolymers, terpolymers etc., may be random,
alternating, graft or block type. Fig.1.1 gives a classification of polyblends in terms of their method of preparation.

Most commercial blends are prepared by mechanical means either on an open roll mill, in an extruder or in a suitable internal mixer. The processing temperature must be well above the glass transition temperature ($T_g$) of each constituent for mixtures of amorphous polymers and above the melting temperature ($T_m$) of mixtures containing semicrystalline polymers, whichever is higher.

Depending on the state of thermal stability of the polymers being mixed, the high processing shear could initiate degradation, resulting in free radicals. If the free radicals react with the other structurally different polymers present, resulting in true chemical graft or block copolymer, the mixture is referred to as a mechanochemical blend.

A chemical polyblend is made by in situ polymerisation and crosslinking of the constituent polymers, giving an interpenetrating crosslinked polymer network of structurally different polymers.
Fig. 1.1: Classification of blends based on the method of preparation
Solution cast polyblends are prepared by dissolving the constituent polymers in a common solvent in such a way that the solutions have about the same viscosity. These solutions are mixed thoroughly and the resulting solution can be film cast to form the solution cast polyblend. A melt processing method can be used for compounding and pelletising the solution cast polyblends.

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.

Rheology of Polymer Blends

Considering the fact that most industrial scale preparations of polymer blends are carried out by mixing of polymer melts, studies on their rheological properties are of paramount importance. In most cases, the blend products have properties imposed by the morphology, created by a particular combination of the thermal and deformational history.
Classification of Polymer Blends

From the rheological point of view, the blends are classified into three groups, those where viscosity shows positive deviation from the log-additivity rule, (PDB) those where the opposite effect is observed (NDB), and the remaining mixed behaviour systems (PNDB).\(^{40}\) To PDB belong the miscible blends and those with strong inter-domain interactions. To NDB belong those where the interactions are weak. To PNDB belong the blends in which there is a concentration dependent transition of structure. The melt flow of polyethylenes and their blends has been reviewed by Plochocki\(^ {41-43}\) and Utracki.\(^ {44,45}\)

Modification of Polymer Blends

One of the reasons for the differences in performance of different resins of the same chemical type is the interface. The most frequent method of modification of this zone is the introduction of a compatibiliser, its presence not only decreases the variability of blend performance but also improves it.

There exist two general routes to compatibility.\(^ {46}\)
i) By adding a third component (compatibiliser) capable of specific interactions and/or chemical reactions with the blend constituents. Block and graft copolymers and a variety of low molecular weight reactive chemicals fall under this category.

The choice of a block or graft copolymer as compatibiliser is based on the miscibility or reactivity of its segments with at least one of the blend components. The influence of these copolymers referred to as 'interfacial agents' has been related to their tendency to be preferentially located at the interface between phases and to the capability of their individual segments to penetrate into the phase to which they are chemically identical or similar. On the other hand reactive chemicals such as co-crosslinking agents do not necessarily act at the interface although they meet the above definition of compatibiliser.

ii) By blending suitably functionalised polymers capable of enhanced specific interactions and/or chemical
reactions. Functionalisation can be carried out in solution or in a suitable internal mixer, and may involve the formation of block or graft copolymers, halogenation, sulfonation, hydroperoxide formation etc. The in situ formed compatibilisers have segments that are chemically identical to those in the respective unreacted homopolymers and are thought to be located preferentially at the interface, thus they may be considered equivalent to the block or graft copolymers that are added separately.

Physical and Mechanical Properties

In a multiphase polymeric system, a property \( P_{c'} \) depends on an average of the properties of the constituents, usually weighed in terms of volume fraction (\( \phi \)).

\[
P_{c'} = \phi_A f(P_A) + \phi_B f(P_B)
\]  (1.4)

The precise form of the equation depends on the particular system, the interactions between the components and on the compatibility.
In the case of miscible systems that are homogeneous the mixtures will be essentially transparent with a single phase and a sharp $T_g$. In such a case the above equation may be written in the following semiempirical form,

$$P_c' = \phi_A P_A + \phi_B P_B + I \phi_A \phi_B$$  \hspace{1cm} (1.5)

where $I$ is an interaction parameter which can be positive, zero or negative as shown in Fig.1.2. When $I$ is positive the property is synergistic, when $I$ is zero the property is additive and when $I$ is negative the property is nonsynergistic.

Equation (1.5) describes in particular, variation with composition of such properties as glass transition temperature, density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties, elastic moduli, viscosity of liquid mixtures and surface tension. Most polymer mixtures are immiscible and the properties of these heterogeneous blends are difficult to predict. Many of
Fig. 1.2: Properties of polymer blends as a function of composition
the equation proposed to account for the behaviour of heterogeneous blends can be expressed by the relation,

\[ \frac{P_C}{P_A} = \frac{1 + AB \phi_B}{1 + B \psi \phi_B} \]  

(1.6)

where \( P_A \) is the property of the continuous matrix. \( A > 0 \) depends on the shape and orientation of the dispersed phase and the nature of the interface, \( B \) is a function of \( A, P_A \) & \( P_B \) and \( \psi \) is a reduced concentration term which is a function of the maximum packing volume fraction of the dispersed phase. This semi-empirical rule of mixing is obeyed by many physical properties such as moduli, impact strength, thermal and oxidative resistance, flame retardance, domain morphology, thermal expansivity, thermal conductivity, compressibility and refractive index. Properties of all polymer blends and the heterogeneous ones in particular, strongly depend on the thermodynamic and rheological properties of the ingredient resins, the method and extent of mixing and processing. These factors taken together define the morphology of the final product and therefore its ultimate properties and performance. These correlations are presented schematically in Fig.1.3.
Polyethylene Blends

Many thousands of tons of plastics are produced yearly all over the world. Among these materials polyethylene plays a very important role as the most extensively used product. Since their discovery in 1933 there has been a continuous rise in consumption to the present level of 25 million tons per annum or 42% of all plastics. This extended period of growth originates in continuous development and modification of these resins, resulting from a widening range of polymerization techniques.

The history of polyethylene can be divided into three periods.
1. The initial period characterised by predominance of the radical polymerization of ethylene \( \text{C}_2 \) at high temperature and pressure.

2. Development of coordination copolymerization of \( \text{C}_2 \) monomer with other \( \alpha \)-olefines.

3. Development of polymer blending technology.

Discoveries in the laboratories of Ziegler and Natta in the early 1950's caused a revolution in polymer and organometallic chemistry. Natta discovered that Ziegler catalysts containing highly ordered transition metal salts in a low valence state (e.g., TiCl₃, VCl₃) polymerise \( \alpha \)-olefines to crystalline stereoisomeric polymers. This discovery led to the commercialisation of high density polyethylene (HDPE), which had to be toughened by copolymerization with butene \( \text{C}_4 \). What followed next was the development of a new class of polymers called the linear low density polyethylene (LLDPE), by Du Pont, Canada in the late 1950s. The polymer was prepared by coordination polymerisation in solution of ethylene with 10 to 20 mol per cent of \( \text{C}_4 \), \( \text{C}_6 \) or \( \text{C}_8 \) comonomers. In 1979 Union Carbide patented the gas phase coordination polymerization process.
The impact of this new technology on the plastics industry has not only made LLDPE popular around the world but also led to an ingress of blending methods for obtaining new polymers with a range of properties for specific end use applications.

Structure of LLDPE

If LDPE is pictured as a highly branched molecule with branches of varying lengths and HDPE as a linear molecule with relatively few or no branches, then LLDPE can be described as molecules having a linear configuration with many short side-chains all of uniform length.58

A comparison of the structures59 of LDPE, LLDPE and HDPE is shown in Fig.1.4

Table 1.1 reports a comparison among the physical, mechanical and application characteristics of LDPE and LLDPE.

The main positive features of LLDPE in comparison to LDPE may be deduced from Table 1.1 as follows:
Fig. 1.4: Structures of LDPE, HDPE and LLDPE
Table 1.1: Comparison among typical characteristics of LDPE and LLDPE used in Blown Films

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>LDPE</th>
<th>LLDPE</th>
</tr>
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<tbody>
<tr>
<td>MFI (g/10 min.)</td>
<td>1.6-2.2</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.920</td>
<td>0.918</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>110</td>
<td>125-130</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>60-65</td>
<td>65-70</td>
</tr>
<tr>
<td>Maximum stretch ratio at 190°C</td>
<td>120-160</td>
<td>800-1000</td>
</tr>
<tr>
<td>Processability</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Impact strength:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal* (J/cm)</td>
<td>6</td>
<td>25</td>
</tr>
<tr>
<td>Transverse* (J/cm)</td>
<td>25</td>
<td>40</td>
</tr>
</tbody>
</table>

* Determined according to ASTM test methods on films of 30 µm thickness (1:1.6 blow ratio) for LDPE and LLDPE.
a) Heat resistance considerably higher

b) Higher crystallinity and consequently a greater degree of stiffness

c) Excellent stretchability which permits thinner films to be obtained

d) Higher and better balanced impact resistance properties.

On the other hand the high melt viscosity of LLDPE associated with its long regular molecular chains makes processability difficult. Many extruders now running LDPE have insufficient torque capability to run LLDPE. Furthermore melt fracture may also occur due to high shear stress in the die. The best solution to this problem is to mix LLDPE with conventional LDPE. The resulting blends combine the good mechanical properties of LLDPE and processing properties of LDPE.

Objectives and Scope of this Work

Polyolefine blends have been extensively studied with a view to improving the properties and
processability of the homopolymers involved. The benefits claimed include, for example, improvement in impact strength, environmental stress cracking, optical properties, crystallisation rate, low temperature impact strength, rheological properties and overall mechanical behaviour. A further reason for the study of such blends is that mixtures of such polymers often occur in plastics scrap and waste and affect the possible reuse of such low cost material.

With the introduction of LLDPE, the polyolefine industry is poised for another leap. Its sufficient compatibility with conventional polyethylene (HDPE and LDPE) enables the formation of blown films and other products consisting of a combination of various types of polyethylene in the form of blends and/or composite multilayer structures. Of these, it is the blends of LDPE and LLDPE which are likely to become the most useful especially for the manufacture of blown films. LLDPE gives a greater degree of stiffness and higher tensile strength compared to LDPE and also has a more regular crystalline structure, higher melting point and better fracture resistance at low temperature. This provides the opportunity for improving the performance of LDPE with
LLDPE. If the mechanical and rheological properties of these blends are clearly understood, it can revolutionise the blown film industry. It was with this aim that the present study on LDPE/LLDPE blends was undertaken.

In the present study, the mechanical properties of the blends of various grades of LDPE and LLDPE are proposed to be studied. The rheological and processing properties of the blends are also proposed to be studied in detail. At high shear rates encountered in the processing equipments, the viscosity of LLDPE is considerably greater compared to LDPE and this can cause difficulties in the forming of film at the die exit, and also in the drawing of the films uniformly from the die. Investigation on the rheological properties will answer the question whether conventional processing machines used for LDPE itself can be used for processing of LDPE/LLDPE blends or whether any modification is necessary.

In order to improve the mechanical and processing behaviour of polymers they are sometimes crosslinked by addition of organic peroxides. Creep and tensile properties, mechanical stability at high
temperature and ductile-brittle failure can be improved by introducing a low level of crosslinking. However, no such studies have been reported so far on polyolefine blends.

Mechanical and rheological behaviour of chemically crosslinked LDPE/LLDPE blends are also proposed to be investigated. Studies on the processing and rheological behaviour of two phase blends is a challenging field. Conventional equipments like a capillary rheometer may not reveal the behaviour of the melt under complex shearing conditions encountered in actual processing operations. Shear and temperature can be varied over a wide range in a Brabender Plasticorder. Rheological evaluation of LDPE/LLDPE blends have also been done using the Brabender plasticorder.

The effect of modifiers in improving the mechanical behaviour of the blends is also proposed to be investigated. Since both LDPE and LLDPE are crystalline polymers, rubbery modifiers may be able to improve properties such as toughness, stress crack resistance etc. of the blends.
REFERENCES


