Chapter 1

INTRODUCTION
Studies on the future of plastics production and the associated occurrence of wastes originating from these products have shown that, by the year 2000, plastics will account for more than 30% of the volume of controlled waste dumps. In view of the fact that most plastics require at least 300 years before starting to decompose and that capacity of controlled waste dumps will be exhausted in the near future, it is vital to seek a new technical solution. The need for a rapid solution has arisen due to the following reasons.

1. The increase in price of basic raw materials for the manufacture of polymers.

2. The very low percentage use of plastic wastes.

3. The limited capacity for storing plastics wastes at dumps.

4. The disposal of plastics wastes by combustion is very expensive and requires a complicated and expensive system for controlling the combustion process. Such a system must include a thermal process which does not produce dioxines, furanes or other chemicals which add
to environmental problems such as acid rain and deterioration of ozone layer.

These factors point towards recycling of plastics as the only solution to the problem of handling plastic wastes. The present method of recycling sorted and mostly clean plastics cannot be expected to handle the ever increasing problem of plastics wastes. Hence, new methods should be aimed at recycling of unsorted plastics wastes.

On the basis of analysis, the average composition of the mixed plastics waste can be something like 60-70% polyolefins (HDPE, LDPE, LLDPE and PP), 15-25% PVC and the remaining PS and other types of plastics. Thus polyolefin blends form a major part of all plastics wastes. The present study on polyolefin blends was undertaken to gain a realistic understanding of the problems of recycling of unsorted plastics wastes. Further, polyolefin blends are widely used for optimising the properties and process-ability of individual components and a detailed study of such blends will be very rewarding.

POLYMER BLENDS

Polymer blends are mixtures of structurally different homopolymers, co-polymers, terpolymers and the
like. The copolymers, terpolymers etc., may be random, alternating, graft or block type. Given the economical and technical uncertainties associated with synthesising new polymeric materials, the development of polymer mixtures to achieve a desired combination of properties has obvious attractions.

One of the major areas of studies on polymer blends is the dependence of the mechanical properties on composition. This is due to the fact these complex systems exhibit a behaviour that does not simply follow the sum of the properties of the components. The mechanical properties depend on a number of factors, the most important one being the miscibility of the components. Polymer blends can be homogeneous (miscible) or heterogeneous (multiphase).

MISCIBILITY

Most of the polymer blends form heterogeneous systems which in a few cases present good characteristics. In particular, the size domains of the dispersed phase, its dispersibility and its interfacial interactions control the physical properties of the polymer blends.\(^1\)-\(^3\) The heterogeneity can exist in amorphous, crystalline or both phases.\(^4\)
In general, miscible polymer blends will phase separate on increasing the temperature or molecular weight of the resins.\textsuperscript{5,6}

Many polymer pairs are known to be miscible or partially miscible, and many have become commercially important. The criteria for polymer/polymer miscibility are embodied by the equation for the free energy of mixing,

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]

where \( \Delta G_m \) is the change in Gibbs free energy, \( \Delta H_m \) the change in enthalpy, \( \Delta S_m \) the change in entropy upon mixing and \( T \) the absolute temperature. The necessary condition for miscibility is that \( \Delta G_m < 0 \). The combinatorial entropy of mixing depends on the number of molecules present\textsuperscript{7} according to,

\[ \Delta S_m / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 \]

where \( n_1 \) and \( n_2 \) represent the number of molecules and \( \phi_1 \) and \( \phi_2 \) represent the corresponding mole fractions of the components. Therefore, when the molar mass gets large the number of molecules becomes small, and the combinatorial entropy of mixing becomes negligibly small. Hence, two
polymers can be expected to be miscible only when there is a very close match in cohesive energy density or in specific interactions, which produce a favourable enthalpy of mixing.

CLASSIFICATION OF POLYMER BLENDS

Polymer blends may be classified based on the method of preparation given in Fig.1.1.

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

Frequently during such a process one tries to compatibilise the blend by shear/temperature grafting with or without radical initiators or by addition of compatibilisers. Such mixtures are referred as polymer alloys. The distinction between polymer blends (PB) and polymer alloys (PA) is quantitative and refers to the extent of interpenetration of domains.
FIG. 1.1 CLASSIFICATION OF POLYMER BLENDS BASED ON METHODS OF PREPARATION.
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 system. 

The following definitions are assigned for the various classes of polymer blends:

Polymer blends (PB): the all inclusive term for any mixture of homopolymers and copolymers.

Homologous polymer blends: a subclass of PB limited to mixtures of chemically identical polymers differing in molar mass.

Polymer alloys (PA): a subclass of PB reserved for polymer mixtures with stabilized morphologies.

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

Immiscible polymer blends: a subclass of PB referring to those blends that exhibit two or more phases at all compositions and temperature.
Partially miscible polymer blends: a subclass of PB including those blends that exhibit a 'window' of miscibility ie., only at certain concentrations and temperature.

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 subclass 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.

PHYSICAL AND MECHANICAL PROPERTIES OF POLYMER BLENDS

The physical properties such as $T_g$, density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties, elastic modulus and viscosity of miscible blends vary smoothly with composition, and can be described by the equation,

$$ P = p_1 \phi_1 + p_2 \phi_2 + I_1 \phi_2 $$
where $P$ is the property of interest, $\varnothing$ is the composition and $I$ is the interaction term, which can be positive, zero or negative.\(^{10}\)

when $I > 0$, the property is synergistic,

$I = 0$, the property is additive

$I < 0$, the property is non-synergistic

The properties of the polymer blends as a function of composition is given in Fig.1.2. Properties of heterogeneous blends are more difficult to predict. The property depends on additional factors such as shape and orientation of the dispersed phase, nature of the interface etc.

**POLYETHYLENE BLENDS**

Copolymerisation of ethylene and $\alpha$-olefins has led to a new polyolefin known as linear low density polyethylene (LLDPE). The structure of LLDPE along with the structures of other commercial polyethylene viz., low density polyethylene (LDPE) and high density polyethylene (HDPE) is given in Fig.1.3. While LLDPE resembles LDPE in density, it is a linear polyethylene containing short side chains and resembles HDPE in structure.
FIG. 1.2 PROPERTIES OF POLYMER BLENDS AS A FUNCTION OF COMPOSITION.
FIG. 1.3 STRUCTURE OF LDPE, HDPE and LLDPE.
In recent years blends of various polyolefins have received more and more attention for two main reasons. The first is that polyolefins form most of the plastic wastes and their recycling lead to mixtures without separation.\textsuperscript{11} The second is that the blends lead to new materials with improved processing and mechanical properties for specific purposes.\textsuperscript{1,2,12} The advantages obtained by blending are improvement in impact strength, environmental stress cracking, optical properties, crystallisation rate, low temperature impact strength, rheological properties and overall mechanical behaviour.\textsuperscript{13}

Some of the polyethylene blends have become commercially important and certain properties of the blends are better than those of the parent polymers. Unfortunately, sometimes failure results from poor mechanical properties as a consequence of incompatibility.\textsuperscript{14-18} In low density polyethylene (LDPE)/isotactic polypropylene (PP) blends tensile properties are different from the generally observed behaviour.\textsuperscript{19} This was related to the morphological features induced in the material by the mixing procedure adopted. The influence of mixing parameters on mechanical properties of LDPE/PP blends was reported by Rizzo.\textsuperscript{20}
Several studies have been performed in order to investigate the mechanical properties of polyethylene blends. For HDPE/LDPE blends, the results are somehow contradictory, both a severe incompatibility and semi-compatibility as seen from the elongation at break have been reported. For semicompatible blends the mechanical properties of the blends are intermediate between those of the homopolymers.

Densities measured for incompatible blends have been reported to agree with values calculated from the simple additivity relation given by the equation:

\[ \frac{1}{\rho_b} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \]

where \( \rho_b \) is the density of the blend, \( \rho_1 \) and \( \rho_2 \) are the densities and \( w_1 \) and \( w_2 \) the corresponding weight fractions of the components.

The density of compatible blends may be up to 5% higher than the additive values. The increase in density or negative excess volume of mixing observed for compatible blends is indicative of strong intermolecular interactions favouring better packing between molecules.
Polyethylenes are generally crystalline. The closer packing of molecules causes an increased density. The decreased intermolecular distance will increase the secondary forces holding the chain together and increase the value of properties such as tensile strength, stiffness and softening point.

Linear low density polyethylene (LLDPE) has acquired great commercial importance because of its superior mechanical behaviour compared to low density polyethylene (LDPE) and high density polyethylene (HDPE).\textsuperscript{32} LLDPE being a comparatively new material there is considerable interest in its blends with LDPE or HDPE. Blends of LDPE and LLDPE are now regarded as excellent materials for film manufacture because they combine the processability of LDPE and the good mechanical properties and environmental stress cracking resistance of LLDPE.\textsuperscript{33-35}

The low production cost of LLDPE is also one of the factors in its commercial success. However, despite the advantages of pure LLDPE, blending it with other polyethylenes is a common practice in industry. The reasons include:
1. The higher viscous and less shear sensitive melt properties of LLDPE.

2. The physical and mechanical properties of the blends can fill the gap existing among various pure polyethylenes.

3. Financial incentives.

4. Polyethylene blends occur in plastics wastes and is of interest in recycling of mixed plastics wastes.

Of the three polyethylenes (HDPE, LLDPE and LDPE), HDPE possesses the maximum strength and melting temperature while LLDPE has the highest impact strength. HDPE also has the highest stiffness, but it is considered the most difficult in processing.\textsuperscript{36,37}

While many studies have been undertaken on LDPE/LLDPE and HDPE/LDPE blends, only very few studies are reported on HDPE/LLDPE blends. However, it is reported that a blend of HDPE and LLDPE exhibits a crystallisation exotherm of a single peak which indicates that it is a compatible system,\textsuperscript{38} making the study of these blends most interesting.
The rheology of polyethylene melts has been extensively studied\textsuperscript{15,39-49} but the rheology of LLDPE is less known.\textsuperscript{50-63} Sometimes LLDPE is sold in blends with other polyolefins or EVA.\textsuperscript{64} The rheology of LLDPE blends were studied by Utracki et al.\textsuperscript{65-71} The molecular characteristics and the steady state and the dynamic shear behaviour of LLDPE blended with LDPE and different grades of LLDPE are reported in the literature.\textsuperscript{21-23}

MODIFICATION OF POLYETHYLENE BLENDS

The properties of polyethylene and hence their blends can be modified by adding certain additives or by employing certain modification processes.

Controlled crosslinking of polyolefins has been found to improve creep, tensile properties, mechanical stability at higher temperatures etc.\textsuperscript{72,73} Since crosslinking of polyolefin blends can generate interpenetrating polymer networks, it may improve the properties of the blends. Crosslinking is generally achieved by chemical means or by radiation. Radiation crosslinking is found to affect crystallinity less severely\textsuperscript{74} and radiation crosslinking in the presence of a sensibilising agent\textsuperscript{75} is
suggested as an attractive means of obtaining improvement in properties associated with crosslinking without adversely affecting the mechanical properties.\textsuperscript{76}

The mechanical properties of the incompatible polymer blends can be improved by the use of solid phase dispersants.\textsuperscript{77} Since both HDPE and LLDPE are crystalline polymers, rubbery modifiers improve properties such as toughness, stress crack resistance and environmental stress crack resistance of the blends.

Mineral fillers are frequently used to increase the heat distortion temperature, rigidity and tear resistance of PE and PP matrices. Particulate fillers are added to polymers for a variety of purposes. For example, to enhance mechanical properties, dimensional stability, to control opacity, barrier properties and the like.\textsuperscript{78-81} The performance of filled plastics is not defined by composition alone, the condition of the interface between the polymer and additive being a very important variable.\textsuperscript{82,83} Particulate fillers are often surface modified to control interfacial conditions within the composite.\textsuperscript{84}
OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Following the introduction of linear low density polyethylene (LLDPE) in 1977 interest became focussed on the modification of other polyolefins with LLDPE. The similarity in structure of HDPE and LLDPE makes them ideal components for blending and thus generating a spectrum of new polymer materials.

The present study on HDPE/LLDPE blends was undertaken with the following objectives.

1. To characterise the physical, mechanical and processing behaviour of HDPE/LLDPE blends.

2. To investigate methods of improving the physical and mechanical properties of the blends so as to make them more useful.

3. To study the effect of elastomeric impact modifiers in the blends.

4. To explore the possible use of fillers in the blends for economic advantage.
In the present study, selected grades of HDPE and LLDPE are proposed to be melt mixed over the entire composition range and the mechanical and rheological properties are proposed to be evaluated.

Several modifications are proposed to be done for improving the performance of HDPE/LLDPE blends. A low level of crosslinking in polyethylene that does not affect processing leads to structural modifications that affects its properties significantly. In this study, HDPE/LLDPE blends are proposed to be crosslinked to a low level by chemical means and by irradiation. The mechanical and rheological properties of the modified HDPE/LLDPE blends are proposed to be studied in detail.

Low concentrations of elastomers such as natural rubber (NR), butyl rubber (IIR), ethylene propylene diene rubber (EPDM) and styrene isoprene styrene (SIS) thermoplastic elastomer are proposed to be tried as impact and environmental stress crack modifiers in HDPE/LLDPE blends.
The effect of adding fine particle fillers to HDPE/LLDPE blends on their mechanical properties is also proposed to be evaluated. It is also proposed to study the effect of dispersing them unevenly between the polymeric components.
REFERENCES


