STUDIES ON THE FRACTURE BEHAVIOUR OF POLYMER BLENDS WITH SPECIAL REFERENCE TO PP/HDPE AND PS/HIPS BLENDS

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DECLARATION

I hereby declare that the work presented in this thesis entitled "**Studies on the fracture behaviour of polymer blends with special reference to PP/HDPE and PS/HIPS blends**" is based on the original research work carried out by me under the guidance and supervision of **Dr. P.S. Sreejith,** School of Engineering, Cochin University of Science and Technology and **Dr. K.E. George,** Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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26 – 11 – 2010.

CERTIFICATE

This is to certify that the thesis entitled **"STUDIES ON THE FRACTURE BEHAVIOUR OF POLYMER BLENDS WITH SPECIAL REFERENCE TO PP/HDPE AND PS/HIPS BLENDS"** is based on the original work done by Mr. Deviprasad Varma P.R. under our joint supervision and guidance in the School of Engineering (Faculty of Engineering), Cochin University of Science and Technology, Kochi-22.

No part of this thesis has been presented for any other degree from any other institution.

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ABSTRACT

Investigations on the fracture behaviour of polymer blends is the topic of this thesis. The blends selected are PP/HDPE and PS/HIPS. PP/HDPE blend is chosen due to its commercial importance and PS/HIPS blend is selected to study the transition from brittle fracture to ductile fracture.

PP/HDPE blends were prepared at different compositions by melt blending at 180^0C and fracture failure process was investigated by conducting notch sensitivity test and tensile test at different strain rates. The effects of two types of modifiers (particulate and elastomer) on the fracture behaviour and notch sensitivity of PP/HDPE blends were studied. The modifiers used are calcium carbonate, a hard particulate filler commonly used in plastics and Ethylene Propylene Diene Monomer (EPDM). They were added in 2%, 4% and 6% by weight of the blends.

The study shows that the mechanical properties of PP/HDPE blends can be optimized by selecting proper blend compositions. The selected modifiers are found to alter and improve the fracture behaviour and notch sensitivity of the blends. Particulate fillers like calcium carbonate can be used for making the mechanical behaviour more stable at the various blend compositions. The resistance to notch sensitivity of the blends is found to be marginally lower in the presence of calcium carbonate. The elastomeric modifier EPDM produces a better stability of the mechanical behaviour. A low concentration of EPDM is sufficient to effect such a change. EPDM significantly improves the resistance to notch sensitivity of the blends. The study shows that judicious selection of modifiers can improve the fracture behaviour and notch sensitivity of PP/HDPE blends and help these materials to be used for critical applications.

For investigating the transition in fracture behaviour and failure modes, PS/HIPS blends were selected. The blends were prepared by melt mixing followed by injection moulding to prepare the specimens for conducting tensile, impact and flexure tests. These tests were used to simulate the various conditions which promote failure.

The tensile behaviour of unnotched and notched PS/HIPS blend samples were evaluated at slow speeds. Tensile strengths and moduli were found to increase at the higher testing speed for all the blend combinations whereas maximum strain at break was found to decrease. For a particular speed of testing, the tensile strength and modulus show only a very slight decrease as HIPS content is increased up to about 40%. However, there is a drastic decrease on increasing the HIPS content thereafter.

The maximum strain at break shows only a very slight change up to about 40% HIPS content and thereafter shows a remarkable increase. The notched specimens also follow a comparable trend even though the notch sensitivity is seen high for PS rich blends containing up to 40% HIPS. The notch sensitivity marginally decreases with increase in HIPS content. At the same time, it is found to increase with the increase in strain rate. It is observed that blends containing more than 40% HIPS fail in ductile mode.

The impact characteristics of PS/HIPS blends studied were impact strength, the energy absorbed by the test specimen and impact toughness. Remarkable increase in impact strength is observed as HIPS content in the blend exceeds 40%. The energy absorbed by the test specimens and the impact toughness also show a comparable trend.

Flexural testing which helps to characterize the load bearing capacity was conducted on PS/HIPS blend samples at the two different testing speeds of 5mm/min and 10 mm/min. The flexural strength increases with increase in testing speed for all the blend compositions. At both the speeds, remarkable reduction in flexural strength is observed as HIPS content in the blend exceeds 40%. The flexural strain and flexural energy absorbed by the specimens are found to increase with increase in HIPS content. At both the testing speeds, brittle fracture is observed for PS rich blends whereas HIPS rich blends show ductile mode of failure.

Photoelastic investigations were conducted on PS/HIPS blend samples to analyze their failure modes. A plane polariscope with a broad source of light was utilized for the study. The coloured isochromatic fringes formed indicate the presence of residual stress concentration in the blend samples. The coverage made by the fringes on the test specimens varies with the blend composition and it shows a reducing trend with the increase in HIPS content. This indicates that the presence of residual stress is a contributing factor leading to brittle fracture in PS rich blends and this tendency gradually falls with increase in HIPS content and leads to their ductile mode of failure.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

In the last century, new materials have contributed immensely to industrial and technological development. The list of materials includes a large number of metals, alloys, composites ceramics and polymers. Out of these, polymers have made an important contribution to this developmental process and have established themselves as an important class of engineering materials. What is a macromolecule consisting of a repetitive unit, which may be a chemical group of or a small molecule. Small molecules, which interact to form polymer are called monomers whereas repetitive units in polymer is called mer. These macromolecules may contain hundreds or even tens of thousands of atoms. Polymers are the most rapidly growing materials in terms of use and innovations in processing technology. The main reasons for the widespread use of polymers over other engineering materials like ceramics and metals are their easy processability, lightness, resistance to corrosion etc.

Polymers with high degree of polymerization or a large number of mers are called high polymers and those with low degree of polymerization (e.g. 500 - 600 amu) are called oligomers. The name of the polymer is derived from the name of monomer with a prefix of "poly" attached to it. Plastics and rubber constitute two important classes of polymers.

1.2 PLASTICS

Plastics occupy a major place and pivotal position among engineering materials today, though its use started as a cheap substitute for traditional materials after World War II. Modern age is rightly manned as plastics age as plastics are replacing traditional materials like wood, metals and ceramics in almost all walks of life. In performance characteristics, application prospects and diversity they offer versatility not found in other types of materials. Plastic industry is now a multibillion-dollar industry globally and the product range varies from construction materials to light emitting diodes. Plastics constitute a family of materials, not a single material, with each member of it having its own distinct and special advantages. There are different types of plastics. Plastics can be made hard, soft, tough, transparent, opaque, strong, stiff, and outdoor weather resistant, electrically conductive, biodegradable etc. based on the need. The versatility with which any plastic can be tailor made is a hallmark of the family of plastics.

1.2.1 CLASSIFICATION

1.2.1.1 CLASSIFICATION BASED ON THERMAL BEHAVIOUR

Plastics can be broadly grouped into two types as per their behaviour with change of temperature: thermoplastics and thermosets.

Thermoplastics are usually linear chain polymers held together by secondary forces. On application of heat, the secondary bonding between the polymeric chains breaks down and as a result the material changes into a liquid making the polymers easily mouldable. The temperature at which a polymer becomes soft is known as softening temperature, and as the temperature is increased beyond the softening temperature the plastic melts and hence these materials are not suitable for high temperature applications. These materials usually melt at a few hundred degrees Celsius.

Thermoset polymers have three-dimensional network type structure where bonding in three dimensions is primary. Hence they are hard and rigid at room temperature. As the thermal energy increases, these materials become harder due to formation of more primary bonding between the molecules. Ultimately it decomposes at a specific temperature instead of melting in contrast to what happens in case of thermoplastics. Of course there are speciality thermoplastics suitable for high temperature applications, which are expensive. Scrap plastics can be recycled but thermoset polymers cannot be reused since thermoset polymers are degraded when heated to an elevated temperature

1.2.1.2 CLASSIFICATION BASED ON STRUCTURE

Plastics are large molecules with strong intermolecular forces and entangled chains. When cooled from molten state, different polymers exhibit different tendencies to crystallize at different rates depending on their chemical nature, structural regularity or molecular symmetry. Bulky pendant groups or short chain branches of different lengths hinder molecular packing and inhibit crystallization. Some polymers are amorphous and have very poor tendency to get oriented or ordered on cooling. In a crystalline plastic there are several crystalline and amorphous zones. Crystalline zones are made of intermolecular/intramolecular alignment of orderly arrangement of molecules of chain segments. Polymers showing a high degree crystallinity are termed crystalline polymers. The bulk properties are explained using interlamellar amorphous model in which stacks of lamella are interspaced with and connected by amorphous regions. Highly crystalline polymers are rigid, high melting and less affected by solvent penetration. Crystallinity makes a polymer strong, but also lowers their impact resistance.

At low temperatures molecular motion in an amorphous region is restricted to molecular vibrations, but the chains cannot rotate to move in space. This form is the glassy state of the amorphous region. The glassy state can be thought of as being a super-cooled liquid where the molecular motions have been frozen in. The glassy state is hard, rigid, and brittle like a crystalline solid, but retains the molecular disorder of a liquid. When the material is heated, the polymer will reach a temperature, called the glass transition temperature, when the amorphous region becomes rubbery. When an amorphous polymer is in its rubbery state it is soft and flexible.

Semi-crystalline polymers have both crystalline and amorphous regions. Semi-crystallinity is a desirable property for most plastics because they combine the strength of crystalline polymers with the flexibility of amorphous polymers. Semi-crystalline polymers can be tough with an ability to bend without breaking; isolated lamellar single crystals are obtained by crystallization from dilute solution. When crystals are formed from the melt, chain entanglements are extremely important. In this case the solid is more irregular with polymer chains meandering in and out of ordered crystalline portions. The crystalline portion is in the lamellae; the amorphous portion is outside the lamellae. Polymers such as this are said to be semi-crystalline. The crystals are small and connected to the amorphous regions by polymer chains, so there may be no sharp well-defined boundaries between the two types of regions. For some polymers, such as poly (vinyl alcohol), there is a fairly distinct separation between the crystalline and amorphous regions. Though, in the other cases, the structure is basically is crystalline with uniformly distributed flaws and imperfections.

The mechanical properties of semi crystalline polymers are strongly determined by the crystallites, which usually enhance their stiffness (for example in polypropylene). Amorphous polymers are either very brittle (polystyrene) or very tough (polycarbonate). It is quite difficult to predict the mechanical properties of a semi crystalline material since it is determined by many parameters (such as its percentage of crystallites). It is more feasible to understand the mechanical properties of an amorphous polymer.

1.2.1.3 CLASSIFICATION BASED ON APPLICATION

Polymers are classified on the basis of their application as commodity plastics [PP, PE's, PS and PVC], technical plastics [PC, PBT, PET, PA, ASA, SAN, PMMA, PUR etc] and high-performance plastics [LCP, PEEK, PEI, PPS, PAR, PES etc]. A study conducted by the plastic industry in 1975 showed that by the year 1995, high performance plastics will occupy about 50% of market share of polymer industry and commodity plastics and technical will account for 10% and 40% respectively. But the true picture of 1995 was entirely different. Commodity plastics were worth 81% of the polymer market while high performance plastics accounted for 0.25%. This was due to the fact that the commodity plastics were modified to meet the high performance needs expected from technical and speciality plastics. This shows the growing importance of commodity plastics in the years to come.

The commodity plastics - polyethylene (PE), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC), share 80% of the market volume. The largest group of commodity thermoplastics is polyolefin's. The present day statistics shows that commodity plastics occupy a key position with more than 80% market share (fig.1.1).

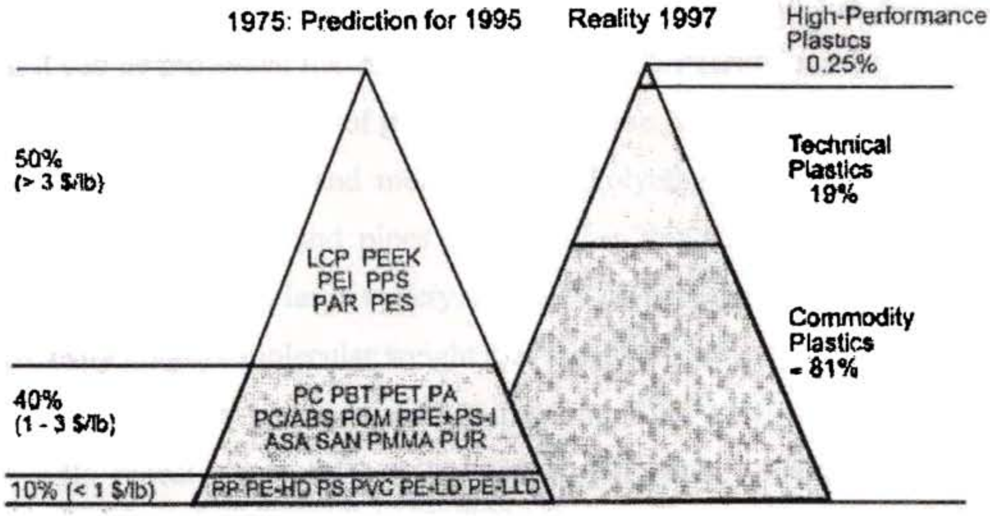

Figure 1.1: prediction and reality for commodity, technical and high performance plastics [G.W. Ehronsteen, *Polymeric Materials*, Munich, 2001]

The main reason is that processing techniques used for commodity plastics permit a fully automated, easy and reproducible manufacturing of a diversity of products in mass fabrication technology characterized by either continuous processing as in films, profiles, fibres or by short cycle times as in injection or blow moulding. The quest for new materials with special properties is met to a great extent by blending of thermoplastics with other plastics or elastomers and the melt processing technology of thermoplastics can be applied to such blends. Thus polymer blending is a very attractive option compared to development of new polymer materials.

1.2.2 COMMONLY USED THERMOPLASTICS

Polyethylenes are the highest volume plastic in the world. Its high toughness, ductility excellent chemical resistance, low water vapour permeability, and very low water absorption, combined with the ease with which it can be processed make polyethylene of all different density grades an excellent choice for a variety of goods. Polyethylene is limited by its relatively low modulus yield stress and melting point. Polyethylene is used to make containers, bottles, film and pipes among other things. It is an incredibly versatile polymer with a large variety due to its co-polymerization potential, a wide density range, a molecular weight that ranges from very low to very high and the ability to vary molecular weight distribution (MWD).

Its repeat structure is (-CH_2-CH_2-). Polyethylene homopolymer is made up exclusively of carbon and hydrogen atoms and just as the properties of diamond and graphite (which are also materials made up of entirely of carbon and hydrogen atoms) vary tremendously; different grades of polyethylene have markedly different thermal and mechanical properties. While polyethylene is generally a whitish translucent polymer, it is available in grades of density that ranges from 0.91 to 0.97 g/cm^3. The density of a particular grade is governed by the morphology of the backbone- long linear chains with very few side braches can assume a much more dimensionally compact, regular, crystalline structure. The commercially available grades are,

Low density polyethylene (LDPE)
Linear low density polyethylene (LLDPE)

High density polyethylene (HDPE)
Ultra high molecular weight polyethylene (UHMWPE)

Generally, yield strength and melt temperature increase with density, while elongation decreases with increased density. Low-density polyethylene is formed by a free radical polymerization mechanism, which requires fairly high temperature and high pressure. Because of these extreme reaction conditions many branches are formed, which are quite long and hence close packing of the chains are prevented. The crystallinity is low of the order of 40% and the structure is highly amorphous. This material is one of the most widely used plastic accounting for more than 20% of the plastic consumption. Its major application is in packaging films and its outstanding dielectric properties permit its wide acceptance as an insulator. Domestic wires, tubing, squeeze bottles, cold water tanks are also made from this.

High-density polyethylene is one of the highest volume commodity chemicals produced in the world. The most common methods of processing high-density polyethylene is of blow moulding, where resin is turned into bottles (especially for milk and juice), house wares, toys, pails, drums and automotive gas tasks. It is also commonly injection moulded into house wares, toys, food containers, garbage pails, milk crates and cases. HDPE films are commonly found as carry bags in supermarkets and departmental stores and as garbage bags.

When low temperatures and pressures are used during polymerization process, branching is less prominent and a linear polymer with a few short branches is obtained. Commercially two polymerization methods are most commonly practiced: one involves Phillips Catalyst (Chromium Oxide) and the other involves Ziegler Natta Catalyst systems (supported heterogeneous catalysts such as titanium halides, Titanium esters and aluminium alkyds and a chemically inert support such as polyethylene or polypropylene). Molecular weight is governed by primarily though temperature control with elevated temperature resulting in reduced molecular weight. The catalyst support and chemistry also plays an important factor in controlling molecular weight and molecular weight distribution.

Polypropylene (PP) is an extremely versatile plastic and is the lightest homopolymer known. PP is produced from propylene polymerization using Ziegler- Natta catalyst. The presence of methyl group leads to produce products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecule. The isotactic type is comparatively more rigid, stiff and stronger than HDPE. Its melting point is nearly 50°C higher than the melting point of HDPE. Having a much higher concentration of tertiary carbon atoms in its chain, PP is much more prone to oxidation or ageing than HDPE and LDPE. The high melting point of PP allows the moulded articles to be steam sterilized. PP is brittle close to 0°C and hence inferior to HDPE for low temperature applications. Its low density combined with stiffness, strength, fatigue and chemical resistance makes it attractive for replacing many materials in commercial applications. Even though this polymer is highly susceptible to photo-degradation, it is commonly used in producing many materials that are exposed to atmosphere like packaging materials, ropes, moulding crates, machine parts, car components, chairs, golf handles, cabinets, etc. Its excellent fatigue resistance is used for moulding integral hinges as in accelerator pedals. The radiations absorbed by the polymer causes removal of hydrogen atoms attached to tertiary carbon atoms leading to the reduction of molecular weight with modification of the chemical structure.

Polystyrene is a highly popular commodity plastic along with PE and PP. Its popularity is due to its transparency, low density, relatively high modulus, excellent electrical properties, low cost and ease of processing. It is an amorphous polymer and is available in various grades. It is generally brittle in nature. The non pigmented grades have crystal clarity. The outside housing of a computer, model cars and airplanes, form packaging and insulation, plastic drinking cups, toys and the housings of things like hairdryers, and kitchen appliances are all made of polystyrene. Polystyrene is a vinyl polymer. Most commercially available polystyrene grades are amorphous in nature. The amorphous morphology provides not only transparency but the lack of crystalline regions also means that there is no clearly defined temperature at which the plastic melts. Polystyrene is generally solid until its T_G of $\sim 100^0$ C is reached, whereupon further heating softens the plastic gradually from glass to liquid. Also the lack of a heat of crystallization means that high heating and cooling rates can be achieved. These reduce cycle time and thus increase the process economy. Upon cooling, polystyrene does not crystallize. This gives polystyrene low shrinkage values (0.004 to 0.005 mm / min) and high dimensional stability during moulding and foaming operations.

HIPS is a graft polymer made from polystyrene and polybutadiene .The polybutadiene try as best as they can to phase separate, and form little globs. But these little globs are always going to be tied to the polystyrene phase. They act to absorb energy when the polymer gets hit with something. They give the polymer a resilience that normal polystyrene doesn't have. This makes it stronger, not as brittle, and capable of taking harder impacts without breaking than regular polystyrene.

1.2.3 PLASTICS PROCESSING

Polymer processing refers to conversion of polymers into various products. One of the most important advantages of polymers compared to other engineering materials like metals or ceramics is the ease with which the polymers can be converted into products. Thermoplastic polymer forming processes can be described in terms of the following operations:

(1) Production of the polymer in a powder, granular or sheet form
(2) Basic pattern of heating to soften
(3) Mechanical deformation to obtain desired form
(4) Cooling to harden.

During the production process the polymers are mixed with suitable additives in the form of solid or liquid in order to have the finished material with the required properties. In case of thermoset polymers, solid additives like chalk, carbon black, cork dust, paper pulp etc. are added to reduce the brittleness of the material. The flow characteristics are improved by adding liquid additives during processing. Gas additives are used to produce foam plastic components. In thermoset polymer, the curing is done in the mould to form three-dimensional network structure and then cooling is done.

Thermoplastic materials can be softened by heating and reused indefinitely provided the temperature is not so high, which causes decomposition of the material. Extrusion and injection moulding can readily process thermoplast. Thermosetting materials cannot be softened by application of heat. These materials undergo chemical changes when heated and become more rigid. So reusing of these materials is not possible. Moulding and casting are the processes used for such material.

1.2.3.1 MIXING

Mixing is the first step in shaping the plastics. The polymer and various additives like fillers, plasticizers, dyes etc. are mixed intimately in open-roll mill. The two rolls in open-roll mill are kept at different temperatures and they rotate at slightly different speeds. The components of the plastic are blended due to the shearing force acting in the nip region between the rolls. The other method of blending uses drums with internal rotors and blades. An inert atmosphere is preferred during these processes since polymers may oxidize during the shearing action.

1.2.3.2 EXTRUSION

In this process the molten polymer, mixed with additives, is forced through a die. This is usually a continuous process. Granules of polymer mixture are hopper fed into the rear of the cylinder where extrusion process is carried out. The polymer mixture is passed through a heated zone by means of screw mechanism. As the screw rotates the polymer granules are compacted, mixed, heated, forwarded and eventually forced through as open-end dye. This process produces plastic pipes, plastic sheets or any other product, which has constant cross-sectional profile. There are external heaters surrounding the compression cylinder, which create heated zone in the cylinder. When a thin film of sheet is to be produced by this process, an extruded cylinder is produced first using a suitable die. This hot cylinder is inflated by compressed air to give a sleeve of thin film. Fibre, curtain rails, household guttering, polybag etc, are examples of the products obtained from this process. Hollow containers like plastic bottles etc. can be produced by extrusion flow moulding.

1.2.3.3 INJECTION MOULDING

The injection moulding process is one of the most important polymer processes by which polymer resins are converted into useful finished products. A wide variety of complex geometry articles varying from very small parts such as precision gear wheels to relatively large parts such as exterior and interior automotive parts like bumpers can be produced. Injection moulding is so versatile that parts as small as a fraction of a gram and as large as 150 kg are successfully produced in large tonnage automatic machines. Production is at high frequency with virtually no wear of the processing machinery. High production rate, short cycle times and small percentage of scrap are further attractions. During this process, molten plastic is forced (injected) into a mould and cooled until the melt solidifies. When the part is cooled sufficiently, the mould is opened, the part is ejected from the mould and the mould is closed again to repeat the cycle. The original injection moulding machines were based on the pressure die casting technique for metals. The first machine is reported to have been patented in the United States in 1872, specifically for use with the celluloid. This was an important invention but probably before its time because the following years very few developments in injection moulding processes were reported until the 1920's.

The next major development in injection moulding, i.e., the introduction of hydraulically operated machines, did not occur until the late 1930's when a wide range of thermoplastics started to become available.

In principle, injection moulding is a simple process. The thermoplastic material, in the form of granules or powder, is taken from a feed hopper and plasticized in a simple screw extruder, and the molten polymer accumulates as the tip of the reservoir. The screw whose displacement is controlled by the hydraulic pressure pushes this melt forward. The melt flows through the nozzle, which connects the extruder to the mould, passes through the sprue, along the runner, through the gate and into the mould cavity. The sprue is designed to offer as little resistance to flow as possible while minimizing the amount of wasted polymer. The runner is designed to carry melt to the mould cavity. The gate represents the entrance to the mould and its location is of utmost importance to the appearance of the part. The gate is to be made as small as possible for cosmetic reasons as well as for facilitating the separation of the part from the rest of the material solidified in the runner. The melt enters the cold cavity where it begins to solidify as it touches the cold wall. As semi-crystalline polymers solidify, they shrink as a result of increase in density. Pressure is maintained during the cooling process to ensure that the melt continues to flow into the mould. Once solidification is complete the mould plate opens and the part is ejected. Although the screw is being pulled back, it starts to rotate again plasticating more polymers. Mould filling involves high deformation and high cooling rates. A considerable amount of orientation and structure or morphology can be developed in an injection-moulded part. There is a distribution of shrinkage with a local maximum and the shrinkage distribution depends on the flow velocity and there is variation in the flow and transverse direction.

As the melt leaves the gate, the flow front occupies various positions in the mould at different times. The flow at the front is stagnation flow and the flow well behind the front is shear flow. A fluid element near the centrelines will decelerate as it approaches the front and become compressed along the x direction and stretched along the y direction. The element is stretched further at the front and laid up on the wall where it rapidly solidifies in a highly oriented state. The fountain flow associated with the advancing front is extremely important to the properties of materials made by injection moulding. In the case of blends, extensional flow at the front leads to a morphology in which the minor component exists as fibrils.

Pressure is maintained during the cooling process to ensure that the melt continues to flow into the mould. Once solidification is complete, the mould opens and ejects the part. The major advantages of the process include its versatility in moulding a wide range of products, the ease with which automation can be introduced, the possibility of high production rates and the manufacture of articles with close tolerances. The basic injection-moulding concept can also be adapted for use with thermosetting materials. Once the cavity is filled, additional material is forced into the cavity to compensate for an increasing polymer density arising from crystallization and compressibility of the melt.

1.2.4 QUALITY OF MOULDING

The moulded item may contain a range of defects, which include weld lines, sink marks, internal voids, and flash lines and locked- in strains.

When a polymer melt is forced along channels and into mould cavities there is a tendency for the molecular chains to become aligned. This is referred to as orientation and causes anisotropy in the component. In general therefore orientation effects are undesirable although they can seldom be avoided.

Shrinkage is the main problem in precision moulding. It is defined as the difference between the dimensions of the cold mould and the dimensions of the cooled moulding. The result of this is that in addition to the shrinkage effects, if the plastic is crystalline then there will be shrinkage due to the closer packing of the molecules in the crystalline state. Hence the shrinkage of these materials is high, typically 1- 4% as compared with 0.3 - 0.7% for amorphous materials.

Injection pressure has as an important influence on shrinkage. By using high pressures it is possible to compensate for the dimensional changes, which occur in the material due to crystallization and thermal contraction, thus reducing the shrinkage.

The time during which the screw remains forward also has an important effect on shrinkage. The maximum beneficial hold-on time for a particular component may be determined gradually increasing the hold-on time until the weight of the moulding reaches a maximum.

Increasing the gate size will reduce the shrinkage because it increases the time taken for the gate to freeze off. This in turn increases the time during which the injection pressure is available to compensate for shrinkage.

Higher mould temperatures will increase the time taken for the gate to freeze off. This is one method therefore of overcoming mould filling problems due to small gates.

Thick sections in a moulding reduce the cooling rate and promote crystallization. Shrinkage will therefore increase as the part thickness increases.

In general the effect of melt temperature on shrinkage is relatively small. Attempts to remedy shrinkage problems by adjusting melt temperature are generally unproductive and not recommended.

Unequal moulded in stresses and strains in the component can result in warpage. It can be caused by poor part design, poor mould design or incorrect outing condition.

If a moulded article has an unacceptable level of moulded-in strain due to shrinkage and orientation, annealing may be necessary. The purpose of annealing is to accelerate the relaxation of the material, thereby reducing the level of internal stresses and stabilizing the part dimensions.

1.2.5 POLYMER BLENDING

The demands for many applications need a set of properties that no polymers can fulfil. One method to satisfy these demands is by mixing two or more polymers. Mixing two or more polymers to produce blends or alloys is a well established route to achieve a certain amount of physical properties, without the need to synthesise specialised polymer systems.

Developing a critical engineering component involves getting the right material, making a proper design and choosing the correct manufacturing process as shown in figure 1.2.

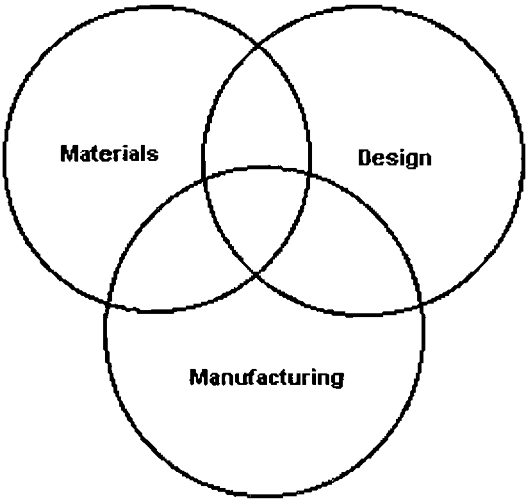

Figure1.2: Interaction of materials, design and manufacturing

One of the most widely used techniques to get the right material in polymers is to select a polymer blend so as to get the attractive properties of both the components. Not-withstanding the attractive properties of polymers, many of them are susceptible to attack by solvents, environment and are notch sensitive leading to fracture failure. It is important to screen common polymers and their blends for notch sensitivity to avoid catastrophic failure due to brittle fracture when they are chosen for critical applications.

The commonly used commodity plastics are Polyethylene (PE), Polypropylene (PP), and Polystyrene (PS). These polymers can be processed without excessive degradation when they contain little impurities. Other important plastics have more problems with degradation such as in the case of Polyacetals and Polyamide. This thesis focuses on blends of Polypropylene (PP), High density polyethylene (HDPE), Polystyrene (PS) and High impact polystyrene (HIPS). Usually the mechanical properties of the pure blends obtained are poor. These properties can be brought back to their original level by adding an additional phase [1-17]. This phase usually is called the compatibiliser.

In this study it is proposed to investigate the fracture behaviour of polymer blends constituted out of the most widely used polymers, High density polyethylene (HDPE), Polypropylene (PP), Polystyrene (PS) and High impact polystyrene (HIPS).

CHAPTER 2

LITERATURE REVIEW

2.1 POLYMERS AND POLYMER BLENDS

During the first half of the twentieth century, the greatest progress in polymer industry was the development of a wide range of new polymers. This was based on the new understanding of polymer synthesis and the development of commercialization of economical manufacturing methods for a range of monomers. Most of the major commodity and engineering plastics in current use were being manufactured in 1950's. By 1970 most of the common monomers had been exploited and then only a few new developments have been taken place in synthesis, generally reserved for specialized polymers and to low volume applications.

During the same period polymer blending began to flourish. It was gradually accepted that new economical monomers were less likely but a range of new materials could be developed by combining different existing polymers. While most monomers available cannot be co polymerized to a product of intermediate properties, their polymers could be melt blended economically. Now polymer blends in one form or another dominate much of polymer practice. This rapid development can be attributed to the following points-

- The opportunity to develop new properties or improve on properties to meet specific customer needs.
- The capacity to reduce material costs with little sacrifice in properties.

- The ability to improve the processibility of materials which are otherwise limited in their ability to be transformed into finished products.
- Permit the much more rapid development of modified polymeric materials to meet emerging needs by by-passing the polymerization steps.

The annual growth rate for blends is about 10% whereas the growth rate for plastics alone is 3%. Polymer blends are mixtures of homopolymers or copolymers of different molecular structure. Immiscible polymer blends possess a minor phase that may undergo severe deformation and acquire an isometric configuration during melt processing. This results on a structure characterized by a distribution of shape factor ratios, concentration and orientation throughout the thickness of the moulded part. For immiscible polymer blends addition of a compatibilizer is found to reduce the interfacial tension and the size of the dispersed phase so that better mechanical properties are achieved [1-3].

The imperatives that encourage one to go for blending are,
a) To maintain a more favourable counter performance ratio, and
b) To achieve reinforcement of a desired property.

An expensive polymer whose property spectrum is much higher than is needed for a specific application is blended with as an inexpensive polymer with a property spectrum of a level that makes the blend suitable for the application at an attractive cost performance ratio. Also the demerits from a poor property of a polymer may be effectively overcome by blending it with another, which has a higher property value. Thus available polymers can be selected appropriately and blended to generate the desired properties without having to develop new polymers and thus investment in new plants can be done away with.

The ultimate behaviour of blends depend on,

1) The extent of phase separation
2) Nature of phases provided by the matrix material
3) Character of the dispersed phase and
4) Interaction between the component polymers

The physical properties of blends can be altered to satisfy a wide range of ratios. A desirable performance can be achieved by proper selection of blend ingredients, followed by control of morphology by appropriate methods of compatibilization, compounding and processing. Blending is known to improve the impact strength, mechanical properties, chemical and solvent resistance to, enhance processibility, abrasion resistance, flame retardancy etc. Improvement in processability is becoming the most important criteria as the emphasis is shifting to high performance, difficult to process specialty resins. The processing temperature, T_p can be above the thermal degradation temperature and blending can reduce the processing temperature by about 60°C.

The ultimate mechanical properties of the blend can be improved by adding a third component having intermediate molecular characteristics between the two polymer species which acts as a compatibilizing agent in their amorphous regions. Depending on the type and molecular parameters of the components and the degree of immiscibility successful compatibilizing agents tried are random copolymers, ethylene propylene rubber (EPR) or ethylene propylene diene monomer (EPDM)

Once the blend components are selected, the properties can be controlled by morphology (which depends on the molecular parameters of the components) and composition, as well as by the compounding and processing methods. In the case of amorphous blends, the morphology is defined by the size and shape of the two phases, their distribution and orientation. This type of morphology is referred to as macro morphology. In blends of semicrystalline polymers, blends affect the crystallinity. This is referred to as micro morphology.

Macro and micro morphology depends as the thermodynamic and rheological properties of the ingredients and the methods of compatibilization as well as on the deformation and thermal histories. The macromorphology of polymer blends describes the form and size of the macromolecular phases formed during compounding or blending. A great majority of polymer blends are immiscible due to the negligibly small entropy of mixing.

The miscibility of two polymers is determined by the free energy of mixing (ΔG_{mix}) which includes both entropic and enthalpic terms (ΔS_{mix} and (ΔH_{mix}).

$$\begin{aligned}\Delta G_{mix} &= \Delta H_{mix} - T\Delta S_{mix} \\ &= \Delta E_{mix} + P\Delta V_{mix} - T\Delta S_{mix}\end{aligned}$$

Flory-Huggins theory is the classical theory for calculating the free energy of mixing [4]. Originally derived for small molecule systems, it assumed that each molecule occupied one site in a lattice. The theory was expanded to model polymer systems by assuming that the polymer consisted of a series of connected segments each of which occupied one lattice site.

Plastics will continue to be one of the world's fastest growing industries, ranked as one of the few billion dollar industries. Its three major processing methods are injection moulding, extrusion and blow moulding. Approximately 32% by weight of all plastics go through injection moulding machines, 36% through extruders and 10% blow moulding machines (extruder and injection moulding types).

The ease of processibility and low cost made polyethylene to the largest group of commodity thermoplastics. Polyethylene (PE) covers 45% of all plastics and one of the reasons for its popularity is the development of blending technology for property modification. Polypropylene (PP) is a versatile polymer that continues to grow rapidly because of its excellent performance and improvements in production economics. The blends of PE with PP have attracted much commercial interest. One of the reasons for adding PE to PP is to improve the low temperature impact behaviour of PP. PP/PE blends find application in automobiles, appliances, house-wares, furniture, sporting goods, toys, packaging, chemical processing equipments and industrial components, most of which are injection moulded. PP/PE blends are immiscible. Due to the immiscible nature of the components, both in the melt as well as solid state, resulting blends show deterioration in impact performance and tensile properties [5].

In many industrial applications of polymeric materials, several criteria play important roles in the selection of resins. In terms of overall performance, these generally include (1) The bulk properties, (2) The surface properties and (3) The processability of the resin. Bulk properties are critical in determining the thermal behaviour and mechanical strength of polymers [6, 7]. On the other hand surface properties play important roles in determining the wettability and adhesion, friction and wear, gloss and scratch resistance, paintability and printability, biocompatibility and antistatic properties [8].

In polymer blends, properties like ductility and impact strength should be improved by compatibilization. Compatibilization is done by the addition of block or graft copolymers with segments capable of interacting with blend constituents. These copolymers lower the interfacial tension and improve adhesion between the matrix and dispersed phase [9, 10]. According to Xanthos (1992) chemical modification of a blend by reactive extrusion can improve the properties of the polymer blend [11].

Hettema *et al.* claim that reduction of rheological mismatch for a blend containing low viscosity PE and high viscosity PP can enhance dispersive mixing.

Gongde Liu *et al.* showed that addition of PP to UHMWPE improved the processability of the blend compared to UHMWPE or its blend with HDPE [12].

According to Deanin and Chung the poor impact resistance at low temperature and poor environmental stress cracking resistance has set limitations to the use of polypropylene. These properties of polypropylene can be improved by incorporation of ethylene during polymerization or by mechanical blending with polyethylene. Propylene-ethylene copolymers give better performance than PP at low temperature but these copolymers require controlled, specialized polymerization during manufacture and so are more expensive. Thus blending of PP and PE is an economic alternative [13].

According to Nolly *et al.* and Bartlett *et al.* samples prepared by compression moulding were less ductile and less strong than those prepared by injection moulding [14, 15].

An increase in the mixing time as well as intensity improved the degree of dispersion but prolonged or intensive mixing also increased the thermal and mechanical degradation. There is an optimum mixing procedure that should be sought [16].

Polyolefins are the most important plastics. Polyethylene and polypropylene have the most products and lies in the first position of plastics. Polyolefin blends are frequently used to get the balanced mechanical and processing properties. The properties of individual polyolefin can be changed in a significant way by mixing with other components. For this reason polyolefin blends have attained widespread commercial applications. Studies have been conducted on the relationship between morphology and properties of polyolefin blends to control the micro – phase separation, morphology and orientation in blends in order to get the desired properties [17 - 19].

Study of properties and morphology of polyolefin blends is of great interest importantly because of their rich and fascinated morphology depending on molecular structure, thermal history and external stress field. The work of Prof. Bevis, oscillating shear stress field has been very important in controlling polymer morphology and mechanical properties.

It was found that HDPE and PP were phase separated in the melt state and form separated crystallites during cooling. However a study of PP/HDPE blends by Inoue and co-workers proposed a single phase mixture of PP/HDPE=60/40 obtained in high shear fields in an injection moulding machine based on the regularly phase separated structure [20].

Macosko *et al.* observed the average diameter of particles of the blend with and without compatibilizer. They noted that less than 10 minutes of mixing even at very low shear rate was enough to reach the final particle size. Most of size reduction occurred very rapidly during the softening of the pellets or powder. The particle size was slightly smaller with the block copolymer present [21].

It is interesting to check the miscibility, morphology and mechanical properties of polymer blends in a high shear rate combined with oscillating shear field during cooling. Experiments were carried out for HDPE/PP blends via oscillating packing injection moulding after subjecting a high shear rate at the nozzle. A great enhancement of tensile strength was achieved for the blends with PP content less than 10 weight percentage [22].

The mechanical properties of polystyrene homopolymer can be modified to produce a tougher, more ductile blend as in the case of rubber modified high impact grades of polystyrene (HIPS).

2.2 IMPORTANT BLENDING PRINCIPLES

Polymer blends may be broadly classified into two – miscible and immiscible blends. Miscible blends are characterized by the presence of a single phase and a single glass transition temperature. They involve thermodynamic solubility. Their properties can be predicted as composition weighed average of the properties of individual components. Immiscible blends are phase separated, exhibiting the glass transition temperature and / or melting temperature of both components. The overall performance of the blend depends on the properties of the individual components as well as the morphology of the blends and the interfacial properties between the blend phases.

During blending of two polymers we have to take care of a few possibilities. Simply adding a polymer to another brings out both good and bad properties of the later. The adverse effects are so pronounced that the resultant material is most likely unusable. The main reason is that most polymer pairs are immiscible and blending leads to a phase separated material. This material has three inherent problems.

i) Poor dispersion of one polymer phase in the other

For most polymer pairs, the interfacial tension is high of the order of 1.5 x 10^{-3} to 1.5 x 10^{-2} J $m^{-2.}$ This high value makes dispersion of one phase in the other by melt blending difficult. When the dispersed phase has large surface area, the interfacial contact between the two phases is small. When this material is subjected to mechanical load, it does not respond efficiently.

ii) Weak interfacial adhesion between the two phases

For most polymer pairs, the Flory parameter is large (0.05 – 0.5) and the interfacial width is narrow (1 – 5 nm). This means that there is little penetration of polymer chains from one phase into the other and vice versa, and consequently few entanglements are formed across the interfaces [23]. The failure of the interface between two glassy polymers thus requires only the breaking of weak van der Waal's bonds. For most incompatibilized blends, the interfaces are probably the most vulnerable locations. When they are subjected to an external stress, the interfaces will most likely fail well before the base polymer components.

iii) Instability of immiscible polymer blends

An immiscible polymer blend is thermodynamically unstable. The state of dispersion of one phase in another is governed by both thermodynamics (interfacial tension) and thermo-mechanics (agitation). It is a result of the competition between the interfacial energy of the system which encourages maximum separation of components, and the external mechanical agitation imposed on it, which is to induce mixing. Agitation produces flow stresses which tend to deform and break domains. Interfacial tension opposes the deformation and break-up of domains and encourages coalescence of the dispersed phase domains when they come in close proximity. When agitation ceases the interfacial tension becomes the driving force for the system to evolve. Each phase will coalesce; minimise the total interfacial area as well as the total interfacial energy of the system. Coalescence is slow in an immiscible polymer blend but is still too fast for most practical applications. Due to the instability of the blends, the morphology of the blend depends on the conditions to which it is subjected. The morphology of an immiscible polymer blend obtained from a screw extruder may not be the same as that when the blend is injection moulded.

Immiscible polymer blends are much more interesting for commercial development since immiscibility allows preserving the good features of each of the base polymer components of the blend. Some properties can be achieved only through immiscible polymer blends. For example the impact strength of a polymer cannot be improved significantly by adding an elastomer miscible with it. Our challenge is to develop processes or techniques that allow control of both the morphology and the interfaces of a phase separated blend. Such processes or techniques are called compatibilization. Polymer blends with intentionally modified morphology and interfaces are called compatibilized blends.

2.3 METHODS FOR BLEND COMPATIBILIZATION

2.3.1 ADDITION OF BLOCK AND GRAFT COPOLYMERS

A compatibilization strategy used in polymer blending is the addition of a pre made block copolymer composed of blocks that are each miscible with one of the homopolymers [24]. These segments need not be identical with the blend components. According to Noolandi and Hong as well as Leibler, the block co polymers prefer to span the interface [25, 26]. The co polymer locates at the interface between immiscible polymer blend components, reducing the interfacial tension between blend components, reducing the resistance to minor phase break-up during melt mixing which reduces the size of the dispersed phase and stabilizing the dispersion against coalescence. This finer morphology and the increased interfacial adhesion result in improved physical properties.

2.3.2 UTILIZATION OF NON-BONDING SPECIFIC INTERACTIONS

Non bonding specific interactions like Hydrogen bonding , ion-dipole, dipole-dipole and donor-acceptor interactions can be employed for the compatibilization of polymer blends. These specific interactions are weak and high concentrations are often required for compatibilization. The addition of large quantities of the compatibilizer may change the properties of the desired phase constituents and/or be uneconomical.

2.3.3 REACTIVE COMPATIBILIZATION

Here the compatibilizers are formed in-situ through ionic or covalent bonding during the melt blending of suitably functionalized polymers [27

- 31]. The in-situ formed co-polymer compatabilizers get located at the interface, reducing the size of the dispersed phase, improving interfacial adhesion between blend phases and the physical properties of the blends. This method has been implemented in a number of commercial products.

According to Utracki all commercial blends made from highly immiscible polymers are compatabilized reactively. A block or graft co-polymer is formed by coupling of reactive groups on each of the immiscible polymers [32].

Ghijsels and Raadsen comment that there are several problems in compatibilizing multiphase structures with block co-polymer in the melt. The viscosity of the block co-polymers is high and thus may be difficult to disperse. Moreover these co-polymers are very expensive and we have to minimise their concentration [33]. Hobbs et al. suggest that the block copolymer added to compatibilize the blend should prefer to lie at the interface rather than form micelles or a separate phase [34].

2.3.4 ADDITION OF LOW MOLECULAR WEIGHT COUPLING AGENTS

Compatibilization of a polymer blend can be achieved by the use of low molecular weight reagents or a mixture of low molecular weight co-agents to obtain interfacial reaction between polymer components. During the process some type of graft or block copolymer is formed which plays the role of compatibilizer. When we consider a blend of two polyolefins, we have to add two different functionalized copolymers which may not produce the required results. In such a case the ability of a reagent to compatibilize the polymer blend in a single reactive step would be an advantage. A free radical initiator like peroxide can promote reactions on a polyolefin chain leading to compatibilization.

2.4 MECHANICAL BEHAVIOUR OF POLYMER BLENDS

The mechanical properties of polymer blends are very important in many applications. Melt mixing of two polymers results in blends which are normally weak and brittle. The incorporation of a dispersed phase into a matrix mostly leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. Improvement of mechanical properties of the blend is usually done by compatibilization which means modification of normally not miscible blends to improve miscibility. The end-use performance has been improved many fold by compatibilization.

Several methods are known to improve the properties of polymers. Many polymer additives are needed to improve the properties like processability and life time (lubricants or stabilizers), strength (mineral fillers such as chalk, clay, glass beads, mica or glass fiber reinforcement), appearance and colour (pigments), conductivity (conducting fillers like aluminium flakes or carbon) or flammability (flame retardants).

A large part of studies on blending of polymers deals with attempts to obtain a combination of properties of different polymers. But the mechanical properties of the blends are usually worse instead of better for many combinations of polymers. The conventional methods for the improvement of these properties are often expensive and do not always meet the required demands. In principle compatibilization is influenced by molecular weight distribution and concentration of the compatibilizer in the dispersed phase in complex ways to influence final blend properties. The best known effect of compatibilization is the reduction in interfacial tension in the melt. It causes an emulsifying effect which leads to an extremely fine dispersion of one phase in the other. A second effect is the increase in adhesion at phase boundaries giving improved stress transfer. A third effect is the inhibition of coalescence of the dispersed phase by modifying the phase boundary interface. These and other effects such as modification of rheology may occur simultaneously which complicates the ongoing of the whole process.

The complexity of interaction of the compatibilizer with the morphology of the blend was studied by Lester and Hope. They mixed HDPE with Nylon 6, Nylon 66, Nylon 6-3T and Polyethylene terephthalate PET with and without low levels of various proprietary compatibilizing agents. The study by SEM as well as tensile testing showed that finest dispersion of the blend did not show highest levels of ultimate elongation [35].

Barendsen *et al.* studied the compatibilization of PE/PS blend by adding (PS-g-LDPE) graft copolymer of LDPE with PS to the blends of LDPE and PS. They found that adding 7.5% by weight copolymer caused a substantial reduction in the size of the dispersed phase [36].

It was opined by Herkens *et al.* that difference in the detailed fine structure of copolymers gave rise to large effects on the impact strength, and on the magnitude of the tensile modulus of the blends [37].

Nolley *et al.* used copolymers of propylene and ethylene (EP) displaying residual crystallinity due to long ethylene sequence as compatibilizer for propylene / low density polyethylene (PP/LDPE) blends. They found that the amorphous copolymer was less effective as compatibilizing agent [38]. According to Ho and Salovy (1973), a 5% addition of ethylene-propylene rubbers (EPR) to a blend of HDPE/PP was necessary to obtain a linear relation between tensile strength and composition [39].

Utraki *et al.* studied the influence of addition of hydrogenated poly (styrene-b-isoprene) di-block copolymer (SEB) to a blend [40]. Paul and Barlow independently reviewed the use of block copolymers for the compatibilization of immiscible polymer blends. Addition to PET/HDPE blends variously affected the different physical properties, modulus and yield strength. Addition of block copolymers of the same chemical nature as the two homopolymers of a blend is an obvious choice which when optimized will lead to enhancement of properties [41, 42].

Shilov *et al.* analysed the composition of an immiscible polymer blend as a function of linear dimensions. Between a domain of polymer A and a domain of polymer B there exists an interfacial layer, in some cases having a thickness up to 4 nm. This interfacial region can be considered as a third phase which has been stabilized in many commercial polymer alloys through selective cross linking, resulting in reproducibility of performance and processability. The thickness of this layer depends on thermodynamic interaction, macro molecular segment size, concentration and phase conditions. The interfacial tension and the domain adhesion characterize the interface. The interfacial tension is the integral of the Helmholtz free energy change across the interface which gradually changes over the interfacial area from phase A to B, due to a change in composition of the third phase between both phases [43].

Mixing of two or more polymers to produce blends or alloys is a well known method for achieving a specific combination of physical properties. Mixing means break up of droplets of one polymer to obtain a dispersed phase with a very small size of another polymer. This type of mixing is called blending and if the mixture formed has improved mechanical properties, it is called compounding [44].

Blending of polymers became increasingly important after Taylor studied break-up phenomena in liquids [45]. Normally, blending is used to combine the properties of two or more polymers and is performed in melt blending machines or extruders. But the mechanical properties are not as good as expected due to poor interfacial adhesion between the minor and major components. Hence we have to look for ways for improving the mechanical properties of such blends.

Polymers are often referred to as compatible if the mechanical properties of blends made by mixing them will have a certain set of required values. This could mean that the blend is strong enough, tough enough or ductile enough. Compatibility is often referred to as miscibility on a molecular scale. The polymer blend is compatible – if the mixture is stable under normal conditions for its use and no de-mixing should occur, the dispersed phase should have a strong bonding to the surrounding polymer. Adhesion between both phases in a blend can be achieved by addition of a compatibilizer. The compatibilizer is transported to the interface of the dispersed phase by means of mixing and it decreases the interfacial energy.

The morphology of the blends after blending as a function of material and processing parameters have been studied using scanning electron microscopy [46,47]. Blom *et al.* reported that PP & HDPE are incompatible and immiscible and that the latter caused deterioration in the elongation at break and impact strengths [48].

Stehling *et al.* as well as Choudhary *et al.* showed that a block copolymer of the two homo polymers in the blend can act as compatibilizer of HDPE/PP blend. They used ethylene propylene rubber as compatibilizer for HDPE/PP blends to success [49, 50].

Deanin and Sansone (1978), Lovinger and Williams as well as Bartlett *et al.* (1982) reported that the addition of PP to HDPE resulted in a decrease in impact strength and elongation at break [51 - 53].

Nearly all polymer pairs are immiscible and incompatible. This results in materials which have poor mechanical properties and undergo phase separation. Consequently these materials cannot be used alone or unmodified but need to be compatibilized in some way [54].

2.5 MODELS FOR UNDERSTANDING MECHANICAL BEHAVIOUR

As an aid to the understanding of the shape of stress-strain curves, it is helpful to look at the curves of simple models. Four simple models are shown in fig along with their stress- strain curves for two rates of elongation. A spring has a constant modulus independent of the speed of testing, that is, Hooke's law holds, and the initial slope of the stress- strain curve is a constant proportional to the modulus, A dashpot, on the other hand, has no modulus, but the force resisting motion is proportional to the speed of testing, shown in case B of figure.

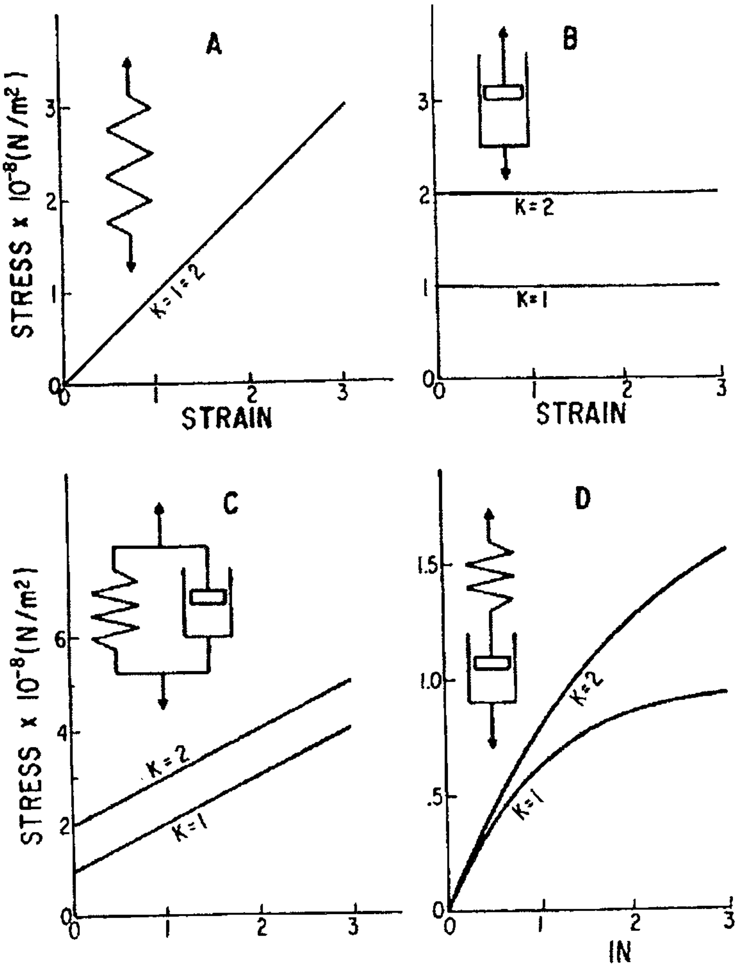

Figure 2.1: Mechanical models for describing viscoelastic nature and their responses.

The Voigt or Kelvin model (case C) has a stress- strain curve given by,

$$\sigma = K\eta + E\varepsilon$$

Where K is the speed of testing $d\varepsilon/dt$, η is the viscosity of the dashpot, and E is the modulus of the spring. Because of the dashpot, the stress starts at some value greater than zero, and as the spring stretches, the stress increases. The slope of the line is the modulus of the spring.

The Maxwell unit (case D) has a more complex stress- strain curve, which is given by:

$$\sigma = K\eta\ [1 - \exp\ (E\varepsilon/K\eta)\ ]$$

The initial slope gives the modulus, which is independent of the speed of deformation since the first part of the curve corresponds to stretching the spring. At higher renovations the slopes of the curves decrease, and their magnitude depends upon the speed of testing when the dashpot begins to relax out part of the stress. Eventually the spring slopes stretching, and all the elongation comes from motion in the dashpot. Actual materials generally show more complex behaviour than these modes. However, the brittle polymers have curves similar to spring up to the point of failure, and many less brittle polymers show curves similar to the Maxwell unit. None of the models show yield points characteristic of many ductile polymers.

2.6 FRACTURE FAILURE PROCESS IN POLYMERS

If a plastic moulding fails in the performance of its normal function it is usually due to one of the two factors – excessive deformation or fracture. For plastics more often than not it will be excessive creep deformation which is the limiting factor. However, fracture if it occurs can have more catastrophic results [55]. Therefore it is essential that designers recognize what is likely to cause premature failure so that steps can be taken to avoid this.

Fractures are usually classified as brittle or ductile. Although any type of fracture is serious, brittle fractures are potentially more dangerous because is no observable deformation of the material prior to or during breakage. When a material fails in a ductile fashion large non recoverable deformations are evident and these serve as warning that all is not well. In polymeric materials, fracture may be ductile of brittle depending on such variables as the straining rate, the temperature and the stress system. The principal causes of fracture are the application of a stress in a very short period of time (impact), the prolonged action of a steady stress (creep rupture) or the continuous application of a cyclically varying stress (fatigue). In all cases the fracture processes will be accelerated if the plastic is in an aggressive environment.

When tensile stress is applied to an amorphous (glassy) polymer such as polystyrene (PS), crazes may be observed to occur before failure. Crazes are like cracks in a sense that they are wedge shaped and form perpendicular to the applied stress. However they may be differentiated from cracks by the fact that they contain polymeric material which is stretched in a highly oriented manner perpendicular to the plane of the craze, i.e., parallel to the applied stress direction. Another major distinguishing feature is that unlike cracks, they are able to bear stress. Under static loading, the strain at which crazes start to form, decreases as the applied stress decreases. At constant strain rate testing the crazes always start to form at a well defined stress level [55]. As with all aspects of the behavior of plastics other factors such as temperature will influence the levels of stress and strain involved. Even a relatively low stress may induce crazing after a period of time, although in some glassy plastics there is a lower stress limit below which crazes will never occur. This is clearly an important stress for design considerations. However, the presence of certain liquids (organic solvents) can initiate crazing at stresses far below this stress limit. This phenomenon of solvent crazing has been the cause of many catastrophic service failures because it is almost impossible to design against its occurrence.

The mechanical properties of polymers are greatly affected by temperature and strain rate, and the load-elongation curve at a constant strain rate changes with increasing temperature as shown schematically (not necessarily to scale) in figure.

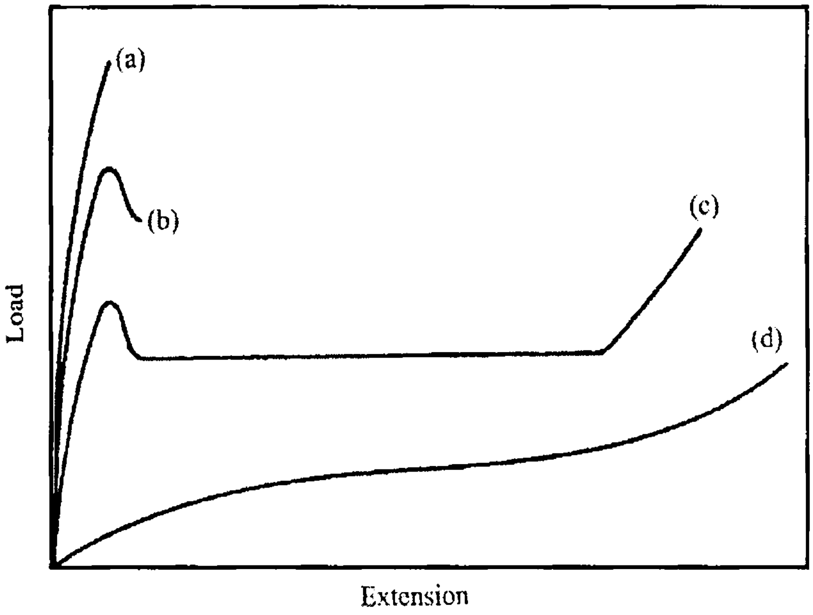

Figure 2.2: Schematic figure showing the load-elongation curve of a polymer at a constant rate but at different temperatures (a < b < c < d).

At low temperatures the load rises approximately linearly with increasing elongation up to the breaking point, when the polymer fractures in brittle manner. At higher temperatures a yield point is observed and the load falls before failure, sometimes with the appearance of a neck: i.e. ductile failure, but still at quite low strains (typically 10-20 percent). At still higher temperatures, under certain conditions, strain hardening occurs, the neck stabilizes and cold drawing ensues. The extensions in this case are generally very large, up to 1000 percent. Finally, at even higher temperatures, homogeneous deformation is observed, with a very large extension at break. In an amorphous polymer this rubber-like behaviour occurs above the glass transition temperature so the stress levels are very low.

For polymers the situation is clearly more complicated than that for the brittle-ductile transition is metals, as there are in general four regions of behaviour and not two. It is of considerable value to discuss the factors that influence the brittle-ductile transition, and then to consider further factors that are involved in the observation of necking and cold drawing.

Ductile and brittle behaviour are most simply defined from the stress-strain curve. Brittle behaviour is designated when the specimen fails at its maximum load, at comparatively low strains (say < 10 percent), whereas ductile behaviour shows a peak load followed by failure at a lower stress [56].

The distinction between brittle and ductile failure is also manifested in two other ways: (1) the energy dissipated in fracture; and (2) the nature of the fracture surface. The energy dissipated is an important consideration for practical applications and forms the basis of the Charpy ad Izod impact tests. At the testing speeds under which the practical impact tests are conducted it is difficult to determine the stress-strain curve, so impact strengths are customarily quoted in terms of the fracture energy for a standard specimen.

The appearance of the fracture surface also can be an indication of the distinction between brittle and ductile failure, although the present state of knowledge concerning the crack propagation is not sufficiently extensive to make this distinction more than empirical.

Modern understanding of the fracture behaviour of brittle materials stems from the seminal research of Griffith on the brittle fracture of glass. The Griffith theory of fracture, which is the earliest statement of linear elastic fracture mechanics, has been applied extensively to the fracture of glass and metals, and more recently to polymers, Although it was conceived initially to describe the propagation of crack in perfectly elastic material at small elastic strains (hence linear elastic), subsequent work has shown that it is still applicable for situations including localized plastic deformation at the crack tip which does not lead to general yielding in the specimen.

First, Griffith considered that fracture produces a new surface area and postulated that for fracture; to occur the increase in energy required; to produce the new surface must be balanced by a decrease in elastically spread energy.

Second, to explain the large discrepancy between the measured strength of materials and those based on theoretical considerations, he proposed that the elastically stored energy is not distributed uniformly throughout the specimen but is concentrated in the neighbourhood of small cracks. Fracture thus occurs due to the spreading of cracks that originate in pre-existing flaws.

Design of engineering components requires sound understanding about the fracture behaviour of the materials under loads at various conditions. In conventional design the material is assumed to be homogeneous and defects-free and design practices do not consider prevention of failure initiation at the defects or imperfections, which will be inherently, present or caused in all materials, either during fabrication or in service. So the nature of the original flaw and its subsequent behaviour under loads are of importance. If it is very small, it is possible that most of the life may be spent in an initiation phase or the flaw may not grow at all and in certain cases this could be controlled by yielding and crazing mechanisms. So if flaw size and its behaviour are known, a safe working stress may be computed.

A component with defect may not fail immediately of on loading, but may experience a stable crack growth before final failure. If the load is kept below a certain value, crack may not grow at all. Hence it may be of immense importance if one can predict the load at which instability sets in when defects are present in structures [57].

2.7 SCOPE AND OBJECTIVES OF THE PRESENT WORK

Polymers being an important class of engineering materials today, their fracture behaviour is of great significance in deciding their suitability for critical applications. This study is proposed to be undertaken to investigate the fracture behaviour of widely used thermoplastics PP, HDPE, PS and HIPS and their blends and to suggest methods for improving their resistance to notch sensitivity. The specific objectives of the study are,

(1) To study the fracture behaviour of two ductile semicrystalline thermoplastics PP and HDPE and their blends.

(2) To study the effect of a particulate modifier (e.g. calcium carbonate which is a commonly used particulate filler in polymers) on the fracture behaviour and notch sensitivity of HDPE / PP blends.

(3) To study the effect of a soft modifier (e.g. an elastomeric filler - EPDM) on the fracture behaviour and notch sensitivity of HDPE / PP blends.

(4) To study the fracture behaviour of blends of an amorphous, brittle polymer Polystyrene (PS) and a ductile polymer High Impact Poly Styrene (HIPS).

(5) To conduct Photo elastic investigation to analyse the failure modes of PS/HIPS blends.

CHAPTER 3

MATERIALS AND METHODS

3.1 POLYMERS

1. POLYPROPYLENE HOMOPOLYMER (PP)

REPOL H200MA, with a melt flow index (MFI) of 20 g/10min, was supplied by Reliance Industries Limited, Mumbai, India.

2. HIGH-DENSITY POLYETHYLENE (HDEPE)

HDPE grade Indothene HD 50 MA 180 was supplied by Indian Petro Chemicals Limited, Baroda, India, with density 0.950 g/cm^3 and MFI 18 g/10 min.

3. POLYSTYRENE (PS)

PS grade LGG104 was supplied by LG Plastics with MFI 18 gm/10 min.

4. HIGH IMPACT POLYSTYRENE (HIPS)

HIPS grade LGH 302 was supplied by LG Plastics with MFI 18 gm / 10 min.

3.2 MODIFIERS

1. CALCIUM CARBONATE

Calcium Carbonate used in this study was commercial grade used as filler in polymers.

2. ETHYLENE PROPYLENE DIENE MONOMER (EPDM)

EPDM used in this study was grade 301T supplied by Herdelia Unimers

3.3 POLYMER BLEND PREPARATION

HDPE and PP granules were placed in an air oven set at 100 ^{0} C for 4 hours to remove any moisture present and allowed to cool to room temperature in a desicator. Six blend compositions were selected namely 100% HDPE/0% PP; 80% HDPE/20% PP; 60% HDPE/40% PP; 40% HDPE/60% PP; 20% HDPE/80% PP and 0% HDPE/100% PP and the granules were weighed out. Each mixture was melt blended either with or without the modifiers. The modifiers Calcium Carbonate and EPDM were added in 2%, 4% and 6% by weight of the neat blends. The granules were fed into the mixing chamber of a Thermo Haake Rheomix 600P blender set at 180^0 C. The blender is fitted with Roller Rotor blades counter rotating at 3:2 speed ratio. They were set to rotate at 30 rpm. Blending was continued till the mixing torque stabilized to constant values in all the cases [4]. Afterwards, the modifiers (either $CaCO_3$ or EPDM) were added. A mixing time of 5 minutes was allowed to complete the blending, during which time the torque would become steady.

Figure 3.1: Thermo Haake Rheomix 600P

Thermo Haake has a mother unit Thermo Haake Rheocord 300P. It is fitted with a motor of 4kW capacity and can work at a speed up to 250 rpm. The blending can be done up to a torque of 300 Nm. The blender has a mixing chamber of capacity 120 cm^3 without the rotors and 69 cm^3 with the rotors. The rotors are Roller Rotor type and work counter rotating. The mixing chamber is provided with three separate heaters and can be heated to a temperature of 450 ^{0}C and the rotors can handle a torque of 160 Nm. The best mixing efficiency is obtained when the mixing chamber is about 70% filled. If the melt density of the test substance is known we can determine the sample weight as follows:

Sample weight = melt density x chamber volume x 0.7

= melt density x 69 x 0.7

A sample weight of 40g was chosen for each mixing.

3.4 PREPARATION OF TEST SPECIMENS

The hot polymer blend taken out from the mixing chamber was passed through a laboratory size two roll mill. The sheet form so obtained was cut to small pieces and subjected to injection moulding at 180^0 C in a semiautomatic plunger type injection moulding machine (Texair JIM –1H). Dumbell specimens were prepared (according to ASTM D 638 specification). Specimens for conducting the notch sensitivity test were notched to 1 mm depth before testing.

3.4.1 MOULDS FOR SAMPLE PREPARATION

Moulds for injection moulding of the samples were of low carbon steel. Single gating system was employed. Mould cavities were made for the specimens as per ASTM – D – 638 specification. Moulds for Flexure and Impact tests were of similar configuration.

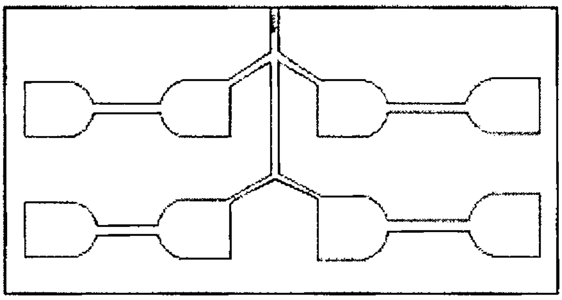

Figure 3.2: Injection mould for preparing test samples

3.5 MEASUREMENTS

3.5.1 TENSILE TEST

The tensile properties of the specimens were determined using dumb bell shaped specimens according to ASTM – D – 638. The length between the jaws at the start of each test was fixed to 40 mm and at least six concordant measurements are taken to represent each data point. A computerised Universal Testing Machine (Schimadzu AG1).

The tensile test was conducted at different crosshead speeds for obtaining various strain rates.
To conduct notch sensitivity test, the specimens were centrally notched to 1 mm depth before testing and the test was conducted at different crosshead speeds for studying the notch sensitivity at various strain rates.

3.5.2 IMPACT TEST

The resistance to impact is one of the key properties of materials. The ability of a material to withstand accidental knocks can decide its success or failure in a particular application. When the design of a component is being considered, knowledge of the impact strength of a prospective material is important even though it cannot be used quantitatively in the design calculations. Instead it serves as a qualitative check that the material is in some desired condition, thought to be appropriate to the envisaged service conditions. Unfortunately, however, it is not possible to attach a unique value to the impact strength of a thermoplastic material. This depends on a wide range of variables including temperature, straining rate, stress system, anisotropy, geometry of component, fabrication conditions, environment and so on. This is a formidable list and certainly enough to discourage any designer who is looking for precise information on which to base a design. Experience has shown that the best the designer can do to avoid premature service failures is to relate, as closely as possible, the conditions pertaining in the specific application to the impact data which is available. This task will be reduced slightly when it is realized that most of the complaints regarding unsatisfactory impact performance arise from sporadic brittle fractures which are uncharacteristic of that material. The key to the problem is then to avoid conditions which are likely to promote brittleness in the material. In general the factors likely to increase the tendency towards brittle fractures are low temperatures, stress concentrations, high strain rates and internal stresses.

For normal use, if a material does not fail in a brittle manner in tests under all conditions likely to be found in service then it may be regarded as tough. In a few applications, impact loading may be the primary stress system experienced by the component in which case the relevant factors need to be studied in greater detail.

3.5.2.1 MODES OF FAILURE UNDER IMPACT

The most convenient classification of failure of thermoplastics materials under impact is due to two classes – brittle or ductile. A brittle failure is a low energy process in which a crack initiates and propagates before any yielding of the material occurs. In a ductile fracture there is yielding, probably localized in the failure region and considerable energy is absorbed.

It is important to realize that both types of failure may be observed in the one material depending on the service conditions. As temperature is reduced, for example, there is often a marked transition from ductile to brittle fractures. The appearance of a failure in service is frequently the only method of classifying the type of failure. Brittle failures usually exhibit smooth, glassy or possibly splintered fracture surfaces. Ductile failures on the other hand normally leave evidence of appreciable deformation and yielding. Identification of the latter is usually aided by stress whitening of material in the failure zone. In practice intermediate failure may also occur. In such cases there will be a change from one type of failure to the other across the fracture surface.

The impact characteristics of the specimens were investigated for the various blend compositions using an impact Testing Machine.

Make and model: Resil Impact Tester (Izod and Charpy) CEAST , Italy.

Figure 3.3: Resil Impact Tester

For applying impact load, a 4J hammer was used.

Hammer striking velocity was maintained at 3.46 m/second.

The test was conducted in the Izod configuration.

The impact characteristics obtained were,

1. Energy absorbed by the test specimen (J)
2. Resilience(KJ/m2)
3. Impact Strength (J/m)

3.5.3 FLEXURE TEST

The flexural properties of the specimens were determined using a computerised universal testing machine (Schimadzu UTM). The simply supported beam configuration was used with a span of 50 mm.

3.5.4 PHOTO ELASTIC INVESTIGATIONS

Photoelasticity is an experimental method to determine stress distribution in a material. The method is mostly used in cases where mathematical methods become quite cumbersome. Unlike the analytical methods of stress determination, photoelasticity gives a fairly accurate picture of stress distribution even around abrupt discontinuities in a material. The method serves as an important tool for determining the critical stress points in a material and is often used for determining stress concentration factors in irregular geometries.

3.5.4.1 PRINCIPLES OF PHOTOELASTICITY

The method is based on the property of birefringence, which is exhibited by certain transparent materials. Birefringence is a property by virtue of which a ray of light passing through a birefringent material experiences two refractive indices. The property of birefringence or double refraction is exhibited by many optical crystals. But photoelastic materials exhibit the property of birefringence only on the application of stress and the magnitude of the refractive indices at each point in the material is directly related to the state of stress at that point. Thus, the first task is to develop a model made out of such materials. The model has a similar geometry to that of the structure on which stress analysis is to be performed. This ensures that the state of stress in the model is similar to state of stress in the structure.

When a ray of plane polarized light is passed through a photoelastic material, it gets resolved along two principal stress directions and each of these components experiences different refractive indices. The difference in the refractive indices leads to a relative phase retardation between the two component waves. The magnitude of the relative retardation is given by the Stress Optic Law:

$$R = Ct\,(\sigma_{11} - \sigma_{22})$$

Where R is the induced retardation, C is the stress optic coefficient, t is the specimen thickness, σ_{11} is the first principal stress, and σ_{22} is the second principal stress.

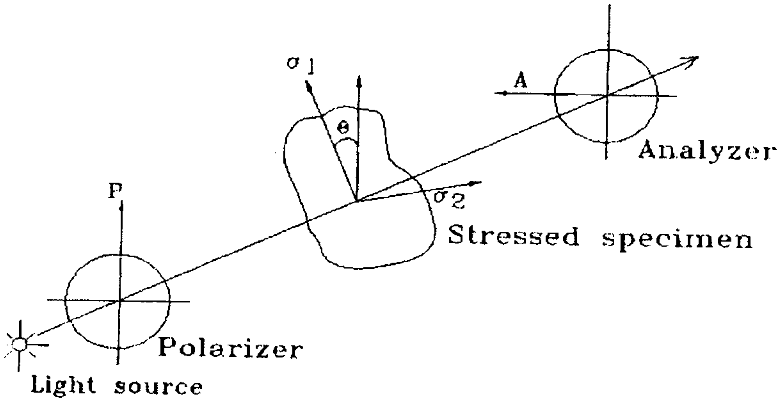

Figure 3.4 **Principle of plane Polariscope.**

The two waves are then brought together in a polariscope. The phenomena of optical interference take place and we get a fringe pattern, which depends on relative retardation. Thus, by studying the fringe pattern, one can determine the state of stress at various points in the material.

Two types of fringes are formed in a plane polariscope. They are isochromatics and isoclinics.

Isochromatics are the locus of points along which the difference in the first and second principal stress remains the same. Thus, they are the lines which join the points with equal maximum shear stress magnitude. Isochromatic fringes are colourful and the fringe colour is related to the difference in principal stresses through the Stress – Optic Law. From the photoelastic stress pattern,Isochromatics provide qualitative information regarding stress distribution within the component.

Isoclinics are locus of points in the specimen along which the principal stresses are in the same direction. They are black in colour and are superimposed on the Isochromatic pattern. They occur whenever either principal stress direction coincides with the axis of polarization of the polarizer. Isoclinics provide information about the directions of principal stresses in the model and provide necessary information for solution of two – dimensional stress problem.

A standard plane polaiscope shows both Isochromatic and Isoclinic fringes and this makes quantitative stress analysis difficult.

3.5.4.2 EXPERIMENTAL PROCEDURE

PS / HIPS mix was prepared at various blend compositions in Thermo – Haake rheomix by melt mixing. Specimens were injection moulded in Texair (JIM - 1H) injection moulding machine at 180^0 Celsius.

A plane polariscope was used for conducting the investigations. The test specimens were placed between the polarisr and analyzer. A broad source of light was used for illuminating the system. The fringe patterns were observed through the analyzer. Isochromatic fringes with distinct colours were visible for each PS/HIPS blend composition. The fringe patterns were photographed for qualitative analysis.

Figure 3.5: Plane polariscope

3.5.5 MELT FLOW STUDIES

The Melt Flow Index (MFI) of polymer blends was determined using a melt flow index apparatus (make CEAST, Italy).

For HDPE/PP blends, the temperature was set at 190^0C and a weight of 2.15 kg was applied. For PS/HIPS blends, the temperature was set at 200^0C and the weight applied was 5 kg.

Figure 3.6: Melt Flow Index apparatus

CHAPTER 4

FRACTURE BEHAVIOUR OF UNMODIFIED AND MODIFIED PP / HDPE BLENDS

4.1 INTRODUCTION

Due to ease of processibility and low cost polyethylenes constitute the largest group of commodity thermoplastics. Polyethelene (PE) covers 45% of all plastics and one of the reasons for its popularity is the development of blending technology for property modification. Polypropylene (PP) is a versatile polymer that continues to grow rapidly because of its excellent performance and improvements in production economics. The blends of PE with PP have attracted much commercial interest. One of the reasons for adding PE to PP is to improve the low temperature impact behaviour of PP.

PP/PE blends are immiscible. From a mechanical point of view PP/HDPE blends have generally been considered as very unsatisfactory materials. They show very poor ultimate mechanical properties in comparison with those of the components. The ultimate mechanical properties of the blend can be improved by adding a third component having intermediate molecular characteristics between the two polymer species which acts as a compatibilizing agent in their amorphous regions. Depending on the type and molecular parameters of the components and the degree of immicibility successful compatibilizing agents tried are random copolymers ethylene propylene rubber (EPR) or ethylene propylene diene monomer (EPDM). Compatibilization of PP/PE blends can be done by addition of copolymer EPR or EPDM, by reactive blending or by post blending treatment using chemical crosslinking, electron beam or by irradiation. Blends of isotactic polypropylene and high density polyethylene with ethylene propylene diene monomer (EPDM) are of particular commercial importance and they constitute a large and important segment of the plastic market. Rubber toughened PP/HDPE blends are important because of the need for thermoplastic materials with the characteristics of vulcanized rubber. The morphology of ternary blends of PP/HDPE/EPDM blends is reported where it is shown that in systems HDPE as the matrix PP lamella entered the EPDM dispersed phase and when HDPE was the dispersed phase, PE lamella entered the PP matrix. The presence of PE did not affect the crystal form of PP. Blending of PP with PE engenders two competing effects. The presence of two immiscible polymers creates a two phase structure that may be detrimental to blend performance at large strains. Also increase of mixing time or intensity not only improves the degree of dispersion but also increases thermal and mechanical degradation. Because of immiscibility in PP/PE blends at large strains, poor ultimate mechanical properties result. Ethylene – propylene copolymer are shown to adhere better to each polymer component than the components adhere to each other.

The following investigations are proposed to be conducted in this section.

(1) Study on the fracture behaviour of polymer blends consisting of two ductile semicrystalline thermoplastics HDPE and PP by studying the effect of blend ratio on the mechanical properties of the blend system.

(2) The effect of a hard modifier (e.g. calcium carbonate which is a commonly used particulate filler in polymers) on the fracture behaviour and notch sensitivity of HDPE / PP blends.

(3) The effect of a soft modifier (e.g. an Elastomeric filler - EPDM) on the fracture behaviour and notch sensitivity of HDPE / PP blends.

4.2 EXPERIMENTAL

4.2.1 MATERIALS

Two ductile polymers, a hard mineral filler and a soft modifier were used for the study.

4.2.1.1 POLYMERS

1. Polypropylene homopolymer (PP)

Poly Propylene (PP) (REPOL H 200 MA) with a melt flow index (MFI) of 20 g /10min was supplied by Reliance Industries Limited, Mumbai, India.

2. High-density polyethylene (HDPE)

HDPE grade Indothene HD 50 MA 180 was supplied by Indian Petro Chemicals Ltd. Baroda ,India, with density 0.950 g/cm^3 and MFI 18 g /10 min.

4.2.1.2 MODIFIERS

1. Calcium carbonate

Calcium Carbonate of commercial grade commonly used as filler in plastics was the hard modifier used for this study.

2. Ethylene propylene diene monomer (EPDM)

EPDM grade 301 T supplied by Herdelia Unimers, India was used as a soft modifier.

4.2.2 SPECIMEN PREPARATION

4.2.2.1 PREPARATION OF POLYMER BLENDS

The polymer blends were prepared by melt mixing HDPE and PP in various compositions using a Torque Rheometer (Thermo Haake Rheomix 600P) attached to Thermo Haake Rheocord 300 set at a chamber temperature of 180^0 C. The rotor speed was set at 30 rpm. A mixing time of 8 minutes was fixed and by that time the mixing torque stabilized to constant values for all the blends.

In the case of modified compounds, modifiers were allowed to mix properly with polymer blends for 3 minutes with continuous torque monitoring. The torque-time curves for melt mixing of different blend compositions were taken and plotted.

4.2.2.2 MOULDING

The hot mix from the mixing chamber was immediately passed through a two roll mill and cut into small pieces. Dumbell specimens were prepared (according to ASTM - D -638 specification) by injection moulding the blends at 180 ^{0}C in a semi automatic plunger type injection moulding machine (Texair JIM -1H). The melt temperature was set to be automatically controlled by the injection moulding machine.

To conduct notch sensitivity test, the specimens were centrally notched to 1 mm depth before testing.

4.2.3 TENSILE TEST

The tensile properties of the specimens were determined using a universal testing machine (Schimadzu UTM) at crosshead speeds of 50 mm/min and 100 mm/min till the specimens failed under tensile load. This was done to study the fracture behaviour of the blend at different strain rates. The length between the jaws at the start of each test was fixed to 40 mm and at least six concordant measurements were taken to represent each data point. The tensile test was conducted for both notched and unnotched specimens.

4.2.4 MELT FLOW STUDIES

The Melt Flow Index (MFI) of PP/HDPE blends of four different compositions were obtained from Melt flow indexer at a temperature of 180^0 C.

4.3 RESULTS AND DISCUSSION

4.3. A. Torque studies

The Torque vs. Time of mixing curves of HDPE / PP blends modified with calcium carbonate are shown in Fig. 4.1. The initial torque for the blend is found to be high which decreases and becomes steady upon melting. When the modifier is added there is a slight increase in torque which stabilizes to a constant value in a couple of minutes.

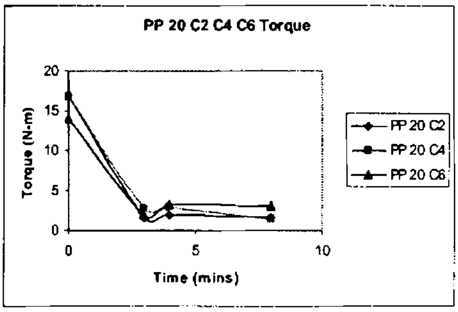

Fig. 4.1.a - PP 20%

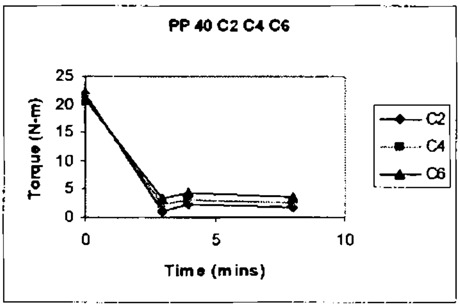

Fig. 4.1.b - PP 40%

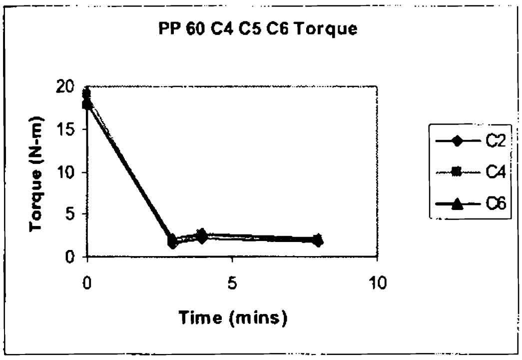

Fig. 4.1.c - PP 60%

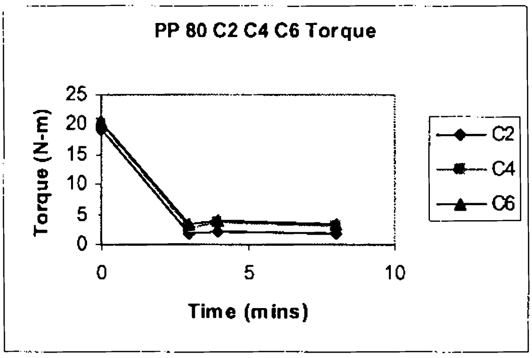

Fig. 4.1.d - PP 80%

Figure 4.1: Torque-Time graphs of PP / HDPE blends containing 2%, 4% and 6% (C2, C4 and C6) of calcium carbonate.

The same trend is seen during the melt blending of PP / HDPE with the addition of EPDM as shown in Fig.4.2.

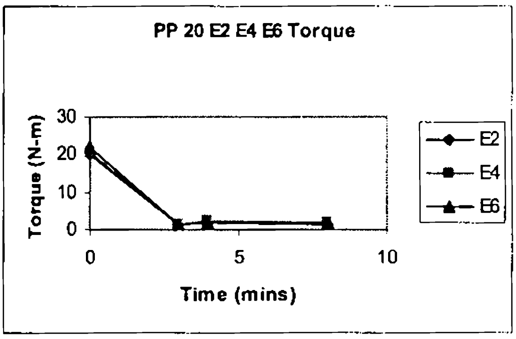

Fig.4.2.a - PP 20%

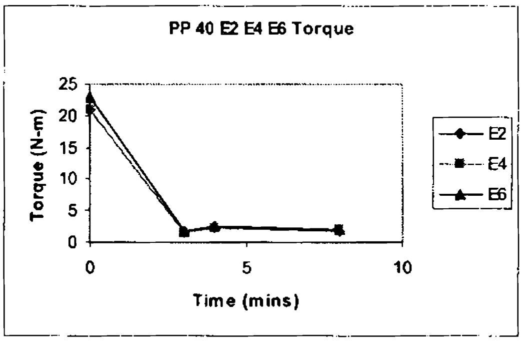

Fig.4.2.b - PP 40%

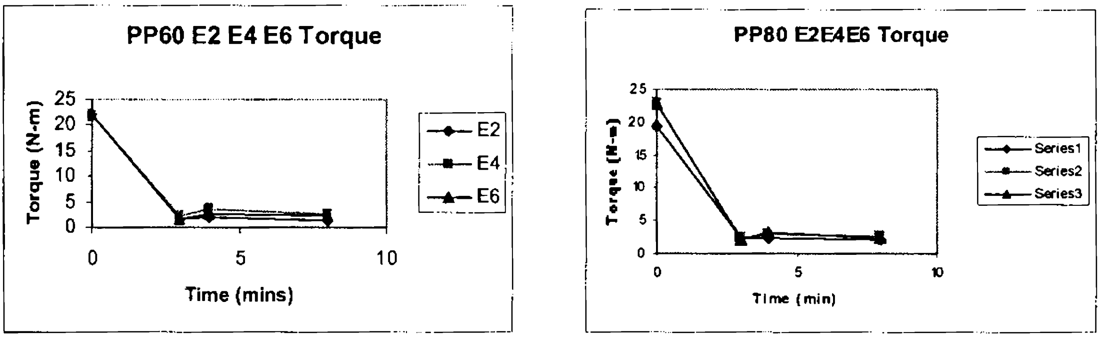

Fig.4.2.c - PP 60%

Fig.4.2.d - PP 80%

Figure 4.2: Torque-Time graphs of PP / HDPE blends containing 2%, 4% and 6% (E2, E4 and E6) of EPDM.

4.3. B. Fracture behaviour of unmodified PP/HDPE blends

The variation of modulus with composition for notched (N) and unnotched (S) PP/HDPE specimens at two testing speeds of 50 mm/min and 100 mm/min are shown in Fig. 4.3.

All the blends show a positive deviation from the additive rule. This shows that the individual crystallinities of the two polymers are not affected in the blend and that they also give rise to improved crystallinity upon blending.

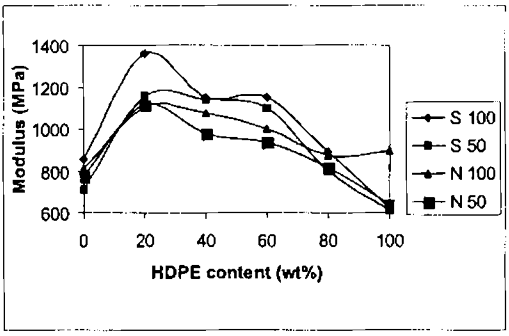

Figure 4.3: Variation of modulus with composition for notched (N) and unnotched (S) PP/HDPE specimens at two testing speeds 50 mm/min (S50) and 100 mm/min (S100).

This shows that the blends can be advantageously used for optimizing the mechanical properties. In the case of both unnotched and notched specimens, higher moduli are observed at higher testing speeds as expected [5,6]. The peak value in all the cases is obtained for 80PP/20HDPE blends. The synergism in mechanical properties may be due to the similarity in the structure of two plastics and their co – crystallization. The fact that the blends with notches also show a positive deviation means that the blends have a good resistance to notch sensitivity.

4.3. C Fracture behaviour of PP/HDPE blends with a mineral filler $CaCO_3$ and an elastomeric modifier EPDM.

4.3. C.1 Effect of Calcium Carbonate

The effect of adding a hard mineral filler $CaCO_3$ at concentrations 2 wt%, 4 wt% and 6 wt% is shown in Fig.4.4.

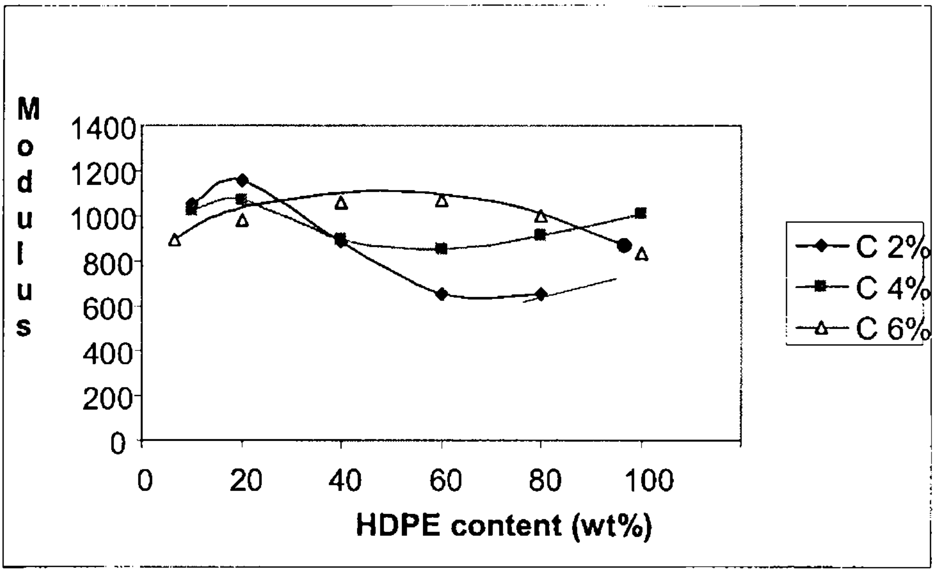

Figure 4.4: Variation of modulus with composition for unnotched PP/HDPE specimens containing different concentrations (2%, 4% and 6% by wt.) of calcium carbonate (C 2, C 4 and C 6) of $CaCo_3$ (C) at a testing speed of 100 mm/min.

The behaviour of positive deviation is maintained in the case of 6wt% modifier and it shows higher modulus in almost all cases compared to neat PP/HDPE blends. The 80/20 PP/HDPE blend shows a positive deviation for all the cases showing again the superiority of this composition. Even though the moduli of the modified specimens are marginally lower than those of the unmodified ones the maximum strain values are marginally higher in the modified samples. Calcium carbonate is widely used as filler in plastics and the study shows that the presence of the filler in controlled amounts does not affect the mechanical behaviour seriously.

The behaviour of notched specimens containing calcium carbonate filler is also similar as shown in Fig.4.5.

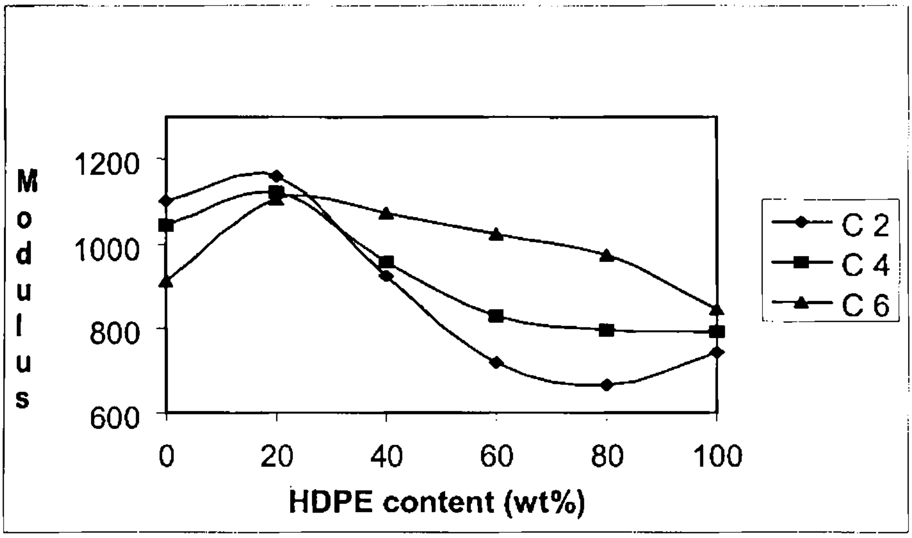

Figure 4.5: Variation of modulus with composition for notched PP/HDPE specimens containing different concentrations (2%, 4% and 6% by wt.) of calcium carbonate (C 2, C 4 and C 6) at a testing speed of 100 mm/min.

In the case of notched specimens also 6 wt% modifier shows the most stable behaviour. 80/20 PP/HDPE blend maintains its superiority in this case also. From figures 4.4 and 4.5, it can be observed that the modifier does not seriously affect the resistance to notch sensitivity of HDPE/PP blends. A minimum concentration of about 5% seems to be necessary to impart a stable behaviour both for notched and unnotched blends. This behaviour may be advantageously used for reducing the cost of the material.

4.3. C.2 Effect of Elastomeric Modifier EPDM

The variation of modulus with composition of unnotched HDPE/PP blends in the presence of 2%, 4% and 6% of the second modifier Ethylene Propylene Diene Monomer (EPDM) is shown in Fig.4.6.

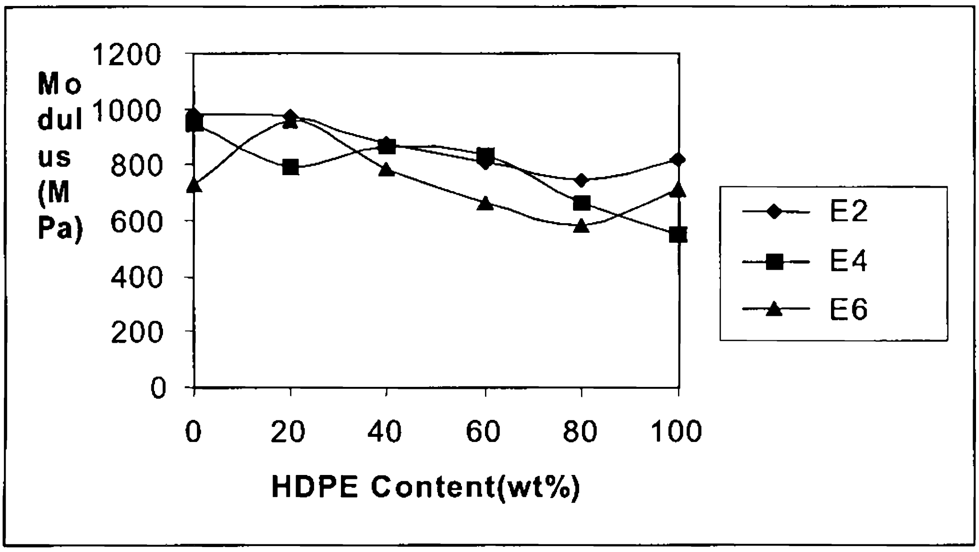

Figure 4.6: Variation of modulus with composition for unnotched PP/HDPE specimens containing different concentrations (2%, 4% and 6% by wt.) of EPDM (E2, E4 and E6) at a testing speed of 100 mm/min.

Unlike the former case EPDM does not produce a positive deviation. However, the moduli values are more or less close to the additive values. But the striking feature of this modifier is that it imparts a significant resistance to notch sensitivity of the blends as in Fig.4.7.

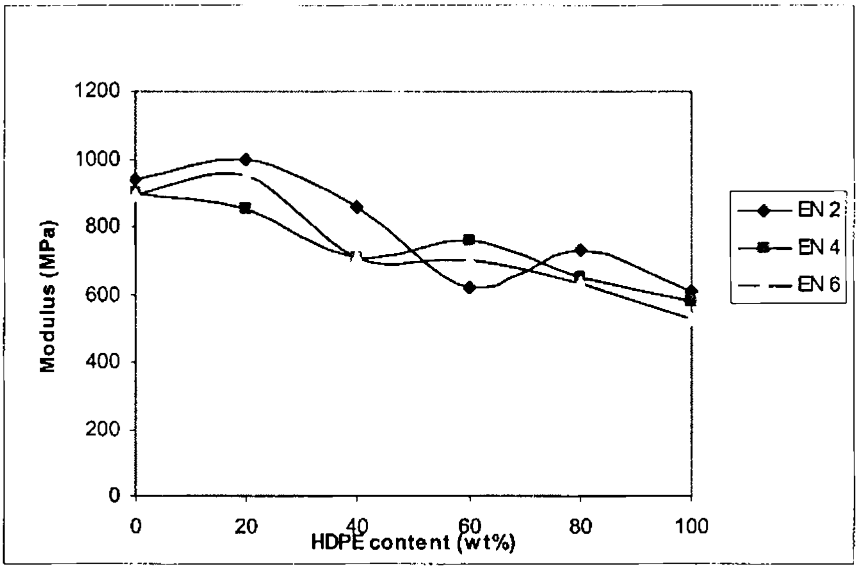

Figure 4.7: Variation of modulus with composition for notched PP/HDPE specimens containing different concentrations (2%, 4% and 6% by wt.) of EPDM (EN2, EN4 and EN6) at a testing speed of 100 mm/min.

A comparison of Fig. 4.6 and Fig 4.7 shows that, both unnotched and notched specimens have almost identical moduli values in the presence of EPDM. It has been reported that the addition of ethylene-propylene rubbers (EPR) to a blend of HDPE/PP results in a linear relation between tensile strength and composition [39].

EPDM is a commonly used compatibilizer for HDPE/PP blends and the present study shows that one another way EPDM can reinforce the blends is by imparting an outstanding resistance to notch sensitivity of the blends. It is also found that about 2% EPDM is sufficient to provide excellent resistance to notch sensitivity. Since the addition of a soft modifier can affect the modulus, the effectiveness of this modifier even at 2% is encouraging.

The affect of the optimum concentrations of the two modifiers on HDPE/PP blends is compared in Fig.4.8.

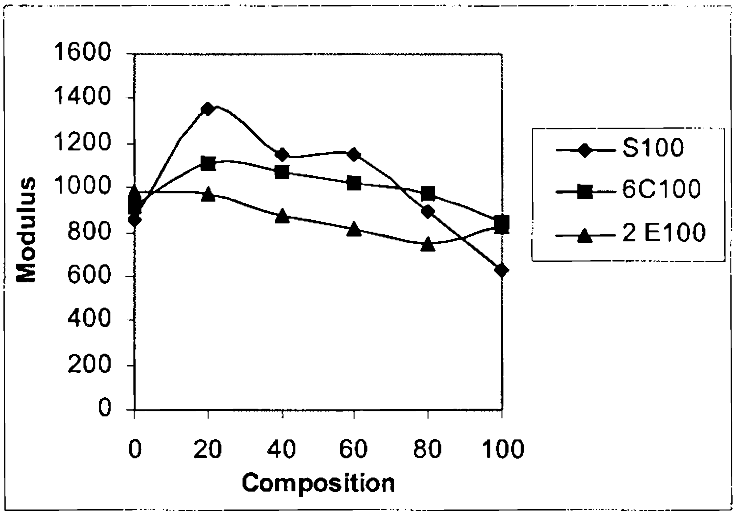

Figure 4.8: Variation of modulus with % HDPE content of unnotched PP/HDPE blends containing 1) no modifier (S 100), 2) 6% Calcium Carbonate (6C 100) and 3) 2% EPDM (2 E 100) at a testing speed of 100 mm/min.

Hard filler like calcium carbonate can be employed for cost reduction without much deterioration in modulus. Soft filler like EPDM can be used in small amounts without serious reduction in modulus.

The elongation at break may be taken as an index of resistance to notch sensitivity. Fig.4.9 shows the variation in elongation at break for notched and unnotched HDPE/PP blend samples with composition.

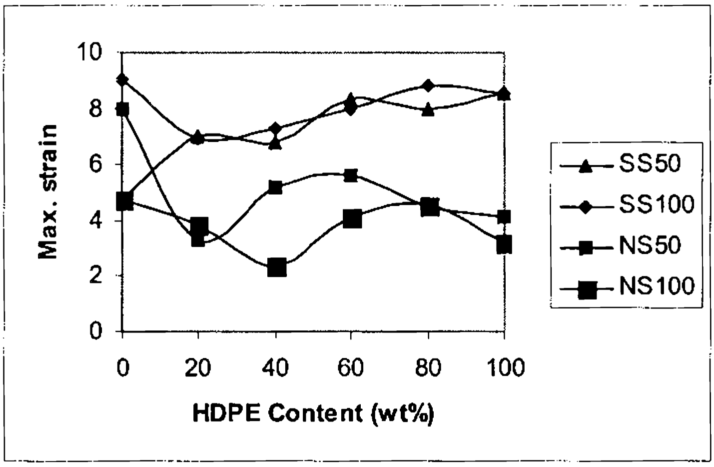

Figure 4.9: Variation of max.strain with composition for notched (N) and unnotched (S) PP/HDPE specimens at the two testing speeds of 50 mm/min (S 50) and 100 mm/min (S 100).

For the unnotched samples, there is not much change in the maximum strain at the two testing speeds. However the picture is different for the notched samples. This shows that the notch sensitivity is very significant in high-speed applications.

The variation of maximum strain with blend composition for PP/HDPE blends modified with calcium carbonate (unnotched and notched samples) at a testing speed of 100mm/min is shown in fig.4.10 and fig.4.11.

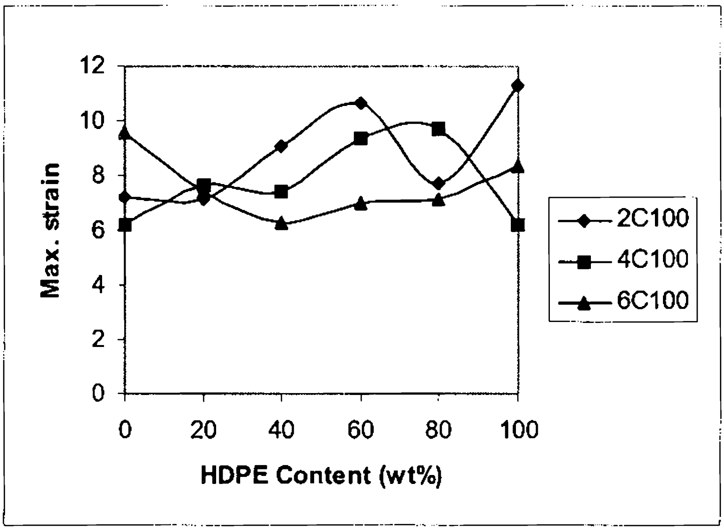

Figure 4.10: Variation of max.strain with composition for unnotched PP/HDPE specimens containing different concentrations of calcium carbonate (2%, 4% and 6% i.e. 2C,4C and 6C) at a testing speed of 100 mm/min.

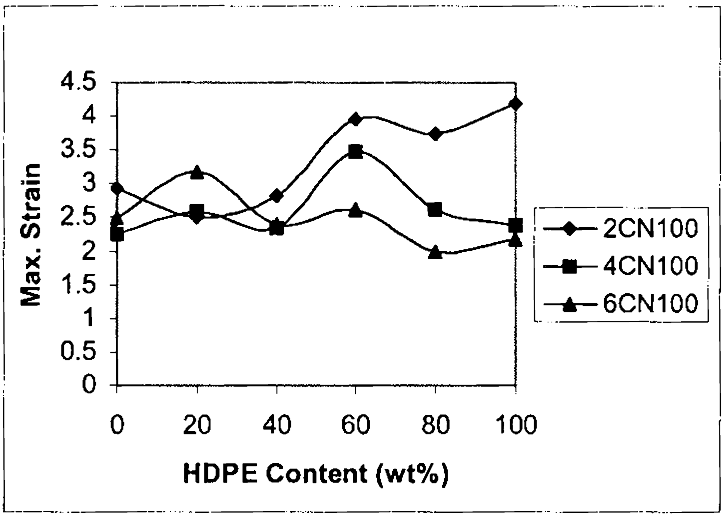

Figure 4.11: Variation of max.strain with composition for notched (N) PP/HDPE specimens containing different concentrations of calcium carbonate (2%, 4% and 6% i.e. 2C, 4C and 6C) at a testing speed of 100 mm/min.

Presence of calcium carbonate seems to impart some stability to the system. For the notched specimens the variation in the maximum strain is a little more pronounced particularly for HDPE rich blends (Fig.4.11).

The variation in maximum strain with EPDM content for HDPE/PP blends at 100mm/min. is shown in Fig.4.12.

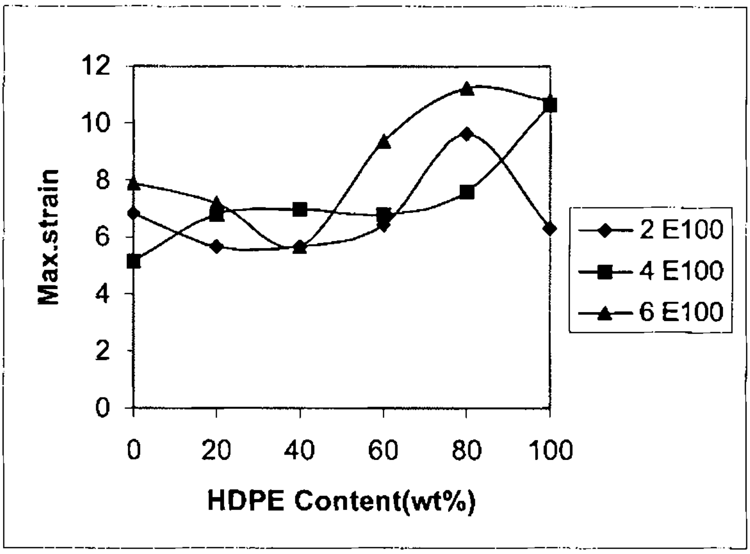

Figure 4.12: Variation of max.strain with composition for unnotched PP/HDPE specimens containing different concentrations of EPDM (2%, 4% and 6% i.e. 2E, 4E and 6E) at a testing speed of 100 mm/min.

It is observed that EPDM gives a better stability to the blends than calcium carbonate. The attractive feature of EPDM is that the stable behaviour is retained even for notched specimens (Figure 4.13).

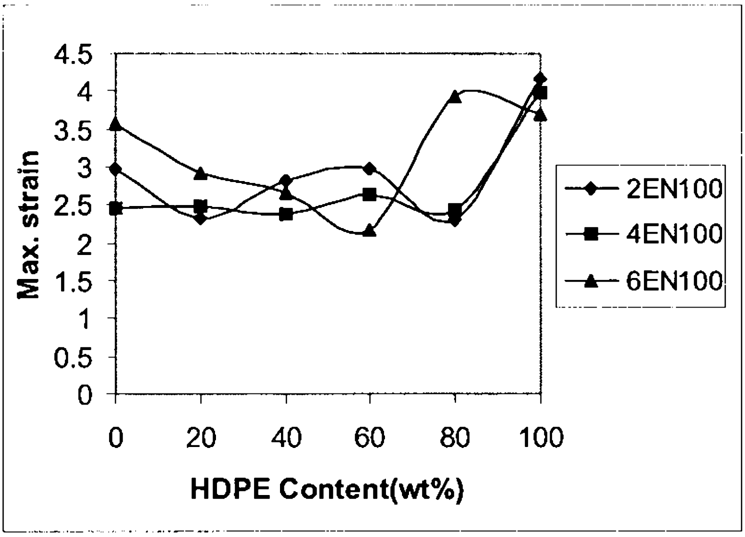

Figure 4.13: Variation of max.strain with composition for notched PP/HDPE specimens (N) containing different concentrations of EPDM (2%, 4% and 6% i.e. 2E, 4E and 6E) at a testing speed of 100 mm/min.

This behaviour is in conformity with the earlier behaviour observed in the case of modulus.

Fig. 4.14 shows a comparison of maximum stain in unnotched HDPE/PP blends with composition with and without modifiers.

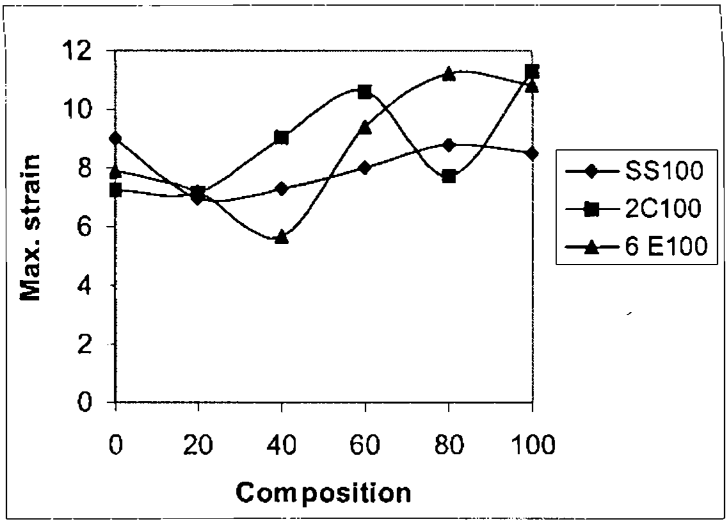

Figure 4.14: Variation of max.strain with composition for unnotched PP/HDPE specimens containing no modifier (SS 100), 2% calcium carbonate (2C 100) and 6% EPDM (6E 100) at a testing speed of 100 mm/min.

It is interesting to note that the maximum strain increases both with the hard filler and the soft filler. This behaviour is not usually observed with single plastics. With a single plastic, the modulus usually increases with the addition of hard filler, while the maximum strain decreases. In the presence of soft filler the modulus usually decreases while the maximum strain decreases. So in the case of these blends, it is observed that both hard and soft fillers can be beneficially used.

4.3. D MELT FLOW STUDIES OF PP/HDPE BLENDS

The Melt Flow Index (MFI) test is used to characterize polymer melts. It is in effect a single point ram extruder test using standard testing conditions. Melt flow studies were conducted on PP/HDPE blends by determining the Melt Flow Index (MFI) of the various blend compositions.

The polymer blend sample was heated in the barrel and then extruded through a standard die using a standard weight (2.15 kg) on the piston, and the weight (in grams) of polymer blend extruded in 10 minutes is quoted as the melt flow index (MFI) of the blend.

The Melt Flow Index (MFI) of PP/HDPE blends at four different compositions were obtained from Melt flow indexer. Variation in MFI values for the various blend compositions is shown in Fig. 4.15.

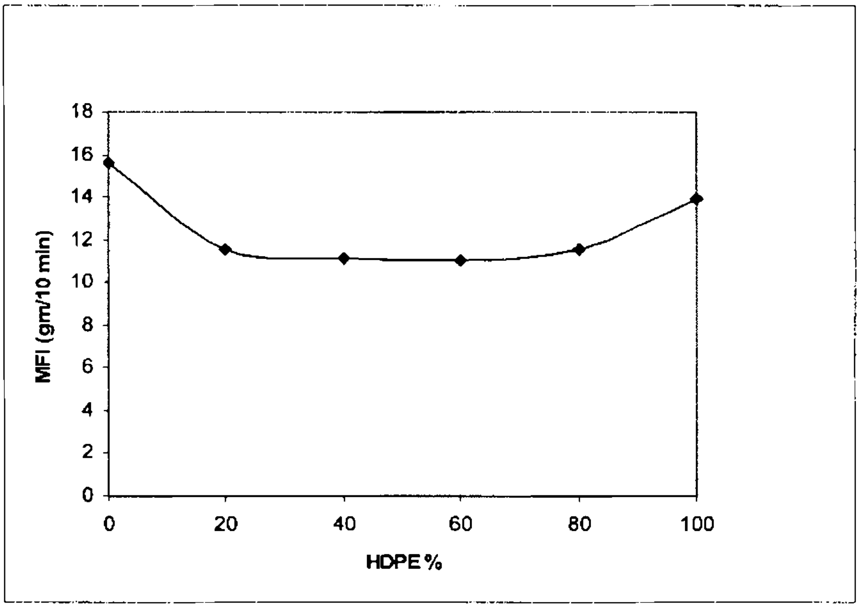

Figure 4.15: Variation of Melt Flow Index with composition for PP/HDPE blends containing 6% calcium carbonate.

It is observed that the MFI values of the blends are lower than that of its constituents.

In the case of high viscosity incompatable polymers, the blend may have significantly lower viscosity than any of the constituents. This behaviour is attributed to the weakness of shear planes at the interface between the phases [61].

4.4 CONCLUSIONS

The present study was undertaken to investigate the mechanical behaviour of the two of the most commonly used thermoplastics, high density polyethylene and polypropylene and their blends.

The study mainly concentrated on the fracture behaviour and notch sensitivity of the blends to explore their utility in critical applications.

HDPE/PP blends form a synergistic system as far as mechanical behaviour is concerned and the blend composition can be selected based on the requirement.

The mechanical properties of HDPE/PP blends can be optimized by selecting proper blend compositions.

The main thrust of the study was to investigate how properly selected modifiers could alter and improve the fracture behaviour and notch sensitivity of the blends. The following conclusions could be drawn from the study.

1. HDPE/PP blends form a synergistic system as far as mechanical behaviour is concerned and the blend composition can be selected based on the requirement. The mechanical properties of PP / HDPE blends can be optimized by selecting proper blend compositions.

2. Particulate filler like calcium carbonate can be efficiently used for making the mechanical behaviour more stable and for cost reduction. Even though the modulus marginally decreases with filler content, the proper filler content can induce a stable mechanical behaviour with some improvement in maximum strain. However the

resistance to notch sensitivity of the blends is marginally lower in the presence of a particulate filler like calcium carbonate.

3. An elastomeric modifier like EPDM can produce a better stability of the mechanical behaviour. A low concentration of EPDM is sufficient to effect such a change. Hence the reduction in moduli is only minimal while there is some increase in the elongation at break. The outstanding advantage of such a modifier is the improvement in the resistance to notch sensitivity of the blends.

4. The study shows that a judicious selection of modifiers can improve the fracture behaviour and notch sensitivity of polymers and their blends and hence help these materials to be used for critical applications.

CHAPTER 5

FRACTURE BEHAVIOUR OF PS/HIPS BLENDS

5.1 INTRODUCTION

Polymers in various forms are widely used in engineering. They can be either amorphous or semicrystalline. A semicrystalline polymer has an amorphous and a crystalline part. The part, which is crystalline, has a more or less ordered structure in which the chains of the polymer are often folded in a uniform random fashion. The mechanical properties of semicrystalline polymers are strongly determined by the crystallites, which usually enhance their stiffness. Amorphous polymers are either very brittle or very tough. In all cases, the occurrence of fracture is a major concern and this is reflected in the large number of tests which are used to simulate the various conditions which promote failure. The use of such tests as standards and quality controls is designed to avoid failures in practice and quite reasonable success is achieved in this regard. The tests are designed to include enough of the circumstances of a real situation to give a realistic measure of how the material will perform in practice.

This section aims to study the fracture behaviour of polymer blends prepared by melt blending of an amorphous, brittle polymer Polystyrene (PS) with a ductile polymer High Impact Poly Styrene (HIPS).

5 A. TENSILE CHARACTERISTICS OF PS/HIPS BLENDS

5A.1 EXPERINENTAL

Blends of PS and HIPS were prepared in the composition of 80% PS/20% HIPS, 60% PS/40% HIPS, 40% PS/60% HIPS and 20% PS/80% HIPS. The blends were prepared by melt mixing the two polymers in the above composition using a Rheomix 600 P attached to Thermo Haake Rheocord 300 set at a chamber temperature of 180^0 C. The rotor speed was set at 30 rpm. The torque-time curves for melt mixing of different polymer mixtures were taken and plotted. A mixing time of 8 minutes was fixed since the torque became steady within that time interval.

The blends so obtained were subjected to injection moulding using a semi automatic injection moulding machine (Texair JIM –1H) at 180^0 C. Dumbell specimens prepared (according to ASTM D 638 specification) were used to study the tensile properties. Specimens for conducting the notch sensitivity test were notched to 1 mm depth before testing.

5A.2 RESULTS AND DISCUSSION

5A.2.1 Torque Studies

The Torque vs. mixing time curves of PS/HIPS blends at various blend compositions are shown in Fig.5.1.

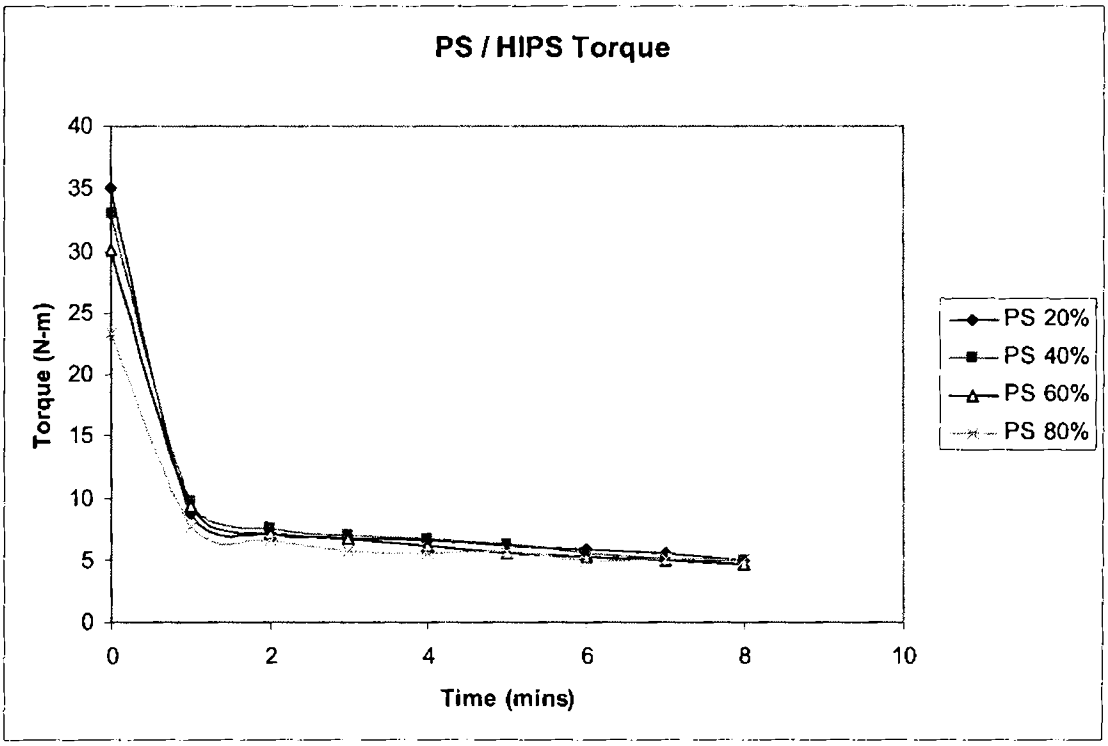

Figure 5.1: Torque-Time graph of various PS/HIPS blend compositions.

The initial torque for the mixture is found to be high which decreases and becomes steady within 4 minutes. This trend is seen for all the blend compositions. The initial high value of the torque is due to the solid nature of the polymers which becomes soft on heating.

When the four blend combinations are considered (80% PS/20% HIPS, 60% PS/40% HIPS, 40% PS/60% HIPS and 20% PS/80% HIPS), it is observed that the Torque-Time curves are different for different blend compositions. As torque stabilized towards completion of mixing, HIPS rich blends show higher torque values compared to PS rich blends.

The stabilization of torque towards the end of mixing indicates that there is no degradation taking place during melt mixing.

5A.2.2 Tensile strength of PS / HIPS blends

The tensile parameters were evaluated at low speeds (5 mm/min and 10 mm/min) till the specimens failed under tensile load.

Fig 5.2 shows the variation in tensile strength of PS / HIPS blends with the blend composition at a testing speed of 5 mm/min.

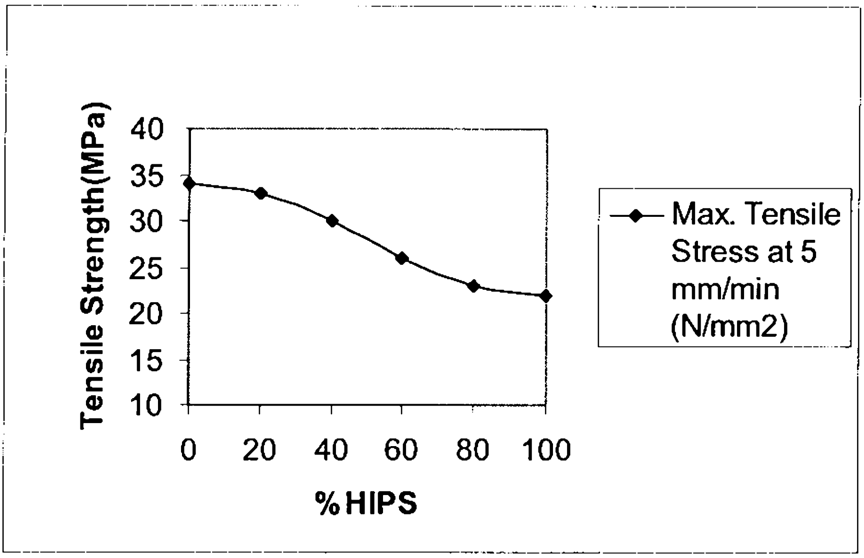

Figure 5.2: Variation in tensile strength of PS/HIPS blends with blend composition at a testing speed of 5 mm/min.

The tensile strength of polystyrene samples prepared by melt blending is found to be 34 MPa (N/mm^2). It is found to change with the addition of HIPS. The tensile strength gradually drops with the increase in HIPS content in the blends. The rate of change in tensile strength is quite slow and gradual initially and this continues up to about 40 % HIPS content in the blends (the value changes from 34 MPa to 30 MPa). The drop in tensile strength becomes more intense as HIPS content exceeds 40 %. This trend continues further up to 100% HIPS content when the tensile strength value reaches 22 MPa.

The variation of tensile strength with HIPS content at a higher strain rate of 10 mm/min is shown in Fig 5.3.

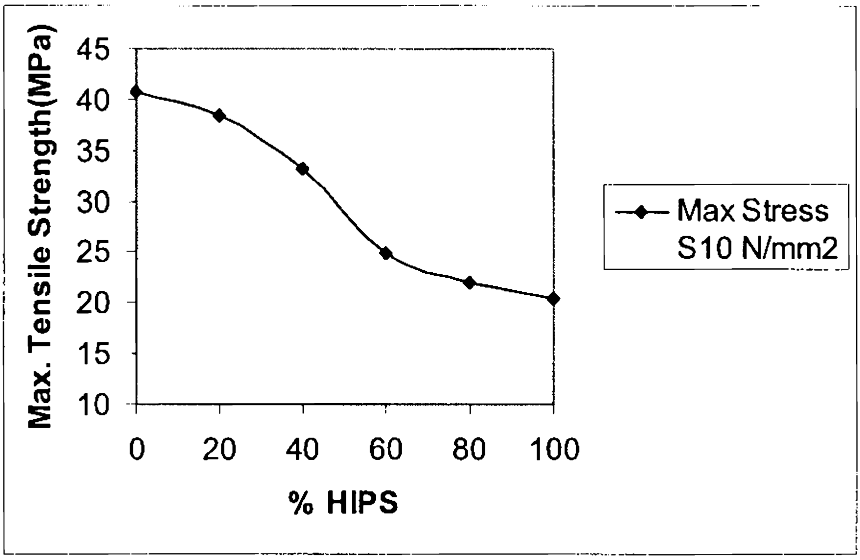

Figure 5.3: Variation in tensile strength of PS/HIPS blends with blend composition at a testing speed of 10 mm/min

It is observed that PS / HIPS blends show higher tensile strength for all the blend compositions than that shown at 5 mm/min. The range is from 40.7MPa to 20.5MPa. Moreover, during the tests, brittle fracture is noted for PS rich blends. The phenomenon of fall in tensile strength with increase in HIPS content is noted at this speed also. The drop in tensile strength is also found to be more rapid for blends having HIPS content more than 40 %. Fig. 5.4 shows a comparison of the variation in tensile strength at the two different testing speeds.

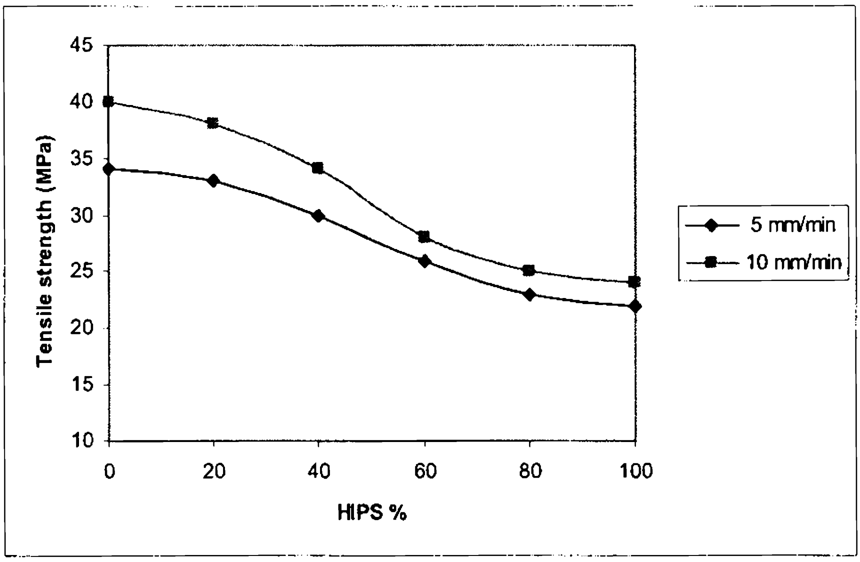

Figure 5.4: Comparison of variation in tensile strength of PS/HIPS blends with blend composition at the two different testing speeds.

5A.2.3 Elongation at break

The variation of elongation at break with the composition of PS / HIPS blends for a testing speed of 5 mm/min is shown in Fig.5.5.

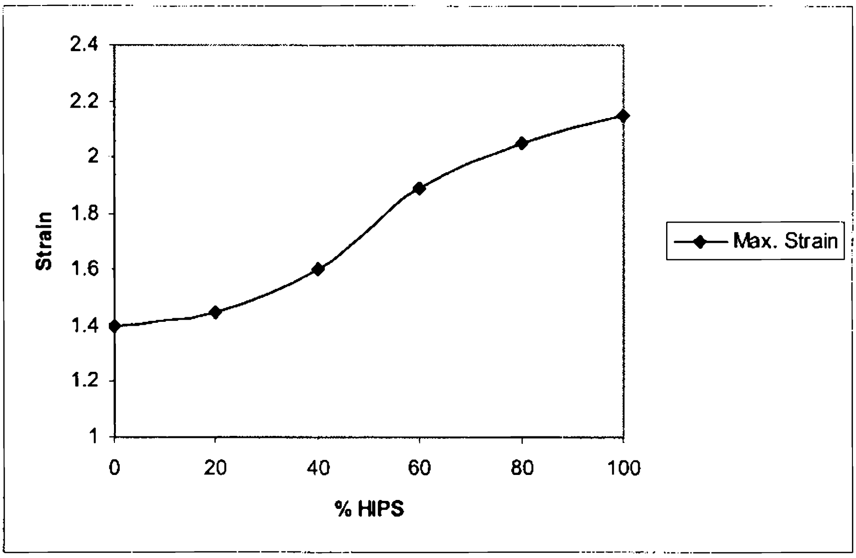

Figure 5.5: Variation of elongation at break with blend composition for PS/HIPS blends at a testing speed of 5 mm/min.

The elongation at break (maximum strain) of PS is found to be 1.4 and that of HIPS 2.15. It is seen that the maximum strain (elongation at break) increases with the content of HIPS in the blend. The ability of specimens to yield before failure increases remarkably when the HIPS content in the blends exceeds 40 %.

The variation of elongation at break with blend composition at a higher testing speed of 10 mm/min is shown in Fig.5.6.

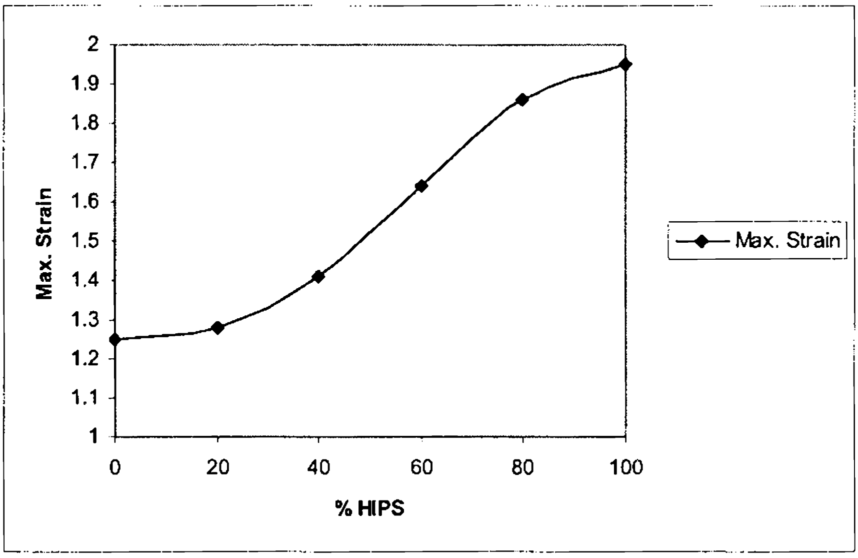

Figure 5.6: Variation of elongation at break with blend composition for PS/HIPS blends at a testing speed of 10 mm/min.

The elongation at break of PS is found to be 1.25. It is seen that the maximum elongation at break increases with HIPS content in the blend. Its value becomes 1.41 at 40% HIPS and thereafter shows an increasing trend reaching a value of 1.95 at 100% HIPS. The ability of specimens to yield before failure increases remarkably when the HIPS content in the blends exceeds 40 %.

Even though the strain values are slightly lower than those that at 5 mm/min, the trend of rapid increase in elongation at break is observed at this speed also, especially when the HIPS content exceeds 40%.

A comparison of the variation in elongation at break at the two different testing speeds is shown in Fig.5.7.

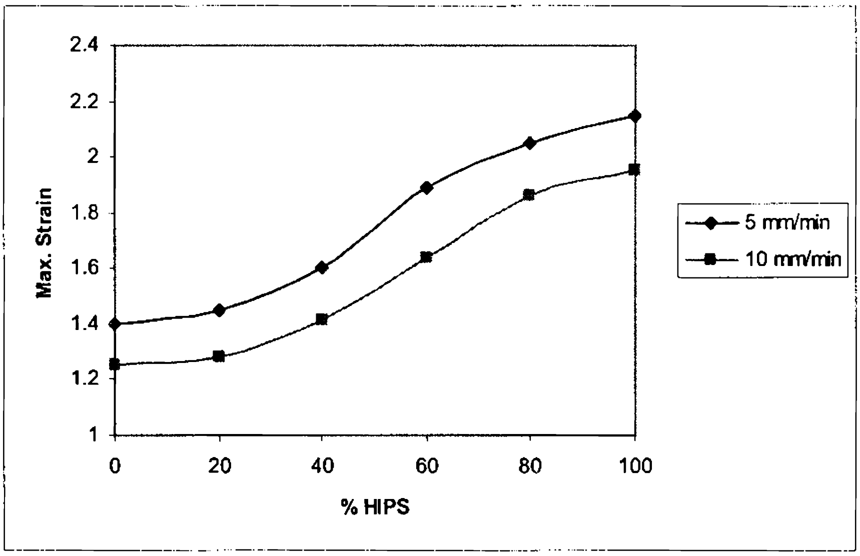

Figure 5.7: Comparison of variation in elongation at break of PS/HIPS blends with blend composition at the two different testing speeds.

5. A 2.4 Tensile Modulus

The variation of tensile modulus at various levels of HIPS content in PS / HIPS blends for a testing speed of 5 mm/min is shown in Fig.5.8.

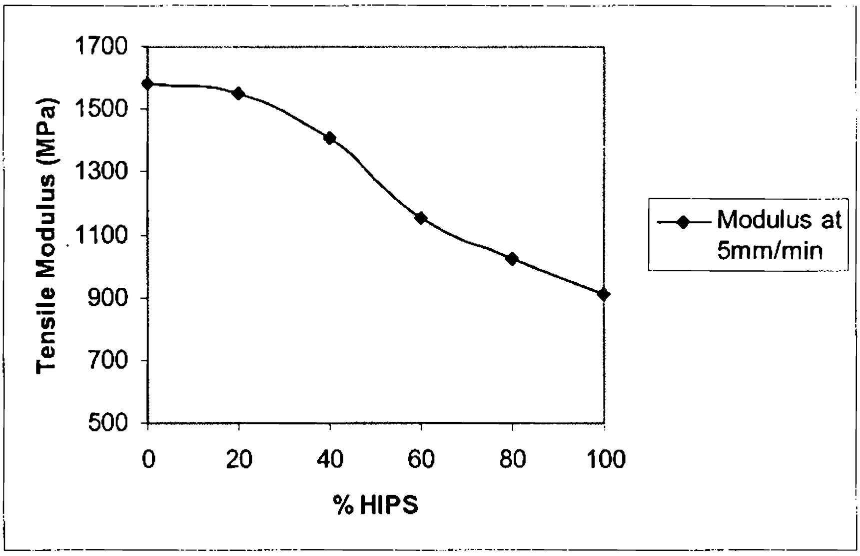

Figure 5.8: Variation of tensile modulus with blend composition for PS/HIPS blends at a testing speed of 5 mm/min.

The tensile modulus is found to drop from 1580 MPa to 1410 MPa for change in HIPS content from 0 % to 40 %. For blends with higher content of HIPS, a rapid drop in modulus is noted, finally attaining a value of 910 MPa.

The plot of variation in tensile modulus at a higher strain rate of 10 mm/min is shown in Fig.5.9 for the various blend compositions.

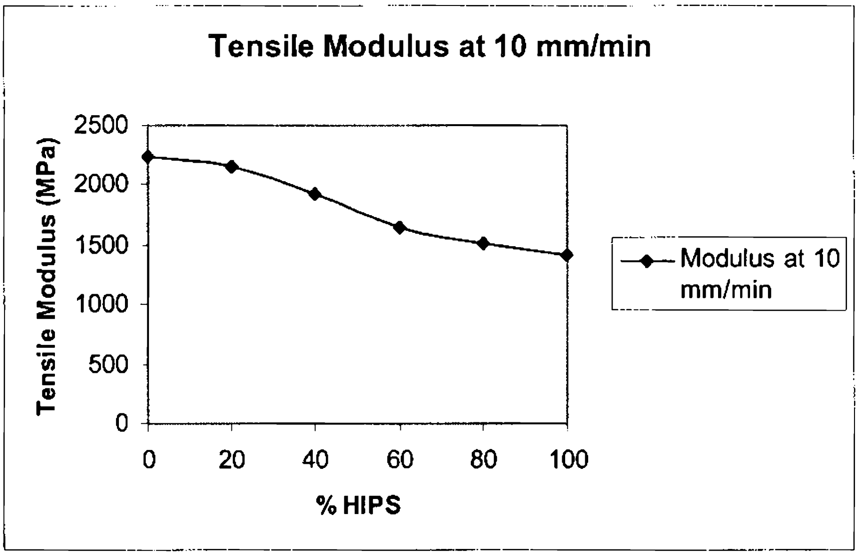

Figure 5.9: Variation of tensile modulus with blend composition for PS/HIPS blends at a testing speed of 10 mm/min.

Slightly higher values of modulli are obtained. During the tests, brittle fracture is observed for PS rich blends containing up to 40 % HIPS. Thereafter the fracture mode shifts to ductile fracture. Finally, the modulus is seen reaching a minimum value of 1410 MPa. A Comparison of variation in tensile modulus with blend composition at the two different testing speeds of 5 mm/min and 10 mm/min is shown in Fig. 5.10.

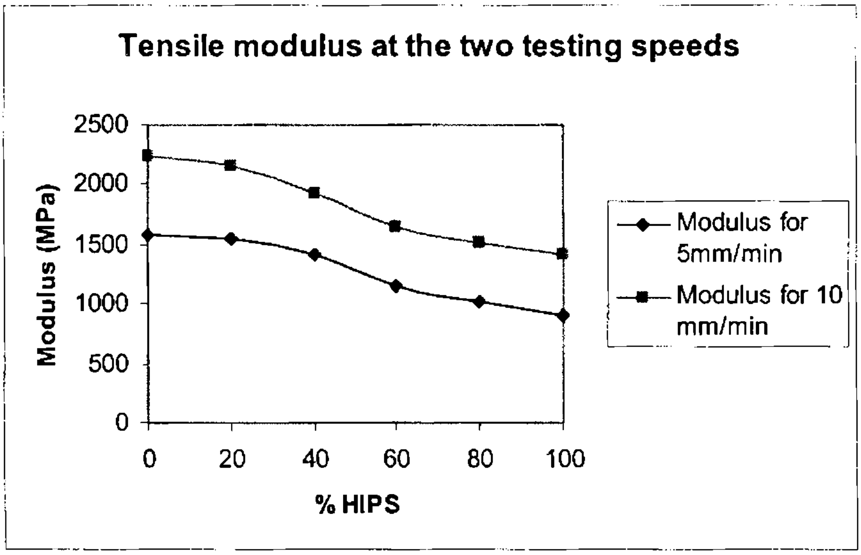

Figure 5.10: Comparison of variation of Tensile modulus with blend composition for PS/HIPS blends at the two testing speeds.

5. B NOTCHED TENSILE TESTS

Blends of PS and HIPS were prepared in the composition of 80% PS/20% HIPS, 60% PS/40% HIPS, 40% PS/60% HIPS and 20% PS/80% HIPS. The blends so obtained were subjected to injection moulding in a semi automatic injection moulding machine (Texair JIM -1H) at 180^0 C. Dumbell specimens prepared (according to ASTM D 638 specification) were centrally notched to 1 mm depth for conducting notch sensitivity tests.

The notched tensile test was conducted at two different speeds (5 mm/min and 10 mm/min) till the specimens failed under tensile load. Tensile parameters were evaluated for the various blend compositions.

5B.1 NOTCHED TENSILE STRENGTH

The variation in tensile strength with blend composition for notched PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min. is shown in Fig. 5.11.

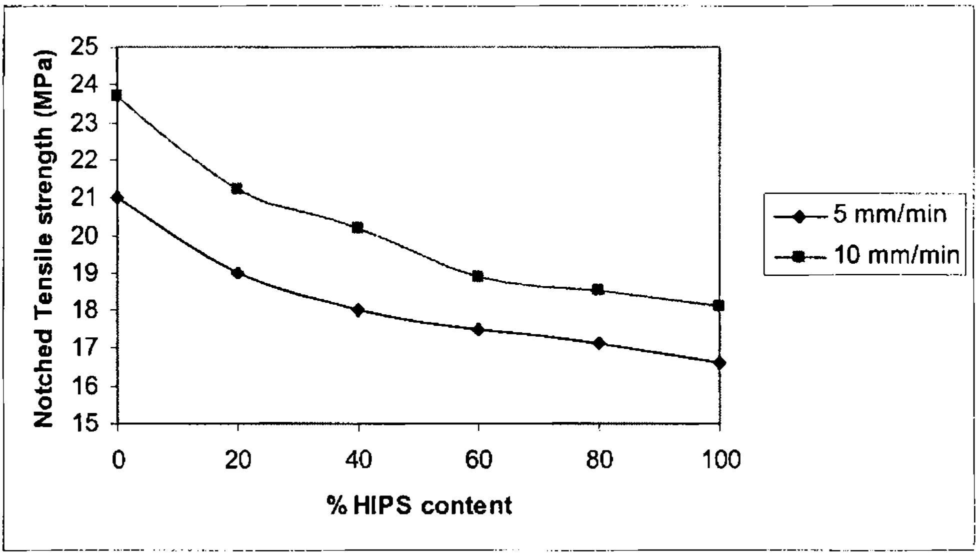

Figure 5.11: Variation in tensile strength with blend composition for notched PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min.

At a strain rate of 5 mm/min, the tensile strength of notched polystyrene samples is found to be 21 MPa (N/mm^2). It is found to change with the addition of HIPS. The tensile strength of the blends drops with the increase in HIPS content. When the HIPS content reaches 40%, its value becomes 18 MPa. As the HIPS content exceeds 40 %, this trend becomes more gradual and continues further up to 100% when it becomes 16.6 MPa.

The plot for 10 mm/min strain rate shown in Fig 5.11 also shows the same trend but higher values of notched tensile strength are noted for all the blend compositions.

5B.2 ELONGATION AT BREAK

The elongation at break may be taken as an index of resistance to notch sensitivity. Figure 5.12 shows the variation in elongation at break for notched PS/HIPS blend samples at the two testing speeds.

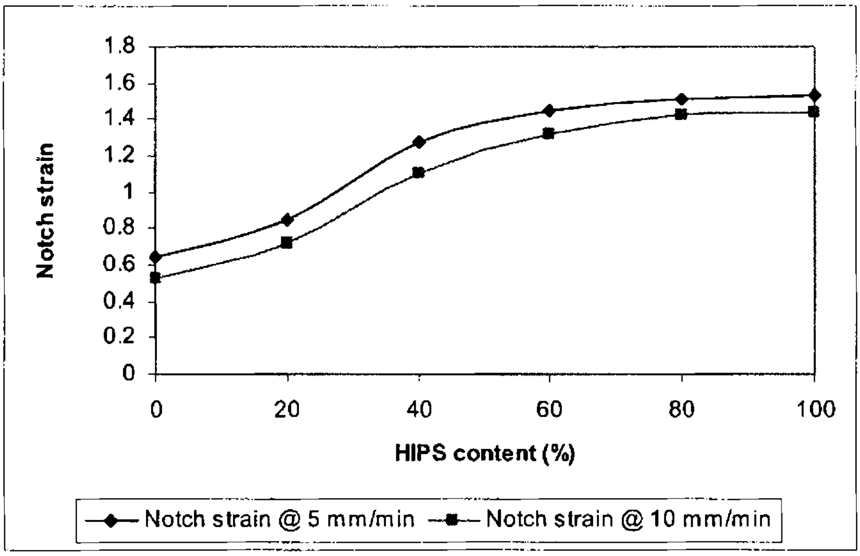

Figure 5.12: Variation in elongation at break with blend composition for notched PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min.

For notched tensile tests at 5 mm/min, it is seen that the elongation at break increases with HIPS content in the blend. Its value changes from 0.64 at 0% HIPS content to 1.28 at 40% HIPS content. The value of elongation at break thereafter increases with HIPS content and finally reaches 1.53. The ability of notched specimens to yield before failure increases remarkably when the HIPS content in the blends exceeds 40 %. Notched tensile tests at a higher speed of 10 mm/min also show the same trend, but lower elongation values were obtained as shown in the figure.

5B.3 NOTCHED MODULUS

The variation of tensile modulus for notched blend samples at various levels of HIPS content for testing speeds of 5 mm/min and 10 mm/min is shown in Fig.5.13.

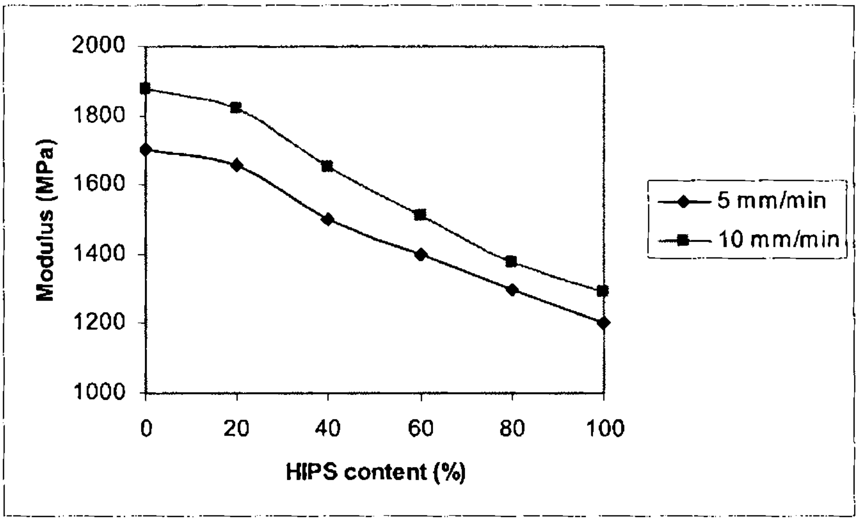

Figure 5.13: Variation in tensile modulus with blend composition for notched PS/HIPS blend samples at the two different testing speeds of 5 mm/min and 10 mm/min.

At 5 mm/min speed, the tensile modulus is found to drop from 1705 MPa to 1502 MPa for change in HIPS content from 0 % to 40 %. For blends with higher content of HIPS, a rapid drop in modulus is noted, finally attaining a value of 1200 MPa.

When the strain rate on the notched specimens is increased by changing the testing speed to 10 mm/min, higher values of tensile modulus are observed. When HIPS content in the blend is increased from 0% to 40%, the modulus is found to change from 1876 MPa to 1652 MPa. Further addition of HIPS in the blend results in a rapid fall of tensile modulus, finally attaining a value of 1294 MPa.

The tensile behaviour of unnotched and notched Polystyrene / High Impact Polystyrene blends is evaluated at slow speed. The tensile modulus, tensile strength and maximum strain remain more or less constant up to about 40% HIPS content and thereafter show a drastic change indicating changes in the morphology of the blend at this composition. The notched specimens also follow a comparable trend even though the notch sensitivity is seen high for PS rich blends containing up to 40% HIPS. The notch sensitivity marginally decreases with HIPS content. The figures suggest that PS / HIPS blends containing more than 40% of HIPS fail in ductile mode.

5C. IMPACT CHARACTERISTICS OF PS/HIPS BLENDS

5C.1 EXPERIMENTAL

The blends of PS and HIPS were prepared in the composition of 80% PS/20% HIPS, 60% PS/40% HIPS, 40% PS/60% HIPS and 20% PS/80% HIPS by melt mixing the two polymers. A computerized blending machine Rheomix 600 P attached to Thermo Haake Rheocord 300 set at a chamber temperature of 180^0 C was used for the melt blending process. The rotor speed was set at 30 rpm.

The blends so obtained were subjected to injection moulding using a semi automatic injection moulding machine (Texair JIM –1H) at 180^0 C. The bars so prepared were loaded in a RESIL impact testing machine and impact strength was measured.

For applying impact load, a 4J hammer was used. Hammer striking velocity was maintained at 3.46 m/second. The test was conducted in the Izod configuration.

5C.2 RESULTS AND DISCUSSION

The impact characteristics of PS/HIPS blends were studied with the aid of injection moulded specimens.
The impact characteristics obtained are,

1. Impact Strength
2. Energy absorbed by the test specimen
3. Resilience

5C.2.1 Impact strength

The variation of impact strength with the composition of PS/HIPS blends is shown in Fig.5.14.

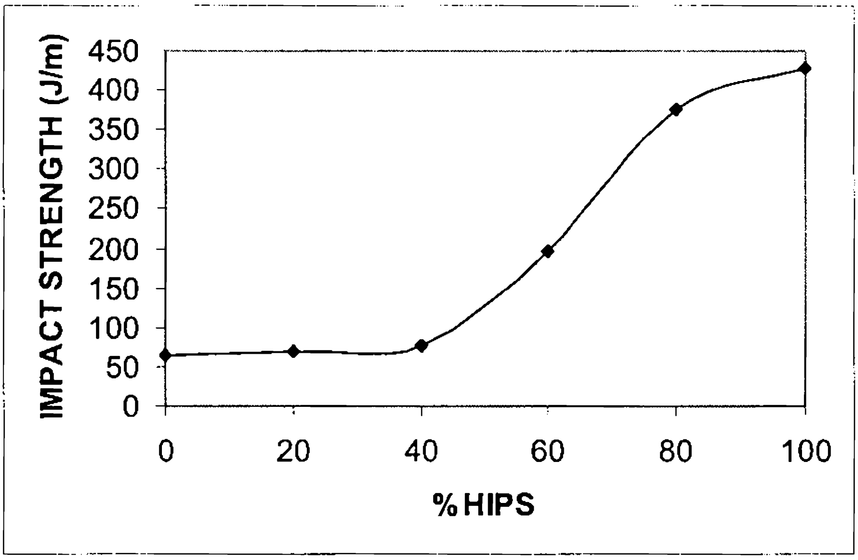

Figure 5.14: Variation of Impact strength with blend composition for PS/HIPS blends.

When the HIPS content varies from 0% to 40%, much change in impact strength is not observed and its value changes from 65.78 J/m to 76.67 J/m only. As the HIPS content in the blend exceeds 40%, a remarkable increase in impact strength is observed, attaining the values 376 J/m and 428 J/m at 80% and 100% HIPS content in the blends.

5C.2.2 Impact energy absorbed

The variation of impact energy absorbed with the blend composition. Is shown in Fig. 5.15 .

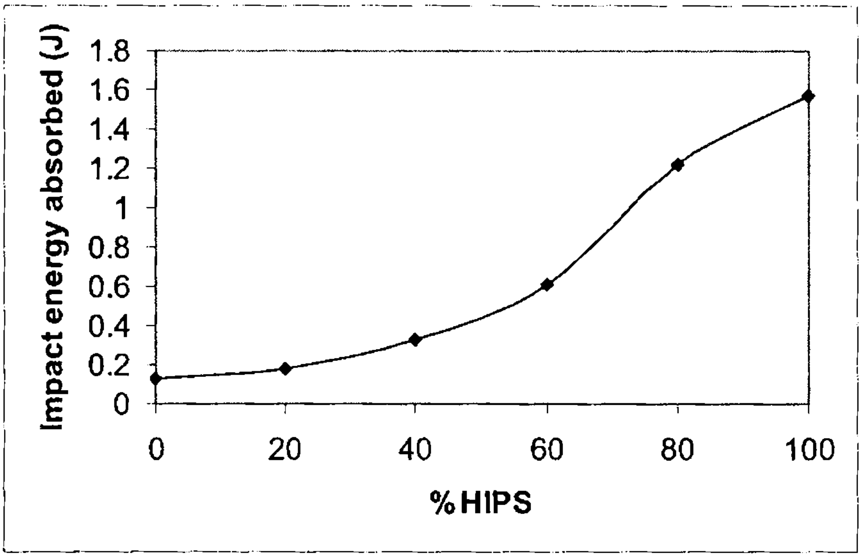

Figure 5.15: Variation of Impact energy absorbed with blend composition for PS/HIPS blends.

Much change is not observed in the impact energy of the blend as HIPS content is increased upto 40%. Its value gradually changes from 0.131 J to 0.33 J during this period. When HIPS content in the blend exceeds 40%, a remarkable increase is seen in the impact energy absorbed, attaining the values 1.22 J and 1.57 J at 80% and 100% HIPS content in the blends.

5C.2.3 Impact toughness

Impact toughness which is a measure of resilience is plotted against the various blend composition values as shown in Fig. 5.16.

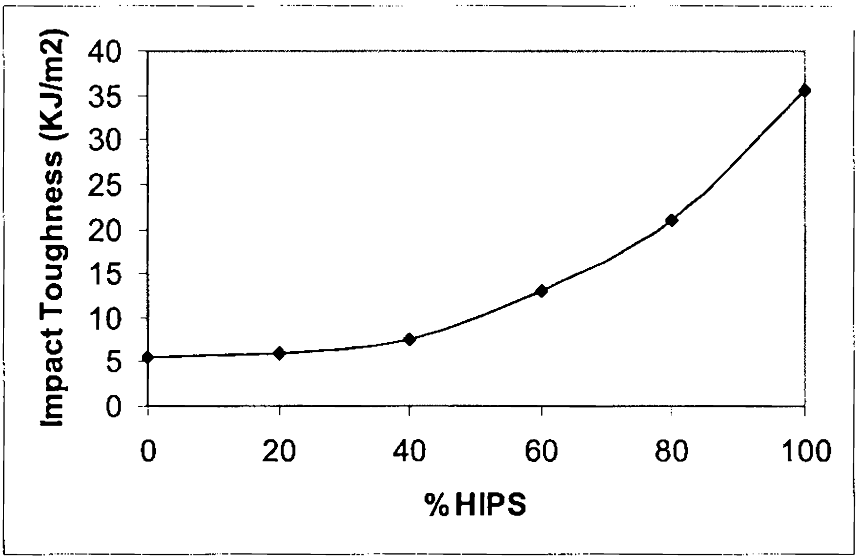

Figure 5.16: Variation of Impact toughness with blend composition for PS/HIPS blends.

The value of impact toughness changes from 5.48 KJ/m^2 to 7.59 KJ/m^2 for a change in HIPS content from 0% to 40%. When the HIPS content in exceeds this value, impact toughness is found to increase at a faster rate. It attains values 21.08 KJ/m^2 and 35.6 KJ/m^2 at 80% and 100% HIPS content in the blend.

5D. FLEXURAL CHARACTERISTICS OF PS/HIPS BLENDS

The flexural properties of the specimens were determined using a computerised universal testing machine (Schimadzu UTM). The simply supported beam configuration was used with a span of 50 mm.

5D.1 EXPERIMENTAL

The blends prepared by melt mixing PS and HIPS in the proportions 80% PS/20% HIPS, 60% PS/40% HIPS, 40% PS/60% HIPS and 20% PS/80% HIPS were subjected to injection moulding in a semi automatic injection moulding machine. The bars so prepared were loaded on a Schmadzu AG II Universal Testing Machine and subjected to three point bending test at the two different testing speeds of 5 mm/min and 10 mm/min.

5D.2 RESULTS AND DISCUSSION

5D.2.1 Flexural strength

Rectangular specimens prepared from blends by injection moulding were subjected to 3 point bending test on a Schmadzu AG II Universal Testing Machine at the two different testing speeds and the results were compared.

The variation of flexural strength with blend composition is shown in Fig. 5.17.

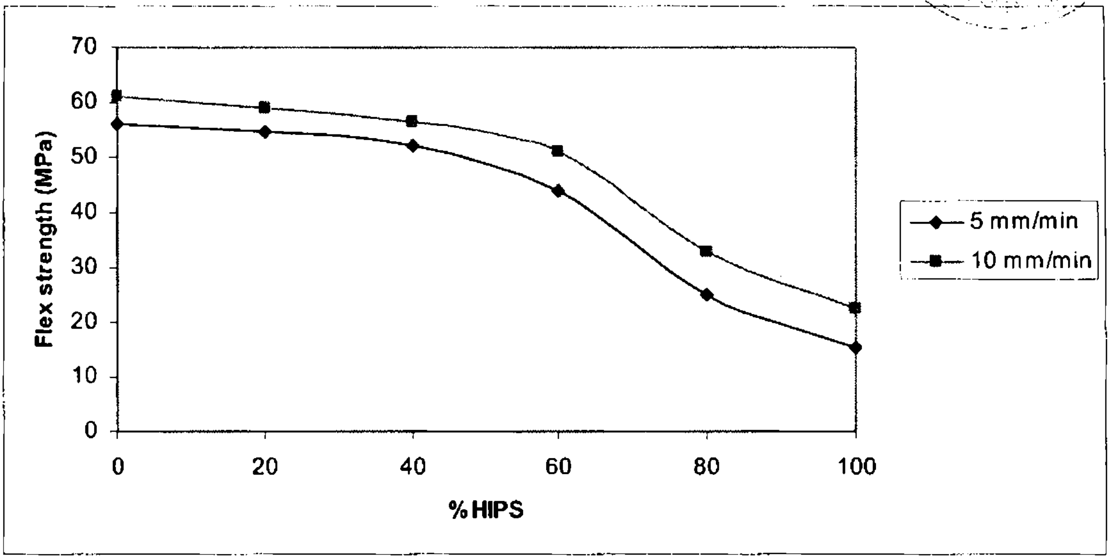

Figure 5.17: Variation in Flexural strength with the blend composition for PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min.

The flexural strength is found to drop with the increase in HIPS content. At a testing speed of 5 mm/min, its value changes from 56.2 MPa to 52.13 MPa as the HIPS content is increased from 0% to 40%. Further addition of HIPS shows a sharp drop in the flexural strength, finally reaching a value of 15.42 MPa at 100% HIPS content in the blend. Higher values of flexural strength are obtained when the speed is increased to 12 mm/min. But, the same trend of faster drop is observed in flexural strength values as HIPS content is increased beyond 40%.

5D.2.2 Flexural strain

The variation in flexural strain with blend composition is shown in Fig. 5.18.

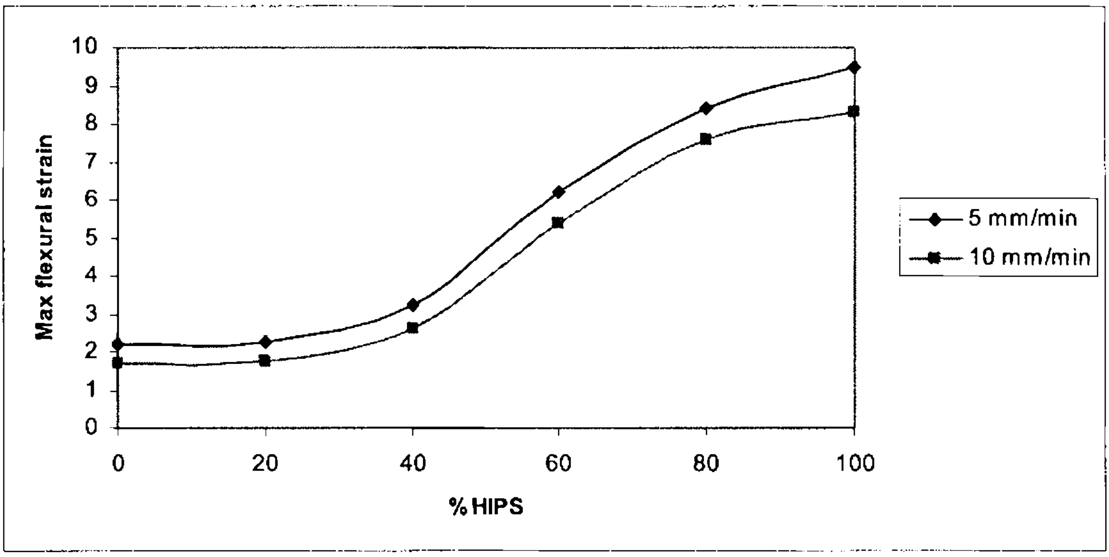

Figure 5.18: Variation in Flexural strain with the blend composition for PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min.

The flexural strain remains more or less steady upto about 40% HIPS content in the blend. As the HIPS content is increased beyond this value, a remarkable change is observed in flexural strain and its value increases from 3.24% to 9.5% by the time the HIPS content reaches 100% in the blend. This trend which is observed at 5 mm/min is seen for the higher testing speed of 10 mm/min also, but lower strain values are obtained.

5D.2.3 Energy absorbed

The amount of energy absorbed by the specimen upto the point of failure gives an important indication about its toughness behaviour. In the case of PS/HIPS blends under investigation, the flexural energy absorbed by the specimens is plotted against the corresponding blend compositions (Fig. 5.19).

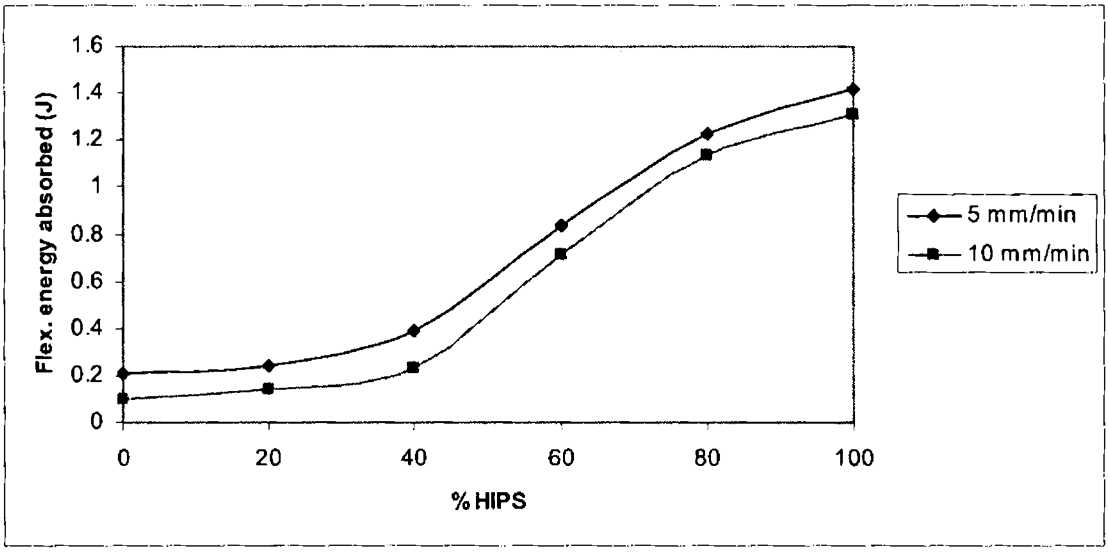

Figure 5.19: Variation in Flexural energy absorbed with the blend composition for PS/HIPS blend samples at testing speeds of 5 mm/min and 10 mm/min.

It is seen that the amount of energy absorbed by the specimens is lower at the testing speed of 10 mm/min than at 5 mm/min for all the blend compositions.

At the testing speed of 5 mm/min, only a slight increase is noted in the energy absorbed by the specimens as the HIPS content is increased upto 40% (0.21 J to o.39 J). Further addition of HIPS shows a remarkable increase in the energy absorbed which changes from 0.39 J at 40% HIPS to 1.42 J at 100% HIPS. Flexural test at the higher speed of 12 mm/min also follows the same trend as shown with slightly lower values for the various blend compositions.

Plot of the Stress- Strain curves obtained during the flexure test of PS/HIPS blends is shown in Fig.5.20.

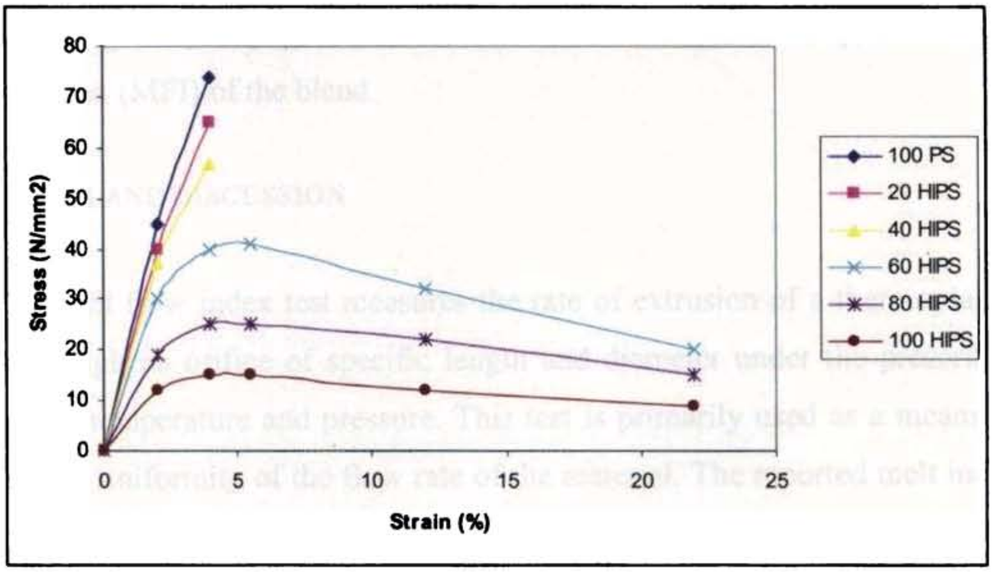

Figure 5.20: Stress-Strain curves for PS/HIPS blends obtained during flexure test.

From the Stress- Strain curves, it is observed that the elongation at break appreciably increases as the HIPS content exceeds 40% in the blends. This indicates their ductile mode of failure whereas high flexural strength and lower elongation in PS rich blends suggest their brittle failure mode.

5 E. MELT FLOW STUDIES OF PS/HIPS BLENDS

The Melt Flow Index (MFI) test is used to characterize polymer melts. It is in effect a single point ram extruder test using standard testing conditions. Melt flow studies were conducted on PS/HIPS blends by determining the Melt Flow Index (MFI) of the various blend compositions.

The polymer blend sample was heated in the barrel (to 180^0 C)and then extruded through a standard die using a standard weight (5 kg) on the piston, and the weight (in grams) of polymer blend extruded in 10 minutes is quoted as the melt flow index (MFI) of the blend.

5E .1 RESULTS AND DISCUSSION

The melt flow index test measures the rate of extrusion of a thermoplastic material through an orifice of specific length and diameter under the prescribed conditions of temperature and pressure. This test is primarily used as a means of measuring the uniformity of the flow rate of the material. The reported melt index values help to distinguish between the different grades of a polymer. A high molecular weight material is more resistant to flow than a low molecular weight material.

Melt flow index of PS/HIPS blends of four different compositions namely 80% PS / 20%HIPS; 60% PS / 40%HIPS; 40% PS / 60%HIPS and 20% PS / 80%HIPS were obtained from Melt flow indexer at a temperature of 180^0 C.
Variation in MFI values for the various blend compositions is shown in Fig 5.21.

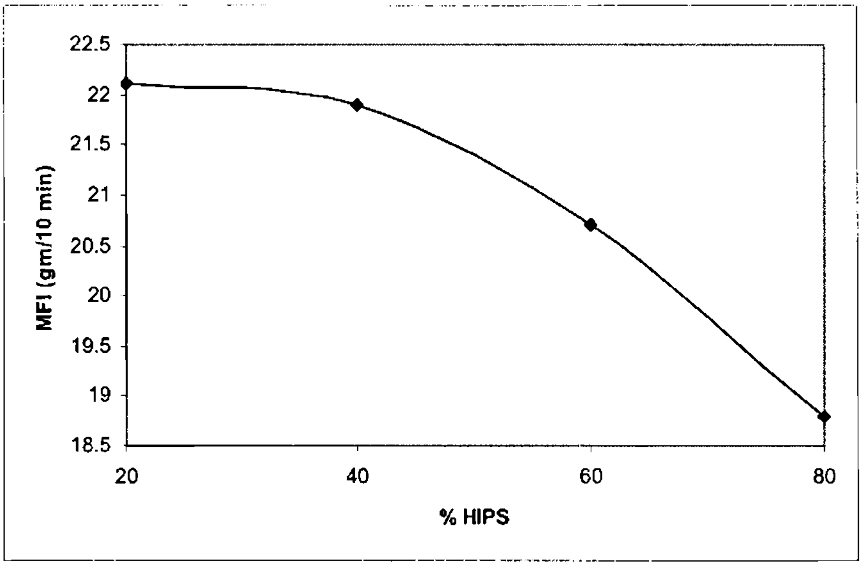

Figure 5.21: Variation of Melt Flow Index for PS/HIPS blends at 180^0 C.

The MFI of 80% PS/20%HIPS blend is obtained as 22.1 gm/10 min. When the HIPS content is increased to 40% as in 60% PS / 40%HIPS blend, the MFI value obtained is 21.9gm/10 min. This reducing trend in MFI was observed for the other blend combinations also which are richer in HIPS content like 20.7gm/10 min for 40% PS / 60%HIPS and 18.8 gm/10 min for 20% PS / 80%HIPS blends.

It is observed that MFI values show a decreasing trend with increase in content of HIPS in the blend samples.

The Melt Flow Index of polymer blends depends upon interfacial adhesion, interfacial thickness and the characteristics of the components forming the blend. When shear stress is applied on polymer blends, there will be interlayer slip along with orientation and disentanglement. When shear stress is applied, the blend undergoes elongational flow. If the interface is strong, the deformation of the dispersed phase will be effectively transferred to the continuous phase. If the interface is weak, interlayer slip occurs.

The psuedoplastic behaviour of a polymer is due to the random and entangled nature of polymer chains [62]. The knowledge of rheological properties of the melt and the blend morphology are important to control the processing parameters for the desired end use applications [63].

The reduction in MFI of polymer blends indicates an increase of shear viscosity. This is probably due to the fact that both phases in a polymer blend have an elastic response and can store a part of the elastic energy supplied to them by the testing apparatus. But discrete domains would dissipate less energy while flowing in the apparatus than the continuous phase that wets the walls. They will offer less resistance to flow and hence will lower viscosity and will be much lower if the dispersed phase gets deformed by the flow [64, 65]. In any polymer melt, flow occurs when polymer molecules slide past each other. The ease of flow depends upon the mobility of moleculer chains and the forces or entanglements holding the molecules together. The compatibility or miscibility between phases is an important factor affecting the rheological characteristics of polymer melts. The dispersion and distribution of the components in the blends as well as the mixing conditions are related. The reduced occurrence of interlayer slip and consequent increase in viscosity may be contributing to the reduced Melt Flow Index of PS/HIPS blends rich in HIPS content.

5 F. RESULTS AND DISCUSSION

Two major mechanisms prevail in determining the fracture resistance of polymeric materials [58]. One primary contribution comes from the energy required to extend polymer chains, or some subsection thereof to the point of rupture. The deformation and fracture energy can be evaluated by two major experiments – stress-strain and impact resistance. In a stress-strain experiment, the sample is elongated until it breaks. The stress is recorded as a function of elongation. This measurement is relatively slow to the order of a few mm per minute. Impact strength measures the material's resistance to a sharp blow and by definition is a faster experiment. In both experiments, energy is absorbed within the sample by viscoelastic deformation of the polymer chains and finally by the creation of new surface areas [59]. Energy may be absorbed by shear yielding, crazing or cracking.

The crack can grow through the polymer either by breaking the chains or by viscoelastic flow of one chain past the other or by a combination of both these processes. While chain scission is important in the deformation and fracture of many polymers, this micro mechanism normally consumes only a small fraction of the fracture energy but its appearance limits the extent of viscoelastic energy dissipation. Thus for tougher materials, chain scission should be delayed or avoided in favour of molecular relaxations [60].

The variation of tensile strength with the blend composition is given in Fig. 5.4. The tensile strength of PS is found to be 34 MPa and that of HIPS is found to be 22 MPa. The addition of HIPS to PS lowers the maximum tensile stress of the blends. The reduction in tensile strength was found to be greater for blends having more than 40% HIPS.

Notched tensile specimens failed under brittle mode and the tensile strength values were much lower than that of unnotched samples for all the blend compositions. This shows a high degree of notch sensitivity in PS / HIPS blends.

The tensile modulus and maximum strain remain more or less steady up to about 40% HIPS and thereafter show a drastic change indicating changes in the morphology of the blend at this composition. The notched specimens also follow a comparable trend even though the notch sensitivity marginally increases with HIPS content. The figures suggest that PS / HIPS blends containing more than 40% of HIPS fail in a ductile mode.

The tensile behaviour of unnotched and notched Polystyrene / High Impact Polystyrene blends was evaluated at slow speed. The tensile modulus, tensile strength and maximum strain remain more or less steady up to about 40% HIPS and thereafter show a drastic change indicating changes in the morphology of the blend at this composition. The notched specimens also follow a comparable trend even though the notch sensitivity is seen high for PS rich blends containing up to 40% HIPS. The notch sensitivity marginally decreases with HIPS content. It is observed that PS / HIPS blends containing more than 40% of HIPS fail in ductile mode.

5.2. CONCLUSIONS

1. The stabilization of torque towards the end of melt blending indicates that there is no degradation taking place during melt mixing.

2. The fracture behaviour of PS/HIPS blends have been investigated by conducting tensile, impact and flexure tests at the various blend compositions.
3. The tests were used to simulate the various conditions which promote failure.
4. Brittle fracture is noted for blends containing upto 40% HIPS. Further addition of HIPS resulted in a transition from brittle to ductile mode of failure.
5. Notch sensitivity is seen higher for PS rich blends and lower for HIPS rich blends.

6. Marginal increase in notch sensitivity is observed as the strain rate is increased.
7. Energy absorbed by the specimens before fracture appreciably increased with the increase in HIPS content.
8. Melt flow studies indicate reduction in MFI values of blends with increase in HIPS content.

CHAPTER 6

PHOTOELASTIC INVESTIGATIONS

6.1 INTRODUCTION

Photoelasticity is an experimental method to determine stress distribution in a material. The method is mostly used in cases where mathematical methods become quite cumbersome. Unlike the analytical methods of stress determination, photoelasticity gives a fairly accurate picture of stress distribution even around abrupt discontinuities in a material. The method serves as an important tool for determining the critical stress points in a material and is often used for determining stress concentration factors in irregular geometries.

Photoelasticity is based on the property of birefringence, which is exhibited by certain transparent materials. Birefringence is a property by virtue of which a ray of light passing through a birefringent material experiences two refractive indices. The property of birefringence or double refraction is exhibited by many optical crystals. But photoelastic materials exhibit the property of birefringence only on the application of stress and the magnitude of the refractive indices at each point in the material is directly related to the state of stress at that point [66]. Thus, the first task is to develop a model made out of such materials. The model has a similar geometry to that of the structure on which stress analysis is to be performed. This ensures that the state of stress in the model is similar to state of stress in the structure.

When a ray of plane polarized light is passed through a photoelastic material, it gets resolved along two principal stress directions and each of these components experience different refractive indices. The difference in the refractive indices leads to a relative phase retardation between the two component waves. The magnitude of the relative retardation is given by the Stress Optic Law:

$$R = Ct\,(\sigma_{11} - \sigma_{22})$$

Where R is the induced retardation, C is the stress optic coefficient, t is the specimen thickness, σ_{11} is the first principal stress, and σ_{22} is the second principal stress.

The two waves are then brought together in a polariscope. The phenomenon of optical interference takes place and we get a fringe pattern, which depends on relative retardation. Thus, by studying the fringe pattern, one can determine the state of stress at various points in the material [67]. Isochromatics and Isoclinics are the two types of fringes observed in a plane polariscope [68].

Isochromatics are the locus of points along which the difference in the first and second principal stress remains the same. Thus, they are the lines which join the points with equal maximum shear stress magnitude. Isochromatic fringes are colourful and the fringe colour is related to the difference in principal stresses through the Stress – Optic Law. From the photoelastic stress pattern, Isochromatics provide qualitative information regarding stress distribution within the component.

Isoclinics are locus of points in the specimen along which the principal stresses are in the same direction. They are black in colour and are superimposed on the Isochromatic pattern. They occur whenever either principal stress direction coincides with the axis of polarization of the polarizer. Isoclinics provide information about the directions of principal stresses in the model and provide necessary information for solution of two – dimensional stress problem.

The fracture behaviour of PS/HIPS blends is proposed to be studied by making use of the principles of photoelasticity. This is proposed to be carried out by observing the fringe patterns created by optical interference as polarized light is made to pass through the transparent specimens having different blend compositions.

6.2 EXPERIMENTAL

6.2.1 SPECIMEN PREPARATION

PS / HIPS blends were prepared at various blend compositions in Thermo – Haake rheomix by melt mixing at 180^0 C. Specimens were prepared by injection moulding in Texair (JIM - 1H) injection moulding machine at 180^0 C. Dumbell specimens were prepared (according to ASTM D 638 specification) and these samples were used for photoelastic investigations of the various blend compositions.

6.2.2 EQUIPMENT AND PROCEDURE

A plane polariscope was used for the photoelastic investigations. The test specimens were placed between the polarisr and analyzer. A broad source of white light was used for illuminating the system. Plane polarized light from the polarizer was allowed to pass through the test specimens. The fringe patterns were observed through the analyzer. Isochromatic fringes with distinct colour patterns were visible for each PS/HIPS blend composition. The fringe patterns were photographed for conducting qualitative analysis.

6.3 RESULTS AND DISCUSSION

As plane polarized light was made to pass through the PS/HIPS blend specimens placed in the plane polariscope, colourful isochromatic fringes were observed.

The fringe pattern obtained for 100%PS / 0%HIPS blend composition is shown in Fig. 6.1.

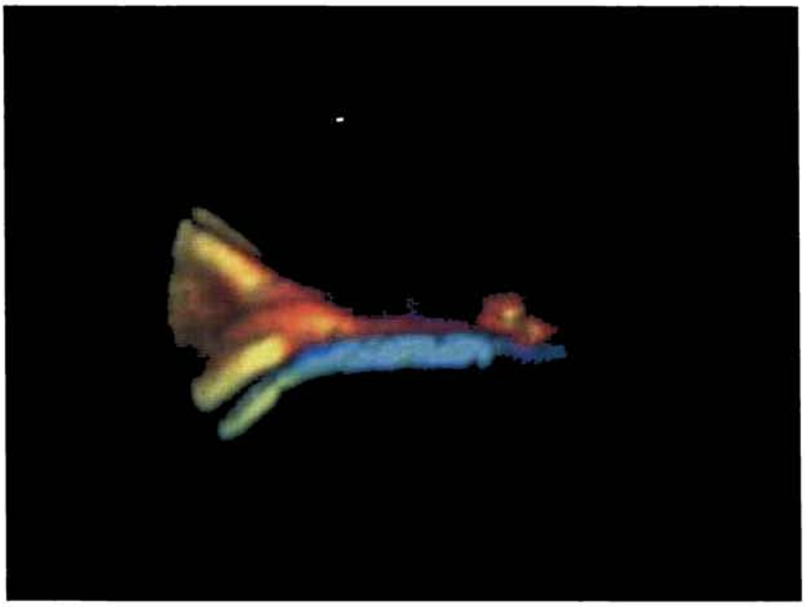

Figure.6.1: Isochromatic fringes obtained for 100% PS/0% HIPS blend sample.

The isochromatic fringes are seen spreading over almost the entire area of the test specimen. They represent points with equal maximum shear stress magnitude. This indicates the presence of a large amount of residual stress in these samples [66, 67]. This fact may be contributing for their highly brittle mode of failure in loaded conditions. Uniform stress regions are identified as the ones having the same colour. Stress concentration points are identified as the points where two colour patterns meet [68, 69].

When the blend composition is changed to 80% PS/20% HIPS, the fringe patterns obtained are shown in Fig.6.2

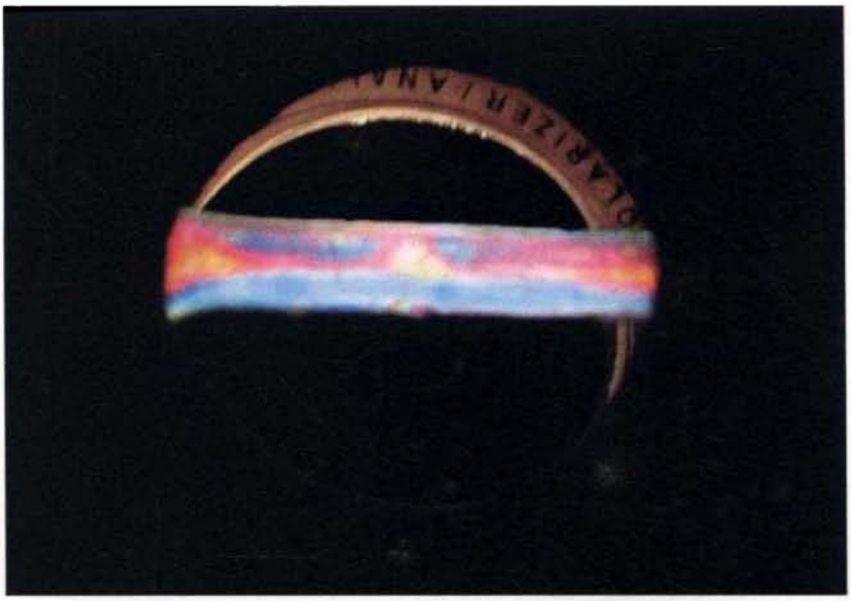

Figure.6.2: Isochromatic fringes obtained for 80% PS/20% HIPS blend sample.

Isochromatic fringes are seen on the test specimen for this blend composition also. Stress concentration points and uniform stress regions can be identified based on fringe colour patterns as in the previous case. But, the area of coverage made on the specimen by the isochromatic fringes show a slight reduction in this case.

This indicates a slight reduction in the amount of residual stress in the blend samples at this composition.

The fringe pattern obtained for 60% PS/40%HIPS blend is shown in Fig.6.3.

Figure. 6.3: Isochromatic fringes obtained for 60% PS/40% HIPS blend sample.

The isochromatic fringes obtained for this blend composition also show the uniform stress regions and stress concentration points. The fringes are seen spreading over a much lesser area over the test specimen. A reduction is observed in the number of interference fringes produced and in its spread over the specimen. This indicates a further reduction in the amount of residual stress inside the blend sample [69, 70].

In PS/HIPS blend samples, reduction in the amount of coloured isochromatic fringes on the specimens with the increase in HIPS content indicates reduction in residual stress. This may be the reason promoting their transition from brittle to ductile mode.

The view of 40% PS/60% HIPS blend sample as seen through the polariscope is given in Fig. 6.4.

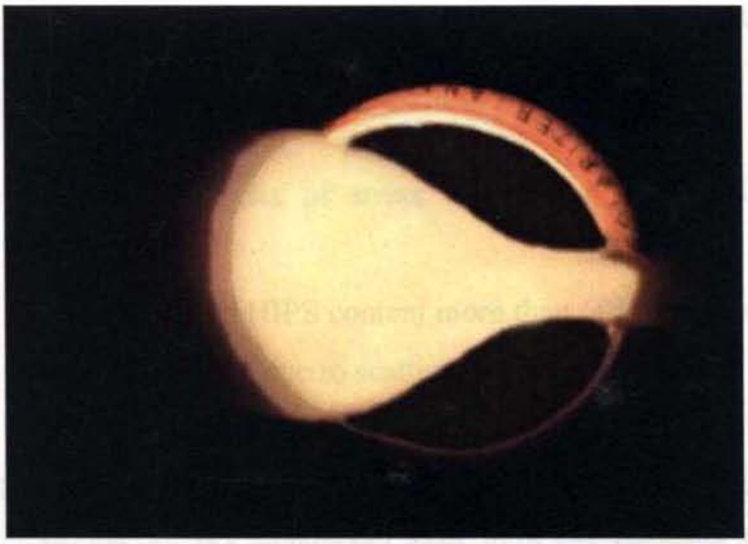

Figure.6.4: View of 40% PS/60% HIPS blend sample through the polariscope.

As evident from the figure, fringes are not obtained at this blend composition. This may be due to the opacity created by the presence of higher content of HIPS (60%) in the blend sample. For the same reason, fringes are not observed for specimens with 80% and 100% HIPS content.

6.4 CONCLUSION

1. As plane polarized light was made to pass through the transparent specimens having different PS/HIPS blend compositions, optical interference takes place and fringes patterns were observed through the plane polariscope using a broad source of light.
2. The fringe patterns obtained on the test specimens indicate the presence of stress concentration in the blend samples. Contours of constant principal stress difference were observed as colourful isochromatic fringes.

3. Stress concentration points and uniform stress regions were identified.
4. The effective area of coverage made by isochromatic fringes on the test specimens were found to vary in accordance with the blend composition.
5. Qualitative analysis of stress distribution in PS/HIPS blends was possible.
6. For samples with HIPS content more than 60%, fringes were not observed - may be due to scattering and opacity.

In PS/HIPS blend samples, reduction in the amount of coloured isochromatic fringes on the specimens seen with the increase in HIPS content indicates reduction in residual stress. This may be the reason promoting the transition from brittle to ductile mode of failure in HIPS rich blends.

CHAPTER 7

SUMMARY AND CONCLUSIONS

7.1 SUMMARY

The fracture behaviour of polymer blends is the main topic of this thesis. The blends selected are PP/HDPE and PS/HIPS. PP/HDPE blend was chosen due to its commercial importance and PS/HIPS was selected to study the transition from brittle fracture to ductile fracture. The preparation of PP/HDPE blends and their modification with two different types of modifiers – calcium carbonate and EPDM are described in the first section. The mechanical properties of the blends were measured as function of the modifier content to find the optimum concentration of the modifier to be added. The fracture characteristics and notch sensitivity were also examined.

PP/HDPE blends were prepared at different compositions by melt blending at 180^0C and fracture failure process was investigated by conducting notch sensitivity test and tensile test at different strain rates. This was done to study the effect of blend ratio on the mechanical properties of the blend system. Afterwards, the effects of two types of modifiers on the fracture behaviour and notch sensitivity of PP/HDPE blends were studied. The modifiers used were calcium carbonate, a hard particulate filler commonly used in plastics and Ethylene Propylene Diene Monomer (EPDM), a soft elastomeric modifier. They were added in 2%, 4% and 6% by weight of the blends. The modified blend samples were subjected to tensile and notch sensitivity tests and tensile parameters were evaluated.

The study shows that PP/HDPE blends form a synergistic system as far as the mechanical behaviour is concerned. The mechanical properties can be optimized by selecting proper blend compositions. The main thrust of the study was to investigate how the properly selected modifiers could alter and improve the fracture behaviour and notch sensitivity of the blends. It is observed that a particulate filler like calcium carbonate can be used for making the mechanical behaviour more stable at the various blend compositions. The resistance to notch sensitivity of the blends is found to be marginally lower in the presence of calcium carbonate. The elastomeric modifier EPDM produces a better stability of the mechanical behaviour. A low concentration of EPDM is sufficient to effect such a change. The reduction in modulus is only minimal while there is some increase in the elongation at break. EPDM shows the outstanding advantage of improvement in the notch sensitivity of the blends. The study shows that judicious selection of modifiers can improve the fracture behaviour and notch sensitivity of PP/HDPE blends and help these materials to be used for critical applications.

Afterwards, the fracture behaviour of blends containing an amorphous, brittle polymer Polystyrene (PS) and a ductile polymer High Impact Polystyrene (HIPS) were studied. PS/HIPS blends were prepared at different compositions by melt blending at 180^0C. Samples prepared by injection moulding were used for conducting tensile, impact and flexure tests. These tests were used to simulate the various conditions which promote failure.

The tensile behaviour of unnotched and notched PS/HIPS blend samples were evaluated at slow speeds. The tests were conducted at speeds 5 mm/min and 10 mm/min. Tensile strengths and moduli were found to increase at the higher testing speed for all the blend combinations whereas maximum strain at break was found to decrease. For a particular speed of testing, the tensile strength and modulus show only a very slight decrease as HIPS content is increased up to about 40% and thereafter show a drastic change indicating changes in the morphology of the blend at this composition. The maximum strain at break show a very slight change up to about 40% HIPS content and thereafter show a remarkable increase. The notched specimens also follow a comparable trend even though the notch sensitivity is seen high for PS rich blends containing up to 40% HIPS. The notch sensitivity marginally decreases with increase in HIPS content. It was found to increase with increase in strain rate. It is observed that blends containing more than 40% HIPS fail in ductile mode.

The impact characteristics of PS/HIPS blends studied were impact strength, the energy absorbed by the test specimen and impact toughness. The test was conducted in the Izod configuration. Only a slight increase was noted in impact strength as HIPS content was increased up to 40%. Remarkable increase in impact strength was observed as HIPS content in the blend exceeded this value. The energy absorbed by the test specimens and the impact toughness also showed a comparable trend. They show a drastic increase as HIPS content exceeds 40%.

Flexural testing which helps to characterize the load bearing capacity was conducted on PS/HIPS blend samples at the two different testing speeds of 5mm/min and 10 mm/min. The simply supported beam configuration was used with a span of 50 mm. The flexural strength showed higher values at the higher testing speed for all the blend compositions. At both the speeds, remarkable reduction in flexural strength is observed as HIPS content in the blend exceeds 40%. The flexural strain and flexural energy absorbed by the specimens are found to increase with increase in HIPS content. At both the testing speeds, brittle fracture is observed for PS rich blends whereas HIPS rich blends show ductile mode of failure.

Photoelastic investigations were conducted on PS/HIPS blend samples prepared at the various blend compositions to analyze their failure modes. This is used as an experimental method to determine the stress distribution in a material. A plane polariscope with a broad source of light was utilized for the study. The test specimens were placed between the polarizer and analyzer. Plane polarized light from the polarizer was allowed to pass through the test specimens. The optical interference fringes formed as plane polarized light was made to pass through the transparent specimens were observed through the analyzer.

Isochromatic fringes with distinct colour patterns were visible. The fringe patterns obtained on the test specimens indicate the presence of residual stress concentration in the blend samples. The coverage made by isochromatic fringes on the test specimens were found to vary in accordance with the blend composition and it shows a reducing trend with increase in HIPS content. This indicates that the presence of residual stress is a contributing factor leading to brittle fracture in PS rich blends and this tendency gradually falls in HIPS rich blends which lead to their ductile mode of failure.

7.2 CONCLUSIONS

1. The mechanical properties of PP/HDPE blends can be optimized by selecting proper blend compositions.

2. Optimum concentration of particulate fillers like calcium carbonate can make the mechanical behaviour more stable.

3. With the addition of elastic modifiers like EPDM, a better stability of mechanical behaviour is obtained at much lower concentrations.

4. EPDM can further improve the resistance to notch sensitivity.

5. The fracture behaviour of PS/HIPS blends investigated by conducting tensile, impact and flexure tests identifies the various conditions which promote failure.

6. Notch sensitivity is seen higher for PS rich blends, but lower for HIPS rich blends. Marginal increase in notch sensitivity is observed as the strain rate is increased.

7. The impact energy absorbed by the test specimens and the impact toughness increases with HIPS content.

8. Brittle fracture is noted for blends containing upto 40% HIPS. Further addition of HIPS results in a transition from brittle to ductile mode of failure. This is evident from both tensile and flexure tests.

9. Photoelastic investigation indicates the presence of residual stress in PS/HIPS blend samples.

10. The presence of residual stress is a contributing factor leading to brittle fracture in PS rich blends and this tendency gradually falls for HIPS rich blends which lead to their ductile mode of failure.

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List of Abbreviations and Symbols

PP	Polypropylene
HDPE	High density polyethylene
PS	Polystyrene
EPDM	Ethylene propylene diene monomer
HIPS	High impact polystyrene
PE	Polyethylene
min	Minute
mm	Milimetre
MPa	Mege Pascal
rpm	Revolutions per minute
T	Temperature
Nm	Newton meter
ΔG_{mix}	Free energy of mixing
ΔS_{mix}	Entropy of mixing
ΔH_{mix}	Enthalpy of mixing

LIST OF PUBLICATIONS BASED ON THE RESEARCH WORK

1. Deviprasad Varma P. R., Sreejith P.S. and K.E. George, "Mechanical behaviour of polymer blends and the effect of modifiers – an experimental investigation", *Proceedings of the national conference on Emerging Trends in Physics, Electronics and Engineering Sciences,* JSS College, Mysore, 25th and 26th September 2006.

2. Deviprasad Varma P. R., Sreejith P.S. and K.E. George, "EPDM as a fracture modifier in HDPE/PP blends", *Proceedings of the international conference – Asia Rub Tech Expo 2006* in November 2006 at Kochi.

3. Deviprasad Varma P. R., Sreejith P.S. and K.E. George, "Effect of blend composition on the tensile behaviour of PS/HIPS blends", *Proceedings of the international conference on Advances in Polymer Technology* CUSAT, Kochi, September 25 – 27, 2008.

4. Deviprasad Varma P. R., Sreejith P.S. and K.E. George, "Photoelastic investigations on the fracture behaviour of PS/HIPS blends", to be presented in the *Second International conference on Materials for the Future* at Trichur in February 2011.

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