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 processibility 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 ($\Delta G_{\text{mix}}$) which includes both entropic and enthalpic terms ($\Delta S_{\text{mix}}$ and $\Delta H_{\text{mix}}$).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

$$= \Delta E_{\text{mix}} + P\Delta V_{\text{mix}} - T\Delta S_{\text{mix}}$$

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-ware, 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 $1.5 \times 10^{-3}$ to $1.5 \times 10^{-2}$ 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
The in-situ formed co-polymer compatibilizers 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 compatibilized 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 $d\varepsilon/dt$, $\eta$ 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 there 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 in 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 and 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 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.