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ABSTRACT

The properties and behavior of plastics is still not well defined like metals and standard data sets for specific service applications are yet to be established. High Density Polyethylene is a plastic class which is expected to sustain extreme service conditions. The above mentioned aspect of exploring the plastics character stimulated the research. Molecular structure of this specified material was studied. Material processing through injection molding was examined .To analyze the impact behavior of this material, a series of experiments were conducted on variety of material samples molded at varying process melt temperatures and were subjected to impact testing with different conditioning environment.

Apart from mechanical testing, thermal characteristic analysis and flow behaviour of various samples was also conducted. To further supplement the outcome of aforementioned lab test series, a real in service product manufactured from same material i.e. Butt Plate of Rifle G3 was also incorporated in this study and different samples were put to Radiographic examination and dynamic impact testing on a specially fabricated test bench. This additional dimension provided an opportunity to validate certain lab test deductions in a real service environment. Butt Plate material model was also simulated utilizing an injection molding analysis program “Mold Flow MPi3”. The predicted results generally agree to theoretical and experimental findings.

The results analysis deduced that Material demonstrated comparatively best impact character in processing temperature range of 230 – 240^{0}C.Impact strength of material reduces when processed at 250^{0}C. Material suitably under service conditions at low temperatures should be carefully examined. Manufacturing process parameters of Butt Plate and its design need minor modifications to get desired working strength.

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INFLUENCE OF PROCESS INDUCED THERMAL DECOMPOSITION ON IMPACT STRENGTH OF INJECTION MOLDED HIGH DENSITY POLYETHYLENE POLYETHLYNE

CHAPTER 1

1.1. INTRODUCTION

Plastics designers, manufacturers and ultimate retailers always try to assure themselves, their customers, and the general public that their product can do what it is supposed to do throughout a prolonged life span and furthermore, do it in a safe and trouble-free manner. Whilst it is accepted that nothing lasts forever but this fact does not over rule the prime responsibility of manufacturer to provide the user a flawless product. The key to performance of plastics products is that it must remain serviceable for a reasonable life cycle, and failure must not occur in a manner that could jeopardise the equipment or purpose it serves. It is a practical necessity to understand the variation in properties and failure of plastic products due to improper control over key parameters in manufacturing process.

There has been a rapid growth in the use of polymers for various industrial and domestic applications and there is every indication that this trend will continue. Main advantages associated with plastics are, high strength to weight ratio, low cost, chemical resistance and ease of processing. However, there are many disadvantages to plastics that lead to unexpected or premature failure if not taken into account. Some of these failures are caused by poor design, selection of wrong material for a particular application and improper material processing.

The processing conditions can have a strong influence on the properties of the product. Polymers are characterized in two broad categories of thermoplastics and thermosets. Quite a few processing techniques are used for polymer materials which mainly include injection molding, blow molding and extrusion. Among these processing methods, injection molding is the most widely used technique for processing of thermoplastics. The complex thermorheological (deformation and flow of matter due to temperature variation) situations that arise by varying the injection molding process temperatures lead to different structural parameters like molecular deformation, residual stress and crystallinity in the finished part.

A better control over process variables would allow for superior control over the service properties of final product. A slight variation in some key process variable like processing melt and mold temperatures can result into significant variations in the mechanical and physical properties of final products. There is a dire need to study the material (High Density Polyethylene), its processing and effects of varying processing temperatures which contribute towards inferior quality and service ultimately part failure.

1.2. RESEARCH OBJECTIVE

To use polymeric products as critical structural components in existing technological applications, it is very important to understand their structure, processing and behavior.The two main forms of mechanical failure are ductile and brittle failure Ductile failure is, by definition, failure at high strain. It is relatively straightforward to manufacture plastic components to avoid ductile failure. However, in practice, ductile materials often fail in a brittle manner, which becomes much more difficult to predict from a theoretical standpoint. Brittle fracture is a low energy process characterised by failure at low strain, with little or no deformation.

Service conditions which definitely influence the overall performance of product and when exceed the designed performance limits can lead to premature failure of product. However this alone is not the root cause of failure. Probably as the experience shows most of the thermoplastic products fail due to manufacturing process related flaws and improper material selection for certain specific application. Process variables of injection molding for HDPE that would maximize the product’s performance are crucial, from a research point of view, because the resulting molecular or physical structures that can influence the mechanical properties are crucial.

The objective of this work is to develop an understanding of the role of processing temperatures in effecting the product's key mechanical property of impact strength as well as molecular structural variations for injection molded high density polyethylene and try to practically verify the theoretical and simulated property profile of injection molded high density polyethylene which influence the impact behaviour of this material

1.3. OVERVIEW OF STUDY

This work was undertaken in following sequential order:-

(1) Literature survey

(2) Study of material's (HDPE) molecular structure

(3) Study of thermoplastic processing technique of injection molding

(4) Preparation of sets of test samples at varied injection melt temperatures and Conduct of:-

   a. Impact testing (ITD labs)
   b. Material Thermogravimetry analysis (TGA) (Chemistry Dept QA University)
   c. Melt flow index (ITD labs)
   d. Tensile tests (Material Sciences Deptt, GIK)
   e. Wide angle X-Ray Diffraction (WAXD) (Polymer Research Centre NESCOM)

(5) To supplement the results obtained from series of lab experiments, an in service real product i.e. Butt Plate of Rifle G3, manufactured from same material was also put to experimental routine to further verify the material's character under dynamic impact loading.

(6) Preparation of molded samples of (Butt Plate of Rifle) at varied molding temperatures keeping all other processing parameters fixed.

(7) Radiography of selected Butt Plates (SUPARCO labs)

(8) Mathematical modeling of service impact loading on Plate

(9) Dynamic impact fatigue testing of Butt Plate samples on specially fabricated test bench

(10) Modelling and Simulation of Butt Plate molding with an injection molding analysis program "Moldflow MPi3" which employs a finite element method.

(11) Discussion, conclusion and recommendations

1.4. LITERATURE REVIEW

Due to ever increasing use of plastic materials, researchers throughout the word are actively involved in research in this field but still there is much more to be done to understand and predict the behaviour and properties of polymers under specific manufacturing techniques and service conditions. Quite an established data is available for metals which have been compiled on the basis of years of research ever since the emergence and use of metals. Polymers are relatively new in their discovery, use and standard property data build up. Over seventy books, research papers and articles related to this topic were consulted to get an insight of the related work. A brief description of few related works already under taken is given in paragraphs below.

1.4.1. M.A. Semeliss and Tuttle [1] at NASA Research Centre have worked on determining the yield and post yield behaviour of high density polyethylene. The research was primarily focused on studying the yield and post-yield material behaviour by two alternate assumption of isotropic material model behaviour and anisotropic material model behaviour. Few conclusions drawn from this work indicate that the annealing process reduces the residual stresses induced during the extrusion process to minimal levels. However, the annealed polyethylene specimens were found to exhibit a pronounced anisotropy. A 30% difference in modulus for the axial and hoop directions existed in the annealed specimens. Two possible explanations of the isotropic post-yield response have been proposed. In the first hypothesis it is suggested that molecular motions associated with plastic strains occur primarily within the amorphous regions of the polymer, and hence the post-yield behaviour is effectively isotropic. If this hypothesis is valid, then no increase in the degree of crystallinity would occur as a result of plastic deformation.

1.4.2. S.G Luckey Jr and J. M. Henshaw in 2000, at Tulsa University USA, studied the reasons for increased crystallinity in High Density Polyethylene.[27]They performed comparative characterization lab analysis for two samples of a product with the help of Atomic force microscopy, Differential scanning calorimetry and wide angle X-ray Diffraction. The difference between crystals of two samples was established and was attributed to processing cooling method.

1.4.3. Sang Sik Yang ,at Pohang University Korea in 2007,studied the thermal and flow induced stresses[33].Deformation at and after ejection has been considered and concluded that thermal stresses are much greater than flow induced stresses. Another work carried out by Rajendra at Philips Chemical Company USA In 2005, indicates an improvement in material properties with temperature increase. Temperature causes the residual stress in the material to relax to some extent [34].

1.4.4. B.A .Grahm and Thompson in 2005 at McMaster University Canada experimented to find out the reason of HDPE degradation during manufacturing process. They found that every short processing history has caused marginal structural changes and inclusion of stabilizer towards higher end of processing temperature was found to be important to inhibit degradation [35].

1.4.5. In 2003, at Drexel University ,Philadelphia USA, D.S.Li and S.R.Kalidindi simulated the tensile behaviour of low and high density polyethylene and observed the crystallographic texture of material. They documented that stress of deformed low density polyethylene relaxes faster than the high density polyethylene [36]

CHAPTER 2

2.1. FUNDAMENTALS OF THERMOPLASTICS

Polymeric materials have been used since early times even though their exact nature was unknown.Polymeres are a class of chemicals that occur naturally and can be made in laboratory. In the 1400s, Christopher Columbus found natives of Haiti playing with balls made from material obtained from a tree. This was natural rubber, which became an important product after Charles Goodyear discovered that the addition of sulphur dramatically improved the properties. However, the use of polymeric materials was still limited to natural-based materials. The first true synthetic polymers were prepared in the early 1900s. We call these plastics because they are pliable, that is, they can be shaped and molded easily. As plastics become easier to mold and shape when they're hot, and melt when they get hot enough, we call them thermoplastics.

2.2. How thermoplastics are made

A chemical reaction that makes polymers is called a polymerization. There are many of these reactions, and they come in all kinds. But all polymerizations have one thing in common: they all start with small molecules, and join them into big giant molecules. We call the original small molecules as monomers. The basic building blocks for the gases from which polymers are derived are hydrogen and carbon atoms. For polyethylene, these atoms are combined to form the ethylene monomer, C_2H_4.

2.2.1. When ethylene is polymerized to make polyethylene, then every atom of the ethylene molecule becomes part of the polymer. The monomer is added to the polymer. The process of polymerization is random; therefore some molecules grow much larger than others. [21]

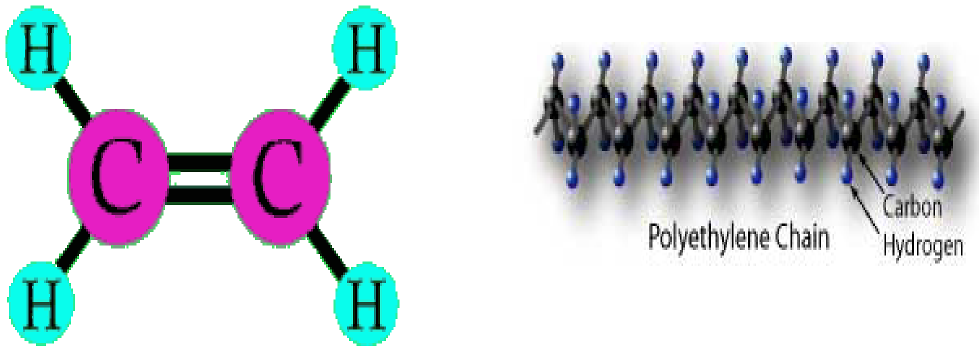


Figure 2.1 Ethylene Molecule[38]

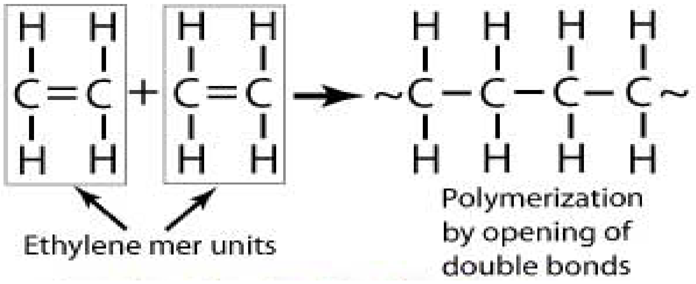


Fig 2.2 Chain Of Ethylene Mer Units [22]

The polymer chain is a three dimensional structure. When stress is applied, these chains stretch and the elongation of polymers can be many times greater than it is in outstretched form.

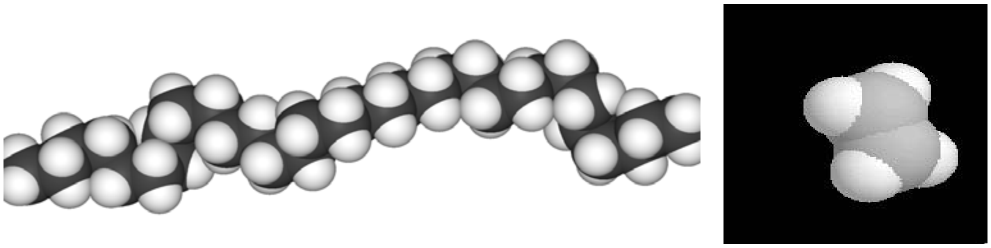


Fig 2.3 Ethylene Molecule Chain 3-D View[11]

2.3. The length of the polymer chain is very important. As the number of carbon atoms in the Chain is increased to beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over 1,000, the solid material

polyethylene is obtained. For polyethylene, the length the chains will stretch before they fold is about 100 angstroms (A metric unit of length equal to one ten billionth of a meter (or 0.0001 micron); used to specify wavelengths of electromagnetic radiation).

2.3.1 Change in state

As the length of the molecules increases, the total binding forces between molecules also increase. Polymer chains may be fairly linear, as in high density polyethylene, or highly branched as in low density polyethylene. For every 100-ethylene units in the polyethylene molecular chain, there can be one to ten short or long branches that radiate three-dimensionally .The degree of polymerization (DP) is the molecular weight of the polymer divided by the molecular weight of the mer. It tells the number of mers in the molecule.

2.4. Thermosets

There is another group of polymers in which a single large network, instead of many molecules is formed during polymerization (fig-2.5).This group is called thermosetting polymers. Since these materials are essentially comprised of one giant molecule, there is no movement between molecules once the mass has set. They will not become plastic when heated.

For this type of network structure to form, the mers must have more than two places for boning to occur; otherwise, only a linear structure is possible. Branching occurs when a chain curls back and bonds to an earlier part of the chain. When this curl breaks, it leaves small chains sprouting from the main carbon backbone. Branched carbon chains cannot line up as close to each other as unbranched chains can. This causes less contact between atoms of different chains. A low density results from the chains being further apart. Lower melting points and tensile strengths are evident, because the intermolecular bonds are weaker and require less energy to break.(10)

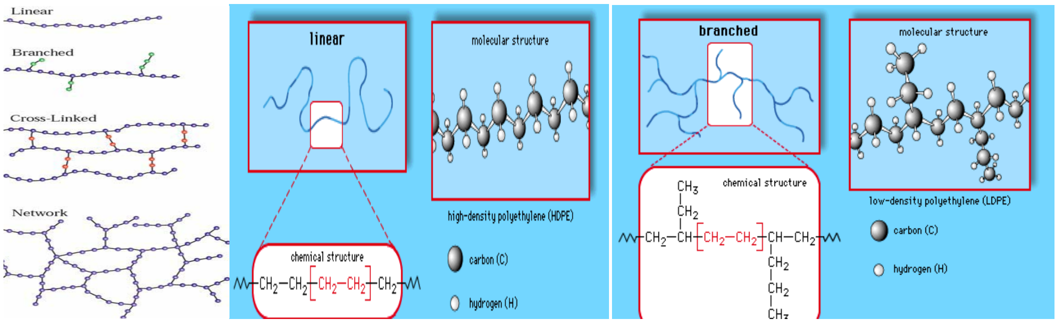


Fig 2.5- Linear,Branched and Network Polymer Chains[39]

2.5 Chemical bond

All chemical bonds involve electrons. This is the physical process responsible for the attractive interactions between atoms and molecules, and which confers stability .When an atom has a nearly full electron shell, it will try to find electrons from another atom so that it can fill its outer shell.

2.6 Covalent Bond

This bond is a form of chemical bonding that is characterized by the sharing of pairs of electrons between atoms, Metals usually have 1, 2, or 3 electrons in their outermost shell. Non-metals have 5, 6, or 7 electrons in their outer shell. With this many electrons in the outer shell, it would require more energy to remove the electrons than would be gained by making new bonds. Therefore, both the atoms involved share a pair of electrons. Each atom gives one of its outer electrons to the electron pair, consequently, both atoms are held near each other since both atoms have a share in the electrons.

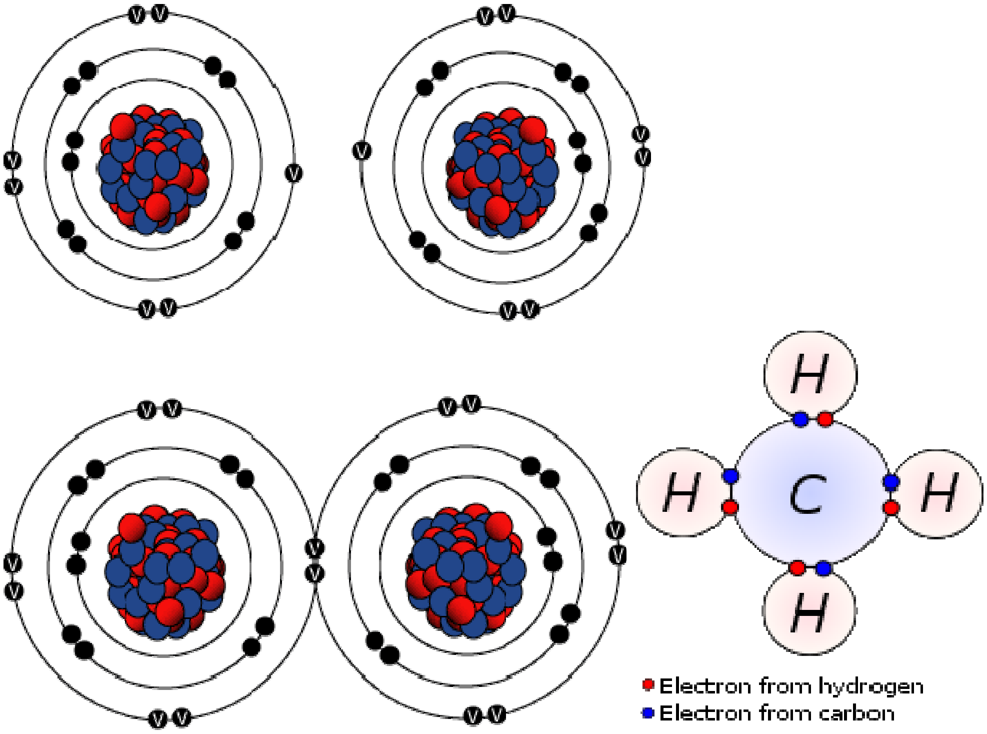


Fig 2.6- Carbon Hydrogen Bond[39]

A carbon-hydrogen bond, also known as a C-H bond is a single bond between carbon and hydrogen atoms, found in polyethylene (fig2.6). More than one electron pair can be formed with half of the electrons coming from one atom and the rest from the other atom. An important feature of this bond is that the electrons are tightly held and equally shared by the participating atoms. In each molecule, the bonds between the atoms are strong but the bonds between molecules are usually weak. This makes many solid materials with covalent bonds brittle. Material with covalent bonds may be solid, liquid or gas at room temperature depending on the number of atoms in the compound. The more atoms in each molecule, the higher a material melting and boiling temperature.

2.7 Van der Waals Bond

The van der Waal bonds occur to some extent in all materials but are particularly important in plastics. These materials are made up of a long string molecules consisting of carbon atoms covalently bonded with other atoms, such as hydrogen, nitrogen, oxygen. The covalent bonds within the molecules are very strong and rupture only under extreme conditions. The bonds between the molecules that allow sliding and rupture to occur are called van der Waal forces (fig2.9)

The hydrogen atoms are bonded to the oxygen atoms showing a positive polarity at the hydrogen-rich end of the molecule and a negative polarity at the other end (fig2.8). A result of this charge imbalance is that water molecules are attracted to each other. This is the force that holds the molecules together in a drop of water. Same concept can be carried on to plastics, except that as molecules become larger, the van der Waal forces between molecules also increase. In polyethylene the molecules are composed of hydrogen and carbon atoms in the same ratio as ethylene gas. But there are more of each type of atom in the polyethylene molecules and as the number of atoms in a molecule increases, the matter passes from a gas to a liquid and finally to a solid. Heat can be used to break the van der Waal

forces between the molecules and change the form of the material from a solid to a liquid.

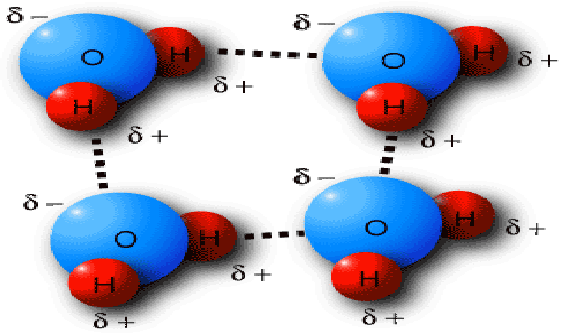


Figure 2.8 Hydrogen-Oxygen Bond[39]

Table 2-1 Some Typical Bond Lengths and Associated Energies

Typical bond lengths in pm and bond energies in kJ/mol. Bond lengths can be converted to Å by division by 100 (1 Å = 100 pm). Data taken from [3].

Bond	Length (pm)	Energy (KJ/mol)
H — Hydrogen		
H–H	74	436
H–C	109	413
H–Cl	127	432
H–Br	141	366
C — Carbon		
C–C	154	348
C=C	134	614
C≡C	120	839
C–Cl	177	330
C–I	214	216

. We have shown the molecule as a straight line and it is called a linear polymer. High Density Polyethylene has linear structure but actually the molecules are not so straight but can be thought of as a mass of worms randomly thrown into a pail. There is considerably more intertwining than there would be with worms, because if we scale up the typical polymer molecule to a diameter of 0.25 in. (0.635 cm), it would be 20 ft (6.1 m) long. Now it may come as a surprise when we say that these chains, often containing 10,000 atoms, may be folded back and forth to form crystals. We know that segments of worms continually coil and uncoil, and we note a similar motion with the polymer molecules. If we pull slowly on the mass of worms, we would find a higher percentage with the long axis parallel to the direction of tension.

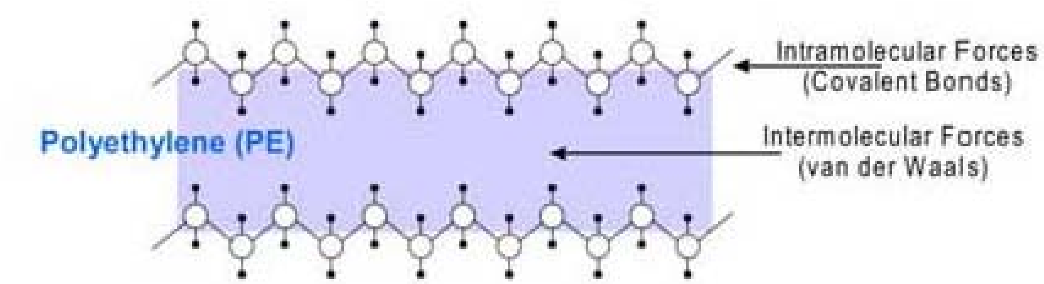


Figure 2.9-Covalent and Vander Waals Bonding

2.8 Molecular weight and its distribution

Atoms of different elements, such as carbon, hydrogen, etc., have different atomic weights. For carbon, the atomic weight is 12 and for hydrogen it is one. The molecular weight of the ethylene unit is the sum of the weight of its six atoms (two carbon atoms x 12 + four hydrogen x 1) or 28. During polymerization, a mixture of molecular chains of widely varying lengths is produced. Some may be short; others may be extremely long containing several thousand monomer units. The relative distribution of large, medium and small molecular chains in the polymer is important to its properties. When the distribution is made up of chains close to the average length, the polymer is said to have a “narrow molecular weight distribution.” polymer with “broad

molecular weight distribution" are having a wider variety of chain lengths. In general, polymer with narrow molecular weight distributions have good low-temperature impact strength and polymer with broad molecular weight distributions generally have greater stress cracking resistance and greater ease of processing (Figure 2.10).

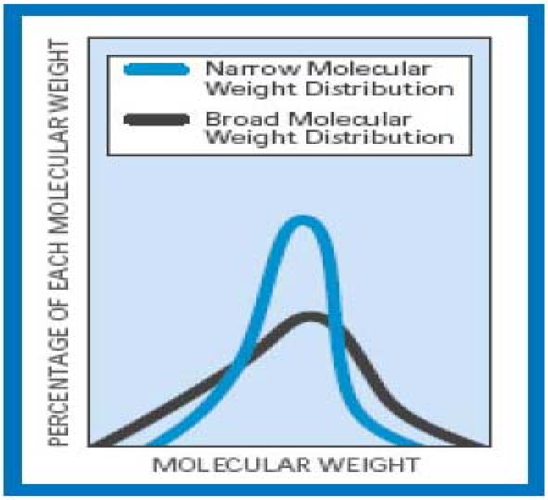


Figure 2.10, Schematic of Molecular Weight Distribution

2.9 Crystalline Polymers.

If the structure of the polymer backbone is a regular, ordered structure then the polymer can tightly pack into an ordered crystalline structure. A crystal is a regular, repeating arrangement of atoms or molecules like in polyethylene (fig 2.11). These possess sharp melting point, strength, higher density but low impact resistance and low permeability to gas. Thermoplastics never crystallize completely, as metals do.(21)

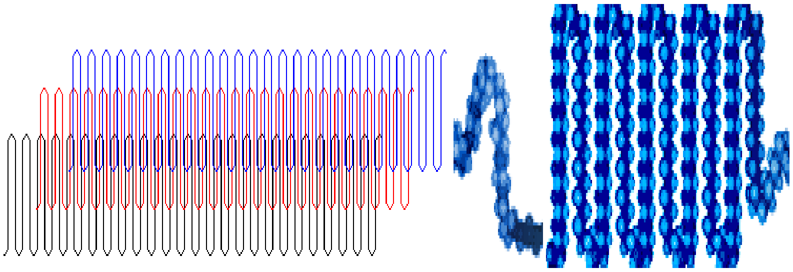


Figure 2.11, Crystaline Polymer Chain[30]

Various techniques are being used nowadays for the determination of polymer crystallinity. Among them Differential Scanning Calorimeter (DSC), Wide angle X-ray Diffraction (WAXD) and density measurements are the most common techniques employ. Increased density is directly related to crystallinity (27)

.

2.10 Effects of Degree of crystallinity and Molecular Weight on Polyethylene State

The percentage of the polymer that is crystalline is called the percent crystallinity. The percent crystallinity has an important influence on the properties of the polymer. A totally crystalline polymer would be very hard and brittle. HDPE has linear molecular chains with comparatively few side chain branches. Therefore, the chains are packed more closely together. The result is crystallinity up to 90 percent. LDPE resins generally have crystallinity from 60 percent to 75 percent.

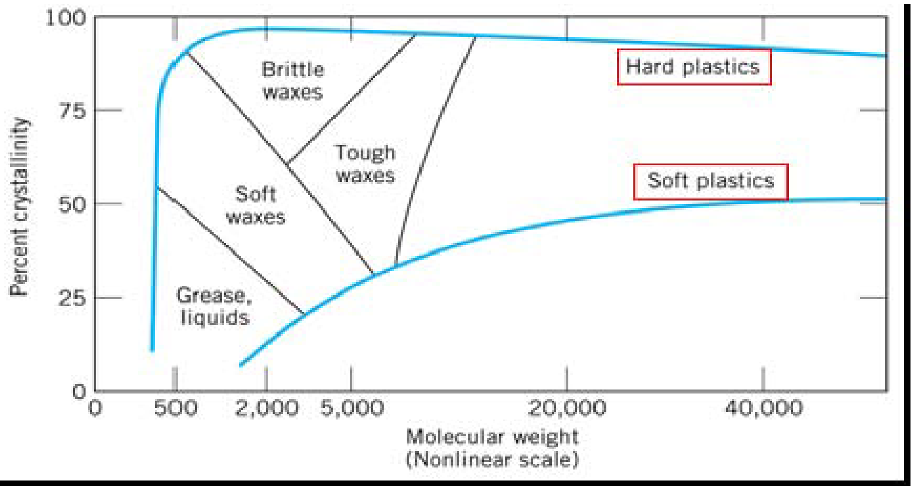


Figure 2.12 Relation Ship Of Molecular Weight,Percent Crystalinity And Physical Properties of Polymer[39]

2.11 Amorphous Polymers.

Amorphous polymers are a family of polymers that are characterized by entangled polymer chains that are loosely bound. The term amorphous indicates that there is no preferred orientation of the molecules, relative to each other. These do not have sharp melting point. The physical properties of

amorphous Polymers are identical in all directions along any axis so they are said to have isotropic properties. Even crystalline polymers will have some amorphous portion. This portion usually makes up 40-70% of the polymer sample.

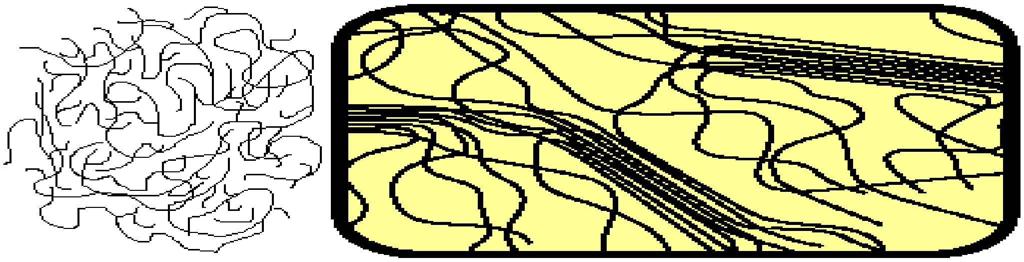


Figure 2.13, Amorphous Polymers structure[39]

2.12 Semi Crystalline Polymers.

Semi-crystalline polymers have both crystalline and amorphous regions. 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, there is a fairly distinct separation between the crystalline and amorphous regions. In other cases (e.g., HDPE) the structure basically is crystalline with uniformly-distributed-imperfections (20). Impact strength will decrease as crystallinity increases. Impacting of all crystalline materials will have a tendency to transmit energy along the face of the crystals where they break. Seventy- percent crystalline PP has a notched izod of 2.8 ft-lb/in. Increasing the crystallinity to 95% reduces impact to .9 ft-lb/in(31)

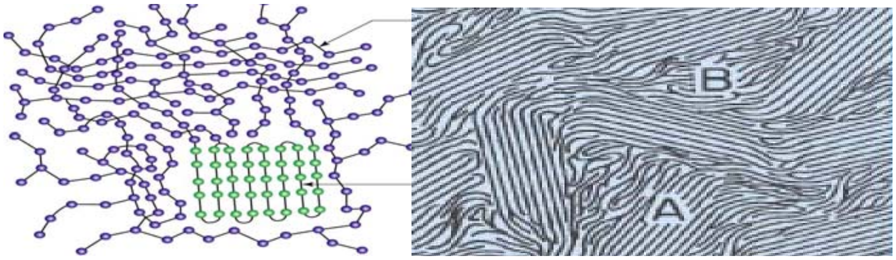


Fig 2.14 Semi Crystalline Polymer Structure[39]

2.13 FACTORS EFFECTING THE PROPERTIES OF PLASTICS

Plastic parts are always subjected to various external natural and applied factors throughout their life cycle (Fig 2.15).If proper design, material selection and processing technique is not taken into account then there are likely chances that the product will fail in premature manner without delivery of intended services

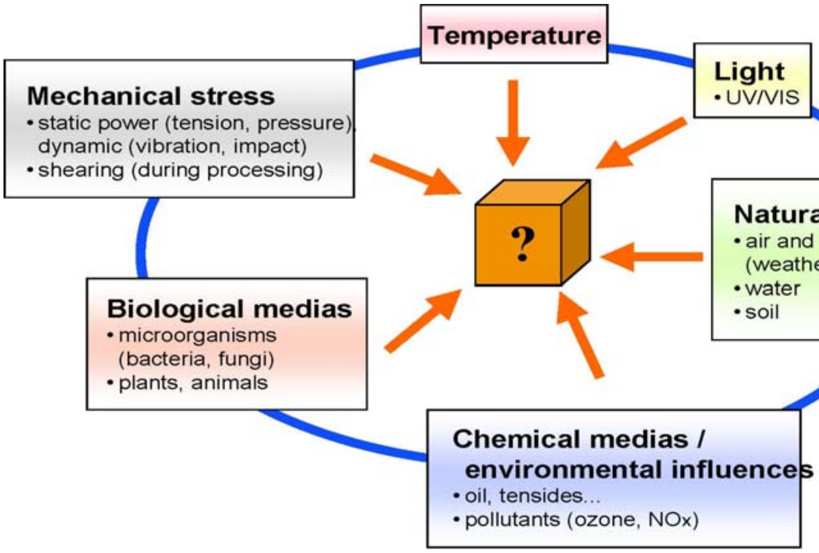
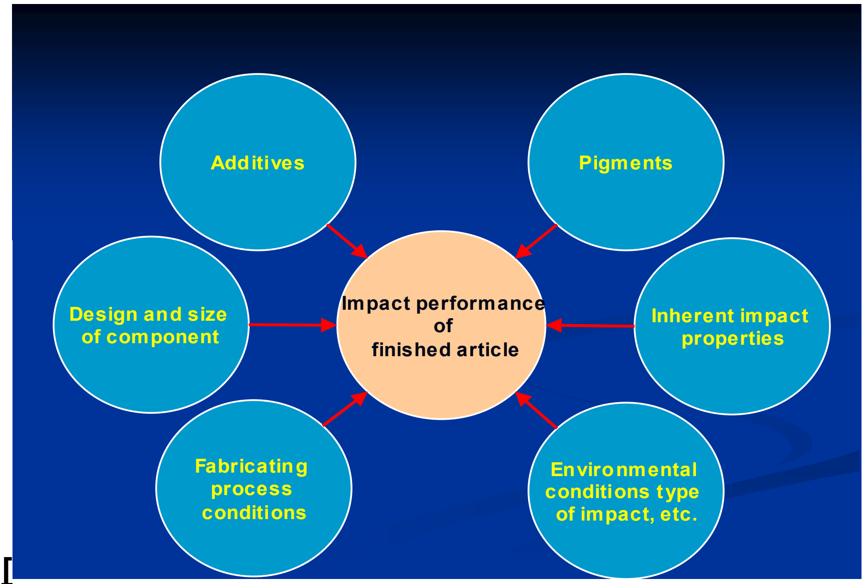


Figure 2.15 Factors Influincing the product in its life cycle[24]



[

Figure 2.15 1 Factors contributing to change in impact character [29]

2.13.1 Effect of temperature on plastics

Most plastic materials are affected by quite small changes in temperature (20). The effect of temperature on a polymer is striking. They are related to the behaviour of a typical glass. When the glass is cooled, the thermal agitation of the molecule decreases and the material becomes viscous. Finally the chain becomes locked in place and the glass becomes brittle. The same phenomenon occurs in polymers. The temperature at which chain movement decreases to a low value is quiet aptly called the glass transition temp, designated as T_g. The glass transition region thus represents a range of temperatures over which the glass undergoes both thermal and physical Changes. Plastic parts having service temperatures below T_g become hard and brittle while conditions above T_g make them soft.(7)

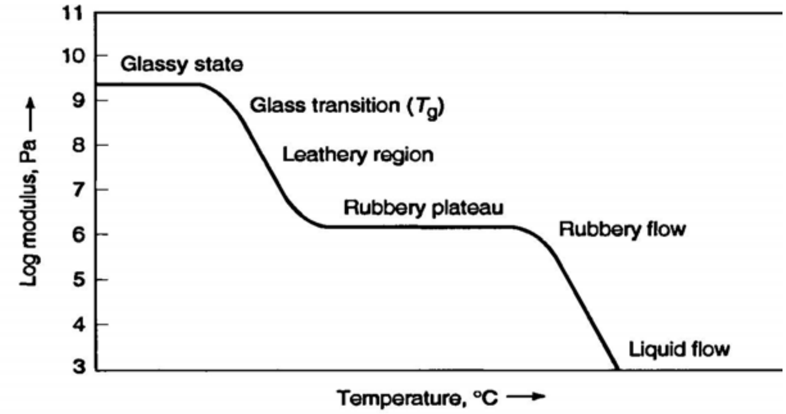
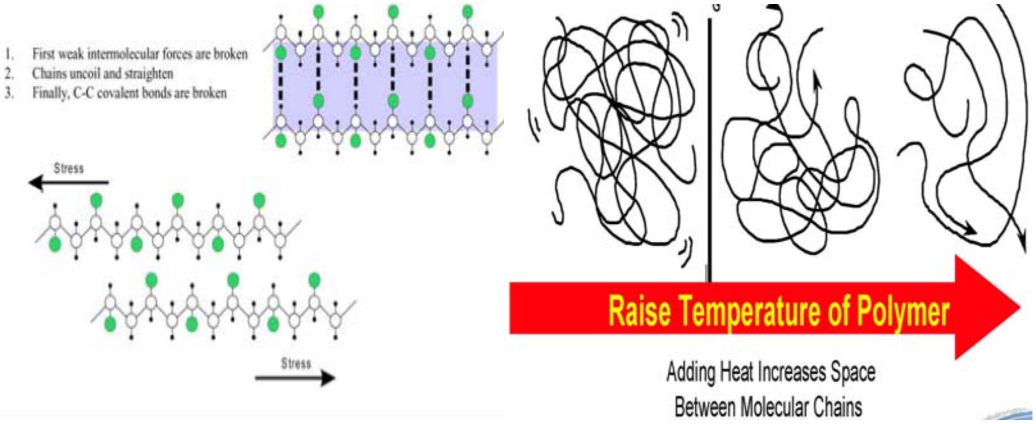


Figure 2.15 ,Temperature effect on Polymer

At relatively high temperature, the polymer chains can move around easily. So, when we take a piece of the polymer and bend it, the molecules, being in motion already, have no trouble moving into new positions to relieve the stress we have placed on them. But if we try to bend sample of a polymer below its T_g, the polymer chains won't be able to move into new positions to

relieve the stress which we have placed on them. So, one of two things will happen. Either the chains are strong enough to resist the force we apply, and the sample won't bend or the force we apply will be too much for the motionless polymer chains to resist, and being unable to move around to relieve the stress, the polymer sample will break or shatter.

This change in mobility with temperature happens because the phenomenon we call "heat" is really a form of kinetic energy; that is, the energy of objects in motion. It is actually an effect of random motion of molecules, whether they are polymer molecules or small molecules. Things are "hot" when their molecules have lots of kinetic energy and move around very fast. Things are "cold" when their molecules lack kinetic energy and move around slowly, or not at all. Chain mobility within the material depends on the anisotropic character induced during processing (8).



<u>Figure 2.16 Chain Motion In Plastics</u>

For polyethylene, the density and crystallinity are directly related, the higher the degree of crystallinity, the higher the density. Higher density, in turn, influences numerous properties. As density increases, heat softening point, resistance to gas and moisture vapor permeation and stiffness increase.

However, increased density generally results in a reduction of stress cracking resistance and low temperature toughness.

2.14 Polymer Decomposition

Molecular deterioration is a result of overheating or shear during processing (12). At high temperatures the components of the long chain backbone of the plastics can begin to separate (the phenomenon often called molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the processing and service temperature of plastics as much as the possibility of mechanical property loss. The chemical reactions involved in thermal degradation lead to physical property changes relative to the initially specified properties. Thermal decomposition generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and increased brittleness.[2]

2.15 The Mechanism of Thermal Decomposition In thermoplstics most types of decompositions follow a similar basic pattern. The conventional model for thermal decomposition involves the major steps of initiation, propagation and branching.[2]

2.16 Initiation. The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain as a result of energy input from heat. This creates a highly reactive and unstable polymer 'free radical' (R*) and a hydrogen atom with an unpaired electron (H*).

2.17 Propagation. The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical (R*) reacts with an oxygen (O2) molecule to form a proxy radical (ROO*) which can then remove a hydrogen atom from another polymer chain to form a hydro peroxide (ROOH) and so regenerates the free radical (R*). The hydro peroxide can then split into two new free radicals, (RO*) + (*OH), which will continue to propagate the reaction to other polymer molecules.(Fig 2.17) The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain.(24)

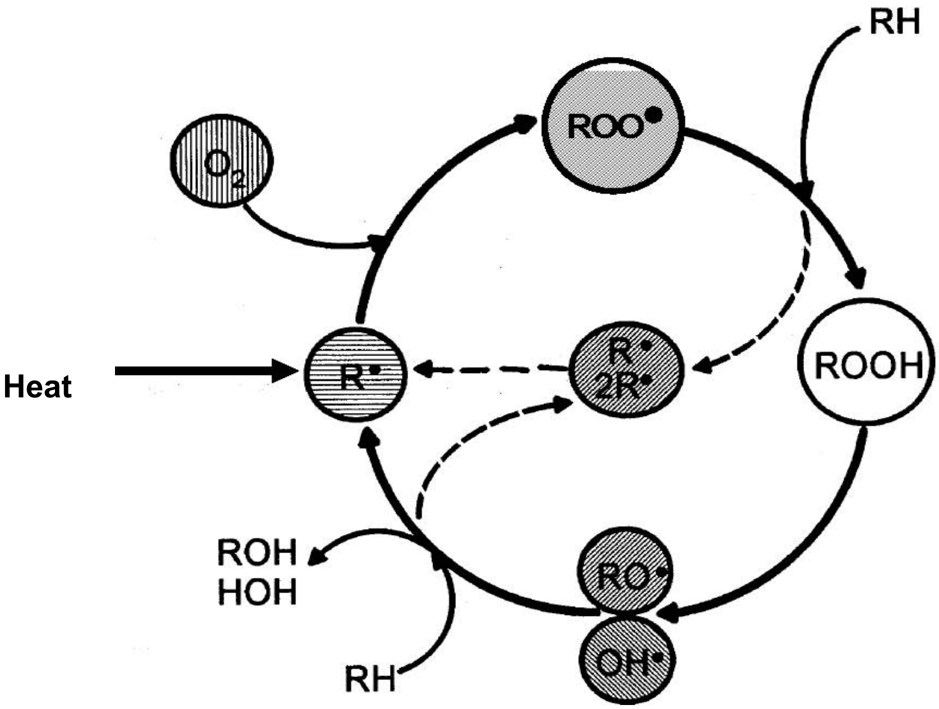


Figure 2.17 PLASTICS DECOMPOSITION PROCESS[40]

CHAPTER 3

THERMOPLASTICS - MATERIAL PROPERTIES AND PROCESSING

3.1 Density. It is the measure of mass per unit volume. The density of a crystalline form of a given polymer is greater than its amorphous density. For High Density Polyethylene, the theoretical crystalline density is 1 g/cc and 0.85 g/cubic centimetre for the amorphous density.(4)

3.2 Melt Flow Rate. It is the measure of fluidity of the molten plastic under specified conditions of temperature and applied force. It gives a qualitative idea of the molecular weight of the part. Melt flow rate is inversely related to the plastic's average molecular weight, as the average molecular weight increases, MFR decreases and vice versa.

3.3 Anisotropy and Isotropy. In a single crystal, the physical and mechanical properties often differ with orientation. In crystalline structure the atoms slip over one another or distort in relation to one another easier in some directions than others. When the properties of a material vary with different orientations, the material is said to be anisotropic. Alternately, when the properties of a material are the same in all directions, the material is said to be isotropic. When a material is processed, the chains are usually distorted and elongated in one or more directions which makes the material anisotropic.

3.4 Failure Behaviour, Brittle and Ductile.

3.4.1 Brittle Failure Materials that fail at rather low elongations and stresses below the yield stress can be considered to have undergone brittle failure. Brittleness results from shorter molecular chain length (thus lower molecular weight) and crystallization (21). As a result, the physical integrity of the part becomes substantially less than the specification. Failure typically can start at a defect or portions where stresses are concentrated. Once a crack is formed,

it will grow as a result of stress concentrations at the crack tip. This can be stimulated by degradation of the polymer. Brittle failure in tension may be induced by either an increase in yield stress, or an increase in crystallinity.[32]

3.4.2 Ductile failure. This is exhibited by yielding of the polymer or slip of the molecular chains past one another. This is most often indicated by a maximum deformation in the tensile stress-strain test or what is termed the yield point. Above this point, the material may exhibit lateral contraction upon further extension, termed necking. Molecules in the necked region become oriented and results in increased local stiffness The ductile materials will absorb more energy before fracturing than the brittle.

3.5 PROCESSING OF THERMOPLASTICS

Processing involves the conversion of the solid polymer into a desirable size and shape. There are a number of methods to shape the polymer, including injection molding, extrusion and blow molding. The plastic material is heated to the appropriate temperature for it to flow. The material is shaped, and then it is cooled so as to preserve the desired shape (Fig 3.5) In this work our prime focus is on injection molding technique and we will explain it in next paragraphs.

3.6 Injection Molding

This is one of the most commonly and widely used polymeric fabrication processes for the thermoplastic polymers. Basic process involves heating a thermoplastic material until it melts. Force it into a hollow (cooled) cavity under pressure to fill the mold. When cool, remove the finished part. Unlike molten metals, polymer melts have a high viscosity and cannot simply be poured into a mold. Instead a large force must be used to inject the polymer into the hollow mold cavity. The process allows rapid, automated production of a wide variety of articles including complex shaped curvatures.

Plastic pellets are poured in the hopper, and finished parts emerge from the dies. Although the injection molding process apparently looks simple, Injection molding is a very complex process because the polymer experiences

a complex thermorheological change during molding that influences the frozen-in free volume, crystallinity, molecular orientation and residual stresses inside the part. These generally govern the final part properties (25). Therefore it is highly desirable to anticipate the effect of process parameters on the resulting mechanical properties of the finished part .It involves complex interplay between the processing conditions, mold geometry and material properties[37].Major process variables are temperature, and Pressure .

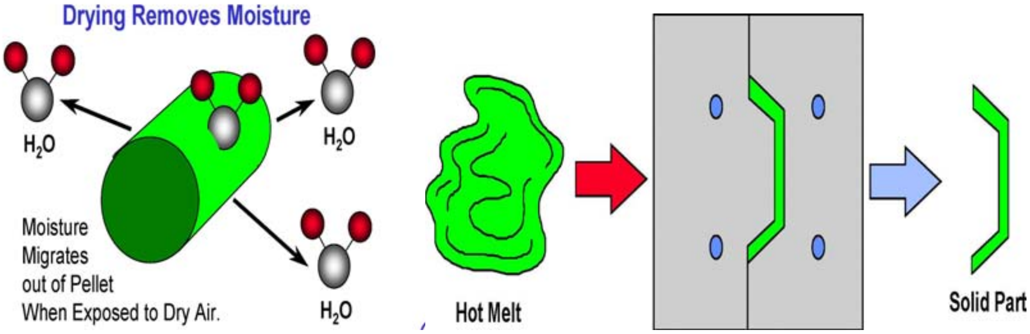


Figure 3.2 Moisture Removal From Raw Material Before Molding(left)

Hot Molten Material Molded in Die and Solid Part Ejected(right)

3.6.1 Injection system.

A material hopper acts as an input buffer. A heated chamber melts the material and injector forces the now viscous fluid into the mold(Fig 3.4).Basically the screw extends from the hopper to the injection chamber. Along the length of the screw chamber, heater bands are used to melt the plastic, as the screw turns, it moves raw solid plastic from the hopper, to the injection chamber. The build-up of pressure in the injection chamber forces the screw back until enough for a shot has accumulated. The screw is forced forward to inject the plastic into the mold.

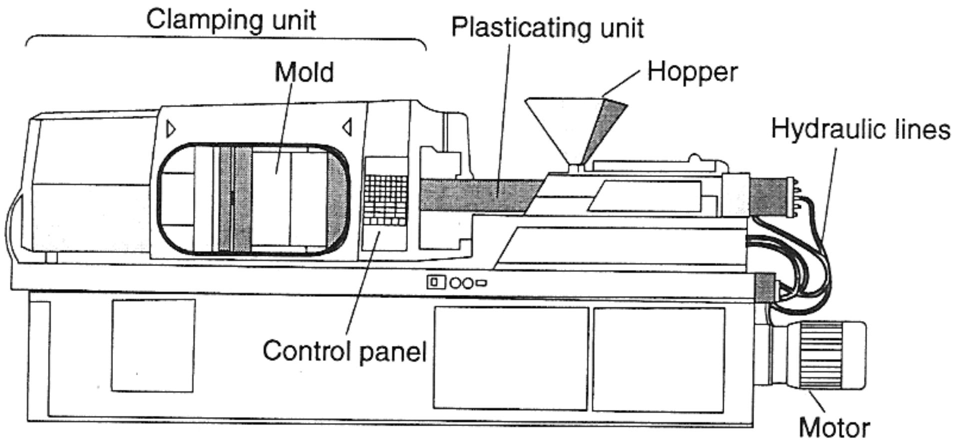


Figure 3.3 Basic Layout of Injection Molding Machine[40]

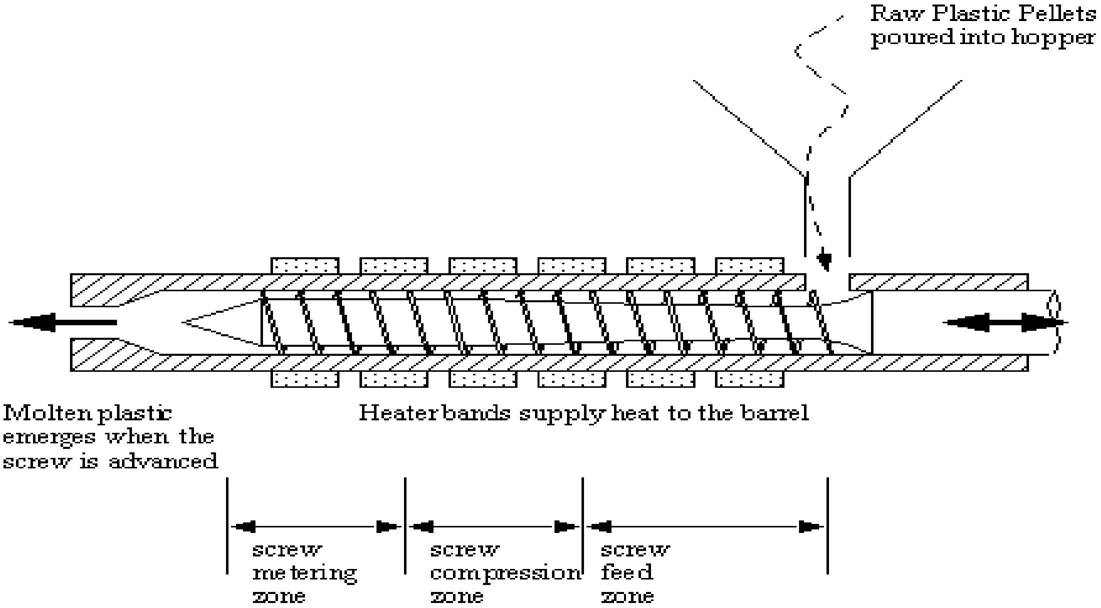


Figure 3.4 Stages of Material Heating[40]

Purpose of the screw is to generate a homogenous melt .Typical zones can be identified on the screw. Feed zone has a screw with large cavities to carry more material .In Compression zone depths of the screw thread reduces, leading to elevated pressures, and pressure induced melting. Metering zone has small and uniform threads to provide controlled quantities. This also serves as a final mixing stage. The heat capacity and melting point temperatures of various materials determine the energy required to melt the

plastic and the energy to be removed for solidification (and for ejection).Cross-linking, branching, and possibly chain extension occurs with high-density polyethylene, even for the short processing history imparted by the injection molding machine (6) High barrel temperature leads to material degradation and lower temperatures can cause part distortion and insufficient material flow(19)

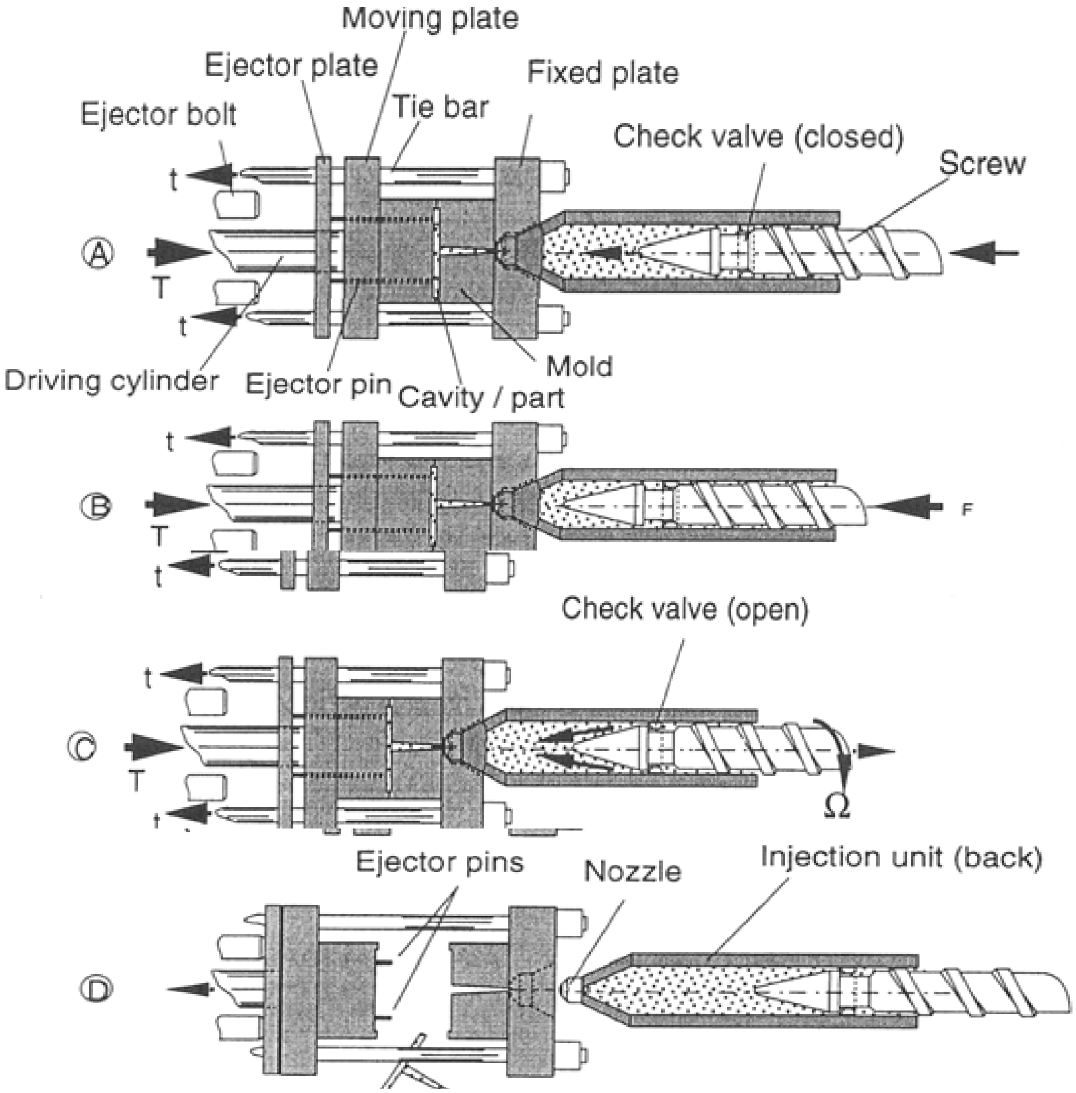


Figure 3.5 Typical phases during injection molding – (A) closing of the mold and melting of the plastic resin, (B) injection of melt into the mold, (C) holding and cooling (D) removal of the part[40]

3.7 Injection Molding Cycle

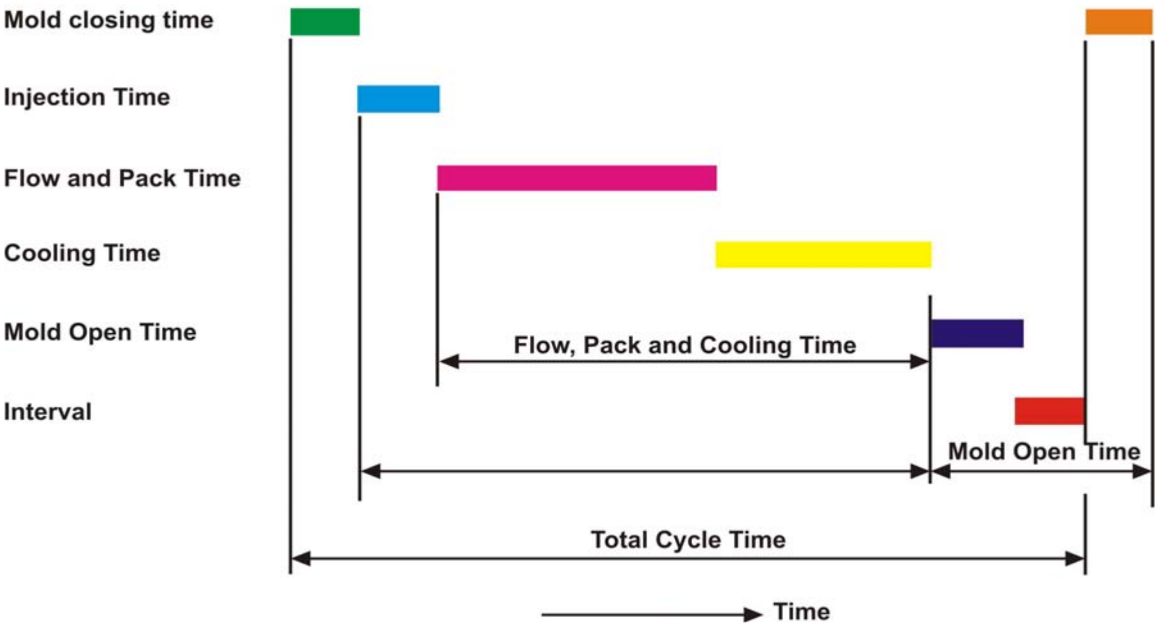


Figure 3.6 Injection Molding Cycle

3.8 Few Common Molding Defects

3.8.1 Weld Lines. When a weld line forms, the thin frozen layers at the front of each flow path meet, melt, and then freeze again with the rest of the plastic. The orientation of the plastic at the weld is therefore perpendicular to the flow path. The weld line occurs where two flow fronts meet, and the polymer molecules are misaligned. It is the sharp difference in molecular orientation at the weld which causes the significant decrease in strength at this point.

3.8.2 Meld Lines. A meld line occurs when two flow fronts blend together at an oblique angle. The orientation of the plastic molecules is therefore more uniform than the orientation after a weld line has formed. Fig 3.7shows the length of a part where a meld line forms. The red arrows show the direction of plastic flow. The white lines represent the orientation of the polymer molecules after the meld line has formed. Meld lines are normally stronger than weld lines and are often much less

visible. The term weld line is often used to mean both weld and meld lines.

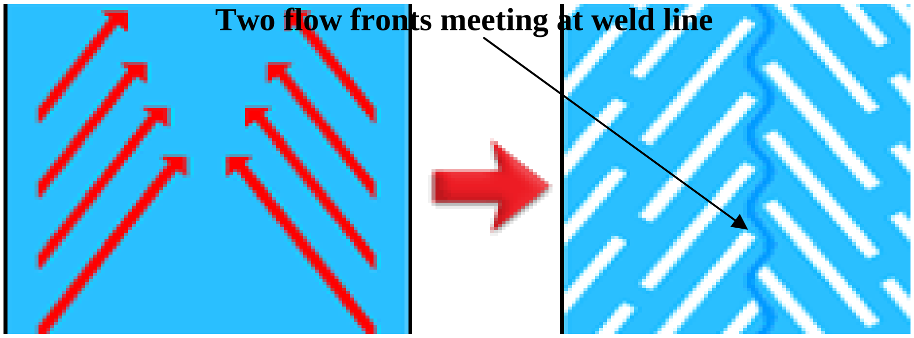


Figure 3.7 Two Flow Fronts Meeting At Oblique Angle To Create Meld Line[30]

3.8.3. Bubble A spherical, internal void caused by air or other gas trapped within a molded plastic product. A bubble differs from a blister in that the bubble is contained within the part, whereas a blister is on or near the surface of the part and generally causes deformation of the surface.

CHAPTER 4

THERMOPLASTICS IMPACT BEHAVIOUR

Up to this point of our work we have under stood the construction, physical and mechanical properties and injection molding process of thermoplastics. During this theoretical quest of exploring the various physical and molecular structure related phenomena which could ultimately alter the material properties, we have somewhat established the causes of thermoplastics impact behaviour changes under improper processing melt conditions. In the subsequent work we will focus on studying and evaluating the changes in important properties of Impact and fatigue.

In our subsequent work we will narrow down our focus on exploring the material character of HDPE after it has gone through the mold processing stage In the experimental phase we have adopted a two dimensional approach .In first phase we have carried out an extensive series of different experiments on lab specimen of material and in the second phase we have included a real product ie Butt Plate of Rifle G-3 which is manufactured with same material which we have selected.

4.1 Impact Strength

In many cases it is not possible even qualitatively to evaluate a design or make a significant comparison of structural materials on the basis of static strengths alone. A survey made in 1930 showed that over 95 percent structural failures were caused by dynamic forces (26). Impact stress is characterized by a high rate of change with time and is non repetitive. On impact, the kinetic energy of colliding bodies is absorbed by deformations in the material. Designer should always be aware of possibility of brittle fracture in impact.[38]

Total deformation at the end of short time impact is the sum of an elastic and a viscous (permanent) deformation. This time is often called the action time. If the action time is extremely short, as in impact, flow is reduced or eliminated. The solid tends to behave as a Hookian body, elongation at break is relatively small, and the energy absorbed in the process of rupture (area under stress-strain curve) tends to be small. In other words, application of load under impact conditions tends to result in brittle behaviour. Indeed, impact leads to a characteristic brittle fracture in a material that otherwise undergoes plastic flow or a long neck down at low rates of loading. It is also well known that brittle behaviour is fostered by decrease in temperature (26).

4.2 Molecular Structural Interpretation of Impact Fracture.

Brittle fracture will result when load is applied so fast that flow cannot occur. This phenomenon is described in Fig4.1. On application of impact load, the structural units that are separated by this force travel some distance and bond again to a next-neighbour unit. The average time required for the process is also the time required for the bond to attain the activation energy.

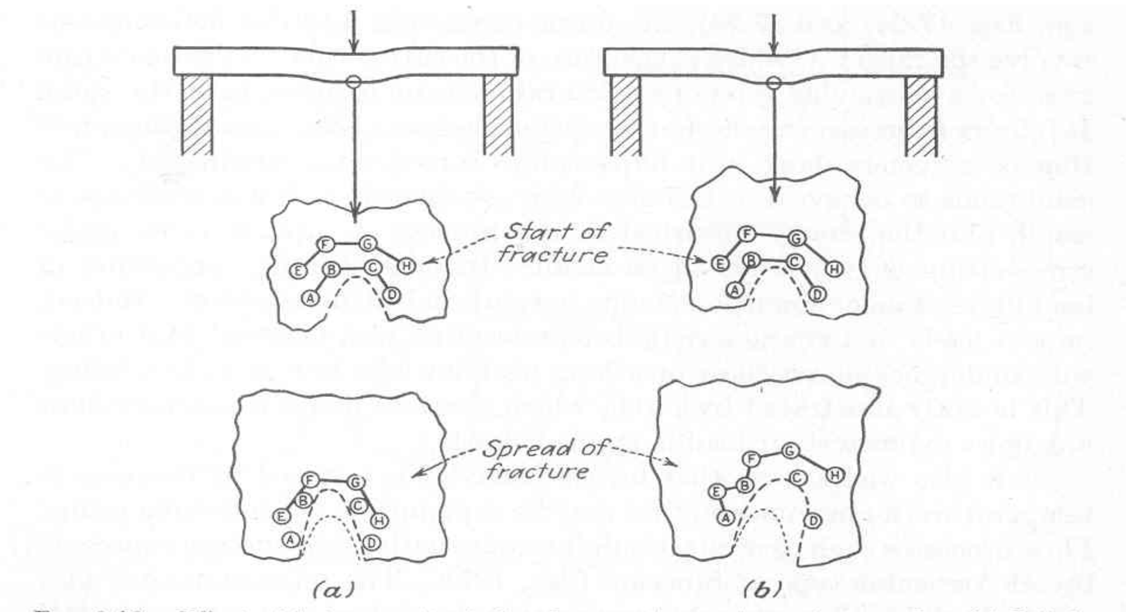


Figure 4.1 (a) Brittle fracture, strain propagated in small volume with steep localized wave front ,uniform relaxation times (b) High impact resistance, strain dissipated over large volume in all directions ,wide distribution of relaxation time[40]

While working out the impact strength of a specimen, dividing by the cross section does not yield a constant value for specimens which differ in shape. This implies that the impact strength will depend upon how large a volume of the specimen is able to participate in absorbing the energy of a blow. It may be assumed that there is a large absorption volume when the material is capable of rapid distortion without fracture. A structural interpretation may be made as follows:

4.2.1 <u>Crystal Structure Fracture</u> Consider a crystalline body in which all the structural elements along a given plane are attracted to one another by bonds identical in magnitude, type, extensibility, and relaxation times. Two successive layers of the structural elements in the crystal are shown schematically as A-B-C-D and E-F-G-H. (Fig 4.1) Assume now that under impact a stress is built up just sufficient to break the bonds in A-B-G-D. The crack then starts forward. Either the bonds will not have time to re-form, or they will do so with new neighbours in a symmetrical fashion so that the stress wave will progress in one direction only and will maintain a sharp front. When it reaches the layer E--F-G-H, the process will be repeated. .Thus only a small volume of the material will participate in resisting stress, and if this is originally great enough to cause fracture, the fracture tends to continue across the entire specimen. The material is brittle.

4.2.2 <u>Amorphous Structure Fracture</u> By contrast, consider an amorphous material or, for example, a linear-polymeric product with crystalline and amorphous regions. Here the bonding between elements is irregular with respect to magnitude, type, relaxation times, and extensibility. when fracture starts and breaks the bonds of A-B-C-D, A and B have (by assumption) short relaxation times and rebond quickly to next neighbours E and F; but C and D are assumed to possess long relaxation times and to require relatively large amounts of energy to become activated sufficiently to rebond to new neighbours. The right-hand side of the stress front is accordingly pictured to be left open so that the fracture spreads in this direction. As a consequence,

the impact fans out, the stress concentration is reduced, and the volume participating in energy absorption is large. The material is tough rather than brittle. Impact strength is particularly sensitive to notch effects as well as localized stresses "frozen into" the material during manufacture (26).

4.3 IMPACT ENERGY

We have modelled our analysis of impact behaviour on injection molded high density polyethylene Butt Plate .The mathematical modelling has been done as a vertically falling mass which is subjected to impact loading .In fact this is the actual service loading condition which this product experiences during use. Law of conservation of energy is explained in Fig 4.2 for a free falling mass.

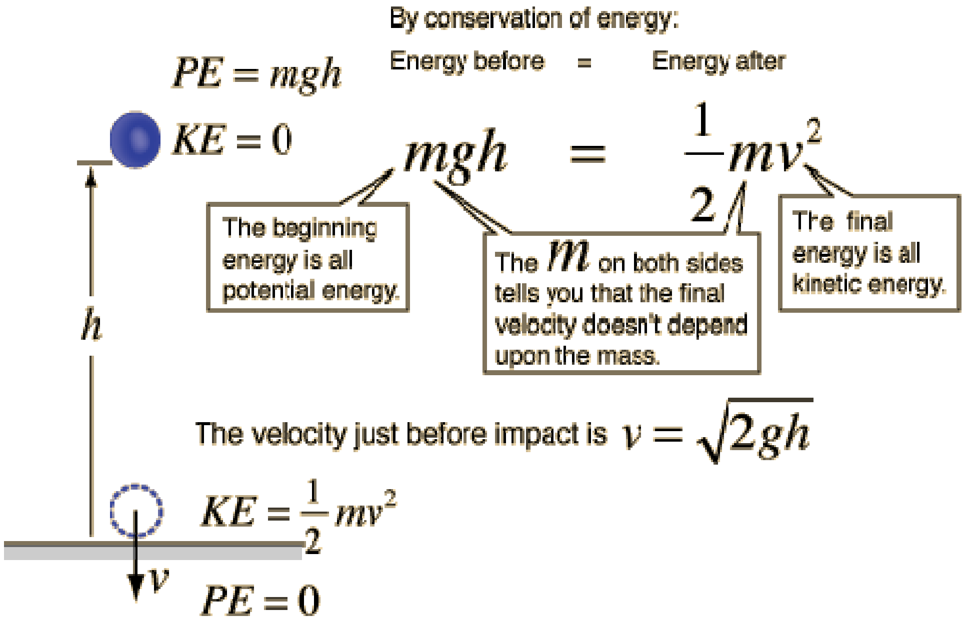


Figure 4.2 Law of conservation of energy ,the potential energy is converted into kinetic energy before impact

In impact, the change in momentum is equal to the impact force times the duration of the impact

$\Delta(mv) = F\Delta t$

$$\text{Or} \quad F = \Delta(mv)/\Delta t \qquad (1)$$

more accurately: $\Delta(mv) = \int F(t)dt$

For clear understanding we have simplified our model of vertically falling Butt Plate on ground (Fig 4.3)

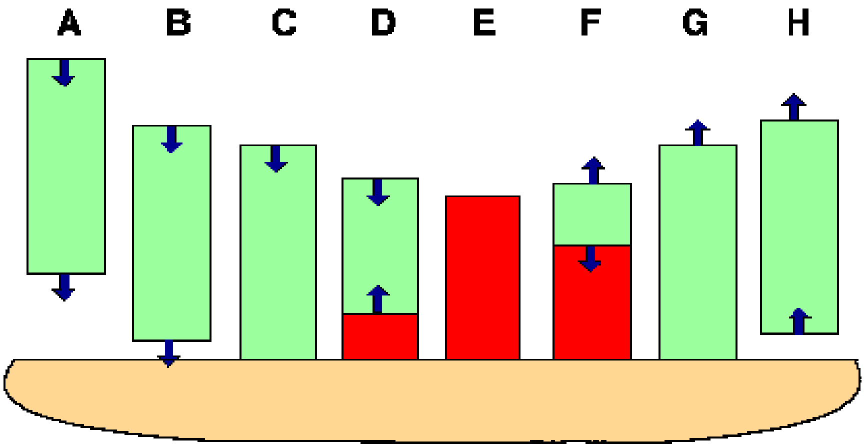


Figure 4.3 schematic of a free falling plate on ground

At moments A and B, the Butt plate is in free fall and has no force acting upon it and it is in an unstressed state (indicated by green). C is the moment when it hits the ground. At the moment D, bottom is stresses but the top of the plate is not. Indicated by red strip at the bottom at point E the whole plate in under stress. A shock wave moves up through the body at the speed of sound (i.e. the speed of sound in the solid, which can be much higher than the speed in air and normally *very much* higher than the 'fall speed' of the object itself.

At the moment E, the compression wave has reached the top of the plate and every particle in the plate is momentarily standing still; all kinetic energy has been transformed into potential (i.e. elastic) energy. At this moment, the top is un-compressed and thus a decompression wave starts to move *downwards* through the plate again at the speed of sound. At the moment G, the decompression wave has hit the ground. The plate is now again unstressed and moving upwards. At H, the object is free of the ground and rebounding.

4.3.1 Duration of Impact

The region behind the shock front (red in the picture) is *uniformly* stressed. i.e. the stress at the bottom of the plate during the impact, and therefore the force of the impact (stress × cross-section of the plate) is constant during the impact.

Duration of Impact $\Delta t=2L/\sigma$ (2)

Where "L" is height or thickness of plate and "σ"is speed of sound or shock wave

The speed of impact is given by conservation of energy:

Potential energy at full height = KE at impact

$1/2mv^2=mgh$ (3)

Where g is the acceleration of gravity 9.8 m/s^2

From Eq (3) Impact Velocity $V_{impact}=2gh$ (4)

With the help of these expressions we can calculate the impact energy being imparted on Butt Plate in a single blow when falling vertically down with complete weight of rifle acting on it.

Key inputs have been physically measured as given below:-

Mass of rifle acting on Butt Plate during impact m = 4.4Kg

Height of fall of Butt Plate L = 0.76m

Putting values in Eq(3) and (4) we get

Speed of impact =3.86m/s

Impact energy =32.8J

From Eq (2) it is clear that the impact duration increases with increase in height or thickness 'L" of the plate. From Eq(1) it is evident that impact force acting on plate is inversely proportional to impact duration "Δt".The intensity

or magnitude of impact will be more severe on sections where part thickness confronting the impact shock wave is less.

4.4 Impact Fatigue

The impact strength ordinarily quoted is based on a single blow. Such single-blow impact strength is no more informative about ability to withstand shock than a single static-stress cycle would be in describing behaviour under frequently repeated cyclic stress. It was important to know how well the material will withstand repeated impact and to determine what might be called an "impact-fatigue limit," i.e., an impact with which the material can be struck indefinitely without measurable or observable damage.

CHAPTER 5

EXPERIMENTAL INVESTIGATIONS

5.1 Material Details of important material properties used during this study are tabulated in table 5.1 below.

Table 5.1 TYPICAL PROPERTIES OF MATERIAL USED FOR STUDY

Comercial Name	Lupolen HDPE
Manufacturer	Basell Polyfine
Density	.96g/cc
Melt flow	0.85g/10 min (220C^{0}/5Kg load)
Tensile modulus	1000MPa
Melt point	131C^{0}

5.2 MPACT TESTING To get more reliable results tests were carried out on variety of different samples under different temperature conditions (18)

Test Sample Preparation

5.3. Injection molding apparatus RN 350 injection molding machine was used for injection molding of test specimen. for IZOD and Charpy impact tests. This machine has Injection melt temperature limits .0-300, and injection pressure range of 0-15 bars(fig 5.5).

Figure 5.1 Injection molding set-up for preparation of test specimen-ITD Labs

5.4. Notched and un- notched Test specimen were injection molded with variable melt temperatures keeping all other parameters constant as per ASTM, D 256 and ISO293 standard [9]. Images of Impact specimen, notched and un-notched are shown in figure 5.2 and dimensions are given in table5.2

Table 5.2, DIMENSIONS OF IMPACT TEST SPECIMEN

Test Specimen type	Length (mm)	Width (mm)	Thickness excluding notch (mm)	Notch depth (mm)	Radius of notch base Mm
Notched	61	12.7	10.2	2.5	1
Un-notched	61	12.7	6.4	-	-

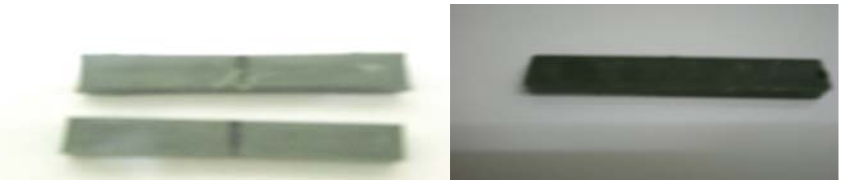


Figure 5.2 Notched (left) and un-notched (right) molded specimen for IZOD impact test

Fig 5.3 IZOD Test apparatus ,Avery –Denison LS 102DE,15 J Capacity

TABLE 5.3, CHARACTERISTICS OF IMPACT TESTING MACHINE

IMPACT ENERGY J	VELOCITY AT IMPACT m/s	PERMISSIBLE ERROR J
2.7	3.46	0.025
5	3.46	0.05
15	3.46	0.2

Calculation of Impact Strength

Impact strength of un-notched test specimen is given as

$$\frac{A}{x.y} \times 1000 \left(KJ/m^2\right)$$

Where A is the impact energy (Joules) absorbed by the test specimen

x is width of test specimen in mm

y is thickness of test specimen in mm

Impact strength of notched test specimen is given as

$$\frac{A}{x.y_k} \times 1000 \left(KJ/m^2\right)$$

Where A is the impact energy (Joules) absorbed by the test specimen

x is width of test specimen in mm

Y_k is thickness of test specimen in mm excluding notch depth

5.5 Procedure

5.5.1 IZOD Impact Testing

All test specimens were conditioned at various temperatures before testing:

1. **(1) Ambient temperature and humidity for 72 hours**
2. **(2) Test specimen were conditioned at $55C^0$ for 72 hours**
3. **(3) Test specimen were conditioned at $-20\ C^0$ for 72 hours**

5.6 Fractured test specimen

Impact testing results both for notched and un-notched specimen are tabulated at subsequent pages. The notches are molded along with test specimen through injection process.

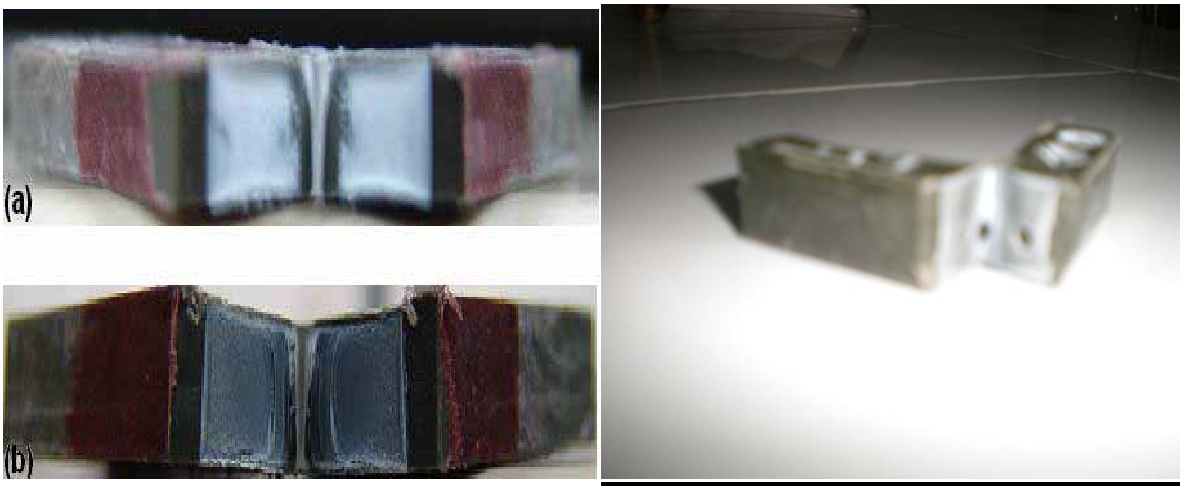


Figure 5.4 Fractured Test Specimen

5.6.1 Results

TABLE 5.4, IMPACT STRENGTHS OF MOLDED NOTCHED SPECIMEN, CONDITIONED AT AMBIENT TEMPERATURE BEFORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	1.65	1.9	1.6	2.35	1.7	1.84	14.20
240	2.4	2.6	0.95	1.45	1.9	1.86	14.35
230	2.7	2.4	2	1.85	2.15	2.22	17.13
220	2.15	2.3	1.75	2.35	1.65	2.04	15.74

TABLE 5.5, IMPACT STRENGTHS OF MOLDED NOTCHED SPECIMEN, CONDITIONED AT 55C^0 FOR 72 HOURS BEBORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	2.3	2.1	2.4	1.9	2.1	2.2	16.98
240	2.6	3.1	2.7	2.9	2.3	2.7	20.33
230	2.4	2.3	1.9	2.4	2.7	2.2	17.13
220	2.6	2.5	2.6	1.9	1.8	2.3	17.17

TABLE 5.6, IMPACT STRENGTHS OF MOLDED NOTCHED SPECIMEN CONDITIONED AT -20C^0 FOR 72 HOURS BEBORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	1.3	1.1	1.1	2.3	1.0	1.36	10.49
240	2.2	2.2	1.9	0.95	1.3	1.71	13.20
230	2.3	1.9	2.2	1.1	1.7	1.84	14.20
220	2.2	2.4	1.3	2.4	1.3	1.92	14.82

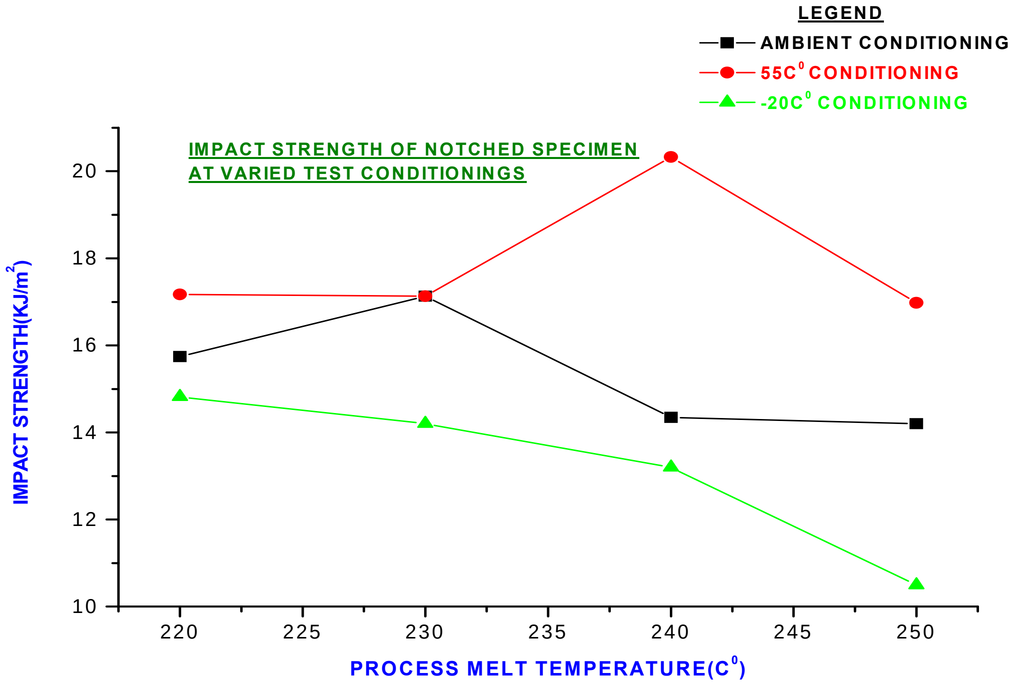


Figure 5.5 Graph of Impact Strengths vs process Temperatures for notched specimen

TABLE 5.7, IMPACT STRENGTHS OF UN- NOTCHED SPECIMEN , CONDITIONED AT AMBIENT TEMPERATURE BEFORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	2.3	2.2	2.5	2.9	1.89	2.35	29.01
240	2.5	2.8	2.5	3.6	2.2	2.72	33.46
230	2.7	3.8	2.4	2.1	2.7	2.74	33.71
220	1.65	0.85	2.4	1.9	1.4	1.64	20.17

TABLE 5.8, IMPACT STRENGTHS OF UN- NOTCHED SPECIMEN CONDITIONED AT 55C^0 FOR 72 HOURS BEBORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	2.7	2.8	1.9	2.3	2.4	2.4	29.52
240	3.3	3.7	2.9	3.1	2.6	3.1	38.13
230	2.9	3.1	3.6	1.9	2.3	2.8	33.95
220	1.4	1.3	1.2	0.7	1.8	1.3	15.74

TABLE 5.9, IMPACT STRENGTHS OF UN- NOTCHED SPECIMEN CONDITIONED AT -20C^0 FOR 72 HOURS BEBORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						**Impact Strength KJ/m²**
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	2.1	2.4	1.3	1.9	1.1	1.76	21.65
240	2.4	2.5	1.9	2.6	3.1	2.50	30.75
230	2.2	3.5	2.3	1.9	3.2	2.62	32.23
220	1.9	1.4	2.1	1.1	1.1	1.52	18.71

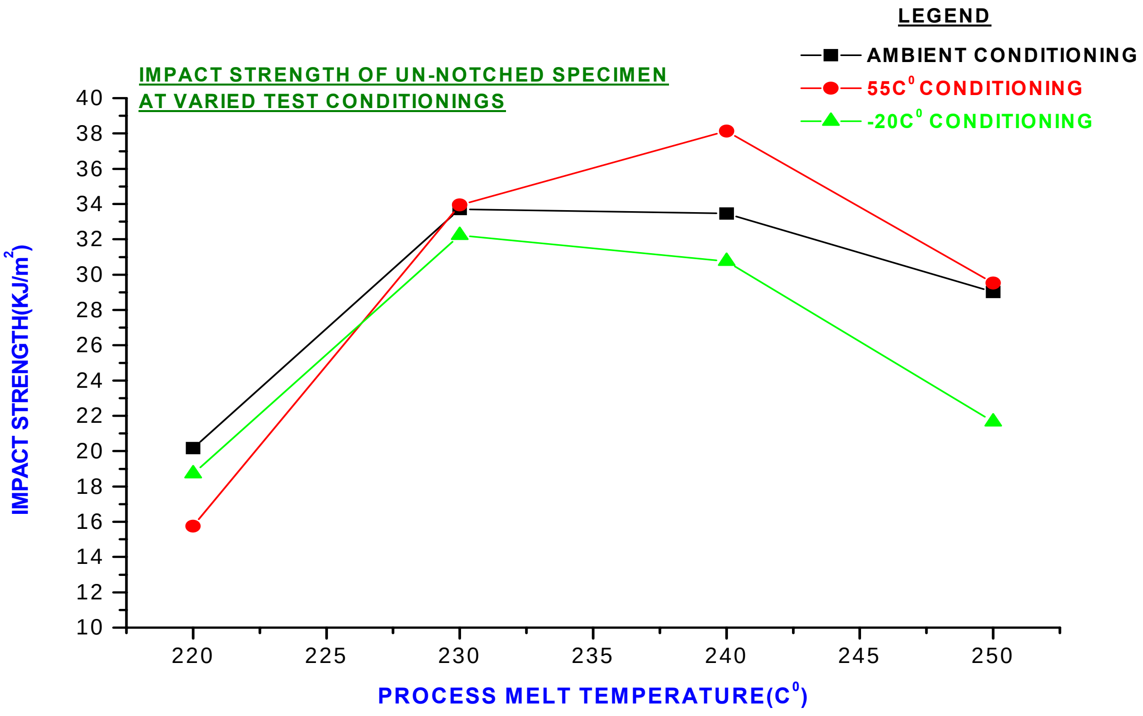


Figure 5.5.1 Graph of Impact Strengths vs process Temperatures for un-notched specimen

5.7 Charpy Impact test

Another sample of test specimen consisting 120 specimen were injection molded as per previous molding details but with the variation of one factor i.e the notch was not molded in the part but it was cut after the molding. Size of both notched and un-notched specimen were same. Results are tabulated below from table 5.10 to 5.17.

5.7.1 Results

TABLE 5.10, IMPACT STRENGTHS OF UN- NOTCHED SPECIMEN CONDITIONED AT AMBIENT TEMPERATURE BEFORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	4.3	4.5	4.4	3.7	1.7	3.72	93
240	5.7	5.8	2.6	5.9	5	5	125
230	5.8	5.6	4.9	5.6	5.9	5.56	139
220	5.1	5.7	2.3	5.5	4.9	4.7	117.5

TABLE 5.11, IMPACT STRENGTHS OF NOTCHED SPECIMEN CONDITIONED AT AMBIENT TEMPERATURE BEFORE TESTING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	0.6	0.5	0.3	0.3	0.4	0.42	32.30
240	0.3	0.6	0.7	0.3	0.6	0.5	38.46
230	0.5	0.4	0.4	0.6	0.4	0.46	35.38
220	0.4	0.38	0.36	0.4	0.3	0.36	28.30

5.8 Material Notch Sensitivity

TABLE 5.12 NOTCH SENSITIVITY OF MATERIAL MOLDED AT DIFFERENT TEMPERATURES AND TESTED AT AMBIENT CONDITIONING

Processing Melt Temp of Specimen (°C)	Impact Strength KJ/m² (Un-Notched)	Impact Strength KJ/m² (Notched)	Notch sensitivity
250	93	32.3	2.87
240	125	38.46	3.25
230	139	35.38	3.92
220	117.5	28.3	4.15

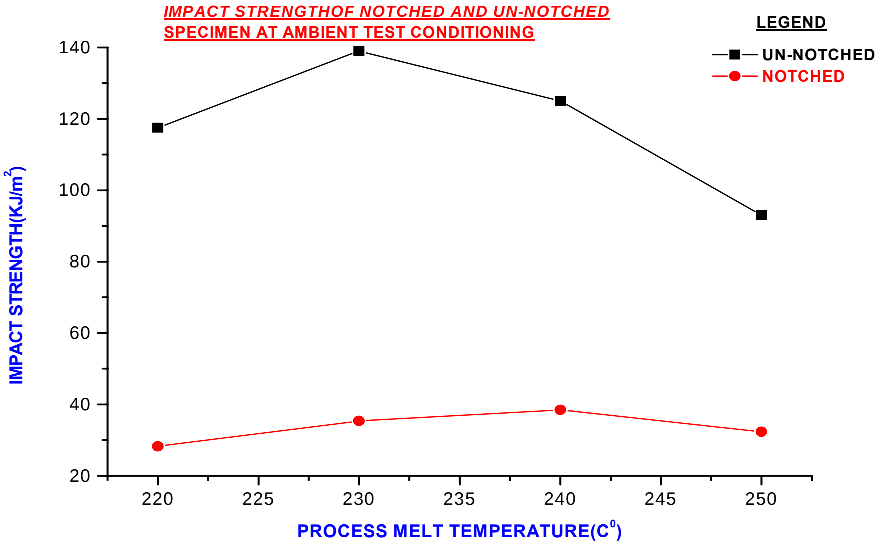


Figure 5.6 Graph of Impact Strengths vs process Temperatures for notched and un-notched specimen Tested at ambient conditioning

5.9 Notch Sensitivity

Is the fraction of the material strength in notched and un-notched configurations. From the results tabulated at 5.12, it is observed that material notch sensitivity has increased at low temperature

TABLE 5.13, IMPACT STRENGTHS OF UN-NOTCHED SPECIMEN TESTED AT 55C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	5.8	5.5	6	3.4	4	4.94	123.5
240	4.7	4.8	5.8	5	3.3	4.72	118
230	6.4	5.8	5	5.4	6.5	5.82	145.5
220	6.7	6.4	5.4	6.1	4	5.72	143

TABLE 5-14, IMPACT STRENGTHS OF NOTCHED SPECIMEN TESTED AT 55C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	0.6	0.5	0.4	0.7	0.35	0.51	39.23
240	0.4	0.65	0.55	0.4	0.48	0.49	38.15
230	0.7	0.3	0.48	0.4	0.5	0.47	36.61
220	0.45	0.6	0.55	0.6	0.35	0.51	39.23

5.10 **Material Notch Sensitivity**

TABLE 5-15 NOTCH SENSITIVITY OF MATERIAL MOLDED AT DIFFERENT TEMPERATURES AND TESTED AT 55C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	Impact Strength KJ/m² (Un-Notched)	Impact Strength KJ/m² (Notched)	Notch sensitivity
250	123.5	39.23	3.14
240	118	38.15	3.09
230	145.5	36.61	3.97
220	143	39.23	3.64

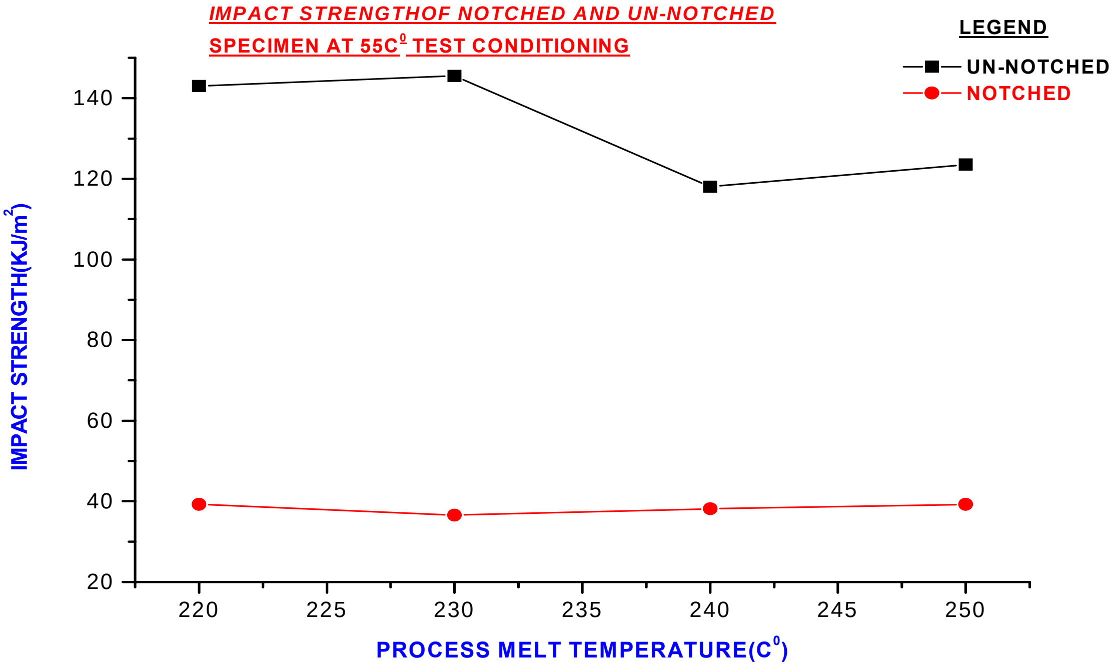


Figure 5.7 Graph of Impact Strengths vs process Temperatures for notched and un-notched specimen Tested at 55^{0}Cconditioning

TABLE 5.16, IMPACT STRENGTHS OF UN-NOTCHED SPECIMEN TESTED AT -20C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	3.5	4	4.5	3.7	3.6	3.86	96.5
240	5.7	5.8	4.8	5.5	6.2	5.6	140
230	4.6	4.8	5	5.4	4.8	4.92	123
220	3.7	4.6	5.1	4	3.8	4.24	106

TABLE 5.17, IMPACT STRENGTHS OF NOTCHED SPECIMEN TESTED AT -20C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	sample wise Impact Energy Absorbed (J)						Impact Strength KJ/m²
	Sample no 1	Sample no 2	Sample no 3	Sample no 4	Sample no 5	Avg	
250	0.4	0.25	0.3	0.4	0.3	0.33	25.38
240	0.3	0.4	0.4	0.32	0.45	0.37	28.76
230	0.7	0.5	0.45	0.4	0.6	0.53	40.76
220	0.35	0.5	0.26	0.27	0.3	0.33	25.84

5.11 Material Notch Sensitivity

TABLE 5.18 NOTCH SENSITIVITY OF MATERIAL MOLDED AT DIFFERENT TEMPERATURES AND TESTED AT -20C^0 CONDITIONING

Processing Melt Temp of Specimen (°C)	Impact Strength KJ/m² (Un-Notched)	Impact Strength KJ/m² (Notched)	Notch sensitivity
250	96.5	25.38	3.80
240	140	28.76	4.86
230	123	40.76	3.01
220	106	25.84	4.10

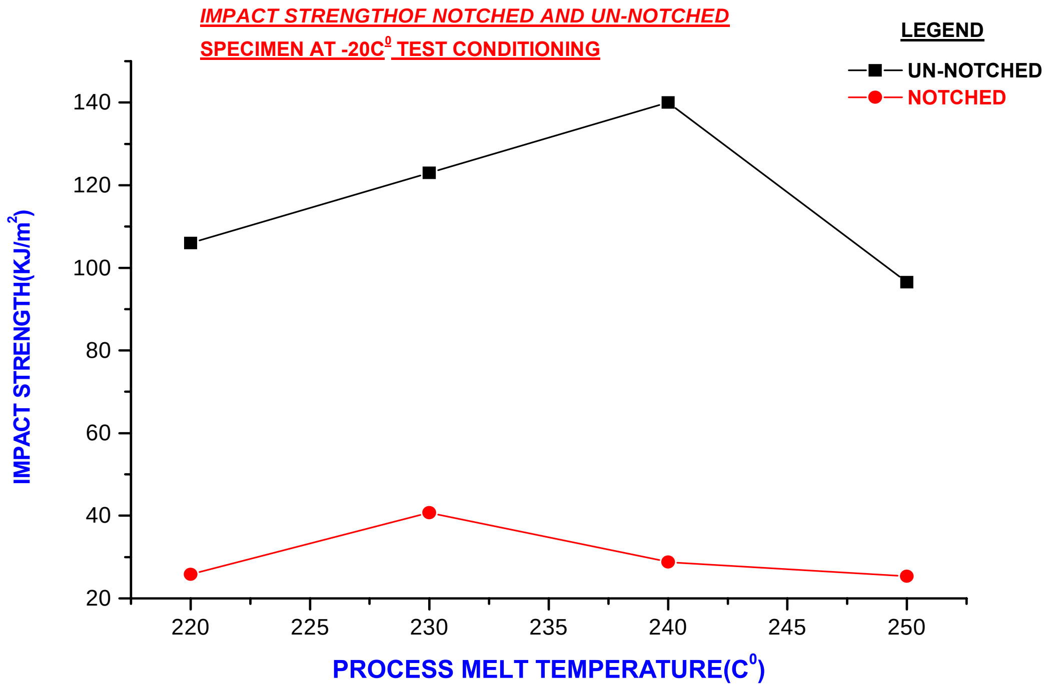


Figure 5.7.1 Graph of Impact Strengths vs process Temperatures for notched and un-notched specimen Tested at -20^{0}Cconditioning

5.12 Stress concentration at notch tip

. **The stress concentration factor (K) at the notch tip is defined by the equation**

$K=1+2\sqrt{c/r}$ (29) where

C is notch depth

r is notch tip radius

For our present model configuration

$K=1+2\sqrt{2.5/1}=4.16$

Stress concentration at notch tip increases with decrease in notch tip radius

5.13 THERMAL ANALYSIS

Thermal Analysis is the generic name for a series of measurement techniques traditionally used to determine changes in material properties with temperature[36]. TG technique was used for analysis of our under study polymer. Among the many uses of TG in the characterization of polymers, determining crystallinity is one of the most important. The main purpose of this test was to characterize, crystallinity of samples.

5.13.1 THERMOGRAVIMETRY (TG)

5.13.2 Sample Preparation

Five different samples were drawn in fine grain shape as per details given in table 5.19 from different samples molded at temperature range of 220-250^{0}C

Table 5.19, SAMPLING DETAILS FOR TG ANALYSIS OF MATERIAL

Sample no	Sample weight(g)	Material Injection Melt Temperature(C^0)
1	19.6760	DRAWN FROM CRACKED BUTT PLATE 250 C^0
2	9.4251	250
3	10.542	240
4	101.321	230
5	12.871	220

Figure 5.8 Grain shaped test sample for TGA

5.13.3 Experimental Set-up

The testing unit was a Mettler TA 3000 DSC system. First sample was taken from Butt plate which has developed cracks and the second sample was taken from a part which was injection molded at processing melt temperature of 250^{0}C. Three other samples were taken from the parts injection molded with same material but at different Injection melt temperatures. Details of samples are appended in table5-19

Figure 5.9 Mettler TA 3000 DSC system

5.13.4 Results TGA thermal degradation curves generated from the thermal analysis are shown from Fig 5.10 to 5.14

Table 5.20 Results generated fron TGA

HEATING TEMPERATURE (C^0)	% REMAINING WT				
	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5
45	100	100	100	100	100
100	100	100	100	100	100
280	100	100	100	100	100
305	98.95	98.50	99.29	98.32	98.56
345	96.06	94.49	98.78	97.67	96.76
385	94.23	80.69	87.72	85.98	89.23
425	81.60	62.31	79.02	80.98	87.34
445	63.91	53.10	71.97	76.54	63.71
465	25.64	45.98	38.29	47.53	45.89
485	4.14	39.79	26.36	42.65	33.37
505	2.50	38.87	17.20	26.74	23.54
525	2.09	38.49	17.74	21.79	17.53
545	1.98	38.46	16.57	23.08	17.19

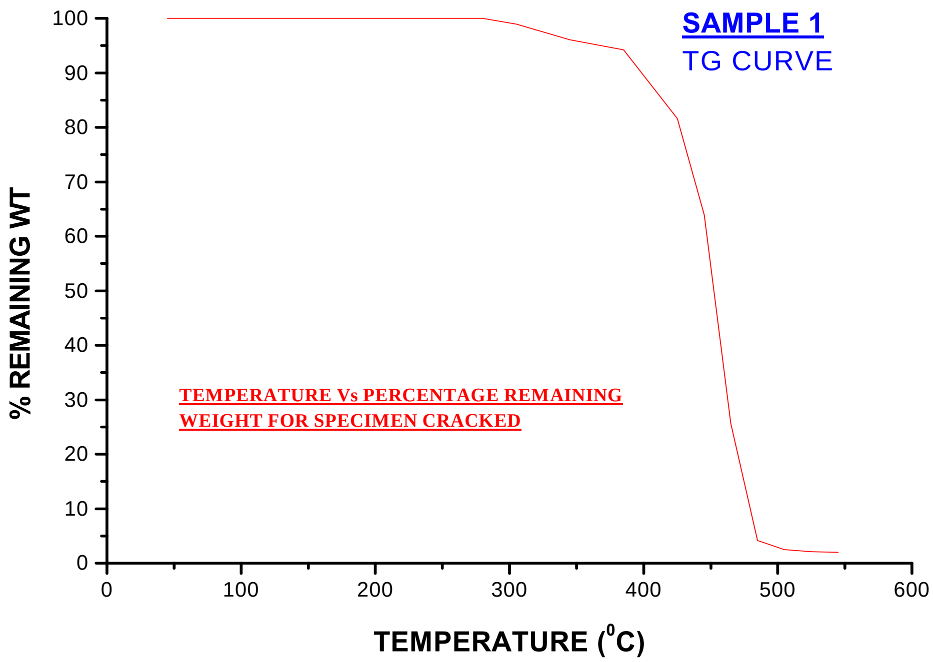


Figure 5.10 Graph of temperature vs % remaining weight of a failed product sample

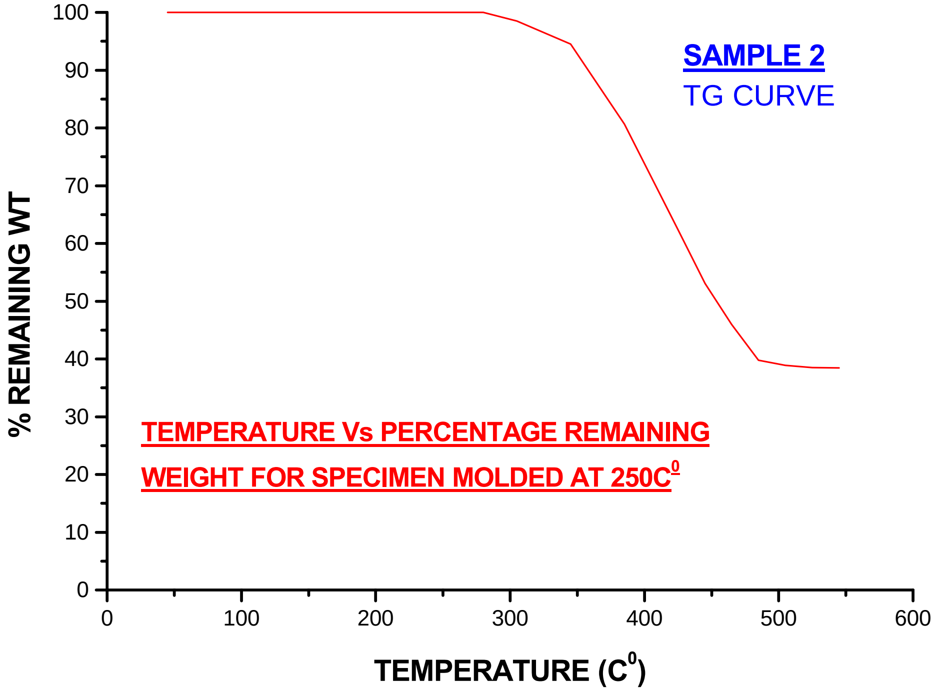


Figure 5.11 Graph of temperature vs % remaining weight of sample molded at 250°C

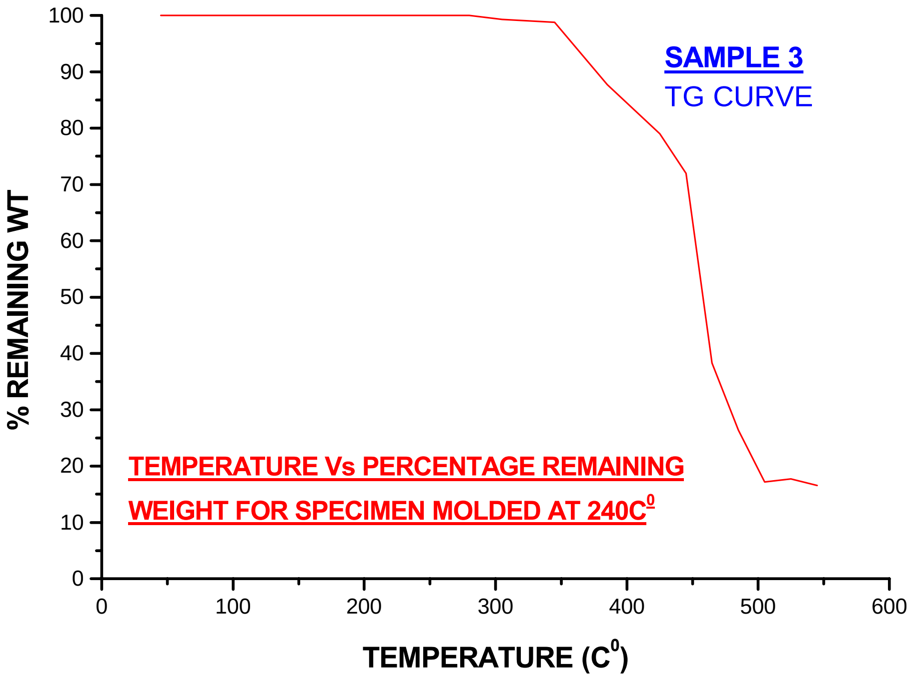


Figure 5.12 Graph of temperature vs % remaining weight of sample molded at 240^{0}C

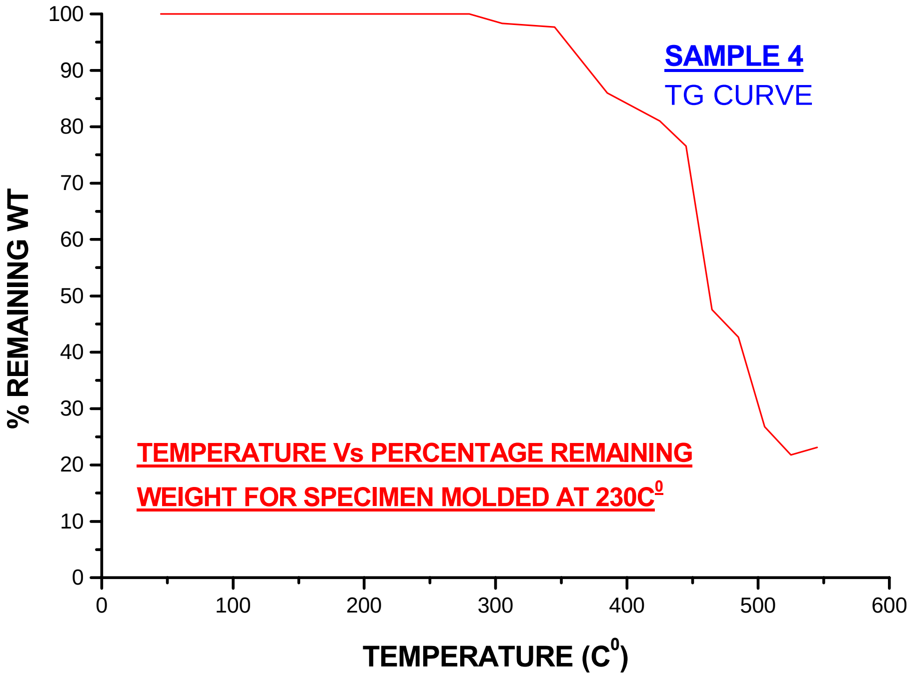


Figure 5.13 Graph of temperature vs % remaining weight of sample molded at 230^{0}C

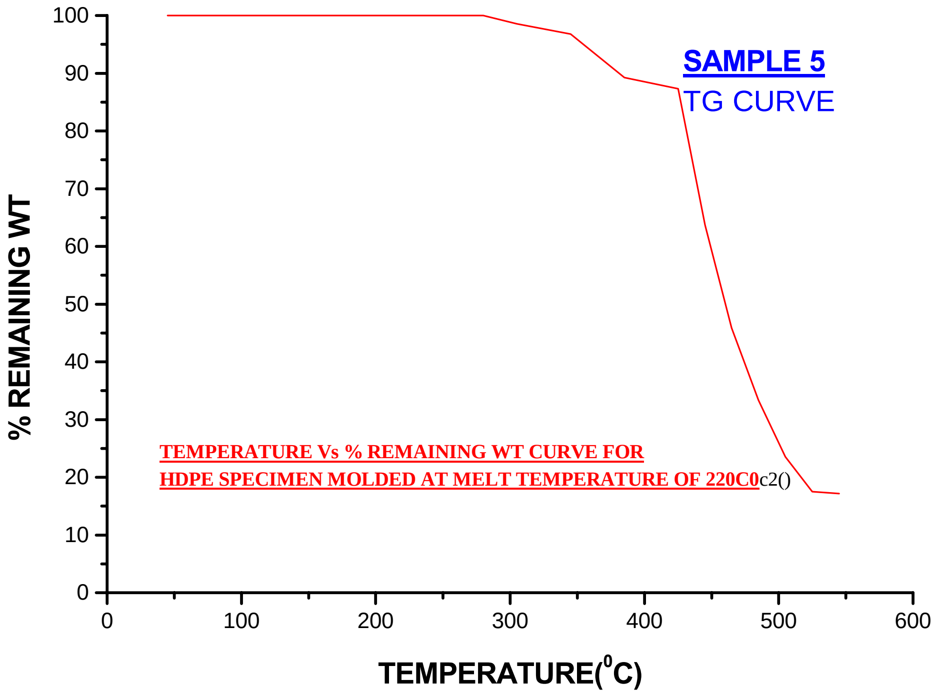


Figure 5.14 Graph of temperature vs % remaining weight of sample molded at 220^{0}C

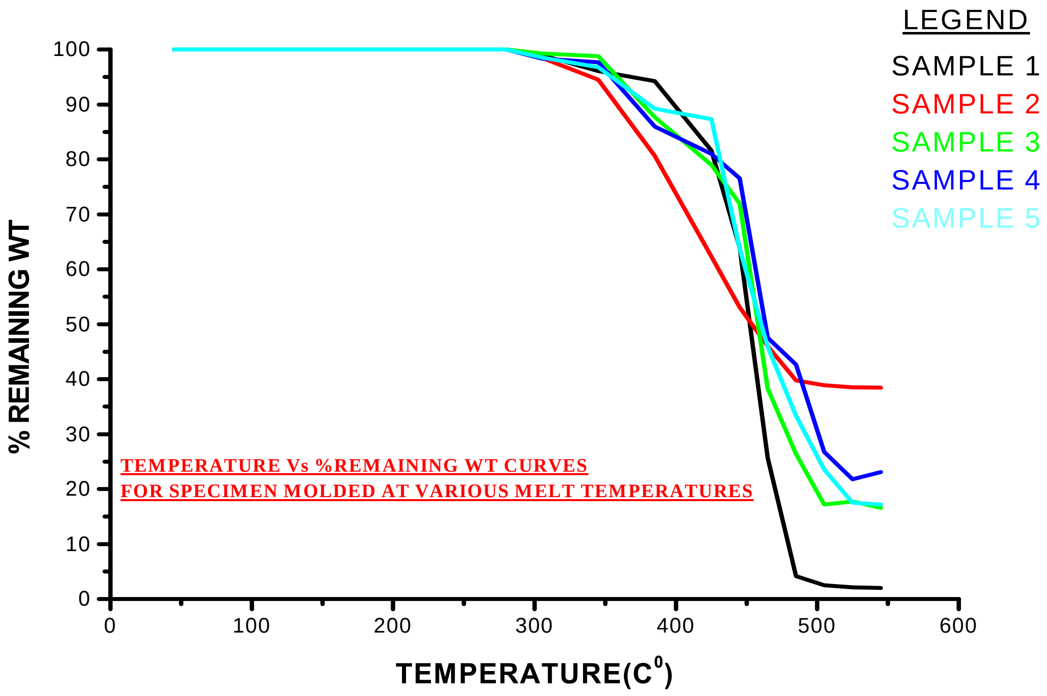


Figure 5.15 Combined Graph of all samples for TGA

5.14 MELT FLOW RATE

The index is used to study the material flow rate under different conditions of temperature These tests were carried out as per ASTM D1238 and ISO 1133 method[16].Melt flow rate measures the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load.

5.14.1 Apparatus

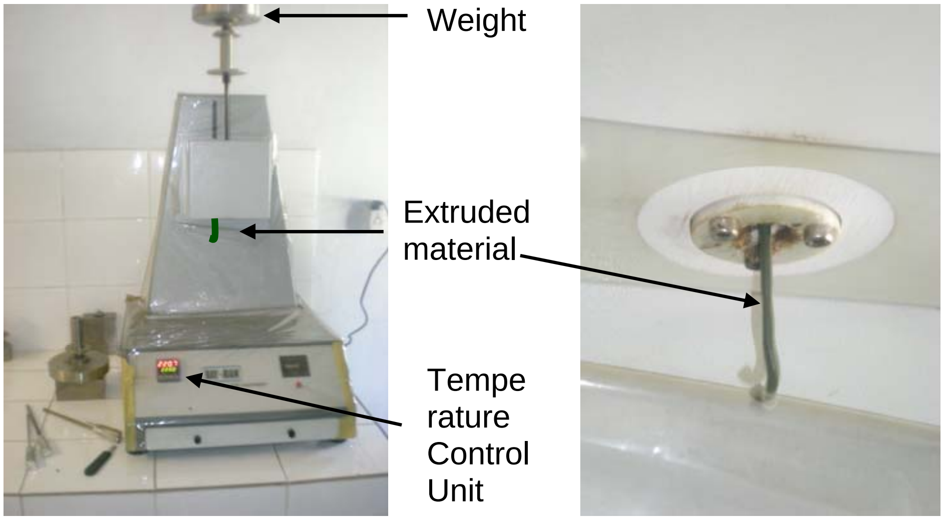


Figure 5.16 MFR apparatus RR/5 MBA

5.14.2 Test procedure

Different test samples were prepared (Fig 5.15) left one from raw material(HDPE) in granular form of particle size 4.96 x 2.9 mm and four other test samples were drawn from an in service injection molded product (Butt Plate of Rifle) molded at four different processing melt temperatures while keeping all other parameters fixed.

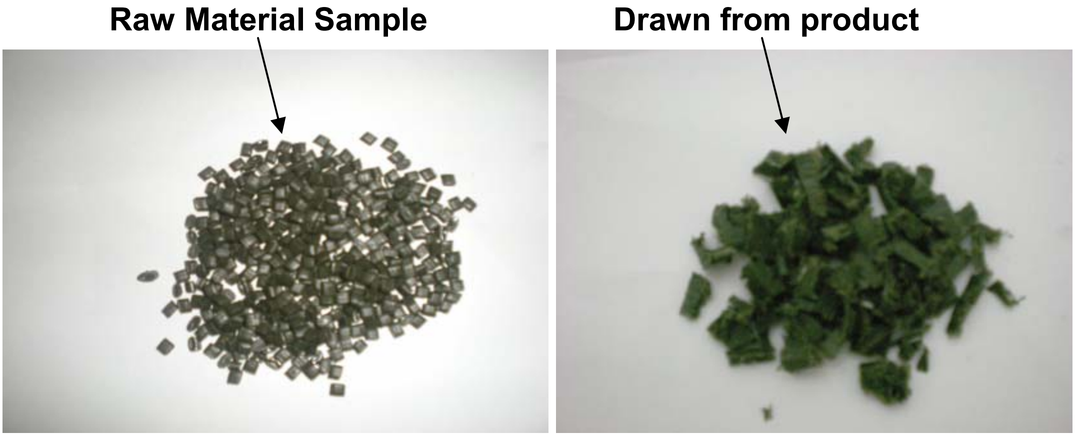


Figure 5.17 MFR Test Samples

Melt flow rate calculations(17)

$$MFR(T,F) = \frac{S \times m}{t}$$

Where

T is test temperature **220^0C**

F is test load **5 Kg**

S is reference time in sec **600 sec**

m is average mass in grams of the cut-offs

t is the cut off time interval **120 sec**

Test temperature (T) and cut-off time interval (t) were kept constant at 220^0C and 120 sec respectively.

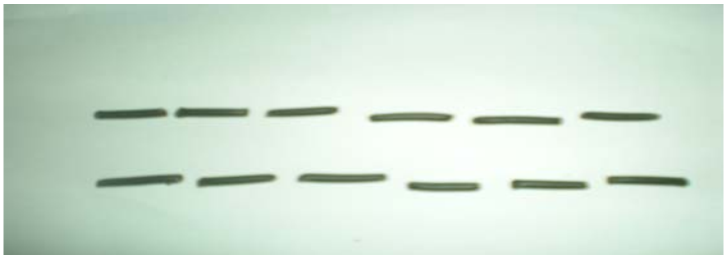


Figure 5.18 Cut offs in solid cylindrical shape

Results

Table 5.21 MFR RESULTS

SAMPLE	Material Melt Temperature (C^0)	average mass of cut-offs (g)	Cut-off time interval (sec)	MFR g/10 min
1	Raw material	0.206	120	1.032
2	250	0.228	120	1.141
3	240	0.212	120	1.061
4	230	0.208	120	1.042
5	220	0.201	120	1.007

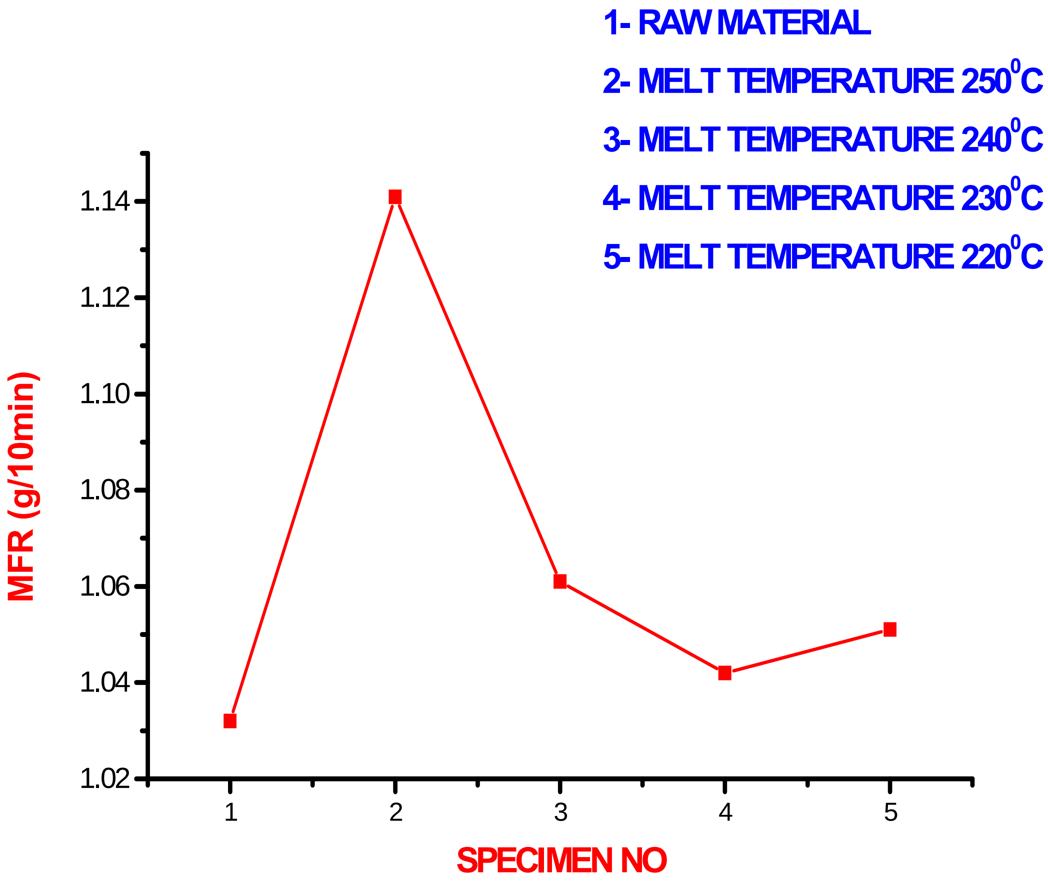
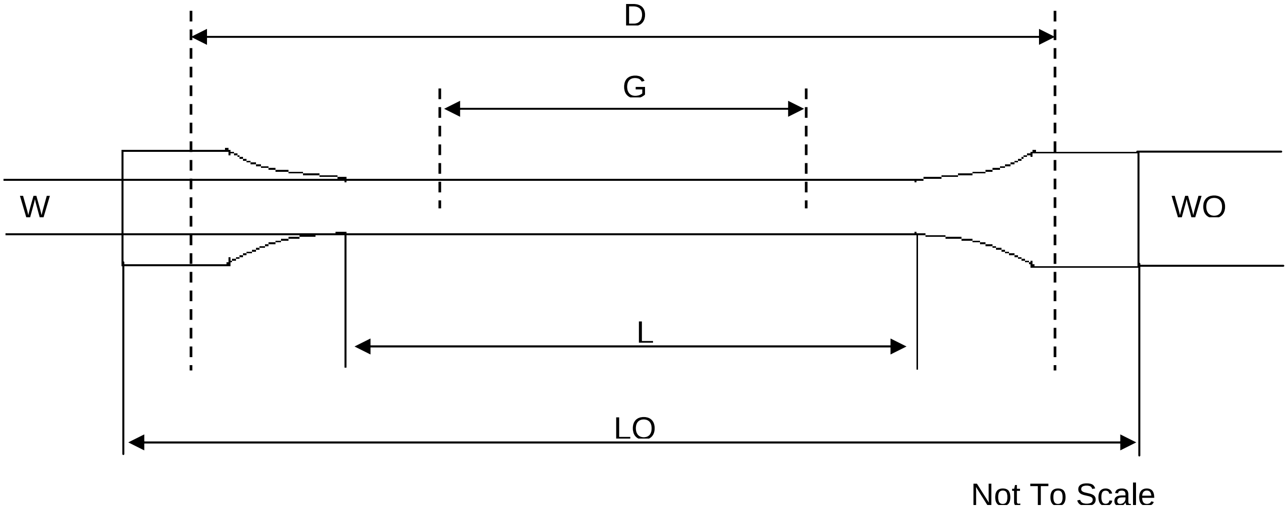


Fig 5.19 Graph of MFR VS Material Melt Temperature

5.15 TENSILE TESTING

5.15.1.Test Specimen Tests were conducted as per ASTM D638.Dumbbell shaped tensile bars were injection-molded using Arburg Allrounder RN 350 injection molding machine equipped with melt temperature and pressure controller. HDPE was first dried in a vacuum chamber at a temperature of 100C^0 for 3 hours and then molded by varying the processing temperatures Molding details are given in Table 5.22 below. During this molding process only one parameter (melt temperature) was changed and all other parameters at the injection molding machine were kept fixed

Fig 5.20 RN 350 injection molding machine



5.15.2. DIMENTIONS OF ASTM D 638 TYPE SPECIMEN.

Length over-all (LO)	**160 mm**
Length of narrow section (L)	**65 mm**
Gauge length (G)	**50 mm**
Distance between grips (D)	**115 mm**
Width over-all (WO)	**20 mm**
Width of narrow section (W)	**10.5 mm**

Table 5.22 Sampling Details For Tensile Testing

TEST SPECIMEN	MOLD TEMPERATURE ^{0}C	INJECTION TIME Sec	HOLDING PRESSURE Psi	MELT TEMPERATURE ^{0}C
B	20	10	120	220
C	20	10	120	230
D	20	10	120	240
E	20	10	120	250

5.15.3 TESTING APARATUS

FIG 5.21 INSTRON UNIVERSAL TESTING 10 KN MACHINE

5.15.4 Test procedure Five test samples at each of four different melt temperatures were molded in RN 350 injection molded machine and subjected to tensile testing at material Science Department Labs, Ghulam Ishaq Khan Institute .Load cell of 10 KN with speed setting of 10 mm per minute was used.

Fig 5.22 Sample before and after tensile loading

5.15.5 RESULTS

Table 5.23 Results of tensile testing

Specimen molding melt temperature(^{0}C)	Yield stress (Mpa)	% increase(+),decrease(-) in Yield stress at stepwise temperature rise (220-250)
220	13.8	-
230	15.2	+ 10 %
240	16	+ 5.3 %
250	16.3	+1.87 %

STRESS STRAIN GRAPHS

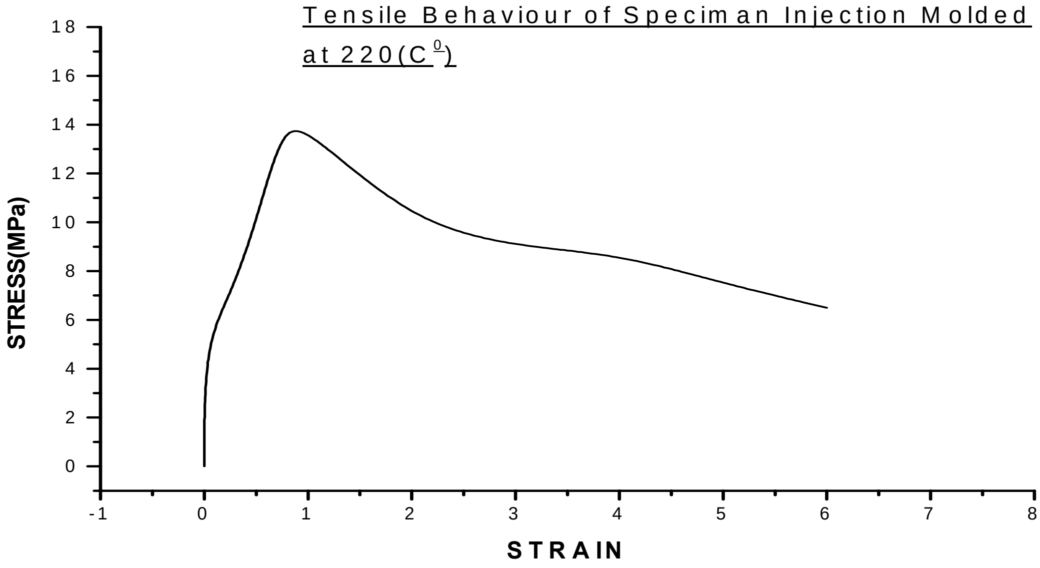


Figure 5.23 Stress vs Strain graph of material molded at 220^{0}C

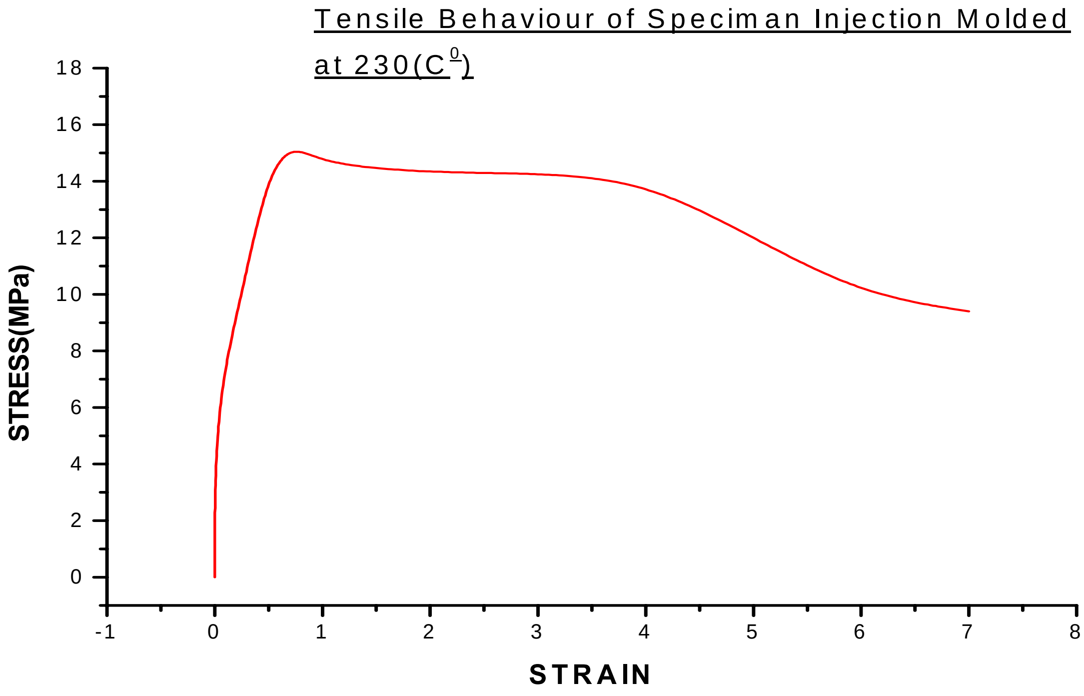


Figure 5.24 Stress vs Strain graph of material molded at 230^{0}C

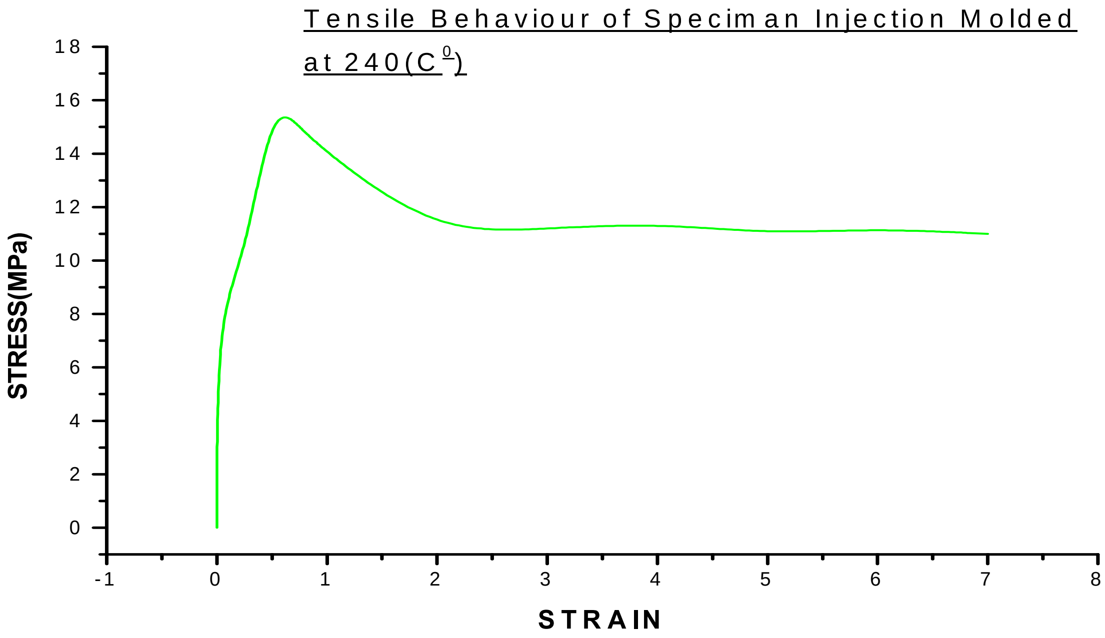


Figure 5.25 tress vs Strain graph of material molded at 240^{0}C

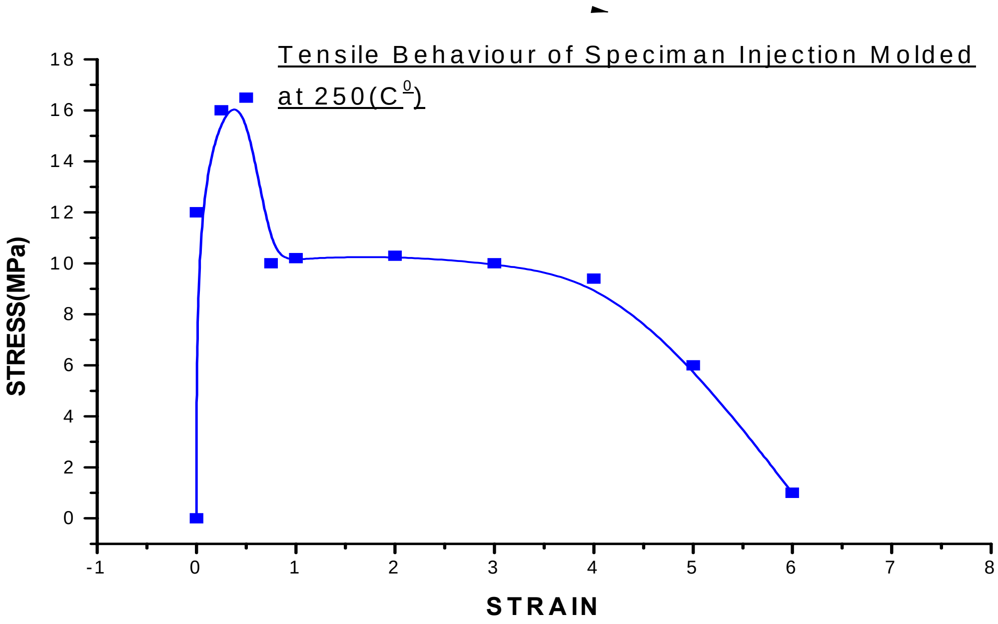


Figure 5.26 Stress vs Strain graph of material molded at 250^{0}C

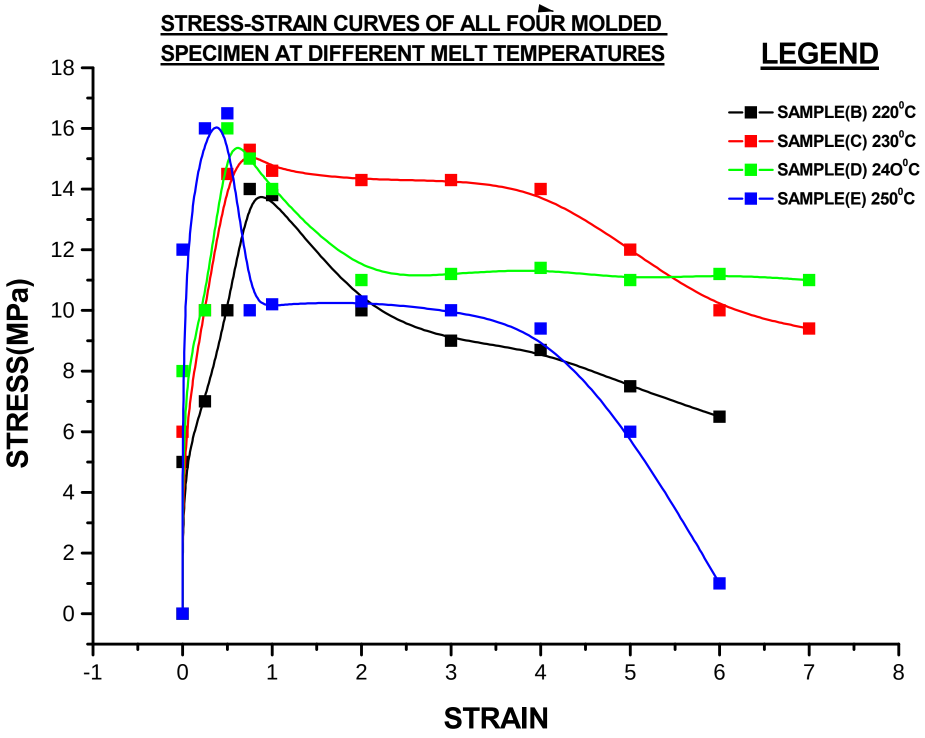


Figure 5.27 Combined Graph of all test samples

5.16 DYNAMIC IMPACT FATIGUE TEST

5.16.1. Experimental Set up

An improvised, non standard test configuration was developed (Fig5.26)and Butt Plate samples molded at various melt temperatures were subjected to cyclic impact loading after conditioning in high and low temperatures to validate impact behavior in realistic conditions. An electric motor and metal stand were fixed to a foundation. A cam was attached to motor through pulley arrangement. The rotating cam further lifts a semi fixed load bar with each rotation and allows to fall down freely once during the same rotation.

5.16.2 Procedure

The setup was build in such a manner as to impart same magnitude of impact which this part approximately experiences during its service life .In section 4.3.1 we have already determined that 32.8J of energy is imparted on Butt Plate in every single blow during its normal service use. We have achieved this energy by setting the mass of falling object as 19.8 Kg, Impact height is fixed at 170 mm and impact frequency is also constant at 60 cycles per minutes. Two plates from each sample were subjected to impact fatigue loading at a time. The tests were continued until a visual crack was observed on surface of the plate. All test samples were Radio graphically examined to check any voids in their internal structure before testing .This was done to eliminate possibility of any other variable contributing to part's mechanical property variation.

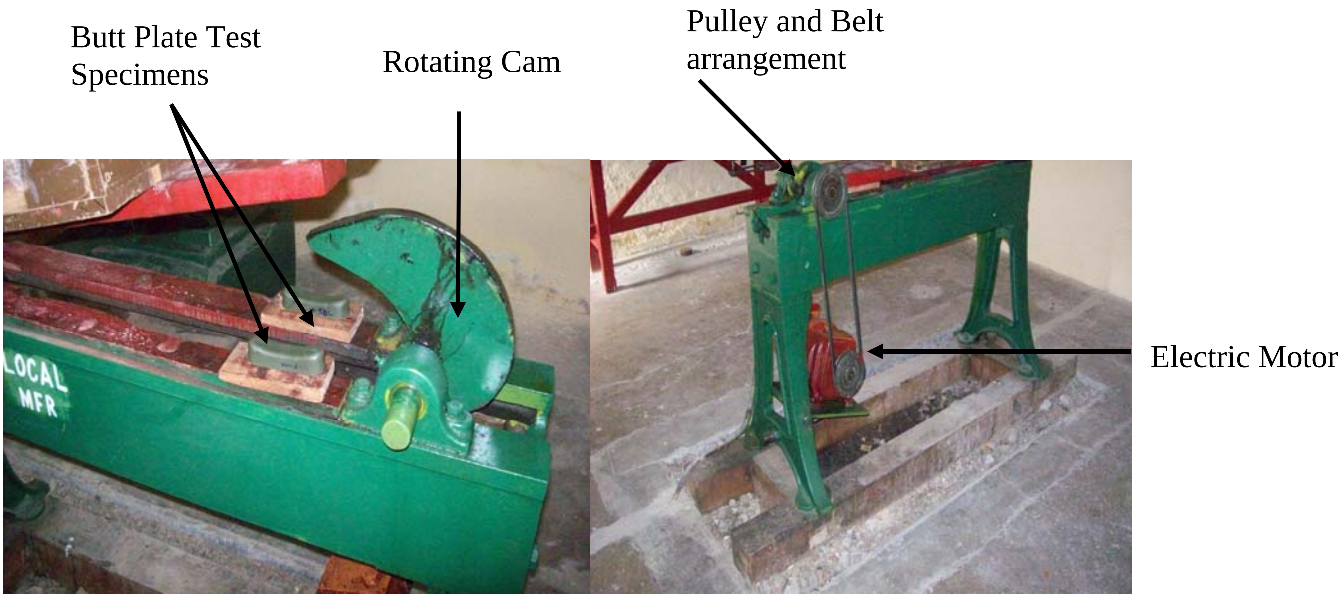


Fig 5.28 Specially fabricated Impact fatigue testing setup

5.16.3 RESULTS

Table 5.24 Results of cyclic impact loading whe samples were conditioned and tested in ambient temperature conditions

Sample no	Material processing temperature ^{0}C	Impact energy joules	No of cycles to failure
1	250	33	9066
2	240	33	11340
3	230	33	9360
4	220	33	8460

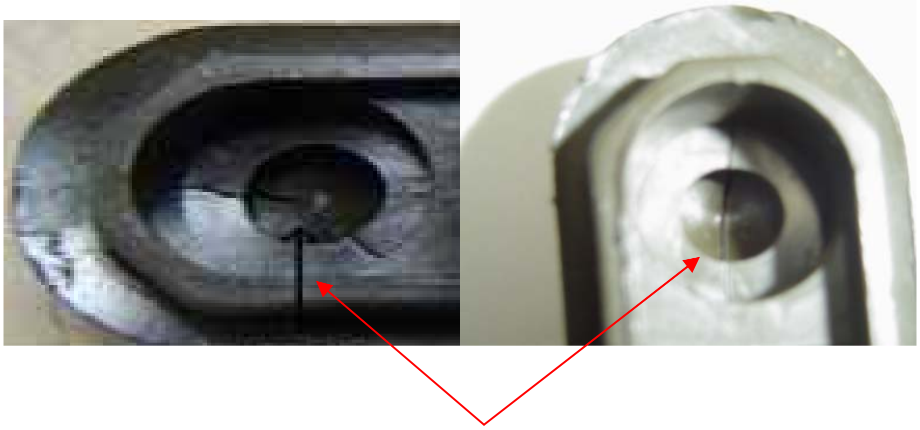


Fig-5.29 Cracks Initiation on Cyclic impact loading

Table 5.25 Results –When test sample was pre-conditioned at 50^{0}C for 24 Hrs and then subjected to cyclic impact loading in normal temperature conditions

Sample no	Material processing temperature ^{0}C	Impact energy joules	No of cycles to failure
1	250	33	7010
2	240	33	11880
3	230	33	9860
4	220	33	7240

Table 5.26 Results –When test sample was pre-conditioned at -20^{0}C for 24 Hrs and then subjected to cyclic impact loading in normal temperature conditions

Sample no	**Material processing temperature** ^{0}C	**Impact energy** joules	**No of cycles to failure**
1	250	33	7080
2	240	33	9680
3	230	33	9060
4	220	33	8700

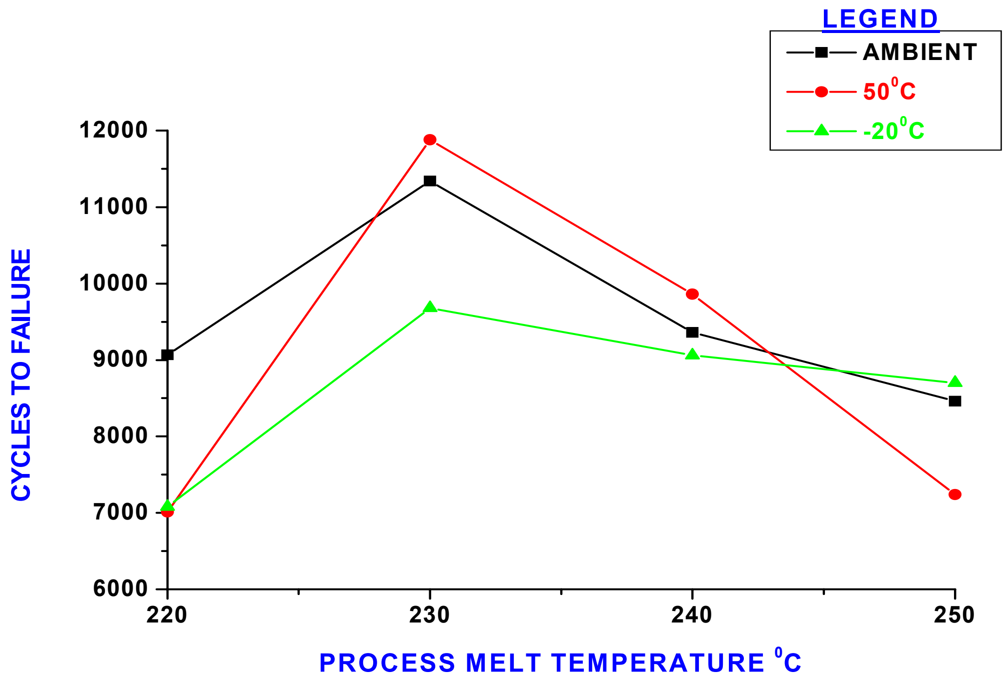


Fig 5.30 Graph of failure cycles vs material process melt temperature

5.17 Microscopy-Wide Angle X-RAY Diffraction

This test was conducted to view microscopically the topographic details of the material .The X-Rays scattering pattern gives a useful information about approximate fractions of crystalline and amorphous regions present in the material structure.

5.17.1 Sampling and procedure

Two material samples were drawn each from Butt Plates processed at 250^{0}C and failed in impact loading and the other sample from material processed at 230^{0}C but sustained the same no of impacts without fail. Results of both samples are shown in Fig 5.26 and 5.27.

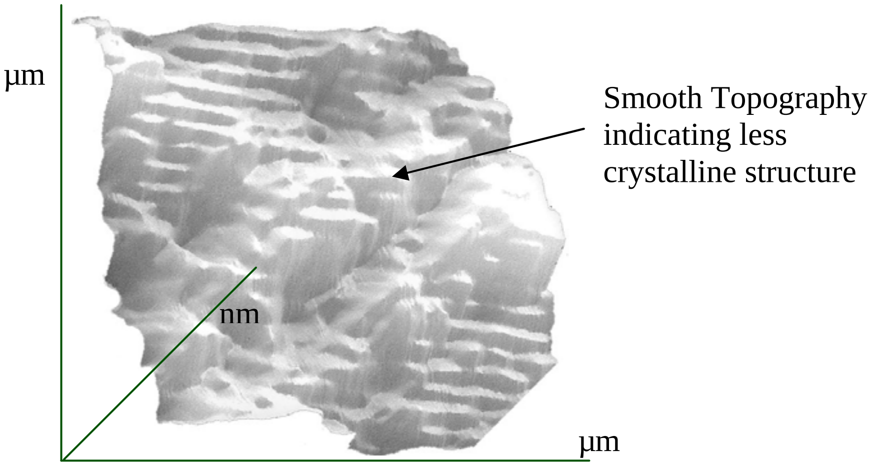


Fig 5.31 Wide angle X-Ray Diffraction material sample processed at 230^{0}C

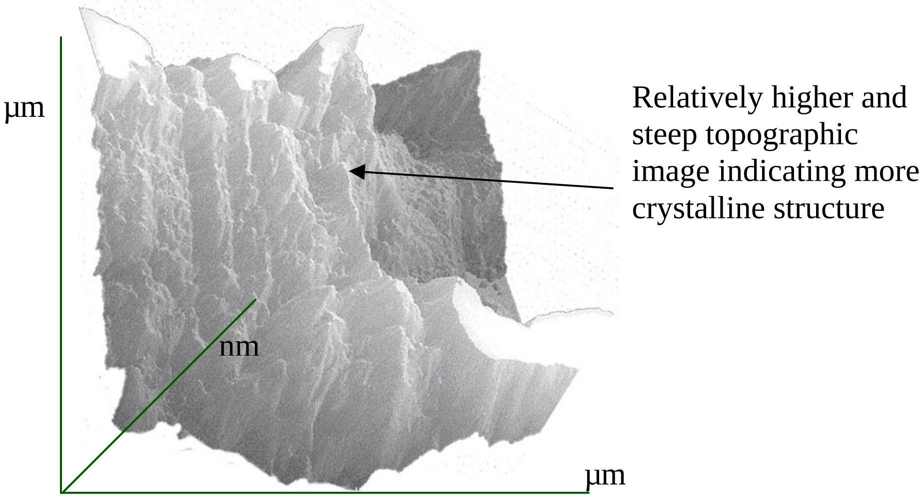


Fig 5.32 Wide angle X-Ray Diffraction scatter of cracked material sample

CHAPTER 6

INJECTION MOLDING SIMULATION

6.1 As already discussed in previous chapters that plastic material undergoes thermal and structural changes during processing. To study and analyze this process we have simulated the injection molding process of Butt Plates using Finite Element Based Programme “MOLD FLOW MPi 3”

6.2. PROCEDURE

(1). A 3D CAD solid model of Butt Plate was prepared in AUTO CAD 2006.

(2). CAD model was converted from DWG file fermata to IGES file format and imported in injection molding analysis programme “MOLD FLOW MPi 3”.

(3). 3D Solid mesh consisting of 4-noded, tetrahedral elements was generated.

(4) All input details of processing parameters were set as per actual process sheet being followed during manufacturing of this part.

(5) Injection molding analysis simulations were run with different material melt temperatures keeping all other parameters fixed.

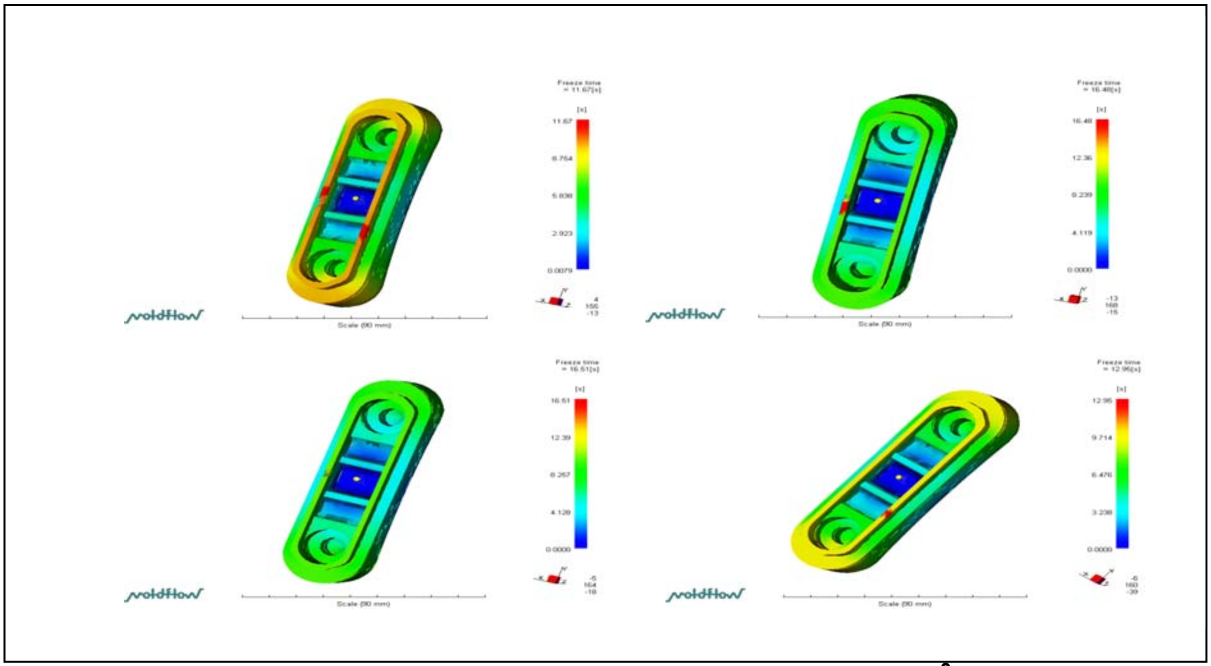


Figure 6.1. Predicted Freeze Time of parts ,molded at 220-250^{0}C   process melt temperature

Freeze Time

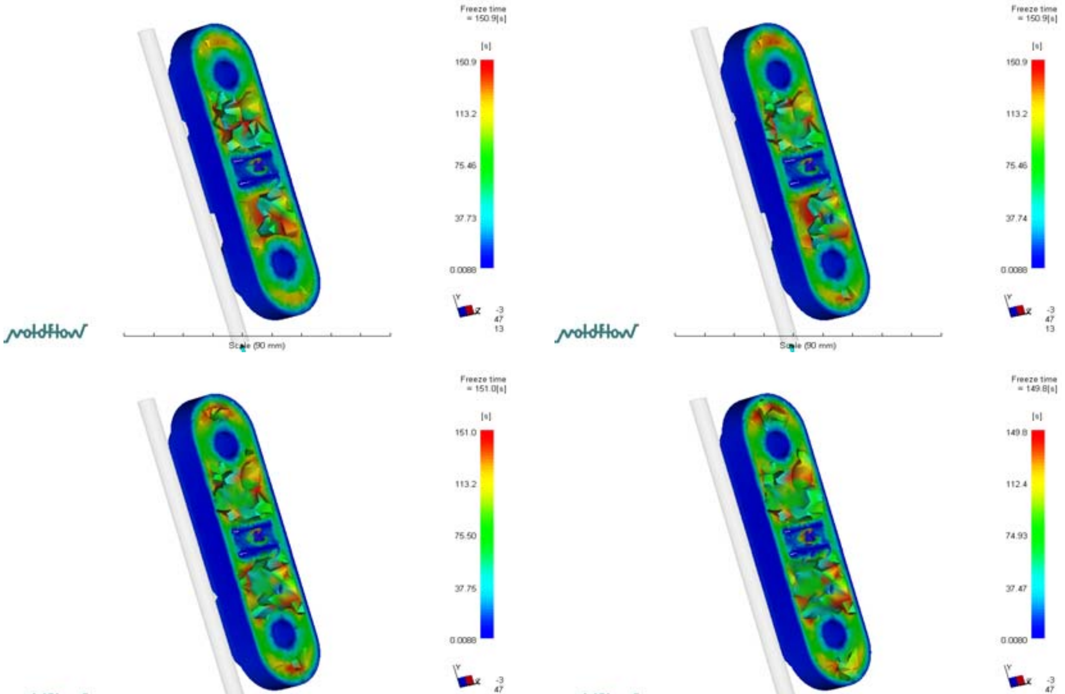


Figure 6.2. Pridicted Freeze Time -cross sectional view

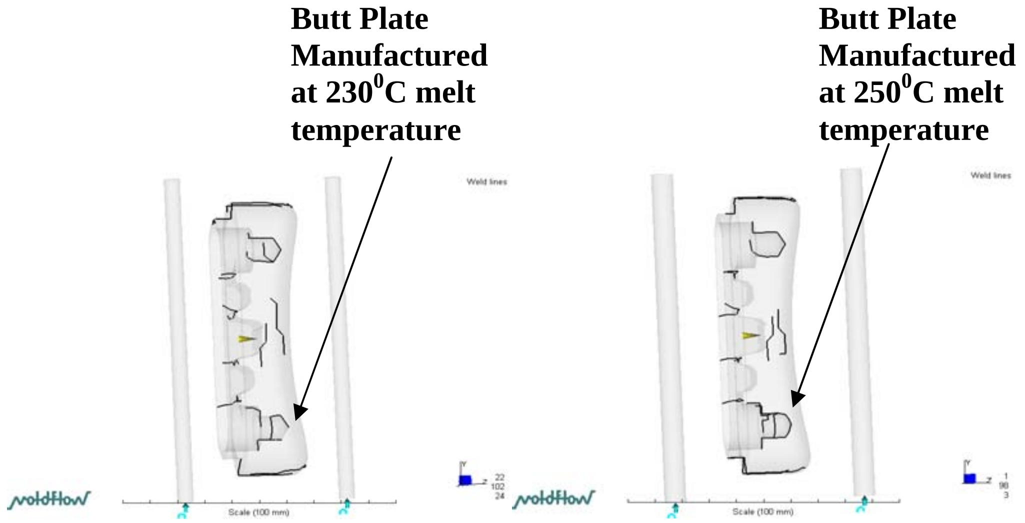


Figure 6.3. Predicted formation of weld lines during injection molding process

6.3 Discussion

6.3.1 Results of Impact testing indicates that the impact strength of material when molded at melt temperature of 230-240^{0}C is relatively high when compared to its strength at 250^{0}C molding. Further variation within this testing temperature range was observed as the impact strength of material reduced by approximately 26%when exposed to low temperature and increased by 19% at high temperature from strength at ambient temperature. As we have established during theoretical discussion that high density thermoplastic materials undergo degradation when processed at improper temperature. Molecular chains are broken with excessive heat content, forcing them to rearrange and adopt more arranged alignment and fraction of crystalline portion increases which in turn makes the material brittle. Relative reduction in material properties when molded at 220^{0}C is an indicator of the possibility that at too low processing temperatures material is not properly melted and hence flow and filling of mold is insufficient.

6.3.2 The impact behaviour of material at varying process temperatures is quite aptly has been evaluated and we can safely say that with

increased processing temperature above 240^0C material's crystallinity increases which increases brittleness and reduces impact strength. Tensile testing results supplement the outcome of impact analysis. For sample molded at 250^0C tensile yield stress is more and curve is steeply declined after this point which indicates material's deformation. Highly crystalline plastics exhibit different tensile curve from amorphous regions [39]. Material deformation is relatively less before fracture which is indicator of brittle character. Yield stress of other material samples molded at relatively low temperatures has reduced. Starting from 220^0C up to 250^0C process melt temperature, the tensile yield stress has increased from 13.8 to 16.3MPa(Table 5.23).Generally 1-1.2 MPa increase in tensile yield stress translates to 1.5 wt% increase in total crystallinity.(28,32)

6.3.3 Results noted from dynamic fatigue loading show that the material molded at 250^0C and 220^0C cracks with less number of loading cycles as compared to martial which was processed in a temperature range of 220-240^0C.This finding is in line with our deductions already drawn from impact and tensile tests. We can also predict the product life with existing material, design and manufacturing configurations.

6.3.4 Melt flow rate measurement is simple and useful technique to predict the comparative change in material molecular structure with different processing temperatures. Melt flow of material sample molded at 250^0C was higher than the other samples processed at lower temperatures. With unsuitably high process melt temperature the material is decomposed and molecular chain lengths have shortened which in turn requires less energy to break intermolecular bonding.

6.3.5 To validate our theoretical assumptions and the out come of experiments so far, we have put the material samples in another type of testing which is different from mechanical testing methods. Thermogravimetry analysis (TGA) measures the % remaining weight of material with increasing temperature. TG curves of different test

samples reveal that % remaining weight of the material sample drawn from already cracked Butt Plate is considerably less than other samples. Material of failed sample has decomposed and short molecular chains are confronted to thermal loading. Due to excessive heat some molecular chains are broken and their molecular weight densities have reduced as compared to other molecules in the structure. Large molecular weight members possess a large volume and hence a large surface. Longer molecular chains have greater molecular weights [39].The intensities of residual fields of force around the two molecules are equal; the large molecule will exert larger total attractive force on surrounding molecules. Now when the plastic is heated, both types of molecules tend to leave due to increased translational energy. However in order to leave the surface and enter a vapour state they must overcome intermolecular attractive forces. That is why the escaping tendency of the larger molecules is less and shorter molecules with lesser molecular weight readily evaporate causing overall weight reduction during heating.

6.3.6 An observation of wide angle X-Ray Diffraction (WAXD) pattern of two different material samples give different microscopic images. Sharp peak topographic pattern indicates more crystalline structure and plane surface indicates amorphous molecular structure[15] A comprehensive experimental investigations through a variety of testing techniques has lead us to conclude that HDPE is decomposed at processing temperature of 250^{0}C and impact strength of material reduces

6.3.6 The injection molding process of Butt Plate was analyzed with the help of finite element based programme “Mold Flow”. All processing parameters were set the same which are being practiced for manufacturing of this in service product, except process melt temperature which was changed for every simulation run to get comparative outcome. The results confirm to our theoretical and experimental deductions. At 250^{0}C processing the part cooling rate is

slow which causes part ejection without sufficient freezing of material. It is recommended that at least 80% material should freeze before ejection (30). Weld lines were observed at areas surrounding the base of hole. This can result into reduced martial strength in this portion and the probability of reduction in strength is further multiplied with the fact that material thickness in this area is already minimum. Too low melt temperature has again indicated different types of problems. Material flow, filling and packing of mold is not sufficient for homogeneous pattern and desired properties.

6.4. Conclusions

(1) **To predict the impact behaviour of HDPE in relation to injection molding induced material decomposition, multidimensional research methodology was adopted. A variety of static and dynamic tests were carried out on samples molded at different temperatures**

(2) **Material demonstrated relatively better impact resistance when molded between 230-240^{0}C When it is molded at recommended temperature of 250^{0}C, its impact strength reduces in entire in use service temperature range of -20 to 55^{0}C This indicates that material has decomposed at high temperature and fraction of crystalline molecular portion has increased .While further evaluating the utility of this material in sub zero temperature environment,it is found that impact strength reduces by almost 26%.This leads us to conclude that material is not suitable for intended service use where low temperatures are encountered.**

(3) **Material is notch sensitive. The failure pattern of Butt Plates during impact fatigue loading clearly leads us to conclude that cracks initiates from areas around the hole and with minimum thickness portions where stresses are concentrated.**

(4) **The inherent mechanical properties of thermoplastics can be manipulated during injection molding process**

(5) **Some experimentally determined material properties were found different from claimed by supplier of this material.**

6.5 Recommendations

(1) Intended service use of this material for applications designed to undergo impact loading, be carefully analyzed.

(2) Butt Plate design be reviewed by filling the holes and functionally verified to validate this modification.

(3) Manufacturing process parameters should be readjusted to get desired working strength of end product.

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