

*Establishing Structure-Property-Relationship In
Polyolefins*

A Major Report submitted towards partial fulfillment of the requirements for the degree

of

**MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY**

Submitted by

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June-2007

CERTIFICATE

This is to certify that the M.E. Major project entitled “**Establishing Structure-Property Relationships In Polyolefins**” completed by Mr. Abhijit Baruah, Department of Applied Chemistry & Polymer Technology, Delhi College Of Engineering, Delhi University, Delhi embodies the original work carried out by him under our joint supervision and guidance. His work has been found excellent for the partial fulfillment of the requirement of the degree of ME in Polymer Technology.

The project has been carried out during the session 2006-2007.

To the best of my knowledge and belief, this work has not been submitted to any other University or Institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

At the outset, I would like to express my sincere thanks to the management of IOC R&D, in general, and Dr. V.K. Chhatwal, DGM (Petrochemicals & Packaging) in particular for providing me this opportunity to work in this esteemed Institute.

I would like to thank *Dr. G.S Kapur, Senior Research Manager, Petrochemicals & Polymers* for giving me the opportunity to work and complete my entire project under his valuable guidance. He not only proposed this interesting work but also gave significant inputs in terms of methodological guidance as the work progressed.

I also like to thank my internal supervisor *Dr. R.C. Sharma & H.O.D Dr. G.L. Verma, Department of Applied Chemistry & Polymer Technology, University of Delhi*, for guiding me and helping me in all the related problems before and during the project period from such a long apart.

I am highly indebted to *Dr. A.S. Sarpal, DGM (AD), Dr. M.I.S Sastry (SRM), Dr. J. Christopher (SRM), Dr.(Mrs) V. Bansal (SRM), Sh. Umesh Srivastva (RM), Sh. M.S Negi (RC)* for their perpetual zeal and valuable guidance and support during the course of my project work. I also acknowledge and express my deepest gratitude to *Mr. L.K. Gupta (Chief Human Resource Manager)* and *Mr. Sanjay Bhagat* for providing me the most suitable environment during the period of my work. Special thanks to *Sh. Ranbir Singh* for his help in his own silent ways.

Lastly, I would like to thank the people that made my stay here in IOCL, Faridabad an exciting and memorable experience forwarding helping hands in all the concerned matters. I convey my special thanks to my teachers, H.O.D. and also the Ph.D. Scholars.

Finally to my parents, sister and friends go my eternal gratitude for their constant love & support.

.....
Abhijit Baruah

Broad Objectives of the Work:

1. To generate detailed base line characterization data at different levels in terms of Molecular/Microscopic, Mesoscopic and Macroscopic properties of commercial PE/PP grades,
2. To characterize and establish structure-property relationships in Polyolefins.
3. To standardize procedures of analytical characterization and testing of Polyethylene, Polypropylene samples.

ABSTRACT

Five commercial samples of polyolefins namely, PP-A, PP-B (both Polypropylene) and LDPE, LLDPE, HDPE have been studied with the aim of developing a deeper understanding of their structure-property relationships. Structural characterization have been carried out at three levels viz., Molecular, Mesoscopic and Macroscopic parameters using a wide range of techniques including Carbon-13 NMR, IR spectroscopy, thermal analysis and High Temperature GPC together with tensile, flexural, impact strength tests, Heat Deflection temperature & Vicat Softening point.

Melting temperatures, Melting Enthalpies and Crystallinity values are found to increase with increasing tensile strength and modulus as a direct result of a more regular and close packing of the molecules. Careful examination of the results shows that the presence of co-monomers in the polymer causes the creation of short chain branches and disrupts the regular packing of the molecular chains.

Analysis of Carbon-13 NMR data shows that PP-A is predominantly Isotactic, PP-B is a co-polymer of Ethylene and Propylene, LDPE contains long PE backbone with mainly hexyl branchings, LLDPE is a copolymer of Ethylene and 1-Butene and HDPE is PE backbone with no branchings.

The analysis of High Temperature GPC data show that the Polypropylene samples have similar molecular weight averages and polydispersity index, but higher than LDPE & LLDPE. HDPE exhibits bimodality in its Molecular weight distribution with high polydispersity index. Also the two PP samples have lower intrinsic viscosities at any given molecular weight than the PE samples.

These differences in Molecular Structure, molecular weight and distribution profile are also reflected in thermal analysis, tensile, flexural and Izod impact tests.

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INTRODUCTION

Polyolefins, primarily polyethylene and polypropylene, comprise the largest share of the U.S. market for polymers. Demand for the newer metallocene polyolefins is expected to grow 20 percent per year through 2006¹.

Professor Giulio Natta produced the first polypropylene resin in Spain in 1954. Natta utilized catalysts developed for the polyethylene industry and applied the technology to propylene gas. Commercial production began in 1957 and polypropylene usage has displayed strong growth from this date². Since the discovery of stereo-selective olefin polymerization in 1954, polypropylene (PP) has been considered a scientific curiosity because it showed scarcely interesting physico-chemical properties due to the low stereo- and regio-regularities of the macromolecules synthesized with the Ziegler–Natta based catalysts, and low crystallinity and melting temperature of the produced materials.³

In 1936, Imperial Chemicals, Inc. (ICI) issued the first patent for the manufacture of high pressure LDPE⁴. The manufacturing of HDPE began with the Ziegler-Natta (ZN) catalyst under low pressure in a 1953 patent⁵. Later development of ZN catalyst led to the production of LLDPE⁶. A HDPE process to make broad molecular weight distribution (MWD) resin was later developed at Phillips Chemicals Company based on the chromium oxide technology⁷. Lately, polyethylene (PE) catalyst development including the metallocene technologies has become more specialized aiming to improve the control of desired molecular weight and MWD and the short chain distribution (SCBD)⁸. These structural differences are the key to the performance of modern day PE resins in any specific applications and process conditions.

With polyolefins available in the market place from a diverse range of reactors, catalysts & co-monomer technologies, a superior understanding of a product in terms of its **Molecular, Mesoscopic & Macroscopic** properties has

become imperative so as to differentiate one's product in the market place. Thus it is important not only to characterize polyolefins from the point of view of chemical structures and basic structure/property relationship and rheological behavior, but also by the characterization of their fracture mechanical behavior.

The Indian market for polyolefins is growing at an exponential rate. New capacities are in the offing. Since early 2000, polyethylenes and polypropylenes made from every single conceivable reactor technology have become available in India. As a result, a large diversity in product grades is available to the customer. The ability to differentiate one's product in the market place with reference to competitor's product and a better understanding of the strength and weakness of one's products is a key factor for ensuring future competitiveness in the polyolefin industry. Without complete analytical support, such in depth product understanding is almost impossible. Increasingly, it is becoming difficult to differentiate products based on simple quality parameters such as MFI, MFR, density and Isotactic index. With polyolefins available in the market place from a diverse range of reactors, catalysts and comonomer technologies, a superior understanding of the product in terms of its molecular, mesoscopic and macroscopic properties has become imperative.

1.1 STRUCTURE-PROPERTY RELATIONSHIP:

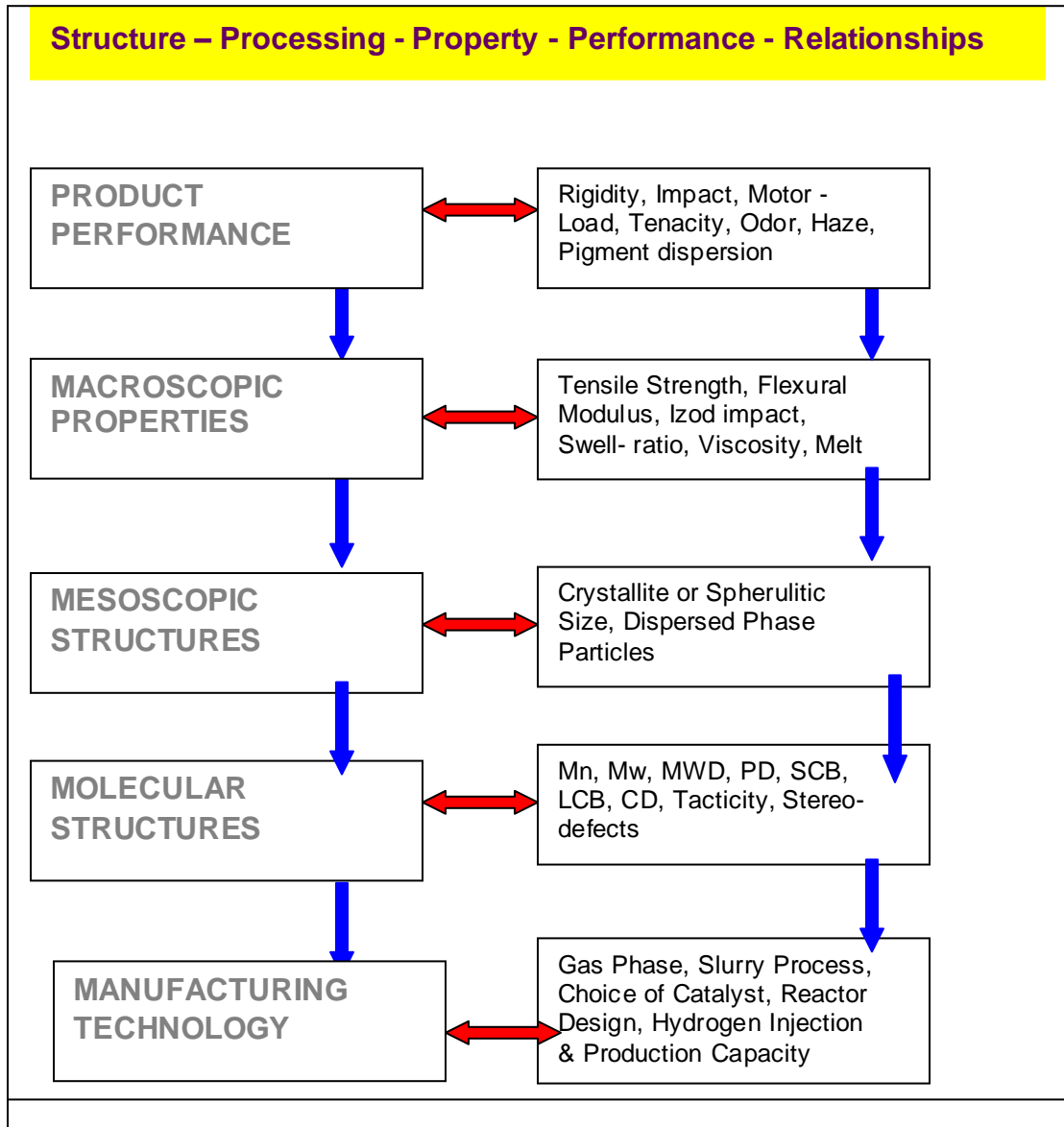
The wide variety of natural, semi-synthetic and synthetic polymers known today exhibit a wide diversity of properties. Some are rigid, hard and strong and dimensionally stable, while others are soft, flexible or largely deformable under stress. Some are soluble and fusible while others are more resistant to heat and solvents and may be even insoluble and infusible. All such properties vary from a polymer of one type to a polymer of another type. They may vary even between samples of the same type of polymer depending on how they are prepared and treated thermo-mechanically before being tested. Depending on the property ranges they exhibit, the polymers are classified as rubber, plastics and fibres.

To find a relation between the structure of a polymer and its physical properties, the factors that largely influence the properties should be primarily considered. **These factors are:** Molecular weight, Polarity, Crystallinity, Molar cohesion, Linearity, and Non-linearity of polymeric chains, Thermo-mechanical history of the polymer and temperature of observation etc. The simple consideration of chemical structure of the repeat units to predict properties, particularly the mechanical behaviour has certain limitations. This is because the chemical structure of individual molecules or segments thereof contributes partly and often indirectly to mechanical properties and a more consequential and direct role is very often played by the supramolecular structure, i.e., the physical arrangement of the chain molecules with respect to each other, more so for crystalline polymers.

The main objective is solving product performance problems through the use of **SP3R chain (Structure – Processing - Property - Performance - Relationships)**. SP3R are established by the detailed characterization of resins at three different length scales: **Molecular, Mesoscopic and Macroscopic**, as shown in the adjacent chart. Subtle differences in any one or more of these structural levels could result in the under performance of a product through the SP3 R chain.

1.2. Molecular Weight and Molecular Weight Distribution:

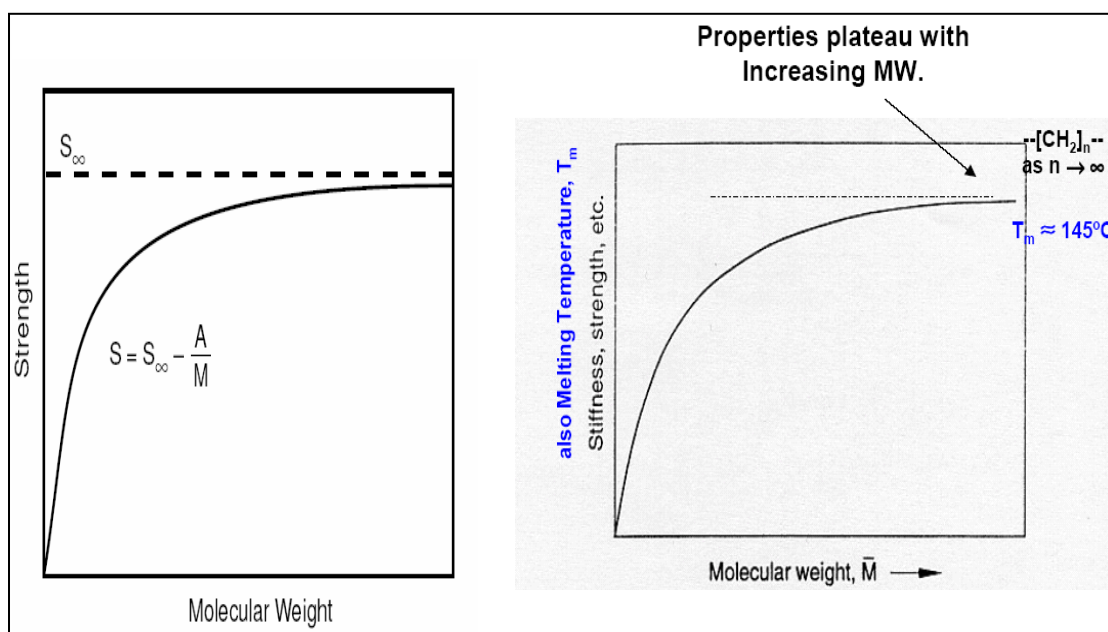
The molecular weight and molecular weight distribution in polymer systems play an important role in determining their bulk properties. Higher molecular weight permits greater degree of chain entanglements resulting in higher melting or softening temperature and tensile strength. For a polymer to be useful it must have transition temperatures to waxes or liquids that are above room temperatures and it must have mechanical properties sufficient to bear design loads.



For example, consider the property of tensile strength. Figure below shows a typical plot of strength as a function of molecular weight. At low molecular weight, the strength is too low for the polymer material to be useful. At high molecular weight, the strength increases eventually saturating to the infinite molecular weight result of S_{∞} . The strength-molecular weight relation can be approximated by the inverse relation:

$$S = S_{\infty} - \frac{A}{M} \quad \dots\dots(1)$$

where A is a constant and M is the molecular weight. Many properties have similar molecular weight dependencies.



Unlike small molecules, however, the molecular weight of a polymer is not one unique value. Rather, a given polymer will have a distribution of molecular weights. The distribution will depend on the way the polymer is produced. So, in case of polymers the distribution of molecular weight, $P(M)$, or the average molecular weight, $\langle M \rangle$ is considered. The figure below gives a typical plot of tensile strength as a function of molecular weight.

Among many possible ways of calculating average molecular weight, three are commonly used: the *Number Average* (M_n), *Weight Average* (M_w), *Z-Average* (M_z) and *Viscosity Average* (M_v) Molecular Weights. The Weight Average is probably the most useful of the three, because it fairly accounts for the contributions of different sized chains to the overall behavior of the polymer, and correlates best with most of the physical properties of interest.

M_n is related to brittleness, flow properties, compression set. M_w is related to strength properties, (tensile, impact resistance). M_z is related to elongation and flexibility. M_{z+1} is related to die-swell.

The ratio of M_w to M_n is known as the Polydispersity Index (**PDI**), and provides a rough indication of the breadth of the distribution. The PDI approaches 1.0

(the lower limit) for special polymers with very narrow MW distributions, but, for typical commercial polymers, is typically greater than 2 (occasionally much greater)⁹⁻¹³.

| Importance of MWD | | |
|-----------------------------------|--------------------------|-------------------------|
| Property/Process Parameter | Effect of High MW | Effect of Low MW |
| <i>Impact Strength</i> | ↑ | ↓ |
| <i>Melt Viscosity</i> | ↑ | ↓ |
| <i>Processing Temp</i> | ↑ | ↓ |
| <i>Flex Life</i> | ↓ | ↑ |
| <i>Brittleness</i> | ↑ | ↓ |
| <i>Drawability</i> | ↓ | ↑ |
| <i>Softening Temp</i> | ↑ | ↓ |
| <i>Stress-crack Resistance</i> | ↓ | ↑ |
| <i>Melt Flow</i> | ↓ | ↑ |

1.3. Linearity and Non-Linearity Of Polymer Chains:

The properties of a polymer would largely depend upon whether its chains are predominantly linear, branched to different extents or cross-linked. Linear polymers are mostly soluble and fusible. Small extents of branching make the otherwise equivalent polymer less resistant to solvents, chemicals and heat, owing to enhanced molecular mobility manifested through the branches or pendent groups. High degrees of branching and ultimate cross-linking make the polymer relatively stiff through greater degree of chain entanglements and ultimately forming giant molecules of a network structure, thus restraining large scale molecular mobility or chain slippage and improving dimensional stability. Polymers thereby become less soluble and less fusible, and ultimately insoluble and infusible. The mechanical strength increases substantially due to cross-linking. Through establishment of cross-links, basic structural changes in the polymer are introduced and consequently basic changes or improvements in properties are often achieved. The established cross-links are covalent bonds and the process limitation is that the shaping of the polymer to a useful article must be accomplished before completion of the

cross-linking. The process is mostly irreversible and regeneration of the heat softenable, uncross-linked structure for reprocessing is seldom possible¹⁴.

1.4 Polymer Morphology

Studies of physical form, arrangement and structure of the molecules of a material system relates to its morphology. Polymer morphology covers the study of arrangement of macromolecules into amorphous and crystalline regions and the overall physical structure of the molecular aggregates.

Different modes of chain growth (and sometimes chain termination) give rise to different configurations including head-to-tail, head-to-head or tail-to-tail arrangements, stereo-specific or random arrangements given by isotactic, syndiotactic and atactic structures in vinyl polymers etc¹⁴.

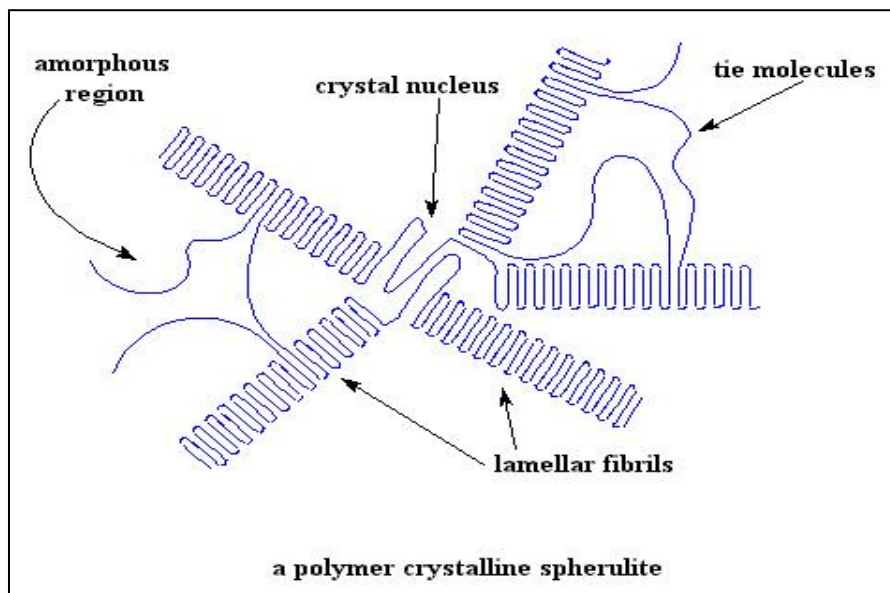
1.4.1 Degree of Crystallinity

Crystallinity is a state of molecular structure referring to a long-range periodic geometric pattern of atomic spacings. Morphological studies about polymers are primarily related to the molecular pattern and physical behaviour of the crystalline regions of crystallizable polymers. Amorphous, semicrystalline and highly crystalline polymers are known, but it is difficult or even impossible to attain 100% crystallinity in bulk polymers. It is also difficult, if not impossible, according to the latest studies based on electron microscopy and other approaches, to obtain solid amorphous polymers completely devoid of any degree of molecular order or crystallinity. A whole spectrum of structures ranging from total disorder, and different kinds and degrees of order to very high degree of order may describe the physical state of a given polymeric system depending on test environment, thermomechanical treatment to which the polymer has been subjected and the chemical environment from which the polymer has been isolated.

Polymer properties depending on % Crystallinity are:

- Density
- Permeability
- Optical properties
- Mechanical properties
- Heat sealing
- Solubility

In semicrystalline polymers, such as PE, the degree of Crystallinity (% Crystallinity) influences the degree of stiffness, hardness and heat resistance. In semicrystalline polymers, some the macromolecules are arranged in crystalline regions, known as crystallites, while the matrix is amorphous. The greater the concentration of these crystallites, i.e., greater the crystallinity, the more rigid is the polymer. Polymers having crystallites in excess of 50% are generally recognized to be crystalline. The predominantly linear chains of high density polyethylene (HDPE) exhibit crystallinity much higher than any other polymer known, even substantially higher than that exhibited by the low density variety; and for the HDPE, the attainable crystallinity is very much close to the upper limit (100%).



| | |
|---------------------------------|-------|
| Polyethylene (low density) | 60-80 |
| Polyethylene (high density) | 80-98 |
| Polypropylene (fibre) | 55-60 |
| Nylon (polyamide fibre) | 55-60 |
| Terylene (polyester fibre) | 55-60 |
| Cellulose (cotton fibre) | 65-70 |
| Cellulose (viscose rayon fibre) | 35-40 |
| <i>Gutta percha</i> | 50-60 |
| Natural rubber (crystallized) | 20-30 |

Also incorporation of rigid bulky groups such as an aromatic ring in the chain makes the polymer stiffer and hence higher melting. The polymer properties are also highly dependent on the spatial disposition of the side groups or side chains. The stereoregular (isotactic) polymers are of high degrees of crystallinity and they exhibit higher strengths and melting points than those exhibited by the corresponding random (atactic) polymers. The lengthening of the substituent group of the higher isotactic poly(α -olefin) homologues decreases the melting point up to polyheptene; from this point the melting point curve follows an increasing trend. The initial falling trend in the melting region is due to repulsion of the bulky side groups in the crystalline region. The upward trend in point is probably a result of developing trends in crystallinity involving relatively long flexible side groups, i.e., a case of side chain crystallinity¹⁴⁻¹⁹.

LITERATURE REVIEW

The continuous growth and demand in the polyolefins market and especially for polyethylene and polypropylene required aggressive research efforts to achieve improved product properties. The scientific and technological developments aimed at a proper.

Combination of the catalyst and the process to achieve the best polymer structure-property design (Figure 2.1 below) tailored to produce specialty materials for specific end-user application²⁰ (Galli and Vecellio, 2004).

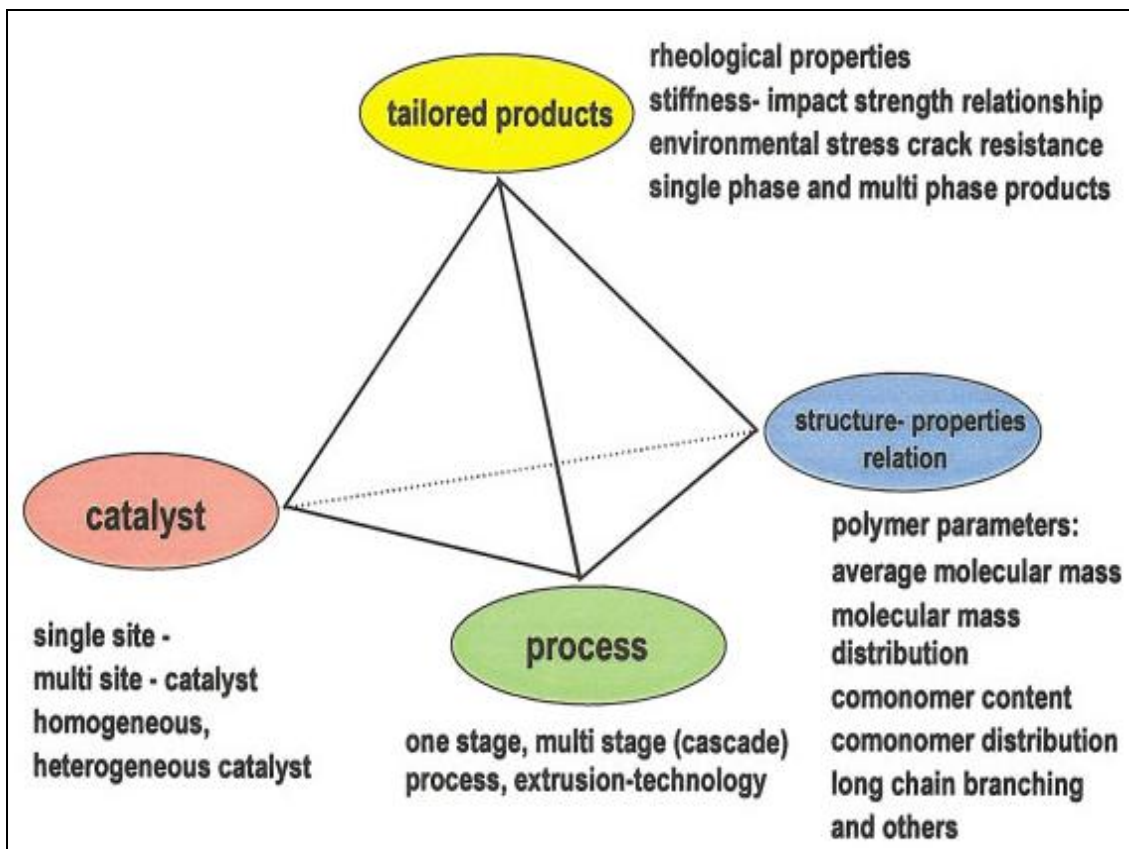


FIGURE 2.1: Technology-product relationship (Galli and Vecellio, 2004)

Increasing the average molecular weight or the degree of polymerization of thermoplastics (such as Polyethylene & Polypropylene) leads to an increase in the tensile strength, impact toughness, creep resistance, wear resistance, and the melting temperature. As the average molecular weight increases, the

melting temperature increases too, resulting in making material processability more difficult. The density, stiffness and strength of polymers are controlled by branching and packing of the chains²¹ (**Askeland and Phule, 2003**).

Therefore, linear low-density polyethylene (LLDPE), which has more branches, is weaker than high-density polyethylene (HDPE). The stiffness of polyethylene depends on the amount of crystallinity, which in turn is determined by the ability of segments in the polymer chain to crystallize. A linear polyethylene is highly crystalline. Addition of small side-groups (methyl) to a linear polyethylene decreases the crystallinity. Longer or bulky (Norborne) side-groups have a better ability to decrease crystallinity (**Ohshima and Tanigaki, 2000**).²²

Qualitative relationships between molecular properties and polymer properties and processability of polymer are described in **Table below**. The molecular structure and molecular weight distribution directly affects end-user properties.

| | <i>Molecular Structure</i> | <i>Molecular Weight (M_w)</i> | <i>Molecular Weight Distribution</i> | <i>Branching Chemicals</i> | <i>Degree of Branching</i> | <i>Degree of Branching Distribution</i> | <i>Long Chain Branching</i> |
|-------------------------------------------|----------------------------|-----------------------------------------|--------------------------------------|----------------------------|----------------------------|-----------------------------------------|-----------------------------|
| <i>Mechanical & Chemical Property</i> | Transparency | ✓ | ✓ | ✓ | ✓ | ✓ | |
| | Tensile Strength | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| | Impact Strength | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| | Rigidity | | | | ✓ | ✓ | |
| | Heat Resistance | | | | ✓ | ✓ | |
| | Cold Resistance | ✓ | ✓ | ✓ | ✓ | ✓ | |
| | Chemical Resistance | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| | Heat Seal | ✓ | ✓ | ✓ | ✓ | ✓ | |
| <i>Processability</i> | Bubble Stability | ✓ | ✓ | | | | ✓ |
| | Draw Down | ✓ | ✓ | | | | ✓ |
| | Extrusion Torque | ✓ | ✓ | | | | ✓ |

Concerning the effects of chain microstructure on mechanical properties, in general it can be stated that the presence of very long highly isotactic sequences tends to result in high values of modulus, tensile strength and hardness, whereas a lower stereoregularity improves impact strength. However a wide variety of reasons play a role in this context, including the molecular mass distribution and the morphology of the crystalline regions²⁰.

Molecular weight significantly affects the strength properties of high polymers. At very high average molecular weights where the strength-molecular weight curve approaches an asymptotic form, this dependence of strength properties on molecular weight decreases. This phenomenon is particularly well investigated in melting point-molecular weight relationships (Boeing, Walker and Meyers, (1961)²³.

Tung (1958)²⁴ reported that polyethylene fractions of molecular weights below 15,000 are very brittle and have very little strength. Also Huff and coworkers (1962)²⁵ reported that isotactic propylene has decreasing tensile yield strength with increasing molecular weight. Shalaeva and Domareva (1962)²⁶ investigated the polydispersity and degree of branching of high-pressure Polyethylene and their effect on mechanical properties.

| POLYMER | PROPERTIES |
|-----------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| HDPE | <p>HDPE has little branching, giving it stronger intermolecular forces and tensile strength than lower density polyethylene. It is also harder and more opaque and can withstand somewhat higher temperatures (120 °C for short periods, 110 °C continuously). The lack of branching is ensured by an appropriate choice of catalyst (e.g. Ziegler-Natta catalysts) and reaction conditions</p> <p>MORE OPAQUE, RIGID NON-WAXY</p> |
| LDPE | <p>It has more branching (on about 2% of the carbon atoms) than HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Also, since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower.</p> <p>MORE TRANSPARENT, FLEXIBLE, WAXY</p> |
| LLDPE | <p>Linear low density polyethylene (LLDPE) is a substantially linear polymer, with significant numbers of short branches, commonly made by copolymerization of ethylene with longer-chain olefins.</p> <p>LLDPE has higher tensile strength and higher impact and puncture resistance than LDPE. It is very flexible and elongates under stress. It can be used to make thinner films, with better environmental stress cracking resistance. It has good resistance to chemicals and to ultraviolet radiation. It has good electrical properties. However it is not as easy to process as LDPE, has lower gloss, and narrower range for heat sealing.</p> |
| Isotactic-PP Syndiotactic-PP Atactic-PP | <p>The Tacticity of a polymer can have a dramatic effect on its physical properties.</p> <p>For example, the melting points of Isotactic, Syndiotactic, and Atactic polypropylene are 160-170 °C, 125-131 °C, and <0 °C, respectively.</p> <p>Atactic polypropylene is a soft, rubbery polymer, while isotactic polypropylene is strong and hard with excellent resistance to stress, cracking, and chemical reaction. Isotactic polypropylene has a high softening point, and is easily crystallized.</p> <p>Syndiotactic polypropylene has only recently been made on a large scale. It is somewhat softer than the isotactic polymer, but also tough and clear. It is stable to gamma radiation and will therefore find applications in medicine.</p> |

POLYMER CHARACTERISTICS AND CHARACTERISATION

3.1 POLYMER MICROSTRUCTURE

New resins are produced to meet the requirements of the final application and processability. Accurate polymer characterization is required to analyze polymer microstructure, which determines the polyolefin properties. The microstructure of polyolefin is defined by its distribution of molecular weight, chemical composition, stereoregularity and long chain branching. Various sophisticated techniques are available for identification and quantification of these microstructures.

Microstructural features are often of tremendous importance in deciding the physical, and to some extent the chemical properties of polymers. The term microstructure does not necessarily infer that the feature of concern occurs at low concentrations. It is more concerned with the particular detail of the structure of the polymer. Some forms of unsaturation may exist at high concentrations, and some at low.

Branching is another aspect of polymer microstructure, which is of great interest. Polyethylene, for example, can contain side chain alkyl groups ranging from methyl to octyl or even higher, which can be identified by techniques such as NMR and Infrared spectroscopy. In case of Polyethylene, however, butyl, hexyl and octyl side-groups, which are of greater interest from the microstructural point of view, all exist at low concentrations usually expressed as the no. of such groups present per 1000 carbon atoms in the polymer chain. Such groups often have a profound effect on the physical properties of Polyethylene and the presence of different types of alkyl side-groups accounts for the fact that many different grades of this polymer are available, each with its own particular physical properties.

Changes in the configuration of branching in a polymer such as the methyl group in Polypropylene lead to changes in its stereochemical configuration and this in turn is a fundamental polymer property affecting its physical and other mechanical characteristics. A specific polymer unit configuration can be converted to its opposite configuration by a simple end-to-end rotation and subsequent translation. Natta introduced the term isotactic to describe adjacent units with the same configuration, and syndiotactic to describe adjacent units with opposite configurations. The measurement of isotacticity, syndiotacticity and the ratio between them (*syndiotactic: isotactic*), known as *tacticity* is the measurement of diad, triad etc. concentrations.

Also, various forms of unsaturation, external vinylidene, trans-olefinic unsaturation (internal double bonds), and terminal vinyl occur in PE and PP, and these are of great interest from the microstructural point of view as the type and amount of unsaturation can profoundly affect polymer properties²⁷⁻²⁸.

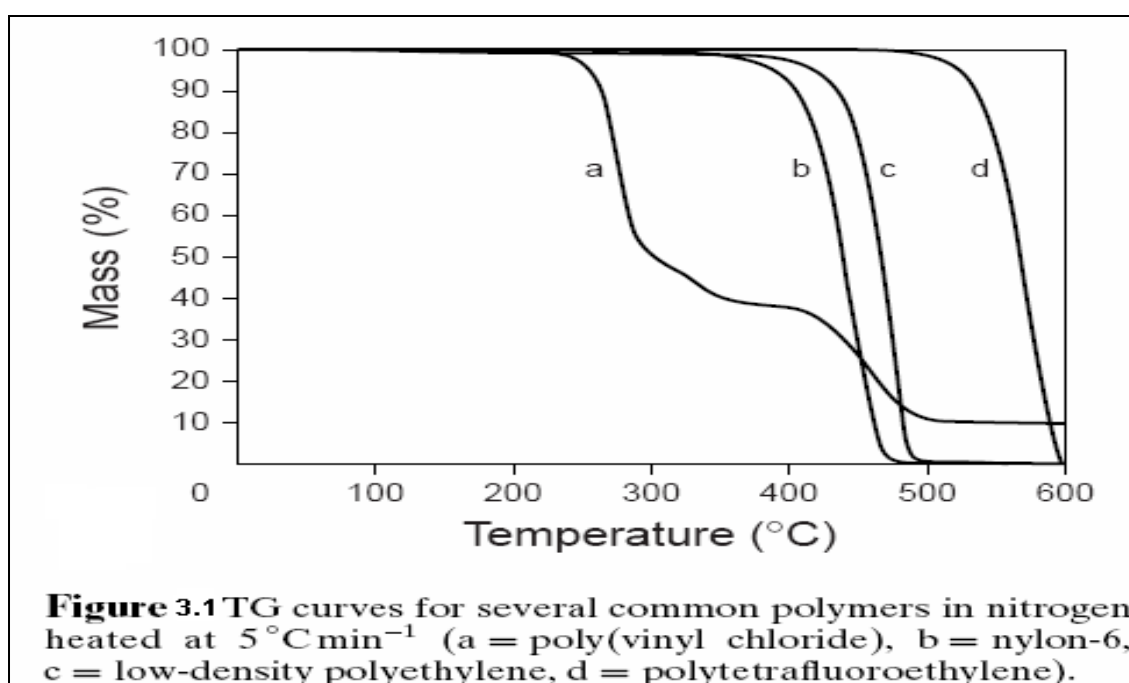
3.2 METHODS OF STUDYING THE SUPRAMOLECULAR STRUCTURE OF POLYMERS (MESOSCOPIC STUDIES)

3.2.1 THERMAL METHODS

Thermal analysis is useful in describing solid-state transitions in polymers and is of pivotal importance to understanding mechanical properties and processing of plastics.

Polymers have different thermal stabilities and thus the qualitative “fingerprint” afforded by TG in terms of temperature range, extent and kinetics of decomposition provides a rapid means to distinguish one polymer from another using only milligram quantities of material. *Thermogravimetric Analysis* or *TGA* is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies upon a high degree of precision in three measurements: **weight, temperature, and temperature change**.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures of the material in an inert atmosphere or in air or oxygen, absorbed moisture content and other volatiles and plasticizer content, ash content, extent of cure for cross-linked polymers, and in suitable cases, the analysis enables identification of polymers taking help of characteristic thermograms. TGA thermograms are obtained by recording change in weight of the test sample as it is held at a constant high temperature or it is dynamically heated in a programmed manner. A curve may be drawn to represent weight loss of the sample as a function of temperature as shown in Fig. 3.1 below.²⁹

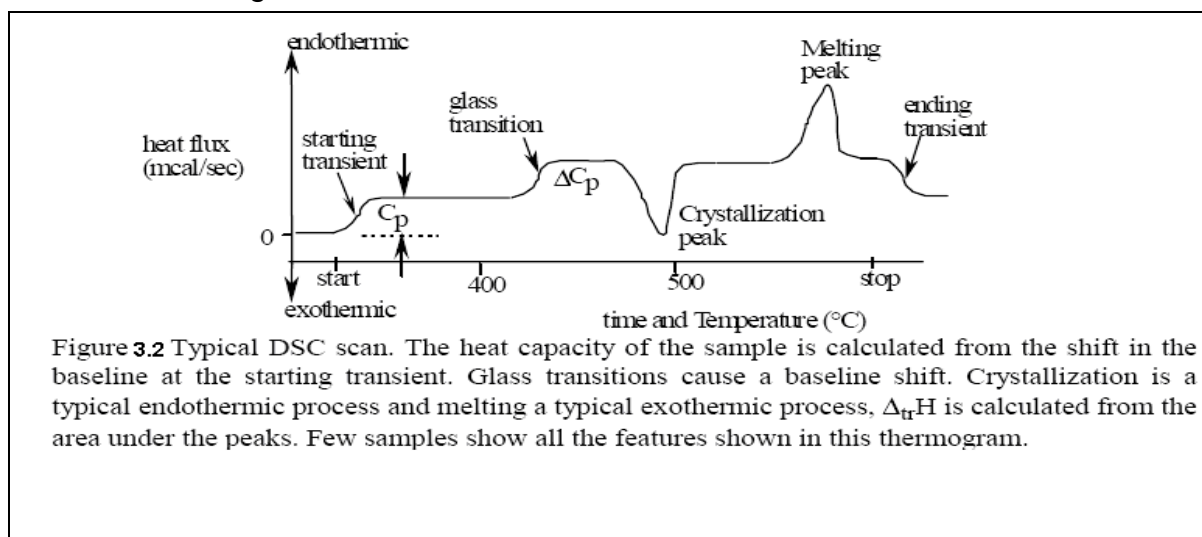


Differential Scanning Calorimetry (DSC) is a common method to locate phase transitions of materials to determine the associated transition enthalpy. The thermal properties obtained from DSC analysis would include the glass transition temperature, crystallization temperatures and endothermic or melting reactions. DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. The basic principle underlying this technique is

that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic.

For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of energy absorbed or released during such transitions. DSC may also be used to observe subtler phase changes, such as glass transitions and melting point. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity, for studying polymer curing, and also in the measurement of quantitative parameters such as heat capacity, heat of fusion or heat of crystallization for crystalline polymers, or change in specific heat at glass transition for amorphous polymers.

For transitions involving latent heat such as fusion, the heat of transition (fusion) is determined by integrating the (heat) energy input over the time interval covering the transition³⁰.



3.2.2 DENSITY

Density is used in many areas of application to designate certain properties of materials or products. In conjunction with other information, the density of a material can provide some indication of possible causes for alterations in product characteristics.

Determining the density of plastics used in engineering can help to monitor the proportion of crystalline phase, because the higher geometric order of crystals makes them denser than the non-crystalline portion.

The Archimedean principle is applied for determining the specific gravity of a solid polymer. A solid immersed in a liquid is exposed to the force of buoyancy. The value of this force is the same as that of the weight of liquid displaced by the volume of the solid

With a hydrostatic balance, it is possible to determine the **specific gravity of a solid** if the density of the liquid causing buoyancy is known:

$$\rho = \frac{W(a) \cdot \rho(fl)}{W(a) - W(fl)}$$

Where **ρ** = specific gravity of the solid

$\rho(fl)$ = density of the liquid

$W(a)$ = weight of the solid in air

$W(fl)$ =weight of the solid in liquid

A solid is buoyed by a corresponding force per cm^3 of its volume when weighed in air, (volume of 1 cm of air has a weight of approximately 1.2mg). Also, the pan for holding and/or immersing the sample during weighing in liquid is rigidly attached to two wires and is immersed approx. 30mm below the surface of the liquid. When a solid sample is weighed in liquid, the attachment wires of the pan hanger assembly are immersed deeper and generate additional buoyancy, which introduces an error in density determination.

This following formula allows for air buoyancy and immersion:

$$\rho = \frac{W(a) \cdot [\rho(fl) - \rho(a)]}{0.99983 \cdot [W(a) - W(fl)]} + \rho(a)$$

Where, $[W(a) - W(fl)] = G = \text{Buoyancy}$

$\rho(a) = 0.0012 \text{ g/cm}^3 = \text{Density of air under standard conditions (T=20}^\circ\text{C, P=101.325 kPa)}$

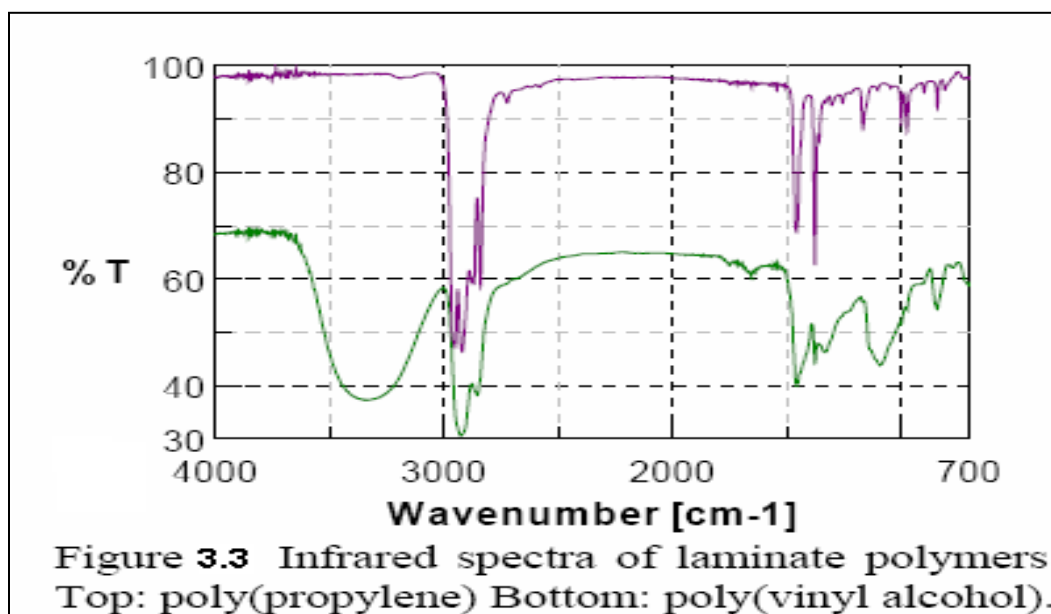
The immersion correction factor is determined exclusively by the geometry of the measuring device setup³¹.

3.3. SPECTROSCOPIC STUDIES OF POLYMERS

3.3.1 FOURIER TRANSFORM-INFRA RED

Fourier transform infrared spectroscopy (IR) is simply the absorption measurement of different infrared (IR) frequencies by a sample positioned in the path of an IR beam. The main goal of the analysis is to determine the chemical composition of the sample.

Infrared spectra of polymers give insight at the molecular level as to the orientations and conformations of the polymer chains. Infrared spectroscopy provides the ability to study the interactions of the vibrational and rotational energies of atoms or groups of atoms within molecules. Infrared spectra reflect vibrational motions that produce a change in the permanent dipole moment of the molecule. Infrared spectroscopy is a powerful qualitative and quantitative tool. There is a large amount of information that can be gained by using infrared spectroscopy for the analysis of polymers. Minor changes to the molecular structure usually result in a spectrum that is clearly distinguishable from the spectrum of the original compound. Thus, they can be used to identify the presence of a specific chemical compound or mixture of compounds²¹. *Spectra can be obtained as either a pressed or cast film, or by attenuated total reflectance. Other instrumental techniques would require the decomposition of the polymer and identification of its fragments.*



The simplest polymer structure would be a chain of methylene units terminated on each end by methyl groups. This is the structure of *Polyethylene*, or *PE*. Since the polymer is composed almost completely of methylene groups, its infrared spectrum would be expected to consist solely of methylene stretches and bends. Four sharp peaks dominate the spectrum: The methylene stretches at 2,920 and 2,850 $[\text{cm}^{-1}]$ and the methylene deformations at 1,464 and 719 $[\text{cm}^{-1}]$. Due to the crystallinity of polyethylene, the 1,464 and 719 $[\text{cm}^{-1}]$ peaks are split, and additional peaks are seen at 1,473 and 731 $[\text{cm}^{-1}]$. High density polyethylene (HDPE) is very regular and is about 70% crystalline. Low density polyethylene (LDPE), on the other hand, is more branched and is only about 50% crystalline. The crystallinity of a polyethylene sample can be determined from the ratio of the 731 to 719 $[\text{cm}^{-1}]$ peaks (ASTM D5576).

The addition of a methyl side group on every other carbon atom in polyethylene gives us *Polypropylene* and quickly complicates the infrared spectrum. In addition to the methylene, we now have methyl and methine groups present. The methyl peaks appear at 2,962/2,952 (split peak), 2,868 and 1,377 $[\text{cm}^{-1}]$. A methyl deformation is also overlapped with the methylene deformation, and this peak has shifted slightly to 1,458 $[\text{cm}^{-1}]$. The methine peaks are weak and of no analytical value³²⁻³³.

3.3.2 CARBON-13 NMR

Nuclear magnetic resonance (NMR) is a very powerful technique for determining chemical structures at the molecular level. It is the fundamental technique for identification of type of branching, chain ends, chemical composition, comonomer sequence distribution, configurational sequence distribution (tacticity) and other stereo-defects during the polymerization.

The use of Carbon-13 Nuclear Magnetic Resonance (NMR) spectroscopy in the molecular characterisation of macromolecules has advanced our knowledge into structural areas that have been nearly impossible to measure by other spectroscopic techniques. Innovative applications have led to determinations of polymer configurational distributions, comonomer sequence distributions and average sequence lengths, structure and distribution of short chain branches and analyses of non-reactive end groups. As a result the importance of ^{13}C NMR to the field of polymer science cannot be overemphasized. The key to the success of ^{13}C NMR studies in defining polymer molecular structure has been a structural sensitivity which encompasses more than just a few functional groups or carbon atoms. A sensitivity to polymer repeat unit sequences of lengths from two to as many as five, seven and even nine contiguous repeat units has been observed.

Detection of long chain branching in Polyethylene can now be made at a level of one per 10,000 carbon atoms, and newer generations of high field, higher sensitivity NMR spectrometers promise to extend this detection limit another order of magnitude.

The internal standard most often used in high-temperature NMR studies of polymers in solution is Hexamethyldisiloxane (HMDS). Tetramethylsilane (TMS) is still the NMR chemical shift standard of choice but its low boiling point frequently precludes its use in NMR studies of polymers. It is preferred to report all polymer chemical shifts with respect to TMS by correcting the HMDS chemical shifts to a TMS standard. The chemical shift difference

between TMS and HMDS is approximately 2 ppm, but the precise difference should be established independently on each spectrometer.

Modern analysis software also allows analysis of the size of peaks to understand how many protons give rise to the peak. This is known as integration—a mathematical process which calculates the area under a graph (essentially what a spectrum is). The analyst must integrate the peak and not measure its height because the peaks also have width—and thus its size is dependent on its area not its height. However, it should be mentioned that the number of protons, or any other observed nucleus, is only proportional to the intensity, or the integral, of the NMR signal, in the very simplest 1-D NMR experiments.

Polymer structure in this discussion will refer to the actual molecular chain structure, i.e., the identity of the repeat unit and its chirality, sequence structures and their distributions, the identity of end groups including numbers & types per molecule, the degree of polymerisation, and the identification of both short – and long-chain branching. For homopolymers, the interest in polymer molecular structure is limited to the degree of polymerisation, chirality and variation in modes of monomer additions, the identity of end groups, and the extent of long-chain branching. Co-polymer structural analyses encompass all of the factors encountered in analyses of homopolymers but with additional complications arising from various possible sequence distributions³⁴⁻³⁹.

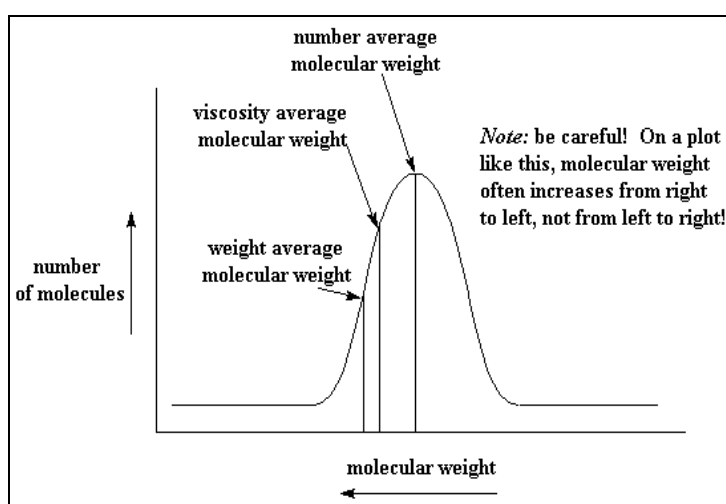
3.3.3 HIGH TEMPERATURE GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC), also known as Size Exclusion Chromatography (SEC) is one of the most powerful and versatile analytical techniques available for understanding and predicting polymer performance. It provides an indirect measure of the polymer molecular weight distribution. GPC is a relative method. **Experiment gives an elution chromatogram, which is converted into molecular weight distribution via a calibration**

curve. The profile of the elution curve is determined by the molecular weight distribution of the sample.

GPC can determine several important parameters. These include number average molecular weight (M_n), weight average molecular weight (M_w), Z weight average molecular weight (M_z), and the most fundamental characteristic of a polymer its molecular weight distribution (Polydispersity index).

Understanding the makeup of a polymer is particularly important due to the variety of resins available for the same purpose, the high cost of specialty resins or compounds, and the value added to the polymer during manufacturing. Also, two



samples of the same polymer resin can have identical tensile strengths and melt viscosities, and yet differ markedly in their ability to be fabricated into usable, durable products. These differences can be attributed to subtle, yet significant variations in the molecular weight distributions of the two resin samples. Such differences, if undetected, can cause serious product defects.

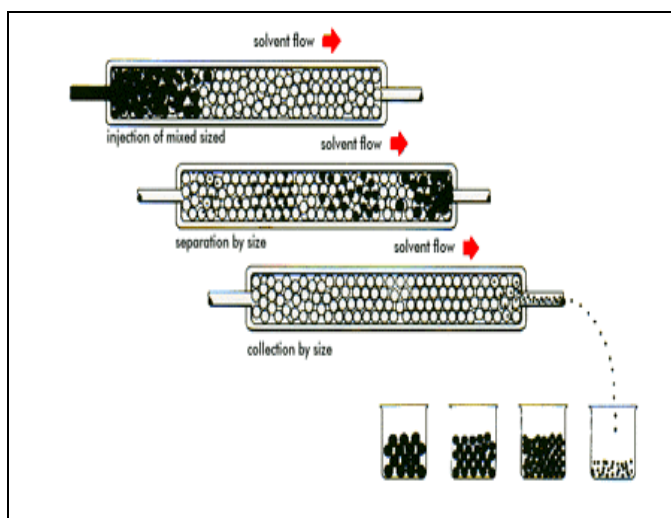
Compared to other chromatographic methods, GPC is characterized by three properties:

- 1. Separation is effected according to molecular size**
- 2. Larger molecules are eluted before small ones**
- 3. Separation takes place in a volume that is smaller than the total volume of the column**

Molecules of various sizes elute from the column at different rates. The column retains low molecular weight material (small black dots) longer than

the high molecular weight material (large black dots). The time it takes for a specific fraction to elute is called its "retention time".

The concentration of the sample in solution depends on the molecular weight, but a concentration of 0.10% (w/v) for a polymer of molecular weight ~100,000, is typical. At times, the sample solution must be heated



to dissolve the sample. For example, some polyolefins need temperatures greater than 120° C to dissolve, and are typically run in 1,2,4 trichlorobenzene at 140 °C⁴⁰⁻⁴⁴.

3.3.3.1 High-Temperature Triple Detector GPC of Polyolefins:

As polymer characterization chemists strive to learn as much as they can about their samples, new detection options are considered. The molecular weight sensitive detectors such as viscometry and light scattering are used in tandem with concentration sensitive detectors such as Refractive Index (RI). Using a triple detector approach provides very meaningful data, as long as the user is able to interpret it all.

The most widely used detector today for GPC analysis is the differential refractometer (DRI). It is a concentration sensitive detector that measures the difference in refractive index (δRI) between the eluent in the reference side, and the sample + eluent in the sample side. The eluent used must dissolve the polymer and provide a significant δRI .

Now, putting a viscometer detector in line with the refractometer provides a way to obtain not only the intrinsic viscosity $[\eta]$ of the polymer, but also the "absolute" molecular weight and estimation of long chain branching. The RI detector is the concentration detector, **(C)**, and the viscometer provides

[η](C). Using the two signals in tandem will provide the intrinsic viscosity at each slice across the elution profile of the polymer.

The light scattering detector, coupled with the refractometer, is another powerful mode of advanced detection. Essentially, a laser beam is focused into a cell (on-line in this case) that contains the sample solution. The incident beam will be scattered by the polymer particles that are in solution. The intensity of scattered light is proportional to the size of the scattering particles. Measuring intensity of scattered light at various angles and determine the radius of the sample, and subsequently, the weight average molecular weight, M_w , very accurately⁴³.

3.3.4 X-RAY DIFFRACTION (XRD)

X-ray Diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, Crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of x-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic decoration within the lattice planes. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material.

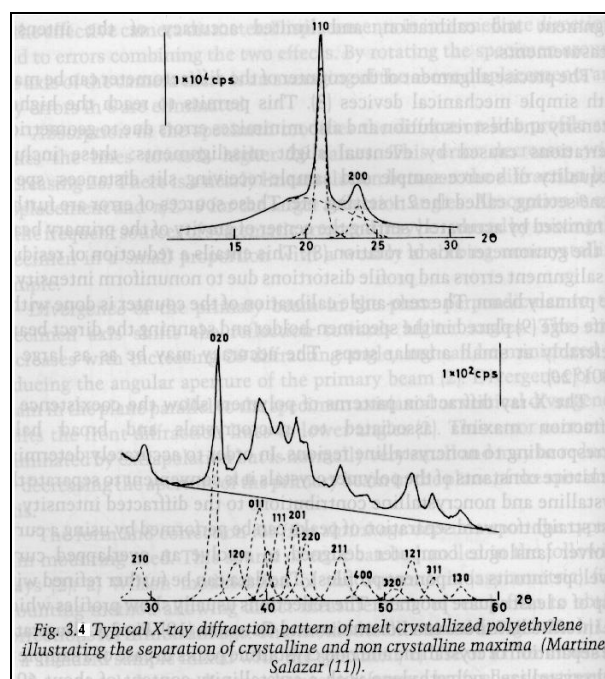


Fig. 3.4 Typical X-ray diffraction pattern of melt crystallized polyethylene illustrating the separation of crystalline and non crystalline maxima (Martinez Salazar (11)).

Polymers are never 100% crystalline. Since the stereochemistry is never perfect, chains contain defects such as branches, & crystallization is highly rate dependent in polymers due to the high viscosity & low transport rates. A primary use of XRD in polymers is determination of the Degree of Crystallinity, by integration of a 1-D XRD pattern (Figure 3.4 for polyethylene).⁴⁵

3.4 MACROSCOPIC (MECHANICAL) PROPERTIES

Due to the favorable combination of easy processability and attractive mechanical properties, the use of polymer materials in diverse applications has assumed large proportions over the last decades. But the ability of a polymer material to deform is determined by the mobility of its molecules, characterized by specific molecular motions and relaxation mechanisms that are accelerated by temperature and stress.

To ensure proper operation under heavy-duty conditions, these applications have to meet specific requirements regarding quality, safety, and mechanical performance (e.g. stiffness, strength and impact resistance).

Mechanical performance is generally optimized by trial-and-error until the functional demands of the design are satisfied. This, however, implies by no means that the final result is fully optimized.

The mechanical performance of polymers is determined by three factors:

1. **Molecular Structure**, which for polymers is characterized by their chemical configuration,
2. **Stereoregularity**, and chain length (distribution); processing, constituting the entire chain of processes that transforms the raw material to the final product, thereby modifying microstructural characteristics such as e.g. molecular orientation and crystallinity;
3. **Geometry**, the product's final functional macroscopic shape obtained as a result of processing.

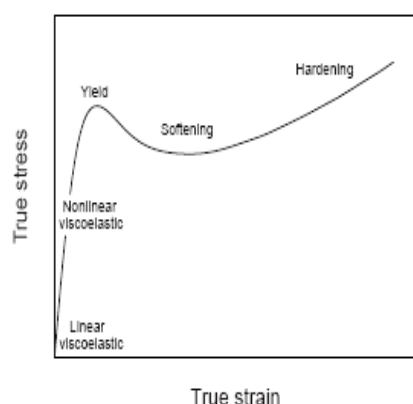
An optimal performance of a product would require an optimization of these three factors.

Also, mechanical properties change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures

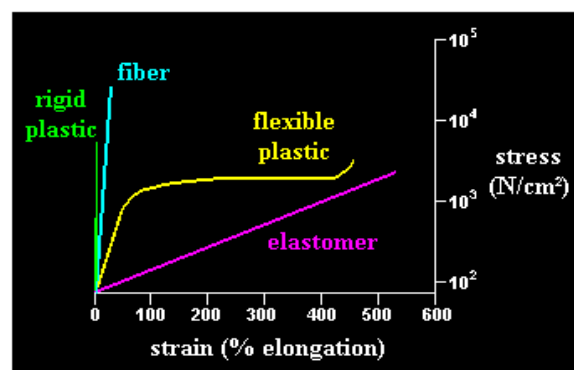
3.4.1 INTRINSIC DEFORMATION BEHAVIOUR

Intrinsic deformation is defined as the materials' true stress-strain response during homogeneous deformation. Since generally strain localization phenomena occur (*like necking, shear banding, crazing and cracking*), the measurement of the intrinsic materials' response requires a special experimental set-up, such as a video-controlled tensile or an uniaxial compression test. Although details of the intrinsic response differ per material, a general representation of the intrinsic deformation of polymers can be recognized, see Figure below.

For small loads the material behaviour is linear viscoelastic, while with increasing load the behaviour becomes progressively nonlinear. At the yield point the deformation becomes irrecoverable since stress-induced plastic flow sets in leading to a structural evolution which reduces the material's resistance to plastic flow: strain softening. Finally, with increasing deformation, molecules become oriented which gives rise to a subsequent increase of stress at large deformations: *Strain Hardening*.



Schematic representation of the intrinsic deformation behaviour of a polymer material.



After Odian, George; *Principles of Polymerization*, 3rd ed., J. Wiley, New York, 1991, p.34.

Many semicrystalline polymers have spherulitic structure and deform in following steps:

- Elongation of amorphous tie chains
- Tilting of lamellar chain folds towards the tensile direction
- Separation of crystalline block segments
- Orientation of segments and tie chains in the tensile direction

3.4.2 MOLECULAR BACKGROUND

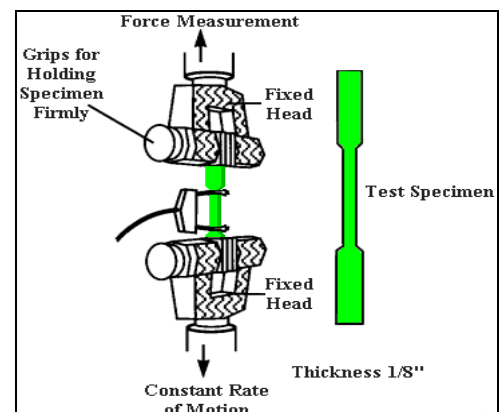
Independent of the stress level or amount of deformation involved, the origin of the deformation of polymer materials lies in their ability to adjust their chain conformation on a molecular level by rotation around single covalent bonds in the main chain. This freedom of rotation is, however, controlled by intramolecular (chain stiffness) and intermolecular (inter-chain) interactions. Together these interactions give rise to an energy barrier that restricts conformational change(s) of the main chain. The rate of conformational changes, i.e. the molecular mobility, is determined totally by the thermal energy available in the system. Increasing the thermal energy increases the rate of change, which on a fixed time scale, allows for larger molecular rearrangements and, thus, accommodation of larger deformations. Since thermal energy is determined by temperature, there will be a relatively strong relation between temperature and mobility, and thus also with macroscopic deformation (in fact polymers are known for their pronounced temperature dependence). In addition to this, there is also a strong influence of stress on molecular mobility since polymers allow for "mechanical" mobility when secondary bonds are broken by applying stress (rather than by increasing the thermal mobility) ⁴⁶⁻⁵⁰.

3.4.3 METHODS OF TESTING

3.4.3.1 TENSILE TEST (ASTM D 638)

Tensile tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point.

Tensile Test is the ***measurement of the ability of a material to withstand forces that tend to pull it apart*** and ***to determine to what extent the material stretches before breaking.***

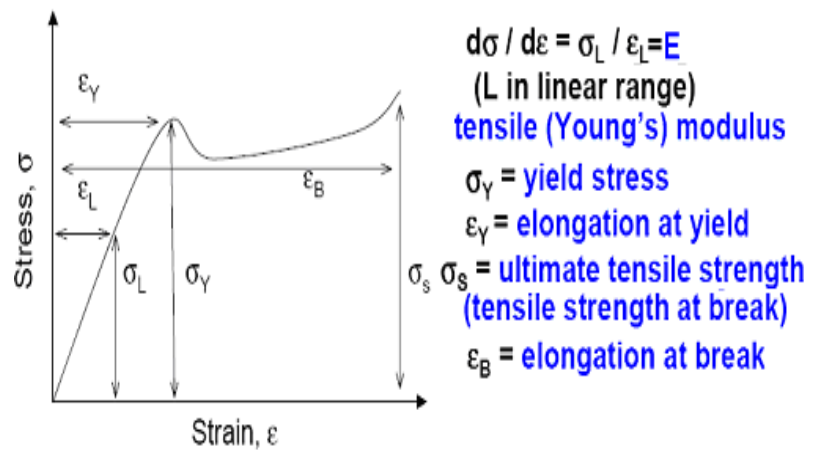


The ductility of a sample is determined by conducting a tensile strength test on a Universal Testing Machine (UTM) like the one seen in the figure. The preferred specimen is a Type-I specimen having a thickness of 0.28 inches or less prepared either by Injection or Compression Moulding.

During the stretching process, the machine measures the **load (F)**, or the force applied to the sample, and the **displacement of the sample (s)**; along with the **original cross sectional area of the sample (A_o)** and the **original length (L_o)**, an engineering **Stress-Strain Curve** can be generated.

When the graph is analyzed, it is found that the strain hardening of the material increases up to a certain maximum point, after which the strain begins to deform the material, softening it until it breaks. Graphically, it is the highest point on the engineering stress-strain curve.

Tensile properties are obtained from features in the curve.



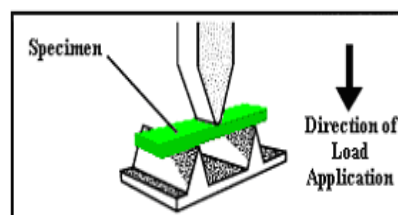
Tensile Test Values:

- (i) Young's Modulus: This is the slope of the linear portion of the stress-strain curve; it is usually specific to each material - a constant, known value.
- (ii) Yield Strength: This is the value of stress at the yield point, which is calculated by plotting Young's Modulus at a specified percent of offset (usually offset = 0.2%).
- (iii) Ultimate Tensile Strength: This is the highest value of stress on the stress-strain curve.
- (iv) Percent Elongation: This is the change in gauge length divided by the original gauge length⁵¹⁻⁵².

3.4.3.2 FLEXURAL STRENGTH TEST (ASTM D 790)

The flexural strength of a material is defined as its **ability to resist bending forces applied perpendicular to its longitudinal axis**. The stresses induced by the flexural load are a **combination of compressive and tensile stresses**. The test beam is under compressive stress at the concave surface and tensile stress at the convex surface.

For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength.



ASTMD790:
Specimen of 1/8" x 1/2" x 5" is placed on two supports and a load is applied at the center. The load at yield is the sample material's flexural strength.

The test is done on an UTM, which operates at a constant rate of crosshead motion over the entire range and error in load measuring system should not exceed 1% of the maximum load expected. The strain rate is 0.01 in/in/min.

The method followed is Procedure A, which is a three-point loading system utilizing central loading on a simple supported beam. A bar of rectangular cross-section rests on two supports and is loaded by means of a loading nose midway between the supports. **This method is useful for Quality Control and specification properties.**

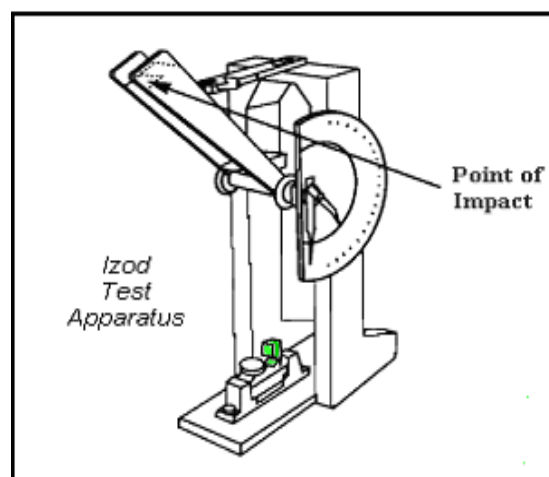
Flexural test result is a plot of load versus displacement or stress versus strain. From this data, a number of properties can be calculated such as flexural modulus and yield strength.

The Flexural Modulus is a measure of the stiffness during the first or initial part of the bending process. It is represented by the slope of the initial straight-line portion of the stress-strain curve and is calculated by dividing the change in stress by the corresponding change in strain⁵³⁻⁵⁴.

3.4.3.3 IZOD IMPACT TEST (ASTM D 256)

Toughness is the ability of polymer to absorb applied energy. Impact energy is a measure of toughness. **Impact tests are designed to measure the resistance to failure of a material to a suddenly applied force such as collision, falling object or instantaneous blow.** The test measures the impact energy, or the energy absorbed prior to fracture.

In Izod test, a specially designed hammer or pendulum released from a specific height strikes the test specimen placed or clamped at the base of the instrument with enough kinetic energy to fracture the specimen. A notched cantilever beam type test specimen, firmly clamped in a vertical position in a vise fixed at the base of the apparatus, is struck horizontally by the pendulum on the top (free) end above the notch. The pendulum continues on its arc after the specimen has been fractured & the remaining energy is measured by the extent of excess swing.



ASTM D256:
A pendulum swings on its track and strikes a notched, cantilevered plastic sample. The energy lost (required to break the sample) as the pendulum continues on its path is measured from the distance of its follow through. Sample thickness is usually 1/8 in. (3.2 mm) but may be up to 1/2 in. (12.3 mm).

Izod specimens can be prepared either by moulding or cutting them from a sheet. Izod test sample usually have a V-notch cut into them, although specimens with no notch as also used on occasion. The notch is cut into the specimen very carefully by a milling machine or lathe. Recommended notch depth is 0.1 inch.

The notch serves as a stress concentration zone and some materials are more sensitive towards notches than others. So, the notch depth and tip radius are therefore very important. *Tough materials absorb a lot of energy, whilst brittle materials tend to absorb very little energy prior to fracture.*

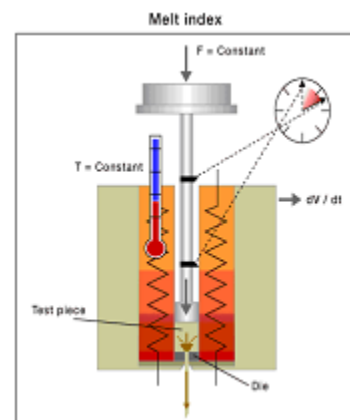
ISO and ASTM standards express impact strengths in different units.

ISO standards report impact strengths in kJ/m^2 , where the impact energy is divided by the cross sectional area at the notch.

ASTM standards call for values to be reported in J/m , where the impact energy is divided by the thickness of the specimen.⁵⁵⁻⁵⁸

3.4.3.4 MELT FLOW INDEX (ASTM D 1238)

The Melt Flow Index (MFI) or Melt Flow Rate (MFR) test measures the **rate of extrusion of a thermoplastic material through an orifice/die of specified length and diameter under prescribed conditions of temperature, load and piston position in the barrel as the timed measurement is being made.**



This test is primarily used as a means of measuring the uniformity of flow rate of material. The reported MFI

values help to distinguish between the different grades of polymer. A high

molecular weight material is more resistant to flow than a low molecular weight material. The flow rate is an empirically defined parameter critically influenced by the physical properties and molecular structure of the polymer and the condition of measurement⁵⁹.

| Polymer Material | Test Temperature, T [°C] | Nominal Load, M [kg] |
|------------------------------------|------------------------------------------|-----------------------------------|
| Polyethylene | 190 | 2.16 |
| Polypropylene | 230 | 2.16 |
| Expected Melt Flow Rate (g/10 min) | Mass of test portion into cylinder, (gm) | Extrudate cut-off interval, (sec) |
| 0.1-0.5 | 3-5 | 240 |
| >0.5-1 | 4-5 | 120 |
| >1-3.5 | 4-5 | 60 |
| >3.5-10.0 | 6-8 | 30 |
| >10.0 | 6-8 | 5-15 |

The MFI is given by the following equation:

$$MFI(T, M) = \frac{t_{ref} \times m}{t}$$

Where, T = test temperature (°C)

M = nominal load (kg)

t_{ref} = reference time (10 min), (s)

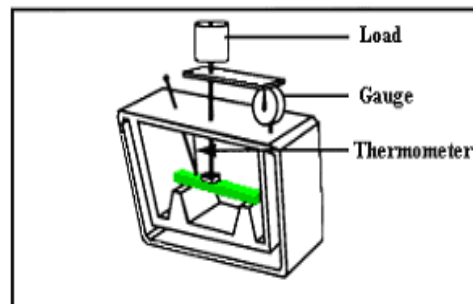
m = average mass of cut-offs (g)

t = time-interval for cut-offs (s)

3.4.3.5 HEAT DEFLECTION TEMPERATURE (ASTM D 648)

The **Heat Deflection Temperature** or **Heat Distortion Temperature (HDT)** is the temperature at which a polymer or plastic sample deforms under a specified load. HDT is defined as the **temperature at which a sample bar of standard dimensions (e.g., 127×14×4 mm) deflects by 0.25 mm (0.01 inch) under a standard flexural load of 0.455 MPa or 1.82 MPa placed at its center.**

The test specimen is loaded in three-point bending in the edgewise or flatwise direction. The selected deflection of 0.25 mm (which is 0.2% additional strain) is selected arbitrarily and has no physical meaning.



ASTM D648: The deflection temperature is the temperature at which a test bar, loaded to a specified bending stress, deflects by 0.01 inch (0.25 mm)

In the case of an amorphous polymer, HDT is slightly (10^0 to 20^0 C) lower than the T_g as determined by thermal techniques while in case of semi-crystalline polymers, HDT is more closely identified with T_m .

HDT is therefore a useful indicator of the temperature limit above which polymers (or commercial grades of plastics) cannot be used for structural (load-supporting) applications.

| Specimen Orientation Parameters | | | | |
|---------------------------------|------------------|-----------|---------------------|---------|
| Orientation | Dimensions (mm) | Span (mm) | Standard Deflection | Diagram |
| Edgewise | 120x9.8-15x3-4.2 | 100 | 0.32 | |
| Flatwise | 80x10x4 | 64 | 0.34 | |

An injection molded plastic part is considered "safe" to remove from its mold once it is near or below the HDT. This means that part deformation will be held within acceptable limits after removal. The molding of plastics by necessity occurs at high temperatures (routinely 200 degrees Celsius or higher) due to the high viscosity of plastics in fluid form. Once plastic is in the mold, it must be cooled to a temperature to which little or no dimensional change will occur after removal. Thus, the heat deflection temperature plays

an important role, as it allows for manufacturers to achieve a much faster molding process than they would otherwise⁶⁰⁻⁶².

3.4.3.6 VICAT SOFTENING POINT (ASTM D 1525)

The Vicat softening temperature (VSP) is the **temperature at which a flat-ended needle of 1mm² circular cross-section will penetrate a thermoplastic specimen to a depth of 1mm under a specified load using a selected uniform rate of temperature rise.**

The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application

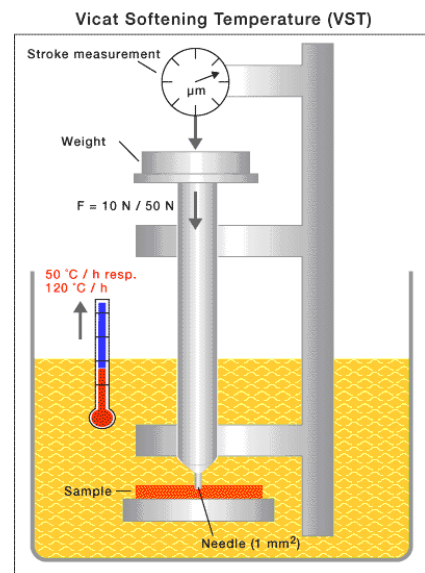
Two different heating rates and two different loads may be used for testing:

Heating rates: **50 °C/hr** or **120 °C/hr**

Loads: **10 N (1 Kg)** or **50N (5 Kg)**

This test is very similar to the HDT test and its usefulness is limited to Quality Control, development and characterization of materials. The data obtained from this test is very useful in comparing the heat-softening qualities of thermoplastic materials, but not recommended for flexible PVC and other

materials. The flat test specimen is molded or cut from a sheet with a minimum thickness and width of 3mm and 10mm respectively⁶³.



Summary of techniques of Polymer Characterization at various levels:

Molecular Characterization:

- High-Temperature-GPC (HT-GPC) with 3-detector system
- Nuclear Magnetic Resonance (NMR)
- Fourier Transform Infra-red Spectrometer (FTIR)
- p-TREF (preparative Temperature Raising Elution Fractionation) – for co monomer distribution in a preparative mode
- High Pressure Liquid Chromatography (HPLC)
- Gas chromatography (GC)

Mesoscopic Characterization:

- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Optical Microscopy (OM)
- X-Ray Diffraction (XRD) – Wide angle
- XRD (WAXD) – 1D and 2D
- Differential Scanning Calorimetry (DSC)
- Thermo-gravimetric Analysis (TGA)

Macroscopic characterization:

SOLID PHASE

- Universal Testing Machine (UTM) for tensile, flexural, compressive strengths, coefficient of friction (COF), peel strength, fibers, films and elastomers
- Heat Deflection Tester (HDT)
- Izod Impact Strength Tester
- Dynamic Mechanical Analyzer (DMA)

MELT PHASE:

- High-shear Capillary Rheometer
- Control-Strain Rheometer
- Control-Stress Rheometer
- Melt flow indexer (MFI)

3.5 EXPERIMENTAL DETAILS

3.5.1 INTRODUCTION

The experimental component of this thesis is based on the objective of detailed characterization of the polymer formulations at three different length scales:

- Molecular Structure,
- Mesoscopic Structure and
- Macroscopic Properties,

so as to understand the performance of a product through the Structure-Property-Performance Relationship chain.

Before discussing the parameters conducted in the experiments, it is necessary to describe the materials that compose the body of this work

3.5.2. MATERIALS

The samples used in the present study were two grades of Polypropylene and three grades of Polyethylene. The Polypropylene grades were produced by Bassell Polyolefins and Dow Chemicals and the Polyethylene grades were from Nova Chemicals. In total five samples were used in the present study. Details of the samples showing their grade, density are listed in Table below. Unfortunately, the processing conditions were not made available to us for commercial reasons.

Table A. Sample Details (* Manufacturers Data)

| Polymer Sample | Density* (g/cm ³) | Company |
|-----------------------------------------|-------------------------------|---------|
| Polypropylene-A | 0.90 | Bassell |
| Polypropylene-B | 0.90 | Dow |
| Low Density Polyethylene (LDPE) | 0.911 | Nova |
| Linear Low Density Polyethylene (LLDPE) | 0.920 | Nova |
| High Density Polyethylene (HDPE) | 0.9634 | Nova |

3.5.3. MOLECULAR CHARACTERISATION

3.5.3.1. FOURIER TRANSFORM INFRA-RED MEASUREMENTS

A Perkin Elmer BX-II IR Fourier Transform spectrophotometer Instrument with Autoimage was employed for determining the molecular structural entities in the polyolefin chains.

The spectra were recorded using films or thin layers of the polyolefin from solutions in the region of 400-4000 cm^{-1} . The polymer films were prepared by dissolving a few polymer pellets in an organic solvent 'Tetralin' with heating and then obtain usable films by evaporating the solvent.

3.5.3.2 CARBON-13 NMR

A 300MHz/52mm Bruker AV300 FT ^{13}C NMR spectrophotometer at 130°C was used for studying the microcomposition and monomer sequence distribution along the polymer chain.

The samples were run as 10 % (w/v) solutions in 1,2,4-trichlorobenzene with DMSO- d_6 as the lock material. All ^{13}C shifts were referenced to Tetramethylsilane (TMS) at 0 ppm. The internal standard used is Hexamethyldisiloxane (HMDS). But it is preferable to report all polymer chemical shifts to with respect to TMS by correcting the HMDS chemical shifts to a TMS standard. The chemical shift difference between TMS and HMDS is approximately 2 ppm.

3.5.3.3 HIGH TEMPERATURE GPC:

The Polypropylene and Polyethylene samples were analyzed on PL Olexis columns with the PL GPC 220 detector. The Polyolefin samples were prepared accurately at concentrations of nominally 2 mg/ml and placed in the PL-SP260 for 6 hours at 150°C. Once the samples had dissolved, they were injected into the system with no further preparation.

| EXPERIMENTAL | DETAILS |
|------------------|---------------------------------------------------------------------|
| Injection Volume | 200 μ L |
| Eluent | TCB+BHT |
| Temperature | 160 $^{\circ}$ C |
| Calibrants | Polystyrene |
| Flow Rate | 1 ml/min |
| Detector | PL GPC 220 (DRI, PL-BV400HT Viscometer and PD2040 Light Scattering) |

3.5.4 MESOSCOPIC CHARACTERISATION

3.5.4.1. DIFFERENTIAL SCANNING CALORIMETRY

The samples were analyzed using two different calorimeters in nitrogen atmosphere in the temperature range of 40-200 $^{\circ}$ C, viz.,

1. Modulated DSC 2920 (TA Instruments), and
2. Perkin Elmer Pyris 6 DSC

A heating rate of 10 $^{\circ}$ C per minute was used for the former while for the latter, the steps followed are:

1. Heat from 40 $^{\circ}$ C to 200 $^{\circ}$ C at 20 $^{\circ}$ C/min
2. Hold for 1 min at 200 $^{\circ}$ C
3. Cool from 200 $^{\circ}$ C to 40 $^{\circ}$ C at 10 $^{\circ}$ C/min
4. Heat from 40 $^{\circ}$ C to 200 $^{\circ}$ C at 10 $^{\circ}$ C/min

Indium was used as the calibration standard and a sample mass of 5 to 6 mg was used for the experiment.

Since the previous thermal history of a polymer affects the measured degree of crystallinity, these samples are evaluated both “*as received*” and after being subjected to a common “*thermal treatment*” designed to impart equivalent thermal history to all three samples. This thermal treatment consists of cooling the sample from 200 $^{\circ}$ C at 10 $^{\circ}$ C/min.

3.5.4.2 THERMOGRAVIMETRIC ANALYSIS

The thermal behavior was investigated using

1. Hi-Res Modulated TGA 2950 (TA Instruments), and
2. Perkin Elmer Pyris 6

The test was carried out in the temperature range of 50°C to 750°C and the heating rates employed were 10°C/min and 20°C/min respectively. The TA Instrument used an Air atmosphere while the Perkin Elmer Instrument used a Nitrogen atmosphere. The typical sample weights used were approximately 6 to 13 mg.

3.5.4.3 XRD ANALYSIS

For recording the XRD of the sample, thin films of the polymer samples, obtained using compression molding, were used. The Compression Moulding was done using an automated Carver Inc. (Washbash, Indiana) press.

The XRD one-dimensional spectrum was recorded on Rigaku D/max 2500 PC diffractometer (Japan) at variable temperatures using 1.54056Å Cu K_α radiation and voltage and current settings of 50 kV and 250 mA respectively. The scanning rate was 1°/min and step-size was 0.01°.

3.5.4.4 DENSITY

A Sartorius BP 221 S Balance is used for measuring the specific gravity of the polymer pellets following Buoyancy Method. The apparent weight of a body in a liquid, i.e., the weight as reduced by the buoyancy force is measured. This value is used in combination with the weight in air to calculate the density.

3.5.5. MACROSCOPIC CHARACTERISATION

3.5.5.1 SPECIMEN PREPARATION

The specimens for the tests (Tensile, Flexural, Impact etc.) were prepared by Injection Moulding on L&T DEMAG PFY40-LNC4P. The processing conditions utilized for the Polypropylene and Polyethylene samples are tabulated below in Table 2.

| Conditions \ Sample | Sample | |
|------------------------|---------------|--------------|
| | POLYPROPYLENE | POLYETHYLENE |
| Cycle Time (sec) | 200 | 200 |
| Blocking Time (sec) | 10 | 10 |
| Pause Time (sec) | 0.05 | 0.05 |
| Cooling Time (sec) | 35 | 30 |
| Injection Delay (sec) | 0.45 | 0.45 |
| Injection Pressure (%) | 80 | 80 |
| Injection Speed (%) | 80 | 75 |
| Holding Pressure (%) | 80 | 80 |
| Holding Time (sec) | 2 | 4 |
| Dosing Delay (sec) | 1 | 1 |
| Dosing Speed (%) | 50 | 50 |
| Nozzle Temperature °C) | 210 | 220 |

Table 2: Processing conditions used for IM of the PP and PE samples

3.5.5.2 TENSILE (ASTM D 638) & FLEXURAL (ASTM D 790) TESTING

Zwick UTS system Z010 was used to determine the flexural and tensile properties. For the tensile test, Dumbbell shaped specimens (ASTM D638-03 type-1) were used having the following dimensions:

GAGE LENGTH = 65 mm
WIDTH = 14 mm
THICKNESS = 4 mm

Flexural tests were accomplished on the rectangular bar samples having dimensions (126 mm × 15 mm × 4 mm) in a Zwick machine with a three-point bending geometry according to ASTM D790.

The crosshead speed used for testing was different for different samples. Both tensile and flexural test average values were calculated from five runs for each sample.

3.5.5.3 HDT (ASTM D 648) /VSP (ASTM D 1525)

Computerized VSP/HDT Apparatus of International Equipments, Mumbai is used as per ASTM D – 1525 and ASTM D - 648 to determine Vicat Softening Temperature and Heat Deflection Temperature of plastics respectively.

The sample dimensions used for HDT were {127 × 4 × 14} mm and the test was done flatwise under a standard flexural load of 0.455 MPa. The temperature of the oil bath is increased at the rate of 2°C per minute. The sample dimensions for VSP were {38 × 10 × 4} mm. The test is performed under a load of 10N (1 kg) and the rate of temperature rise of the bath is 120°C per hour.

3.5.5.4 IZOD IMPACT STRENGTH TESTER (ASTM D 256)

The Izod Impact strength was measured using an ATSFAR Impact Tester instrument on Notched specimens. These specimens were prepared according to ASTM D 256 test procedure, and whose dimensions are as:

If not parallel, the notched surface is machined parallel to its opposite surface within 0.025 mm.

| | |
|----------------|----------|
| Overall Length | 63 mm |
| Width | 12.6 mm |
| Thickness | 4 mm |
| Depth of Notch | 0.25R mm |
| Angle of Notch | 45° |

The average Impact Strength values were calculated from five runs for each sample.

3.5.5.5 MELT FLOW INDEXER (ASTM D 1238)

The Melt Flow Rate was measured following Manual procedures on an Indexer apparatus from International Equipments and DYNISCO Instruments.

The temperature is set and the cylinder is charged with a predetermined amount of material, in the form of pellets, with respect to the anticipated Melt Flow. The material is compressed gradually with a packing rod using only hand pressure. Now the unloaded piston is put on the cylinder and after a preheating time of 4-6 min, the desired weight is put on the piston.

With a slight hand pressure push the piston downwards until a bubble-free filament is extruded. The loaded piston is then allowed to descend under gravity. When the lower mark on the piston reaches the top edge of the cylinder start the stopwatch and at the same time discard the extrudate. The cut-offs are selected at identical time intervals.

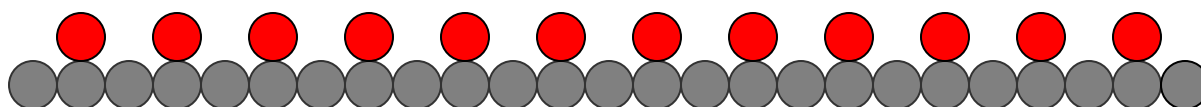
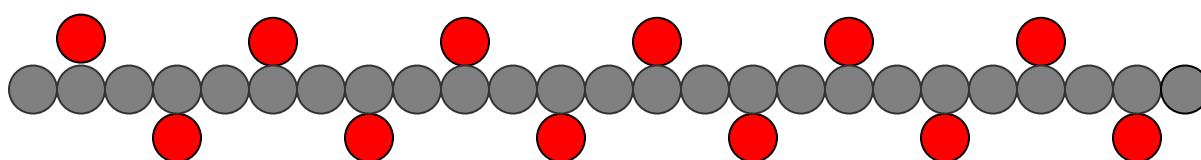
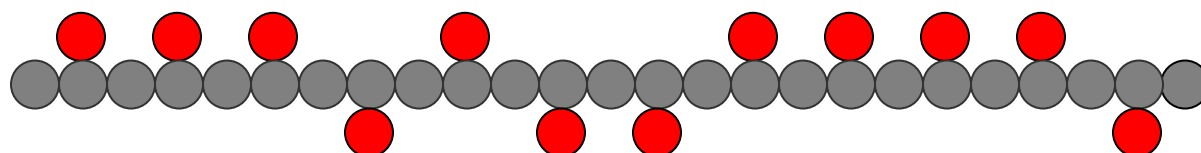
The time intervals depend upon the melt flow of the material. The test results are reported as Melt Flow Rate (MFR) or Melt Flow Index (MFI) having units as "*grams/10 minutes*"

RESULTS AND DISCUSSION

4.1 Carbon-13 NMR Analysis – Microstructure of the Samples

Figures 1 to 5 show the ^{13}C -NMR spectra of the five polyolefin samples under study. The ^{13}C -NMR spectra of PP-A and PP-B samples are shown in figure 1 and 2 respectively. Polypropylene can exist in following stereospecific configurations.

An important concept in understanding the link between the structure of polypropylene and its properties is tacticity. The relative orientation of each methyl group relative to the methyl groups on neighboring monomers has a strong effect on the finished polymer's ability to form crystals, because each methyl group takes up space and constrains backbone bending.

**Isotactic PP****Syndiotactic PP****Atactic PP**

In an Isotactic PP, the relationship between two neighbor monomer is *meso* (m), where as in a Syndiotactic PP, relationship between two neighbor monomers is *racemic* (r). An Atactic PP has sequences of meso and racemic sequences running in a random fashion. Isotactic polypropylene is hard, has a high softening point, and is easily crystallized.

¹³C-NMR spectrum of PP is very sensitive to above configurations and exhibit signals at different chemical shift values depending upon the tacticity of PP. The characteristic ¹³C-NMR Signals in an Isotactic PP are:

Isotactic PP

CH₃ = 21.8 ppm (m m m m)

CH = 28.7 ppm

CH₂ = 46.6 ppm

whereas, a predominately Syndiotactic PP exhibit CH₃ carbon signal at 20.2 ppm (r r r r CH₃). An Atactic PP exhibit number of signals in the range of 20-22 ppm each due to presence of different tetrad sequences like m m m m, m m m r, r m m r, r r r r, etc.

¹³C-NMR spectrum of PP-A sample exhibit sharp signals at 21.73 ppm (CH₃), 29.13 ppm (CH) and 46.71 ppm (CH₂) carbons and indicate that the sample predominately has isotactic configuration. The signals due to other configurational sequences could not be seen.

¹³C-NMR spectrum of PP-B also shows signals at 21.6 ppm (CH₃), 28.95 ppm (CH) and 46.5 ppm (CH₂) carbons characteristic of predominately isotactic PP. However, samples also exhibit other signals of smaller intensity at 20.64 ppm, 24.42 ppm, 30.91 ppm, 37.84 ppm and 46.05 ppm. These signals cannot be assigned to other stereoregular configurations like syndiotactic / atactic, as signals at 24.43, 30.91, & 37.84 ppm are not found in even these sequences. A comparison with the standard chemical shift values, the additional signals have been assigned to the presence of ethylene co-monomer and hence PP-B sample is a copolymer of propylene and ethylene.

Table-1a: Comparison with standard δ values for Carbon assignment

| Chemical shift (standard value) ppm | Carbon assignment | Sequence assignment |
|----------------------------------------|------------------------------------|--------------------------------------|
| 46.53 (46.52) | CH ₂ ($\alpha\alpha$) | PPPP (mmm) |
| 46.05 (46.06) | CH ₂ ($\alpha\alpha$) | PPPE + EPPP (mm) |
| 37.84 (37.91) | CH ₂ ($\alpha\gamma$) | PPEPP (mmm) |
| 30.91 (30.97) | CH | EPP + PPE (m) |
| 28.95 (28.93) | CH | PPP (mm) |
| 24.43 (24.56) | CH ₂ ($\beta\beta$) | PPEPP (mmm) |
| 21.57 & 20.64 (21.83, 20.92) | CH ₃ | PPPPP (mmmm) / PPPE+EPPPP / PPPEP |

The integral intensities of the signals have been used to determine the comonomer sequence distribution at triad level (3 comonomer level) and the percentage of ethylene / propylene comonomer in the sample. The results are shown in Table 1b:

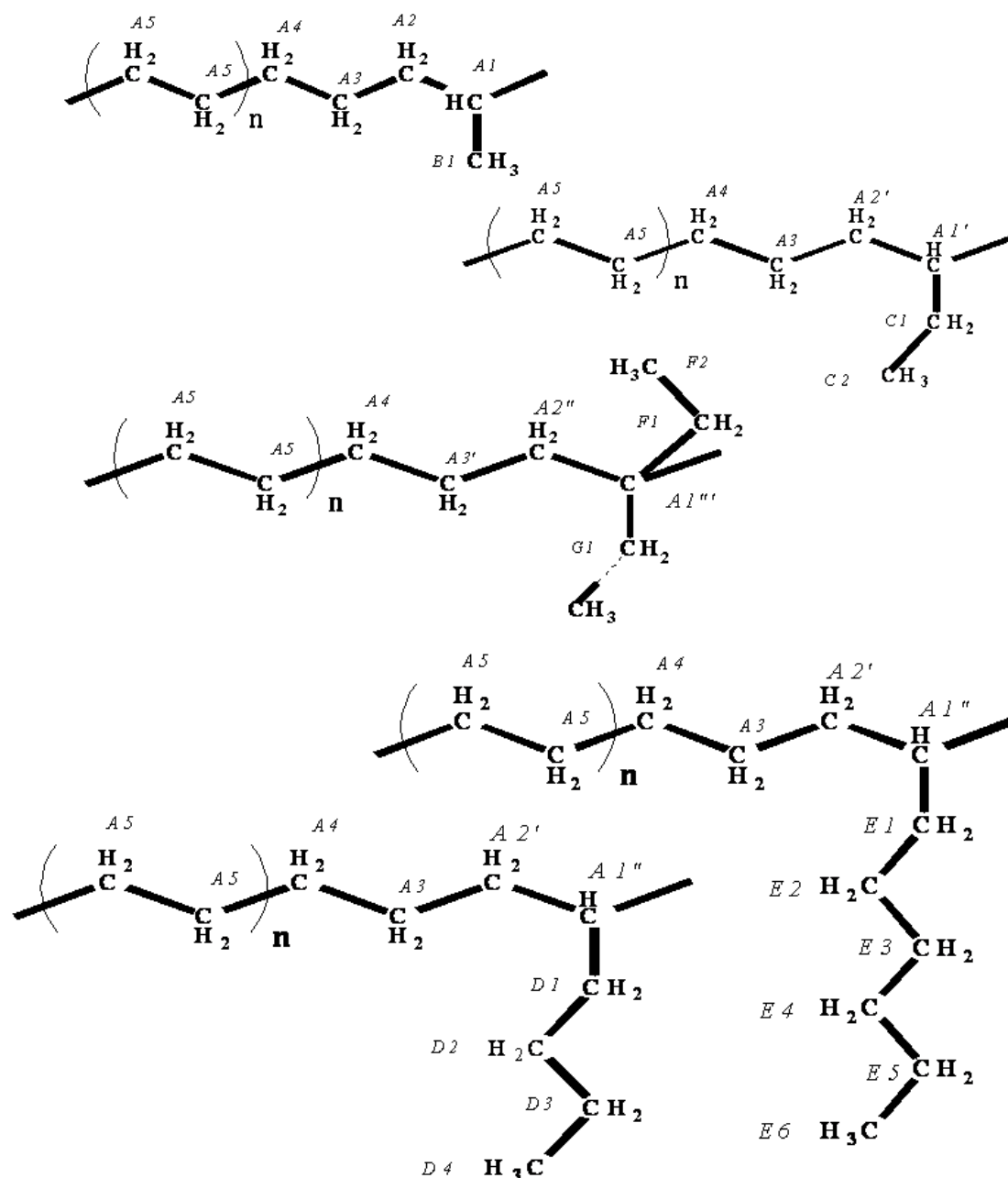
Table-1b: Comonomer Triad Sequence Distribution

| Comonomer Triad Sequences | Mole % |
|---------------------------|--------|
| EEE | 3.94 |
| PEE / EEP | 0.66 |
| PEP | 3.5 |
| EPE | 0.00 |
| EPP | 7.66 |
| PPP | 84.26 |
| ETHYLENE (E) | 8.1 % |
| PROPYLENE (P) | 91.9 % |

13C-NMR spectrum of LDPE sample is shown in Figure 3.

LDPE contains structures and branchings, which are quite complex containing a variety of short chain branches in addition to long chain 'Y' types of branches. Principal types of branches include amyl, butyl, ethyl, 1,3 -diethyl, hexyl and 2-ethyl hexyl. 13C-NMR spectroscopy is very helpful in identification and

quantification of such branchings. Shown below are the structures of LDPE having different types of branched structures along with characteristic carbon-13 chemical shift values, which can be used to identify the same.



A comparison of the ^{13}C -NMR spectrum of the LDPE sample with the characteristic chemical shift values indicate the **absence** of methyl, ethyl, diethyl, ethyl, hexyl types of the branched structures. The spectrum indicate the presence of predominately hexyl **branched** structures,

| CODE | SHIFT (ppm) | CODE | SHIFT (ppm) |
|-------|-------------|------|-------------|
| A1 | 32.8 | D1 | 34.3 |
| A1' | 39.8 | D2 | 27.3 |
| A1'' | 38.2 | D3 | 23.3 |
| A1''' | 39.2 | D4 | 14.0 |
| A2 | 37.4 | E1 | 34.6 |
| A2' | 34.6 | E2 | 27.2 |
| A2'' | 37.4 | E3 | 30.0 |
| A3 | 27.2 | E4 | 32.3 |
| A3' | 25.9 | E5 | 22.8 |
| A4 | 30.6 | E6 | 14.0 |
| A5 | 30.0 | F1 | 29.5 |
| B1 | 20.1 | F2 | 8.1 |
| C1 | 27.0 | G1 | 36.0 |
| C2 | 10.9 | | |

wherein butyl branchings may also be present in very small amount. Integral intensities have been used to calculate number of branchings per 1000 carbon atoms:

Branches per 1000 carbon atoms = 8.8

^{13}C -NMR spectrum of the LLDPE sample is shown in figure 4.

Linear low density polyethylene (LLDPE) is a substantially linear polymer, with significant numbers of short branches, commonly introduced by copolymerization of ethylene with longer-chain olefins like 1-butene, 1-hexene or 1-octene comonomers. The spectrum shows the signals at chemical shift values matching with the presence of an ethyl branched structure.

Introduction of 1-butene units among contiguous ethylene repeat units leads to the presence of an ethyl branch on the polymer backbone, having the following structure:

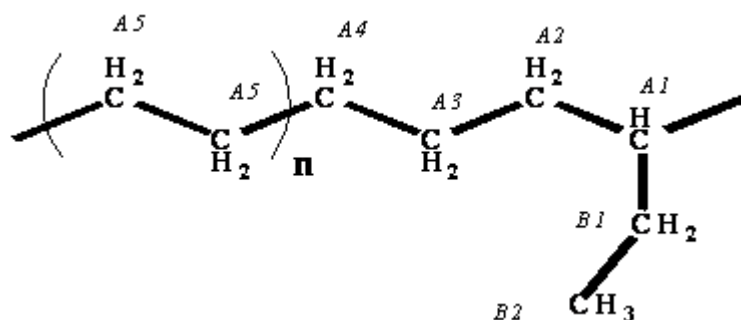


Table 1c: Carbon Assignment

| Carbon (EBE) | Chemical shift obtained (ppm) | Chemical shift standard (ppm) | Assignment |
|--------------|-------------------------------|-------------------------------|--------------------------------------------|
| A1 | 39.51 | 39.8 | CH (EBE) |
| A2 | 33.87 | 34.01 | CH ₂ ($\alpha\delta^+$) EBEE |
| A3 | 27.01 | 27.27 | CH ₂ ($\beta\delta^+$) EBEE |
| A4 | 30.1 | 30.47 | CH ₂ ($\gamma\delta^+$) BEEE |
| A5 | 30.0 | 30.0 | CH ₂ ($\delta+\delta^+$) EEEE |
| B1 | 26.6 | 26.68 | CH ₂ , EBE |
| B2 | 10.9 | 11.1 | CH ₃ , EBE |

Contiguous 1-butene sequences shall lead to 1,3 diethyl and 1,3,5 triethyl branches. It is clear from the spectrum that there are no contiguous 1-butene sequences in the LLDPE sample.

The integral intensities of the signals have been used to determine the comonomer sequence distribution at triad level (3 comonomer level) and the percentage of ethylene / butylene comonomer in the sample. The results are shown in **Table 1d**:

Table 1d: Comonomer Triad sequences

| Comonomer Triad Sequences | Mole % |
|---------------------------|--------|
| <u>EEE</u> | 90.5 |
| <u>BEE</u> / <u>EEB</u> | 7.6 |
| <u>BEB</u> | 0.0 |
| <u>EBE</u> | 1.9 |
| <u>EBP</u> | 0.0 |
| <u>BBB</u> | 0.0 |
| ETHYLENE (E) | 98.1 % |
| 1-BUTENE (B) | 1.9 % |

13C-NMR spectrum of the HDPE sample is shown in figure 5.

The spectrum does not show the presence of any significant (detectable) branches in the sample. The only signal observed is at 30.0 ppm characteristic of long chain polyethylene backbone.

The summary outcome of the NMR measurement is:

| Sample | Nature | Composition and other quantitative parameters |
|--------|---------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| PP-A | Isotactic PP | Other configurational sequences not detectable |
| PP-B | Propylene – ethylene copolymers | <ul style="list-style-type: none">• Principally isotactic PP• Propylene = 91.9, Ethylene = 8.1 mole% |
| LDPE | LDPE with mostly hexyl branches | Branches per 1000 carbon atoms = 8.8 |
| LLDPE | Ethylene / 1-Butene copolymer | Ethylene = 98.1, 1-Butene = 1.9 mole% |
| HDPE | Polyethylene | No detectable branches |

4.2 IR Studies

Figures 6 & 7 show the IR spectrum of PP and PE samples respectively.

FTIR spectrum of the two Polypropylene samples (PP-A and PP-B) in the range 4000-600 cm^{-1} reveals strong bands in the range 2840-3000 cm^{-1} , due to aliphatic C-H stretch along with strong bands near 1455 and 1376 cm^{-1} , due to bending absorptions of CH_2 and CH_3 groups respectively, which are characteristics of Polypropylene. The intensity of the band at 998 cm^{-1} related to helix chains of Polypropylene is very low in PP-B compared to PP-A, which shows that the molecular chains are very short in PP-B.

The IR spectra of the three Polyethylene samples, recorded in the range 4000-600 cm^{-1} shows strong peaks in the range 2840-3000 cm^{-1} , due to aliphatic C-H stretch (methylene stretches) along with strong bands near 1464 and 719 cm^{-1} , due to the methylene (CH_2) deformations, which are characteristics of Polyethylenes. The intensity of the band at 1304 cm^{-1} , a characteristic band for amorphous CH_2 sequences and a reference band for determination of Crystallinity, is low in HDPE compared to LLDPE and LDPE. Thus the polymer Crystallinity is high in HDPE compared to LDPE and LLDPE. Also, the band intensity at 908 cm^{-1} related to the occurrence of terminal vinyl ($-\text{CH}=\text{CH}_2$) groups is higher in HDPE compared to LDPE and LLDPE.

Polyethylenes are branched to different extents depending on their mode of production. Methyl (CH_3) and Ethyl (C_2H_5) groups as side chains absorb at about 1378 cm^{-1} and 769 cm^{-1} respectively. The IR spectrum reveals the presence of Methyl groups in LDPE and LLDPE. LLDPE also shows the existence of Ethyl branchings in its spectra in accordance with ^{13}C -NMR results. HDPE has no Methyl/Ethyl branchings in its structure, again in accordance with the NMR results.

4.3 HIGH TEMPERATURE GPC

GPC is a technique when used with appropriate detector(s) provides an accurate Molecular Weight Distribution of a polymer. This molecular weight distribution may be used to predict important physical properties and processing parameters for extrusion and injection molding.

Polyolefins have melt transition temperature above $100\text{ }^\circ\text{C}$ and must be analyzed at high temperature GPC. The RI/Viscometer combination allows obtaining an accurate molecular weight and branching information, resulting in better prediction of physical properties and processing parameters.

The more crystalline Isotactic and Syndiotactic polypropylene (PP) are required to be run at higher temperature (140 to $150\text{ }^\circ\text{C}$), whereas Atactic PP can be run at lower temperature ($\sim 90\text{ }^\circ\text{C}$). It is also required to add an antioxidant to protect the PP from degradation during the sample preparation.

Figures 8-12 show an overlay of the differential refractive index (DRI), Viscometry and light scattering chromatograms for an injection of each of the samples. The polymer samples eluted as broad Gaussian peaks except the HDPE sample, which had a slight bimodality.

4.3.1 CONVENTIONAL GPC

The samples were first analyzed using conventional GPC using the DRI data only. **Figure 13** shows a conventional GPC calibration for a series of Polystyrene Standards and **Figure 14** show an overlay of MWD calculated for an example injection of each sample.

Table 3: Calculated results for repeat injections of each sample by GPC

| SAMPLE | Molecular Weight Averages, g/mol | | | | | | PD |
|--------|----------------------------------|----------------|----------------|----------------|------------------|----------------|--------|
| | M _P | M _n | M _w | M _z | M _{z+1} | M _v | |
| PP-A | 179198 | 39932 | 337613 | 1282669 | 3142188 | 267443 | 8.4547 |
| | 184960 | 40197 | 351761 | 1269783 | 2749377 | 279064 | 8.7509 |
| PP-B | 220127 | 64012 | 366529 | 1026604 | 1925690 | 303755 | 5.072 |
| | 216671 | 65841 | 367592 | 1031223 | 1964603 | 305060 | 5.583 |
| LDPE | 160409 | 71408 | 311001 | 1008932 | 2169821 | 254727 | 4.3553 |
| | 160409 | 70211 | 315593 | 1039219 | 2205308 | 257511 | 4.4949 |
| LLDPE | 165566 | 67517 | 327731 | 1129691 | 2488571 | 266076 | 4.8541 |
| | 162967 | 70933 | 335178 | 1204917 | 2781813 | 271236 | 4.7253 |
| HDPE | 102992 | 26606 | 341233 | 1824110 | 3697609 | 242932 | 12.825 |
| | 102992 | 26505 | 334424 | 1768699 | 3626568 | 238881 | 12.617 |

4.3.2 MULTI DETECTOR GPC

For the GPC-viscometry calculations, the instrument constants for the detector systems were determined by analysis of a polystyrene narrow standard with a molecular weight of 60,450 gm/mol. Using this analysis the following parameters were obtained:

| | |
|--------------------------------|-----------|
| Interdetector delay (DRI-Visc) | -0.166667 |
| K (Concentration) | 3235.08 |
| K (LS 15) | 107297 |
| K (LS 90) | 27067.3 |
| K (Diff Pressure) | 1.14823 |

These parameters were used in all the calculations performed on the sample

4.3.2.1 GPC/Viscometry

A series of Polystyrene narrow standards were analyzed to generate a Universal Calibration- a plot of Log (molecular weight multiplied by intrinsic viscosity) Vs Retention time. The Universal Calibration curve and data are shown in **Figure 15**

The samples were then analyzed using the Universal Calibration and the Molecular Weight Distributions obtained are shown overlaid in **Figure 16**. **Figure 17** shows the overlaid Mark-Houwink plots for each sample. The molecular weight average data obtained is shown below

| SAMPLE | Molecular Weight Averages, g/mol | | | | | | PD | IV _w | R _{gw} |
|--------|----------------------------------|----------------|----------------|----------------|------------------|----------------|---------|-----------------|-----------------|
| | M _P | M _n | M _w | M _Z | M _{Z+1} | M _V | | | |
| PP-A | 122057 | 39698 | 228138 | 1166295 | 6774060 | 183625 | 5.7468 | 1.3182 | 14.8323 |
| | 138706 | 39789 | 266032 | 1231663 | 5551110 | 213659 | 6.6861 | 1.2462 | 15.1876 |
| PP-B | 157967 | 45956 | 261543 | 742838 | 1473795 | 214412 | 5.6911 | 1.3189 | 16.2543 |
| | 155228 | 48241 | 258635 | 735830 | 1653217 | 214772 | 5.3613 | 1.3301 | 16.1463 |
| LDPE | 82745 | 40006 | 153811 | 516916 | 1696231 | 129919 | 3.8447 | 1.6824 | 14.2738 |
| | 82714 | 40030 | 152070 | 461283 | 982961 | 132392 | 3.7988 | 1.7409 | 14.0601 |
| LLDPE | 80073 | 35366 | 155816 | 551635 | 1391835 | 128404 | 4.4058 | 1.8462 | 14.876 |
| | 79007 | 35899 | 154050 | 509244 | 1136117 | 128195 | 4.2912 | 1.8426 | 14.7674 |
| HDPE | 51193 | 9608 | 157095 | 908244 | 2211137 | 118680 | 16.3493 | 1.7622 | 13.4269 |
| | 49791 | 9617 | 150158 | 727470 | 1483239 | 119432 | 15.6136 | 1.6281 | 12.9355 |

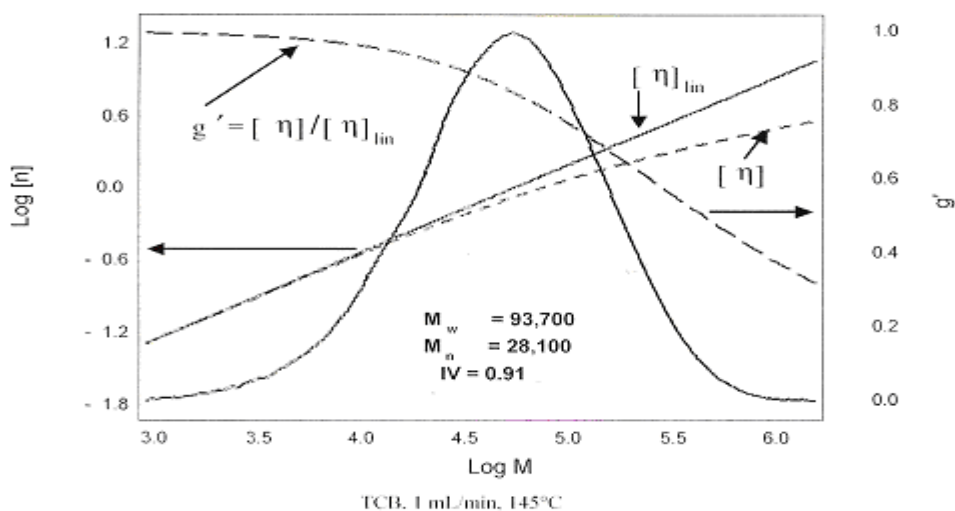
Table 4: Molecular weight average results obtained using GPC/Viscometry

The combination of the RI and Viscometer detectors allows calculation of M_v, the Mark-Houwink constants (K and alpha, α) and the whole polymer Intrinsic Viscosity (IV) in dL/gm. The intrinsic viscosity is zero concentration property and is an indicator of hydrodynamic dimension of the polymer. Hydrodynamic dimensions of a branched polymer are more shrunken compared to its linear counterpart. This analysis also provides information about the Radius of Gyration (R_g) reported in nm, which is an alternate measure of size of the polymer chain.

Branching in Polyolefins: The branching distribution of a polymer is equally important for properties such as tensile strength, tear strength of films, elongation and Crystallinity. The RI/Viscometer detector combination allows one to determine the Intrinsic Viscosity $[\eta]$ of a polymer at each molecular weight increment (slice) in the distribution. **Figure 17** shows such overlaid Mark-Houwink plots for each of the sample.

For a linear polymer, the intrinsic viscosity increases linearly with the molecular weight. For branched polymers, the relationship is non-linear and the deviation from the linearity is a measure of the amount of branching in the polymers.

The plot of **log $[\eta]$ vs. log MW** is also called the '*Viscosity Law Plot*' and provides a wealth of information about the polymer structure. The slope of the plot is called alpha (α) and the intercept is defined as log K, (where K and α are the Mark-Houwink constants). The ratio of the branched plot to the linear plot i.e. $([\eta]/[\eta]_{\text{linear}})$ is called the Branching Index (g'). This Branching Index may be used to calculate branching frequency, the number of branches per 1000 carbons and the branching probability (λ), the number of branch points per unit molecular weight.



VISCOSITY LAW PLOT

For the samples under study, detailed information about branching could not be obtained from the viscosity law plot due to non-availability of linear polyolefin samples.

4.3.2.2 TRIPLE DETECTION

The samples were analyzed using a combination of DRI, Viscometry and Light Scattering data to perform triple detection calculations. Light scattering provides better information about the Mw. Molecular weight distributions are shown in **Fig. 18** and the molecular weight average data is tabulated below (**Table 5**)

Table 5. Molecular weight average results obtained using Triple detection

| SAMPLE | Molecular Weight Averages, g/mol | | | | | | PD | IV _w | Rgw |
|--------|----------------------------------|----------------|----------------|----------------|------------------|----------------|--------|-----------------|--------|
| | M _p | M _n | M _w | M _z | M _{z+1} | M _v | | | |
| PP-A | 153242 | 52413 | 258229 | 743114 | 1428194 | 221635 | 4.9268 | 1.27 | 29.216 |
| | 150403 | 52669 | 258296 | 1017271 | 1428948 | 218472 | 4.9041 | 1.1623 | 26.924 |
| PP-B | 165293 | 55789 | 255794 | 654432 | 1231632 | 219305 | 4.585 | 1.321 | 21.496 |
| | 167353 | 56738 | 267046 | 683907 | 1248672 | 229556 | 4.7066 | 1.3241 | 25.136 |
| LDPE | 87019 | 43524 | 154811 | 442820 | 988011 | 134133 | 3.5569 | 1.6656 | 23.142 |
| | 86442 | 43746 | 153074 | 437581 | 910008 | 132496 | 3.4991 | 1.6402 | 25.323 |
| LLDPE | 81041 | 37811 | 151783 | 477018 | 1023715 | 127944 | 4.0143 | 1.8318 | 23.122 |
| | 805543 | 37880 | 154578 | 497432 | 1099491 | 130181 | 4.0807 | 1.8378 | 21.29 |
| HDPE | 48589 | 9291 | 147236 | 839339 | 2035067 | 108298 | 15.847 | 1.7061 | 25.957 |
| | 48418 | 9816 | 146583 | 709783 | 1447292 | 116738 | 14.932 | 1.6344 | 28.124 |

From the Molecular weight average results obtained from GPC/Viscometry and Triple Detection data, the Mean average values are given in table 6 below. The results show that GPC analyses with a Viscometer, dual angle light scattering detector and a refractive index detectors, provided excellent molecular weight data for the samples

Table 6: Mean average values of Molecular Weight

| SAMPLE | Molecular Weight Averages, g/mol | | | PD |
|---------------|-----------------------------------------|----------------------|----------------------|-----------|
| | M_n | M_w | M_v | |
| PP-A | 46142 | 252674 | 209348 | 5.476 |
| PP-B | 51681 | 260755 | 219511 | 5.045 |
| LDPE | 41827 | 153442 | 132235 | 3.668 |
| LLDPE | 36739 | 154057 | 128681 | 4.193 |
| HDPE | 9583 | 150268 | 115787 | 15.680 |

The samples were analyzed using conventional and GPC/Viscometry and triple detection to yield a range of molecular weight averages. The numbers obtained using GPC/Viscometry and triple detection show differences to those obtained by conventional GPC analysis using the Refractive Index detector data alone. These discrepancies arise from the comparative nature of conventional GPC, which provides results based on the retention behavior of the standards used for the column calibration. As standards used for the calibration and the samples are of different chemistry, they have different sizes in solution at any given molecular weight and since molecular weights are calculated relative to the retention behaviour of the standards and not the molecular size, inaccurate results are obtained.

In GPC/Viscometry and Triple detection, the calibration is generated based on the molecular size in solution, and so more accurate molecular weights are obtained. Differences between the results from GPC/Viscometry and triple detection arise from the sensitivity of the light scattering detector to high molecular weight material (Mw)

The Mark-Houwink plots indicate that the two Polypropylene samples have lower intrinsic viscosities at any given molecular weight than the Polyethylenes Samples. Also, the HDPE sample exhibits bi-modality in its molecular weight distribution with a very high polydispersity index.

4.4 DIFFERENTIAL SCANNING CALORIMETRY

An Endothermic peak was observed in the DSC pattern of all the samples in the temperature range of 80-180 °C. This Endothermic peak is indicative of the melting point of the polymeric materials. **Figures 19-25** show the melting endotherm of the Polyethylene and Polypropylene samples during the initial “as received” heating. And **Figures 21-25** show the DSC curves of the PE and PP samples after “thermal treatment”.

Since the thermal history of a polymer affects the measured degree of crystallinity, these samples are evaluated both ‘as received’ and after being subjected to a common ‘thermal treatment’ to impart equivalent thermal history to all the five samples. This thermal treatment consists of cooling the samples from 150 °C to 40 °C at 10 °C /min.

The Percentage Crystallinity was calculated from the DSC results using the following relation:

$$\% \text{ Crystallinity} = \frac{\Delta H_{f(\text{observed})}}{\Delta H_{f(100\% \text{ crystalline})}} \times 100$$

where $\Delta H_{f(\text{observed})}$ = Enthalpy of fusion of the polymer and is the energy involved in the formation and melting of crystalline regions, and is equal to the area under the melting peak (endo).

$\Delta H_{f(100\% \text{ crystalline})}$ = Enthalpy of fusion of 100 % crystalline material

From literature: $[\Delta H_{f(100\%)}]_{PP} = 209 \text{ J/gm}$

$[\Delta H_{f(100\%)}]_{PE} = 293 \text{ J/gm}$

The results for the five samples studied “AS RECEIVED” are summarized in **Table 7**. After “*Thermal Treatment*” of the polymeric samples, the results show variations from the values initially obtained especially in the crystallinity values. The results are shown in **Table 8**.

Table 7: “As Received” DSC Characterization of PP and PE Samples

| Sample | Melt Onset Temperature (° C) | | Melting Point T_m (° C) | | Enthalpy fusion, ΔH_f (J/gm) | | Crystallinity (%) | |
|--------|------------------------------|--------------|---------------------------|-------------|--------------------------------------|-------------|-------------------|-------------|
| | LAB1 (IOCL) | LAB 2 (IITD) | LAB1 (IOCL) | LAB2 (IITD) | LAB1 (IOCL) | LAB2 (IITD) | LAB1 (IOCL) | LAB2 (IITD) |
| PP-A | 153 | 154.8 | 167 | 168 | 89.57 | 86.1 | 43 | 41 |
| PP-B | 130 | 132.7 | 147 | 151.2 | 68.16 | 61.7 | 33 | 29.5 |
| LDPE | 91 | 102.94 | 123 | 125.16 | 67.23 | 68.15 | 23 | 23 |
| LLDPE | 105 | 110.17 | 124 | 126.79 | 79.2 | 61.72 | 27 | 21 |
| HDPE | 126 | 123.91 | 136.1 | 136.1 | 200.2 | 200.6 | 68 | 68.5 |

Table 8: DSC Characterization of PP and PE Samples after a common “thermal history”

| Sample | Melt Onset Temperature (° C) | Melting Point T_m (° C) | Enthalpy of fusion, ΔH_f (J/gm) | Enthalpy of crystallization ΔH_c (J/gm) | Crystallinity (%) |
|--------|------------------------------|---------------------------|-----------------------------------------|-------------------------------------------------|-------------------|
| PP-A | 156.29 | 166.67 | 119.2 | - 119.4 | 57 |
| PP-B | 137.76 | 149.78 | 87.4 | - 86.8 | 42 |
| LDPE | 109.6 | 123.1 | 73.4 | -72.7 | 25 |
| LLDPE | 110.18 | 122.58 | 84.3 | - 79.8 | 29 |
| HDPE | 124.4 | 136.6 | 189.5 | -207.7 | 65 |

Enthalpy of crystallization (ΔH_c) is the heat of crystallization and is the heat given off by polymer when it crystallizes (exothermic)

In case of Polypropylene, the melting points (endo peak) show slight variations while there’s a prominent increase in the percentage crystallinity values after *thermal treatment*.

A similar trend is observed in case of the Polyethylene with respect to melting point. But though LDPE and LLDPE show an increase in the percentage crystallinity values after thermal treatment, HDPE shows a decrease in the value.

The results reflect elimination of earlier processing thermal history effects. It is reasonable to assume that all of these polymers would now have similar final properties.

By subjecting polymer samples to different “thermal treatments” in the DSC prior to the crystallinity determinations, much may be learned about optimizing processing conditions.

4.5 THERMOGRAVIMETRY (TG)

Figures 26-29 & Figures 30-34 show the TG and DTG of PE and PP samples in Air and Nitrogen atmosphere respectively.

Single step decomposition was observed in all the samples. All the samples were stable up to 300 °C and started losing weight above that temperature. Thermal stability was studied by comparing Initial Decomposition Temperature (T_i), Final Decomposition Temperature (T_f) and Temperature of Maximum Rate of Weight Loss (T_{max}).

- i. Initial Decomposition Temperature (T_i): The temperature at which first weight loss was observed in the TG trace and was noted by extrapolation
- ii. Final Decomposition Temperature (T_f): The temperature at which weight loss virtually stops and is obtained by extrapolation of final portion of TG trace.
- iii. Temperature of Maximum Rate of Weight Loss (T_{max}): T_{max} was evaluated from DTG traces. The temperature corresponding to the peak position of the derivative plot was noted as T_{max} .

The results are summarized in Table 9 and 10 below:

Table 9: TG characterization in Nitrogen atmosphere

| Sample | T _i (°C) | T _{max} (°C) | T _f (°C) | Weight % Residue |
|--------|---------------------|-----------------------|---------------------|------------------|
| PP-A | 458 | 483 | 494 | <0.1 |
| PP-B | 452 | 477 | 491.5 | <0.1 |
| LDPE | 471 | 491 | 502 | <0.1 |
| LLDPE | 467 | 485.5 | 497 | <0.1 |
| HDPE | 479.5 | 496 | 511 | <0.1 |

Table 10: TG characterization in Air atmosphere

| Sample | T _i (°C) | T _{max} (°C) | T _f (°C) | Weight % Residue |
|--------|---------------------|-----------------------|---------------------|------------------|
| PP-A | 314 | 382 | 397 | <0.1 |
| PP-B | 312 | 370 | 386 | <0.1 |
| LDPE | 361 | 378 | 430 | <0.1 |
| LLDPE | 375 | 412 | 441 | <0.1 |
| HDPE | 368.5 | 389 | 452 | <0.1 |

Almost zero weight % residues in all the samples indicate that no inorganic additives / fillers etc are present in these commercial samples.

4.6 XRD ANALYSES OF THE POLYMERS

Figures 35 & 36 show the XRD pattern for the PP & PE samples under analyses. The sharp peaks due to crystalline regions present in the polymers are appearing above the broad signals due to amorphous phases. The polyethylene samples (LDPE, LLDPE and HDPE) shows characteristic crystalline peaks at 2θ value of approx. 22 and 24 degree, whereas

Polypropylene samples exhibit characteristic crystalline peaks at 2θ value of 14, 16, 18, 20 & 25.

% Crystallinity of the samples have been obtained by integrating sharp peaks with respect to the total area under the XRD pattern and the values obtained are provided below:

| Sample | % Degree of Crystallinity |
|--------|---------------------------|
| PP-A | 70.7 |
| PP-B | 65 |
| LDPE | 28.4 |
| LLDPE | 45.3 |
| HDPE | 73.5 |

It can be seen that values of % crystallinity obtained using XRD are higher than those obtained using DSC. But the trend followed is similar to that obtained using DSC results. Some anomaly is observed in the crystallinity values obtained for the Polypropylene samples. There is a need to develop the method of XRD for crystallinity determination by taking standard samples.

4.7 DENSITY

The density of Polypropylene and Polyethylene was measured using Archimedes' Buoyancy principle. The specimen is weighed in air and then weighed when immersed in distilled water at 23 °C using a sinker and wire to hold the sample completely submerged as required.

Density was calculated using the following formula

$$\rho = \frac{W(a) \cdot [\rho(fl) - \rho(a)]}{0.99983 \cdot [W(a) - W(fl)]} + \rho(a)$$

Where,

$[W(a)-W(fl)] = G = \text{Buoyancy}$

ρ = Density of the polymer sample

$\rho(fl)$ = density of the solvent (Distilled water) at measurement temperature

$W(a)$ = weight of the sample in air

$W(fl)$ = weight of the sample in liquid

$\rho(a) = 0.0012 \text{ g/cm}^3 = \text{Density of air under standard conditions (T=20}^\circ\text{C, P=101.325 kPa)}$. The value of $\rho(fl)$ at 23 °C was obtained from literature as 0.9976 gm/cc.

The density of the polymer samples is measured and is shown in Table 11.

Table 11: Average Density as calculated for the 5 samples

| Sample | No. of Pellets | W(a) g | G g | ρ g/cc | P (Average) g/cc |
|--------|----------------|-----------|--------|----------------|------------------------|
| PP-A | 2 | 0.0656 | 0.0737 | 0.8893 | 0.8773 |
| | 4 | 0.1245 | 0.1400 | 0.8885 | |
| | 8 | 0.2582 | 0.2918 | 0.8841 | |
| PP-B | 2 | 0.0346 | 0.0393 | 0.8797 | 0.8711 |
| | 4 | 0.0701 | 0.0820 | 0.8542 | |
| | 8 | 0.1358 | 0.1543 | 0.8794 | |
| LDPE | 2 | 0.0473 | 0.0517 | 0.914 | 0.9112 |
| | 4 | 0.1018 | 0.1115 | 0.9121 | |
| | 8 | 0.1898 | 0.2089 | 0.9076 | |
| LLDPE | 2 | 0.0617 | 0.0685 | 0.8998 | 0.9154 |
| | 4 | 0.1082 | 0.1170 | 0.9238 | |
| | 8 | 0.2341 | 0.2535 | 0.9225 | |
| HDPE | 2 | 0.0517 | 0.0530 | 0.9744 | 0.9634 |
| | 4 | 0.0896 | 0.0944 | 0.9481 | |
| | 8 | 0.1778 | 0.1835 | 0.9679 | |

4.8 MECHANICAL PROPERTIES

4.8.1 MELT FLOW INDEX (MFI)

MFI was measured at 230 °C under a 2.16 kg loading for Polypropylene, and at 190 °C under 2.16 kg loading for Polyethylene according to ASTM D 1238.

The MFI values obtained from two instruments from two laboratories are reported in **Table 12**.

| Sample Name | Temperature/ Load | MFI, g/10 min | |
|-------------|-------------------|--------------------------|---------------------|
| | | International Equipments | Dynisco Instruments |
| PP-A | 230 °C/2.16 kg | 15 | 17.5 |
| PP-B | | 6 | 5 |
| LDPE | 190 °C/2.16 kg | 0.8 | 0.7 |
| LLDPE | | 0.7 | 0.5 |
| HDPE | | 0.7 | 0.7 |

Table 12: MFI values of the 5 samples from two instruments

The MFI values of the Polypropylenes show variations in the results from two different instruments, while not much variation is observed in the Polyethylene samples.

4.8.2 TENSILE & FLEXURAL PROPERTIES

Figures 37-41 shows the Stress-Strain curve (Tensile Properties) and **Figures 42-46** shows the Load vs. Deformation curve (Flexural Properties) for the PE and PP samples.

The tensile modulus and strength at break, as well as the elongation at break are compiled in **Table 13**.

The force per unit area (MPa or psi) required to break a material is the **ultimate tensile strength** or **tensile strength at break**. The **tensile modulus** is the ratio of stress to elastic strain in tension. A high tensile modulus means that the material is rigid - more stress is required to produce a given amount of strain. The **ultimate elongation** of an engineering material is the percentage increase in length that occurs before it breaks under tension.

Table 13: Tensile and Flexural Strength, Modulus and Elongation values for the PE & PP samples

| Sample | TEST | CROSS-HEAD SPEED (mm/min) | STRENGTH AT BREAK (MPa) | MODULUS (MPa) | ELONGATION AT BREAK (%) |
|--------|-----------------|---------------------------|-------------------------|---------------|-------------------------|
| HDPE | Tensile | 100 | 26 ± 0.5 | 234 ± 24 | 69 ± 9 |
| | <i>Flexural</i> | 100 | 26 ± 1 | 419 ± 221 | |
| LDPE | Tensile | 300 | 13 ± 1 | 76 ± 5 | Did not break |
| | <i>Flexural</i> | 300 | 6 ± 0.2 | 158 ± 9 | |
| | <i>Flexural</i> | 500 | 7 ± 0.3 | 189 ± 25 | |
| LLDPE | Tensile | 500 | 16 ± 0.3 | 118 ± 10 | Did not break |
| | <i>Flexural</i> | 500 | 10 ± 1 | 292 ± 24 | |
| | <i>Flexural</i> | 600 | 11 ± 1 | 226 ± 49 | |
| PP-A | Tensile | 10 | 36 ± 1 | 238 ± 63 | 16 ± 2 |
| | <i>Flexural</i> | 10 | 43 ± 1.5 | 1293 ± 47 | |
| | <i>Flexural</i> | 25 | 44 ± 0.4 | 945 ± 217 | |
| PP-B | Tensile | 50 | 27 ± 1 | 157 ± 27 | 148 ± 71 |
| | <i>Flexural</i> | 50 | 28 ± 0.5 | 635 ± 138 | |

The Tensile Strength and Tensile Modulus of the PP-A sample is higher than PP-B, but the percentage elongation is higher for the PP-B sample, which is due to its rubber like character imparted by ethylene comonomer. Similarly in Polyethylene, the tensile strength and modulus is highest for HDPE, then LLDPE and LDPE respectively. The LLDPE and LDPE samples did not break during the tensile test and only the HDPE sample showed a percentage elongation of 70%. The presence of chains provides flexibility to LDPE and LLDPE, whereas more brittle (highest crystallinity) HDPE breaks down.

The Flexural Strength and Modulus of PP-A is greater than that of PP-B. The PP-A samples showed an increase in the Strength but Modulus values are decreased on changing the speed of testing.

The Flexural Strength and Modulus is highest for HDPE, then LLDPE and LDPE respectively. The Strength and Modulus values are increased in LDPE on changing the crosshead speed, while in case of LLDPE, the Flexural Strength is increased but Modulus is decreased.

4.8.3 IZOD IMPACT STRENGTH

The impact strength was calculated by dividing the absorbed energy by the thickness of the specimen according to ASTM D 256. The Izod impact strength was measured for notched specimens and values are reported in terms of Joules per meter and shown in **Table 14**.

Table 14: Izod Impact Strength of PE and PP samples

| SAMPLE | ENERGY (J/m) |
|---------------|---------------------|
| PP-A | 24 ± 6 |
| PP-B | 70 ± 10 |
| LDPE | 448 ± 61 |
| LLDPE | 456 ± 44 |
| HDPE | 190 ± 19 |

The impact strength of PP-B sample is higher than that of the PP-A sample. This is due to the presence of ethylene comonomer in sample PP-B, which due to its rubbery structures increases the impact strength of the polymer.

LDPE has almost equal impact strength compared to LLDPE. As expected, the HDPE has the lowest impact strength amongst polyethylenes and is easy to break.

4.8.4 Heat Deflection Temperature (HDT) & Vicat Softening Point (VSP)

HDT is a useful indicator of the temperature limit above which polymers (or commercial grades of plastics) cannot be used for structural (load-supporting) applications.

Figures 47-51 show the HDT and VSP curves of the PP and PE samples under analyses. The Heat Deflection Temperature and Vicat Softening Point was measured under load and shown in **Table 15**.

Table 15: HDT and VSP of the five PP and PE samples

| Sample | HDT (°C) | VSP (°C) |
|---------------|-----------------|-----------------|
| PP-A | 137.9 | 155.7 |
| PP-B | 114.7 | 131.1 |
| LDPE | 94.3 | 105.5 |
| LLDPE | 99.8 | 121.7 |
| HDPE | 120.5 | 126.3 |

PP-A has higher HDT and VSP compared to PP-B, which can be explained based on their chemical structure. Similarly, LDPE has lower HDT and VSP compared to LLDPE, in which differences in VSP are noticeable. HDPE sample, as expected, has much higher HDT compared to LDPE & LLDPE, whereas in case of VSP, though on higher side, differences between HDPE and LLDPE are not dramatic.

CONCLUSION

With the stated objectives for characterizing and establishing structure-property relationships of polyolefins, five (5) commercial samples namely PP-A, PP-B (both polypropylene), LDPE, LLDPE and HDPE have been subjected to detailed characterization at three levels viz: Molecular, Mesoscopic and Macroscopic.

Structurally, PP-A has been found to be principally Isotactic polypropylene, whereas PP-B has been found to be a copolymer of propylene and ethylene containing principally Isotactic polypropylene sequences and ~ 9 mole% of ethylene comonomer. LDPE has been found to contain long polyethylene backbone with mainly hexyl branchings of the order of ~ 8.9 branches per 1000 carbon atoms. LLDPE has been characterized as a copolymer of ethylene and 1-butene containing ~ 2 mole% butane comonomer. HDPE sample has been characterized as polyethylene backbone with no branchings.

Information about the molecular weight and molecular weight distribution has been obtained using high temperature-GPC with triple detector system (RI, Viscosity and light scattering). Both the polypropylene samples have equal molecular weight and polydispersity index, but higher than their polyethylene counterparts. The two Polypropylene samples have lower intrinsic viscosities at any given molecular weight than the Polyethylenes Samples. LDPE, LLDPE and HDPE samples exhibit almost similar M_w and M_v , however, the HDPE sample exhibits bi-modality in its molecular weight distribution with a very high polydispersity index of the order of 16, whereas LDPE and LLDPE has almost similar polydispersity index (~ 4).

Thermal analyses of the samples shows that PP-A has much higher melting point (~ 166 C) compared to PP-B (~149 C), which is due to different chemical composition of two polypropylene samples. Introduction of ethylene as a comonomer in PP-B lowers the melting point. LLDPE and LLDPE has been

found to have almost similar melting point (~ 123 C), which is correlated to the presence of branchings in both as well as almost similar molecular weight and distribution profile.

PP-A has been found to have higher crystallinity (~ 42%) compared to PP-B (~ 30 %), which can again be correlated to the molecular structural differences. However, crystallinity of both the polypropylene samples have been found to increase proportionally (57 % and 42% respectively) after the common heating history is provided to the samples. Both LDPE and LLDPE have been found to have similar %crystallinity (~ 23-24%), which increases slightly after the thermal treatment. HDPE has been found to have the maximum crystallinity of 68 %, which is expected from the structure of the sample.

Thermal analyses also showed the absence of any inorganic additives / fillers in the commercial samples.

The Tensile Strength and Tensile Modulus of the PP-A sample is higher than PP-B, but the percentage elongation is higher for the PP-B sample, which is due to its rubber like character imparted by ethylene comonomer. Similarly in Polyethylene, the tensile strength and modulus is highest for HDPE, then LLDPE and LDPE respectively. The LLDPE and LDPE samples did not break during the tensile test and only the HDPE sample showed a percentage elongation of 70%. The presence of chains provides flexibility to LDPE and LLDPE, whereas more brittle (highest crystallinity) HDPE breaks down.

The Flexural Strength and Modulus of PP-A is greater than that of PP-B. The PP-A samples showed an increase in the Strength but Modulus values are decreased on changing the speed of testing. The Flexural Strength and Modulus is highest for HDPE, then LLDPE and LDPE respectively. The Strength and Modulus values are increased in LDPE on changing the crosshead speed, while in case of LLDPE, the Flexural Strength is increased but Modulus is decreased.

The structural differences of the samples are also reflected in the IZOD impact test. The impact strength of PP-B sample is higher than that of the PP-A sample. This is due to the presence of ethylene comonomer in sample PP-B, which due to its rubbery structures increases the impact strength of the polymer.

LDPE has almost equal impact strength compared to LLDPE. As expected, the HDPE has the lowest impact strength amongst polyethylenes and is easy to break.

PP-A has higher HDT and VSP compared to PP-B, which can be explained based on their chemical structure. Similarly, LDPE has lower HDT and VSP compared to LLDPE, in which differences in VSP are noticeable. HDPE sample, as expected, has much higher HDT compared to LDPE & LLDPE, whereas in case of VSP, though on higher side, differences between HDPE and LLDPE are not dramatic.

The present study has helped standardize procedures of analytical characterization and testing of Polyethylene, Polypropylene samples for the generation of base line data for the commercial samples in order to establish structure-property relationships, extendable to correlations with performance of the polyolefins.

REFERENCES

1. <http://polymers.msel.nist.gov/highlights/polyolefins.html>
2. http://www.bpf.co.uk/bpfindustry/plastics_materials_polypropylene_PP.cfm
3. Prog. Polym. Sci., 31 (2006), 145–237
4. Fawcett, E. W., Gibson, R. O., Perrin, M. W., Patton, J. G., Williams, E. G., B Patent 471,590, Sept. 6, (1937).
5. Ziegler, K., Ger Patent 878,560 (1953).
6. Boor, J., “Ziegler-Natta Catalysts and Polymerizations”, New York: Academic Press, (1979).
7. McDaniel, M. P., and Johnson, M. M., Macromolecules, 20: 773 (1987).
8. Kaminsky, W., Macromol. Chem. Phys., 197:3907 (1996).
9. http://www.ias.ac.in/initiat/sci_ed/resources/chemistry/MolWeight.pdf
10. <HTTP://plc.cwru.edu/tutorial/enhanced/files/polymers/synth/synth.htm>
11. <http://chem.chem.rochester.edu/~chem421/propmw.htm>
12. <http://www.pslc.ws/mactest/weight.htm>
13. http://en.wikipedia.org/wiki/Molar_mass_distribution
14. P. Ghosh, “Polymer Science & Technology of Plastics and Rubbers”. TMH Pub. Co., Delhi, 1990
15. Edgar, O.W. and R. Hill, *J. Polym. Sci.*, 8 (1952), 1.
16. Frosini, V., Magagnini, P.L., Newman, B.A., *J. Polym. Sci. Polymer Physics Ed.*, 12 23 (1974)
17. Mandelkern, L. *Crystallization of Polymers*, McGraw-Hill, New York, 1964.
18. Odian, George; *Principles of Polymerization*, 3rd ed., John Wiley & Sons, New York, 1991, p.27
19. <http://www.pslc.ws/mactest/crystal.htm>
20. Galli, P.; Vecellio, G., 2004, Polyolefins: The Most Promising Large-Volume Materials for the 21st Century, *Journal of Polymer Science: Part A: Polymer Chemistry*, 42, 396–415
21. Askeland, D.; Phule, P. 2003, *The Science and Engineering of Materials*, Fourth Edition, Brooks/Cole, Thomson Learning Inc.
22. Ohshima, M.; Tanigaki, M., 2000, Quality Control of Polymer Production Processes, *Journal of Process Control*, 10,135–148
23. *J. Appl. Polymer Sci.*, 16 (1961) 384
24. Tung, L. H., *SPE Tech. Papers*, 1958,p. 959

REFERENCES

25. *J. Appl. Polymer Sci.*, 8(1964) 825
26. Shalaeva L. H., Domareva N. M., *Soviet Plastics*, (6) June (1962)
27. Natta, G., Dannusso, F., *J. Polym. Sci.*, 34 3 (1959)
28. Bovey, F.A., *Polymer Conformation and Configuration*, Academic Press, New York (1969)
29. D. M. Price, D. J. Hourston, and F. Dumont, *Encyclopedia of Analytical Chemistry*, pp. 8094–8105, Ó John Wiley & Sons Ltd, Chichester, 2000
30. <http://www.msm.cam.ac.uk/phase-trans/2002/Thermal2.pdf>
31. www.sartorius.com
32. http://www.jascoinc.com/literature/pdf/appnotes/IR_01.04.pdf
33. <http://www.thefreelibrary.com/Identification+of+polymers+by+IR+spectroscopy-a0119376722>
34. F.A.Bovey, *Polymer Preprints*, 10 (1), 9 (1969)
35. DeRosa, C., Auriemma, F., Capitani, D., Caporaso, L., Talarico, G., *Polymer*, 41(2000), 2141-2148
36. Randall, J.C., *Rev. Macromol. Chem. Phys.*, C29(2 & 3), 201-317 (1989)
37. Randall, J.C., *Polymer Sequence Determination: Carbon 13 NMR method*, Academic, New York, 1977
38. <http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-cnmr-1.html>
39. www.eng.uc.edu/%7Egbeaucag/Classes/Analysis/Chapter6.pdf
40. Berger, H.L. and Schultz, A.R., *J. Polym. Sci.*, A 2(1965), 3643
41. Alteget, K.H., *Advances in Chromatogr.* 79(1968), 3
42. Müller, G., Arndt, K.F., Schröder, E. *Polymer Characterization*, Hanser Publishers, 1988
43. <http://www.waters.com/WatersDivision/contentd.asp?watersit=JDRS-5LW9ZN#cal2>
44. <http://www.answers.com/gel%20permeation%20chromatography>
45. http://www.eaglabs.com/techniques/analytical_techniques/xrd.php
46. Van Melick, H.G.H., Govaert, L.E., Meijer, H.E.H. (2003). *Polymer*, 44, 2493–2502.
47. G'Sell, C., Hiver, J.M., Dahoun, A., Souahi, A. (1992). *J. Mat. Sci.*, 27, 5031–5039.

REFERENCES

48. Arruda, E.M., Boyce, M.C. (1993). *Int. J. Plast.*, 9, 697–720.
49. Boyce, M.C., Arruda, E.M., Jayachandran, R. (1994). *Pol. Eng. Sci.*, 34, 716–725.
50. http://www.eng.buffalo.edu/Courses/ce435/2001/Plastic_Microwave/MicrowaveReport_files
51. <http://www.cvgs.k12.va.us/Nuclear/tensile%2520specimens.jpg>
52. http://www.plasticsmag.com/article_images/Tensile%2520Test.JPG
53. <http://www.testedandproven.com/flexural.html>
54. www.matweb.com
55. Aklonis, J.J., *J. Chem. Ed.*, 58, 892-897
56. www.matweb.com/reference/izod-impact.asp
57. www.azom.com
58. <http://info.lu.farmingdale.edu/depts/met/met206/index.html>
59. http://en.wikipedia.org/wiki/Melt_Flow_Index
60. http://en.wikipedia.org/wiki/Heat_Deflection_Temperature
61. www.ides.co/property_descriptions/ASTMD648.asp
62. www.matweb.com/deflection-temperature.asp
63. www.ides.co/property_descriptions/ASTMD1525.asp

FIGURES

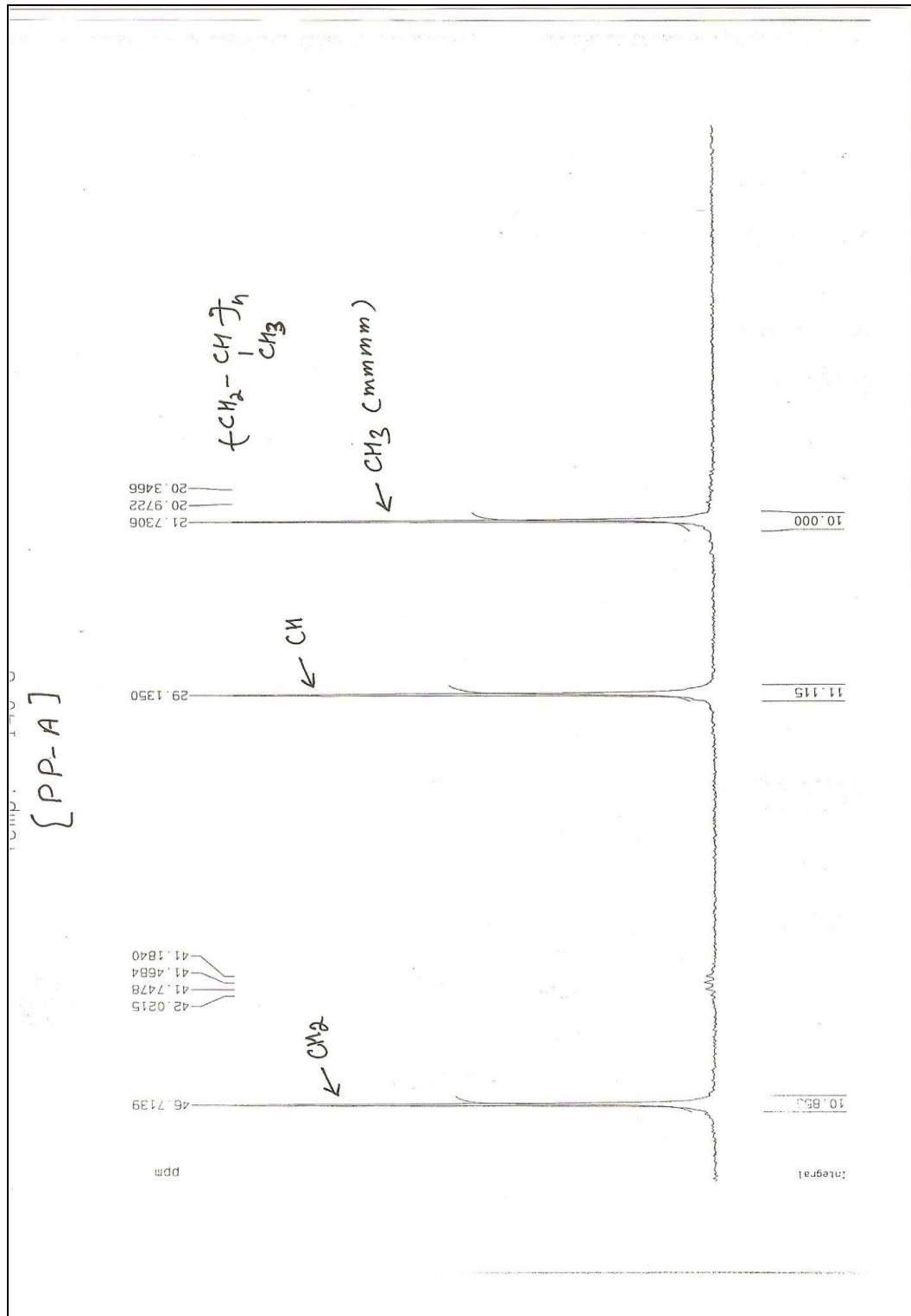


FIGURE 1: C-13 NMR SPECTRA OF PP-A

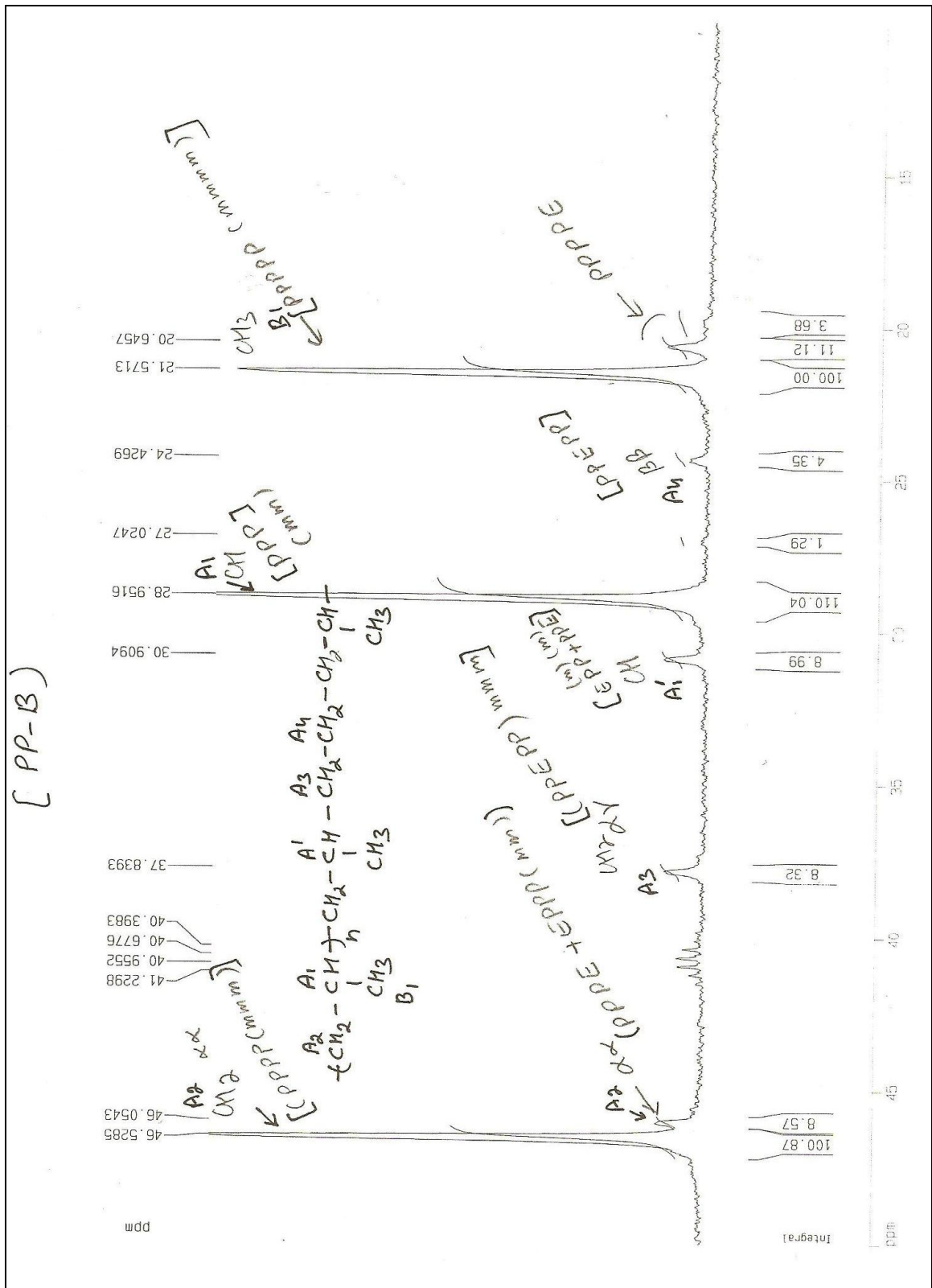


FIGURE 2: C-13 NMR SPECTRA OF PP-B

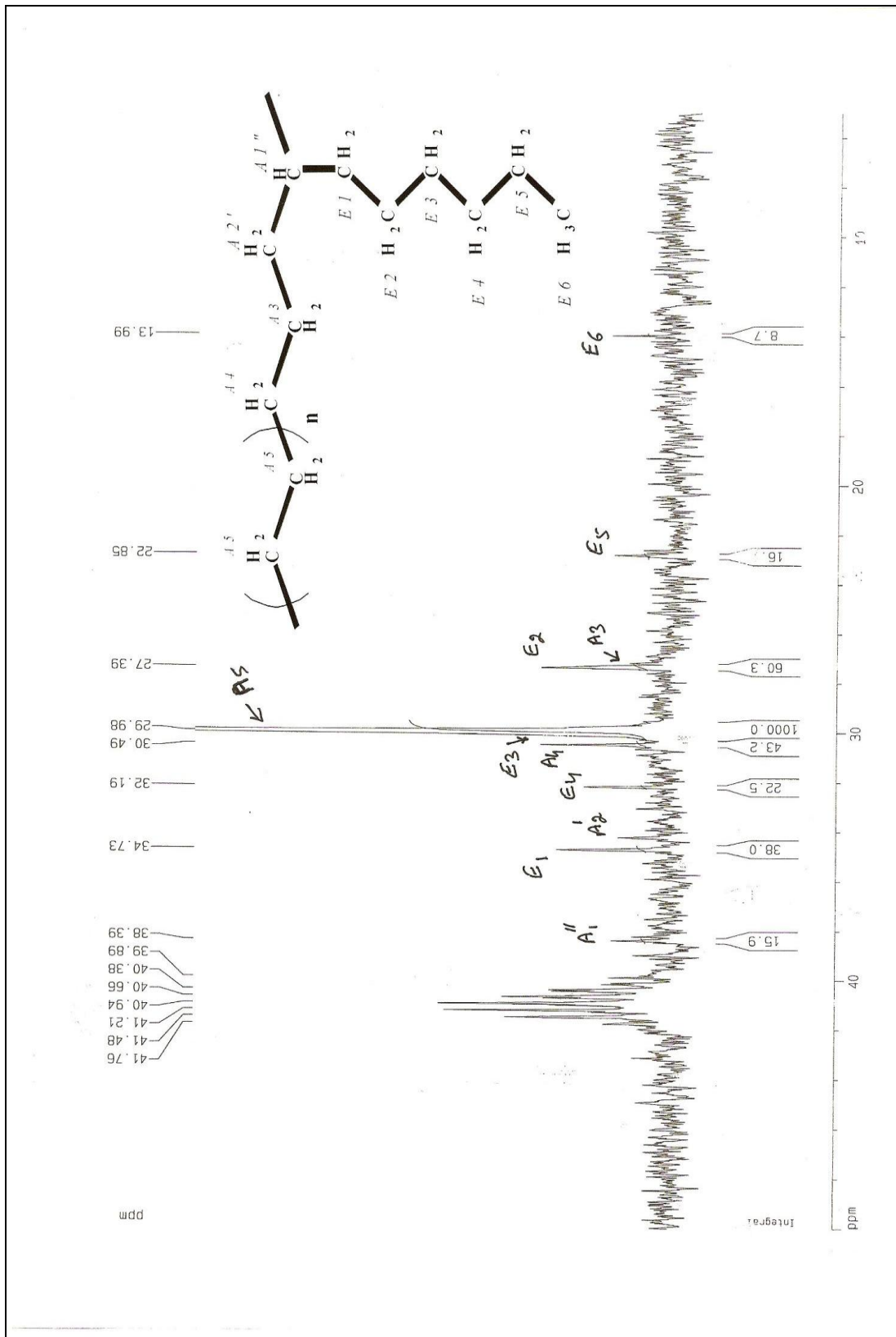


FIGURE 3: C-13 NMR SPECTRA OF LDPE

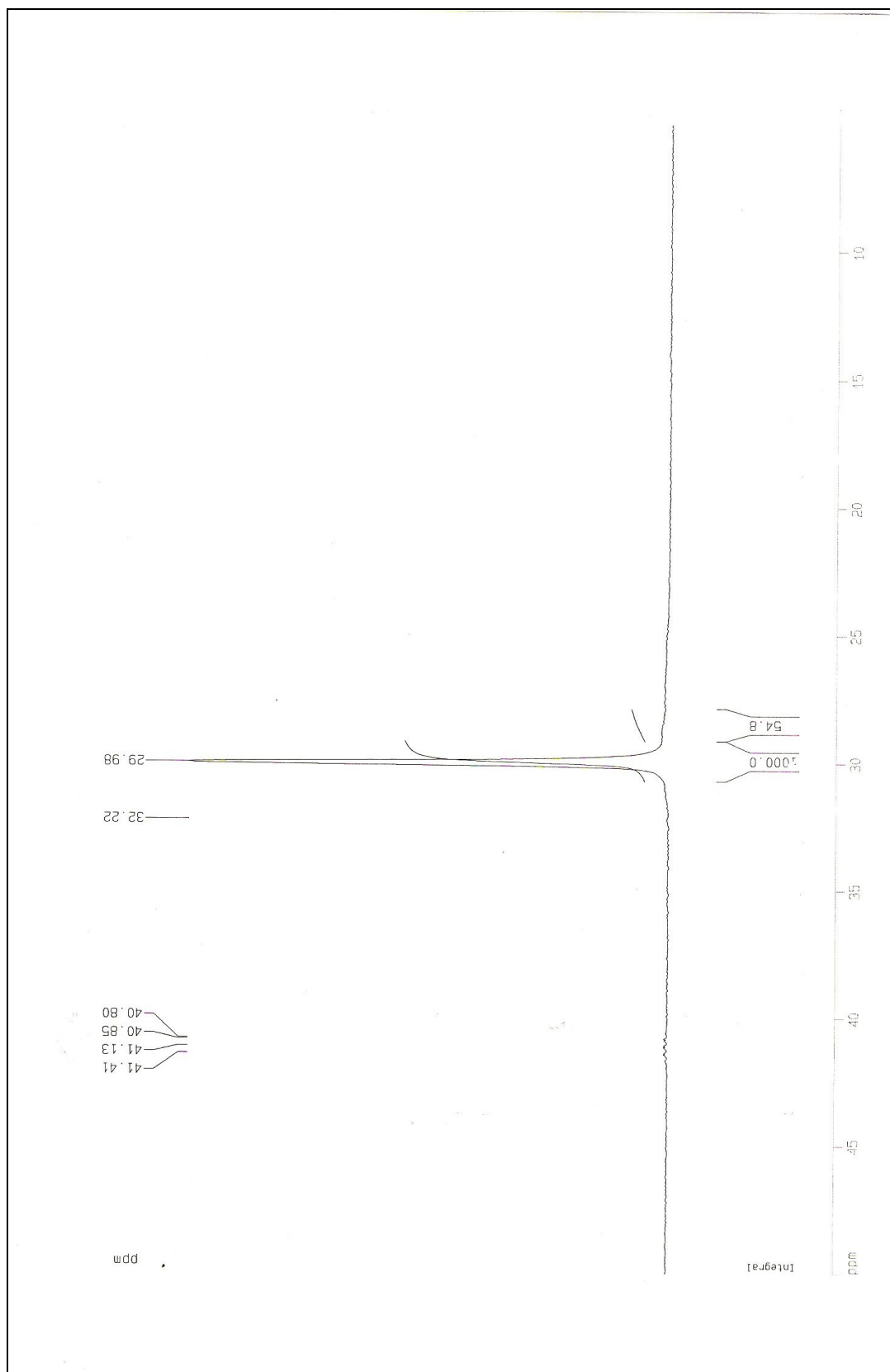


FIGURE 5: C-13 NMR SPECTRA OF HDPE

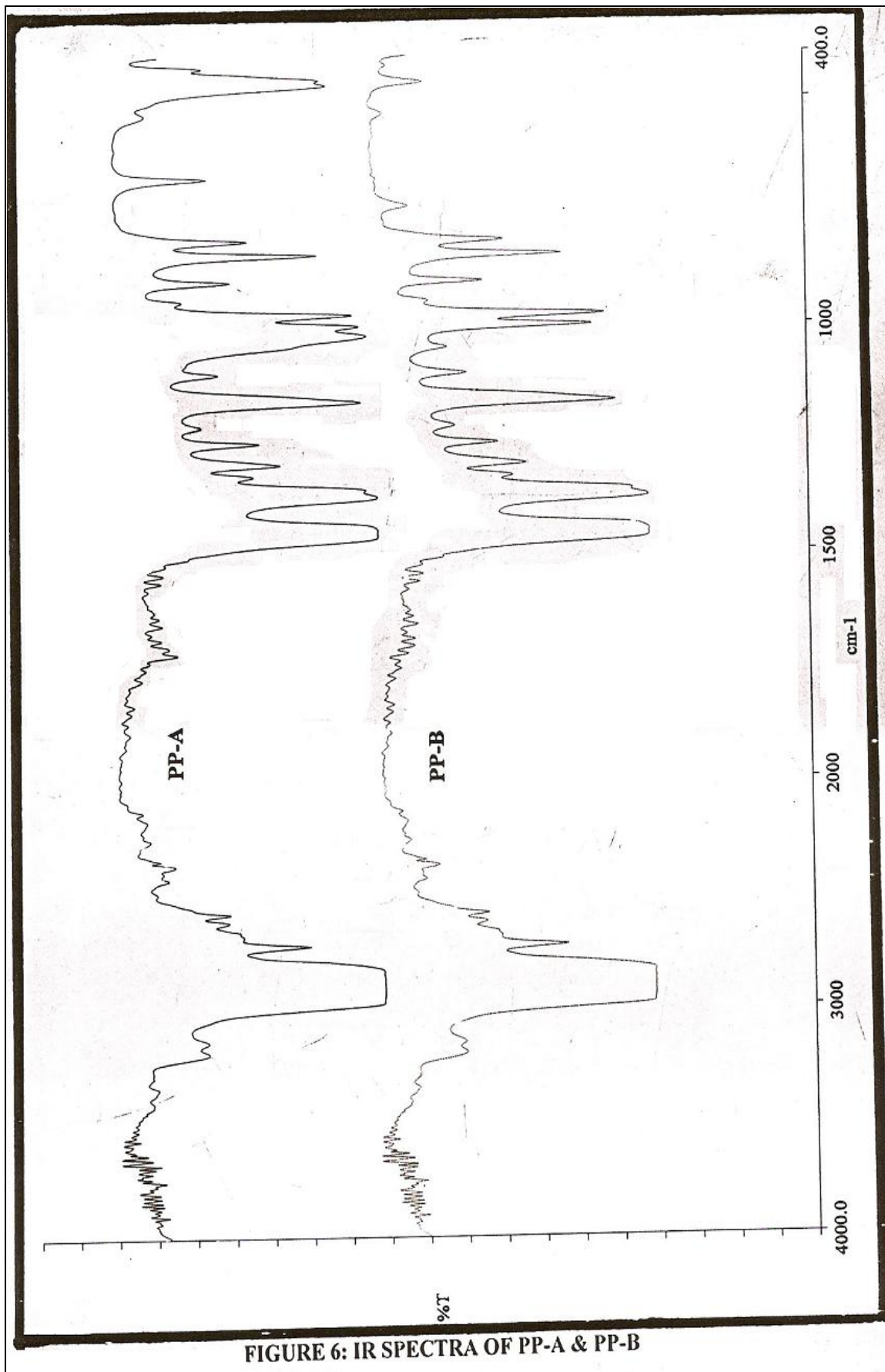


FIGURE 6: IR SPECTRA OF PP-A & PP-B

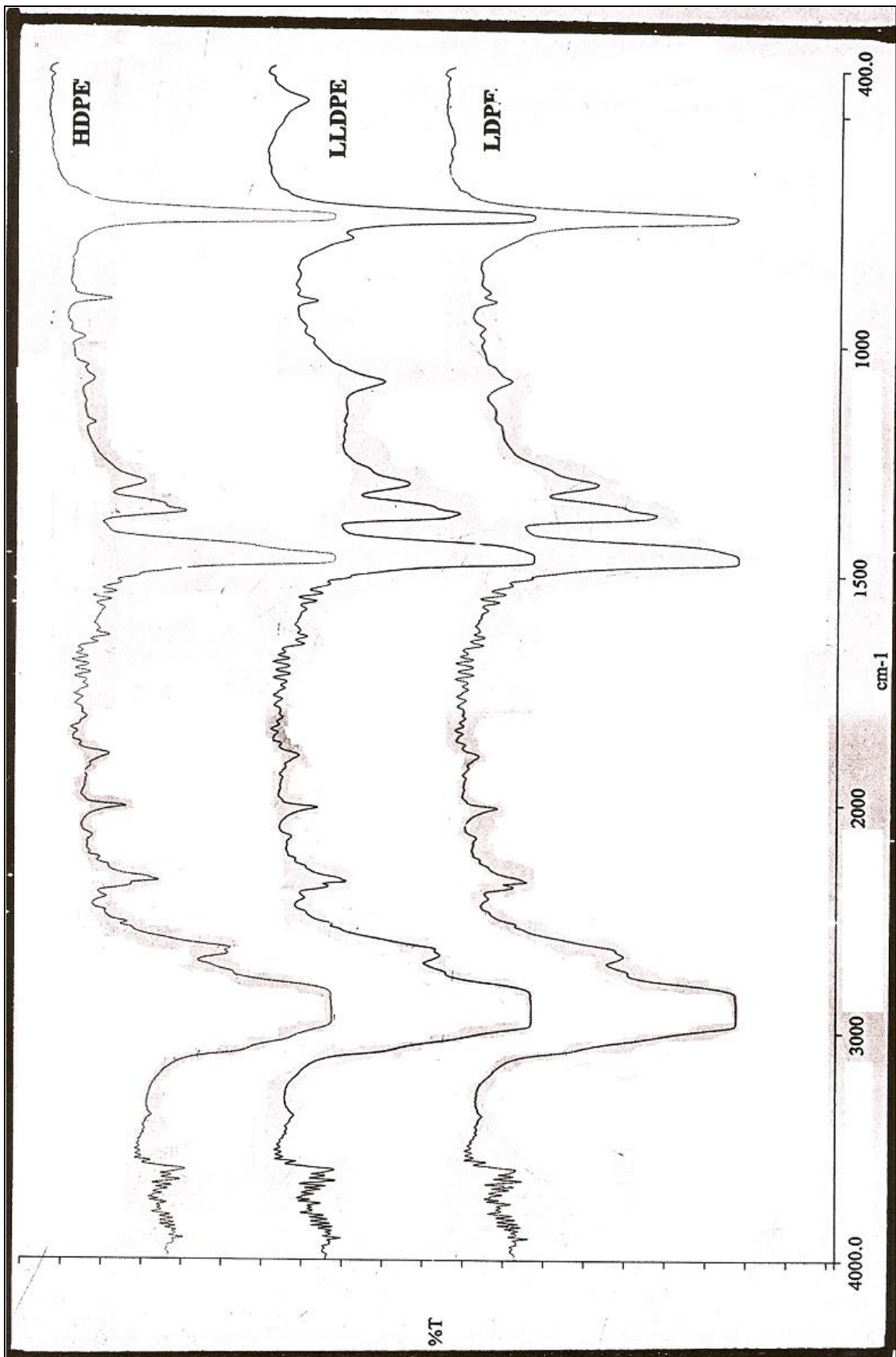


FIGURE 7: IR SPECTRA OF LDPE,LLDPE,HDPE

Figure 8: Overlaid Chromatogram of Sample PP-A

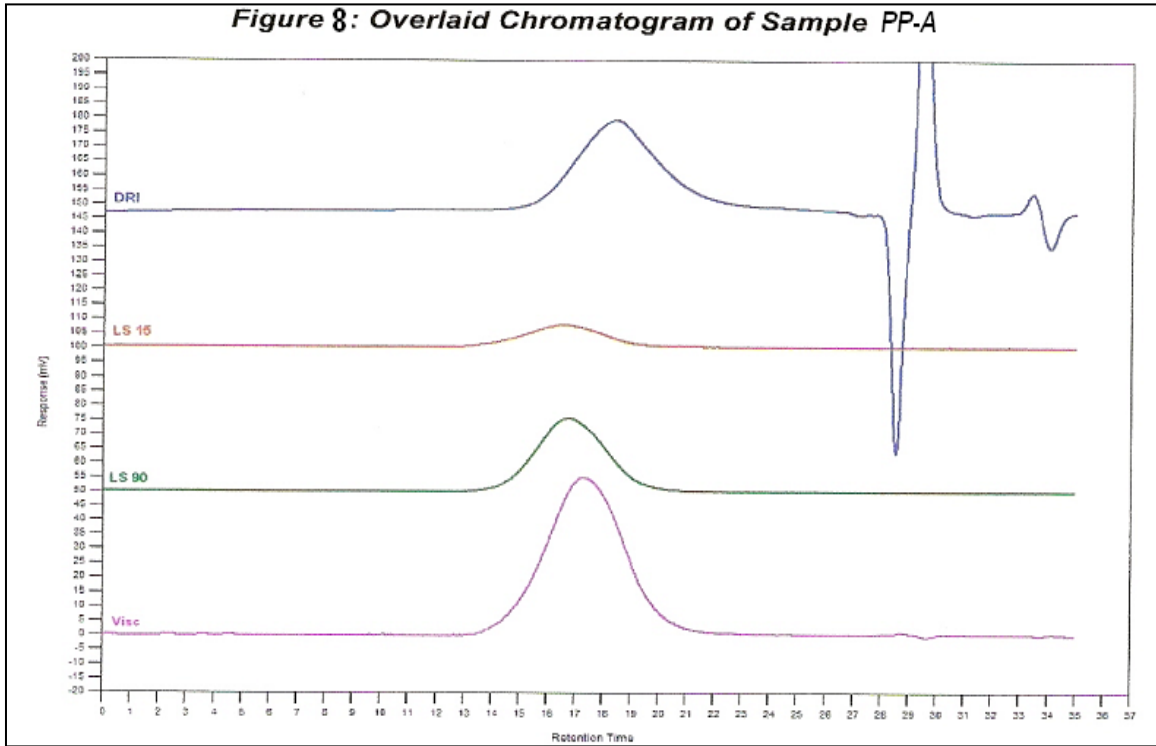


Figure 9: Overlaid Chromatogram of Sample PP-B

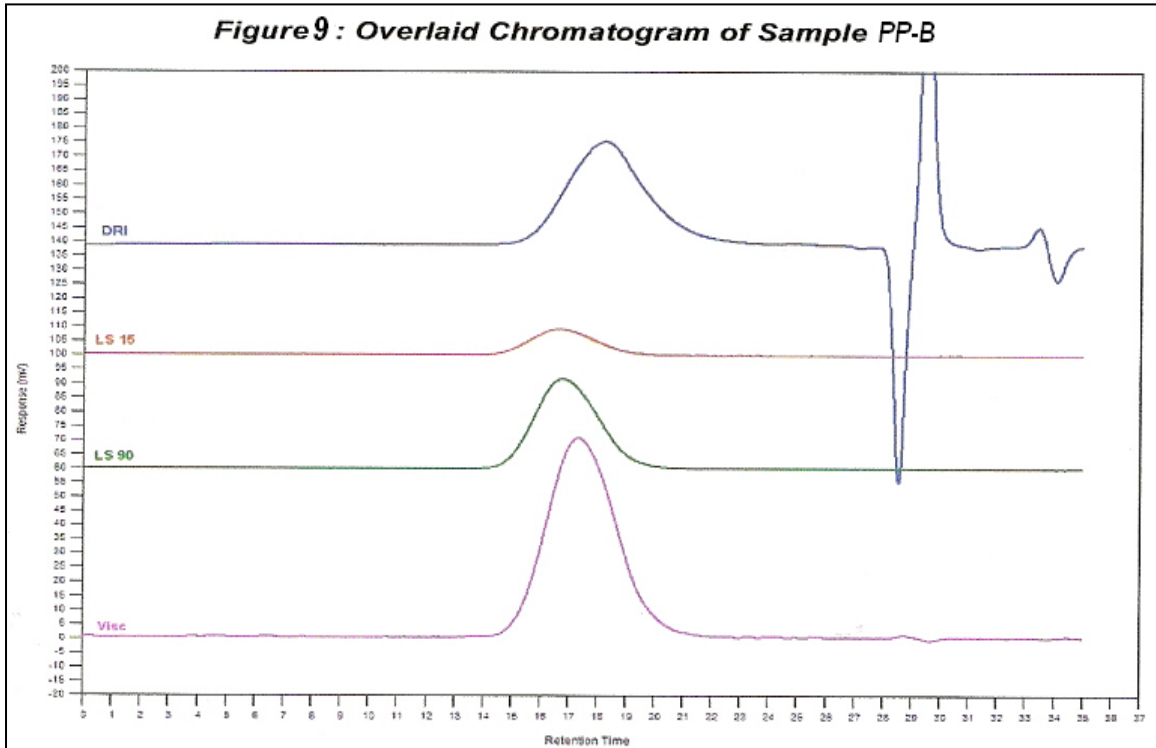


Figure10: Overlaid Chromatogram of Sample LDPE

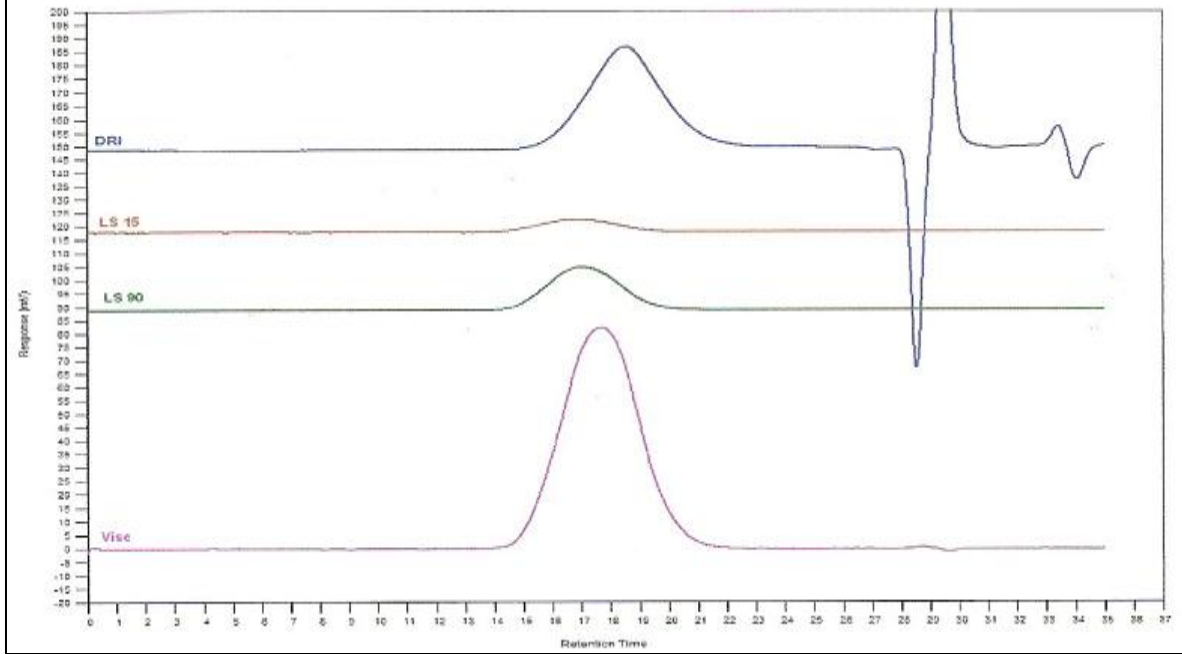
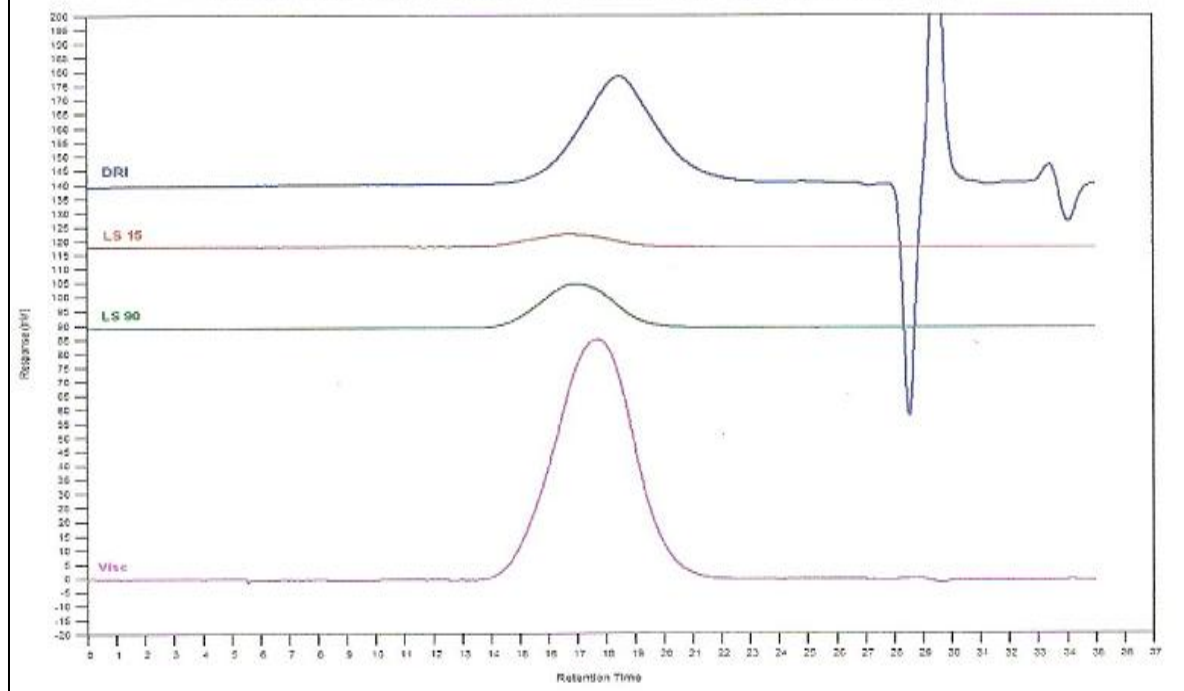


Figure11: Overlaid Chromatogram of Sample LLDPE



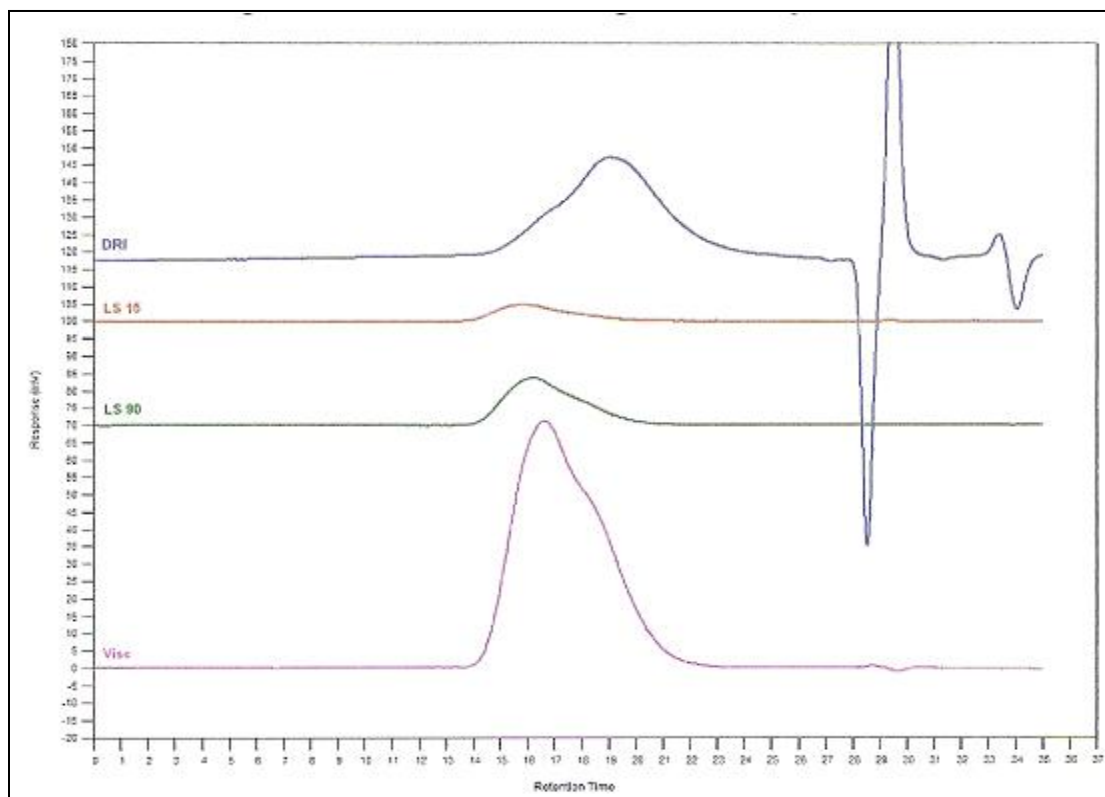


FIGURE 12: Overlaid Chromatogram of Sample HDPE

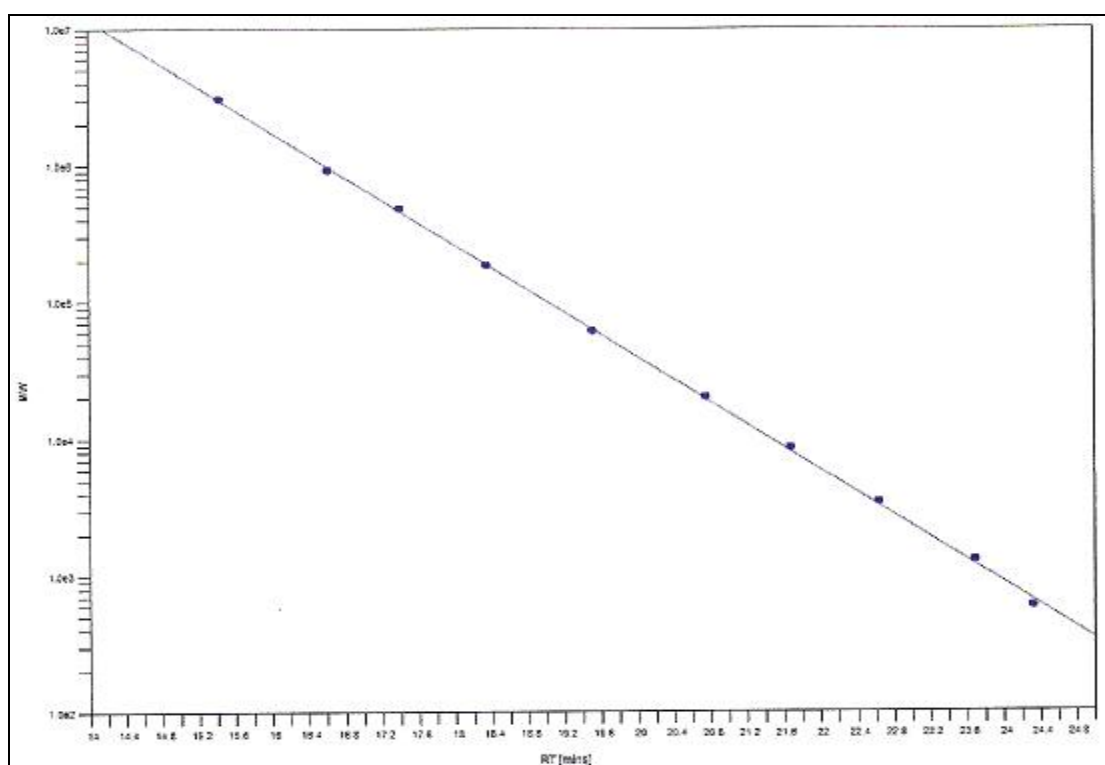


FIGURE 13: Conventional GPC calibration for a series of Polystyrene Standards.

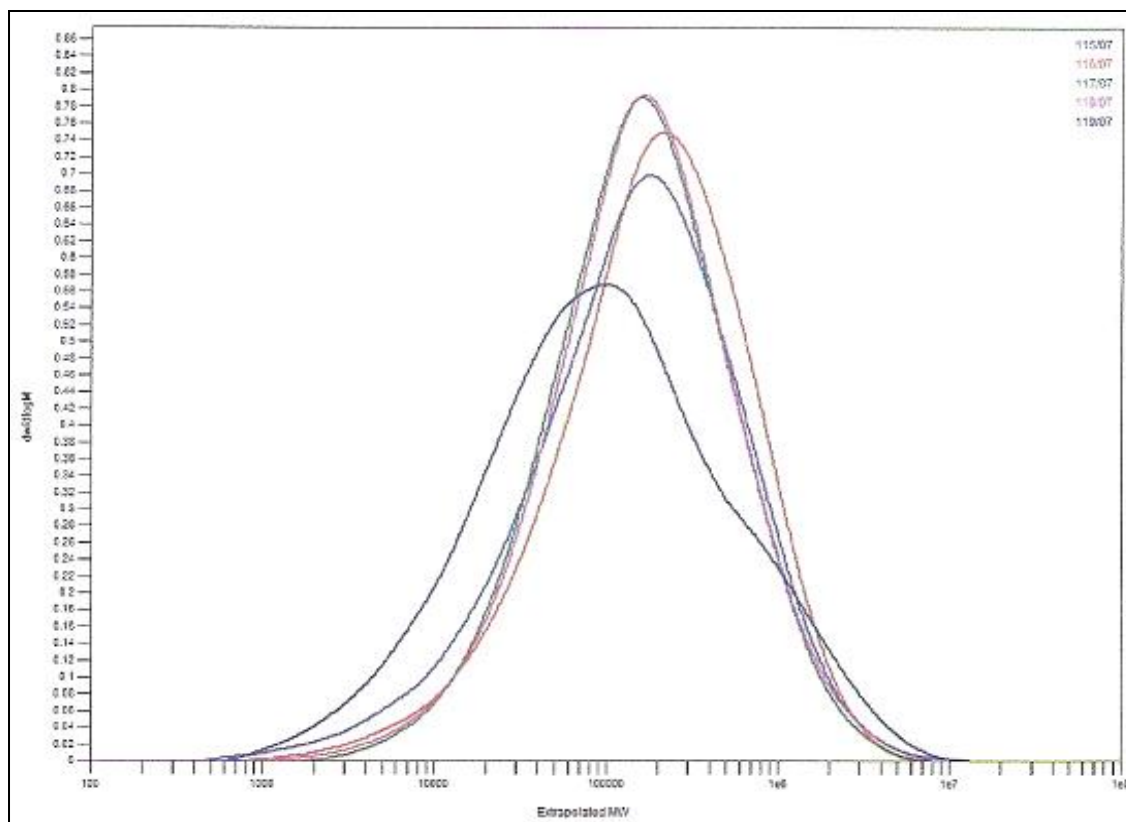


Figure 14: Overlaid MWD plot of injections of 5 samples by conventional GPC

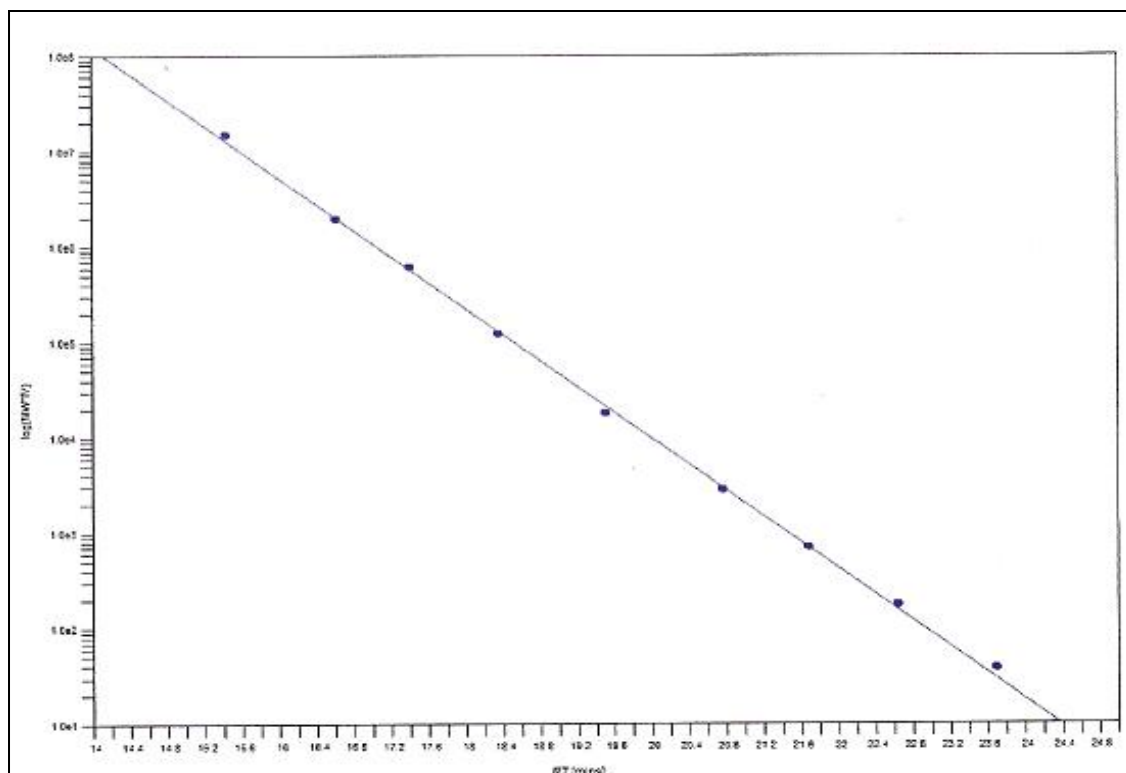


Figure 15: Universal Calibration Plot

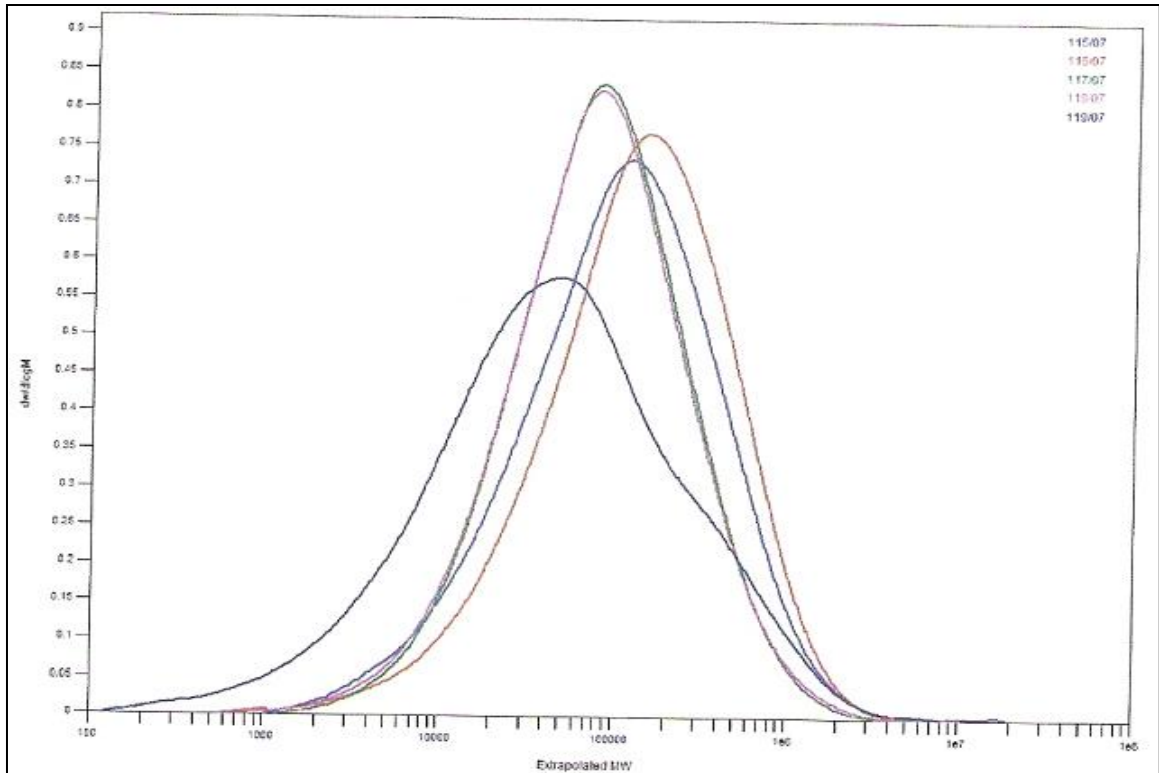
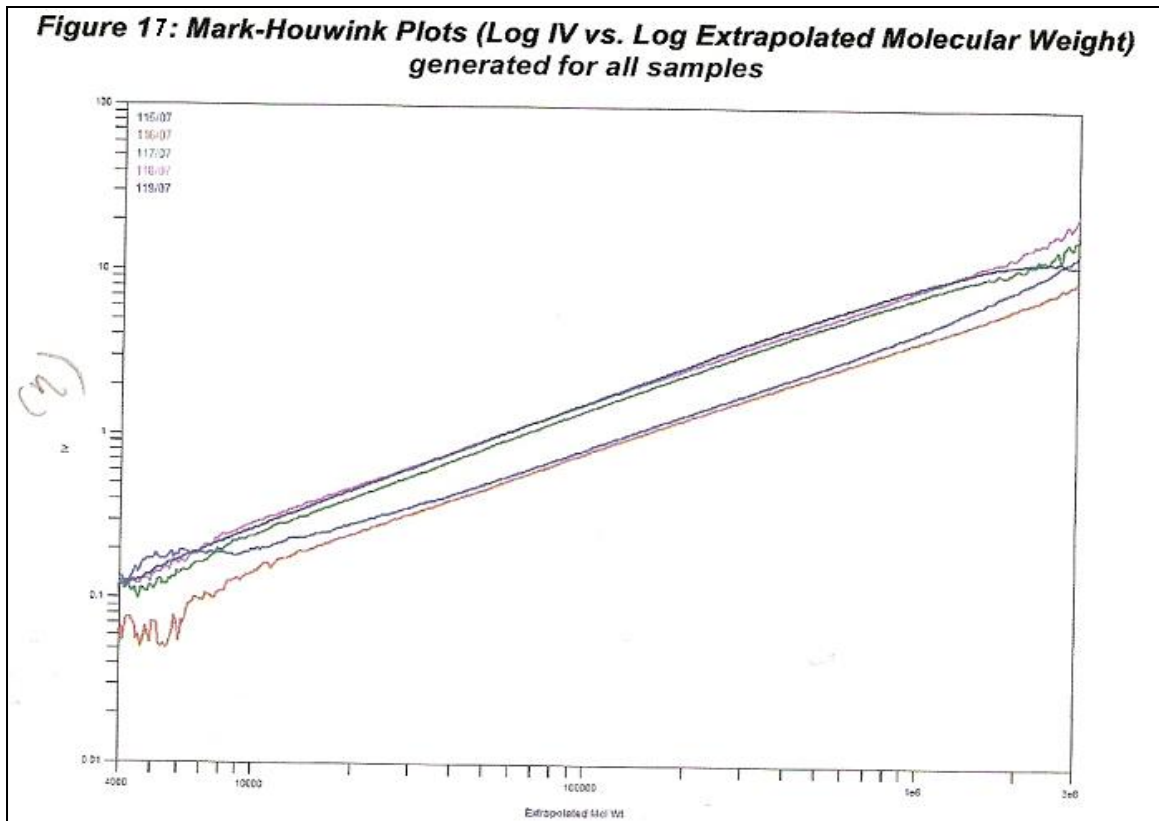


Figure 16: Overlaid MWD plot of injections of 5 samples by GPC/Viscometry



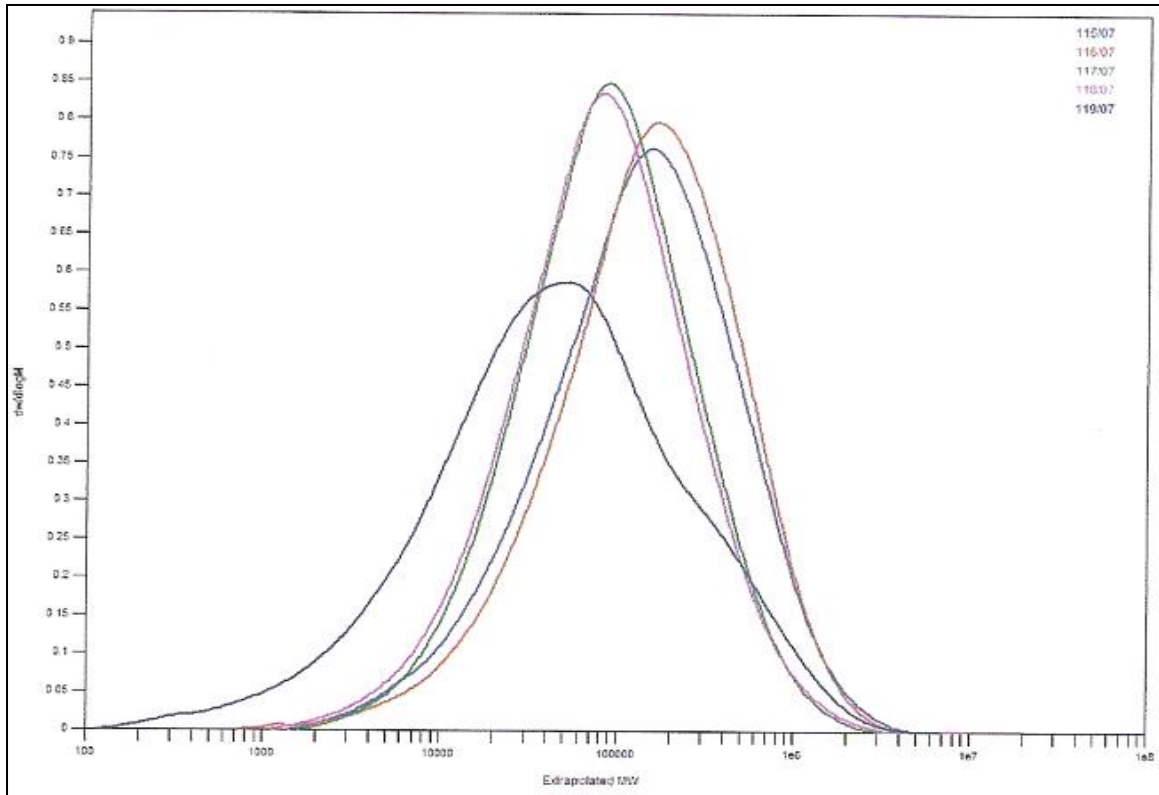


Figure 18: Overlaid MWD plot of injections of 5 samples by Triple Detection

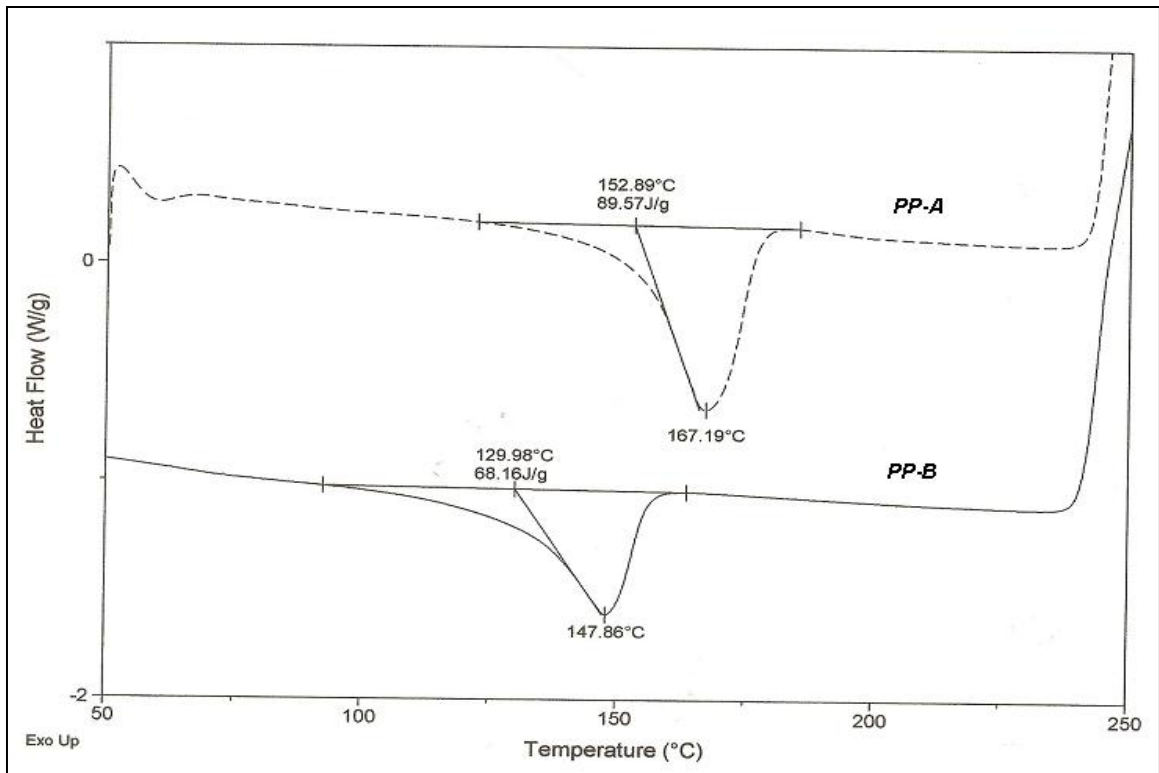


Figure 19: DSC Curves of PP-A & PP-B "as received"

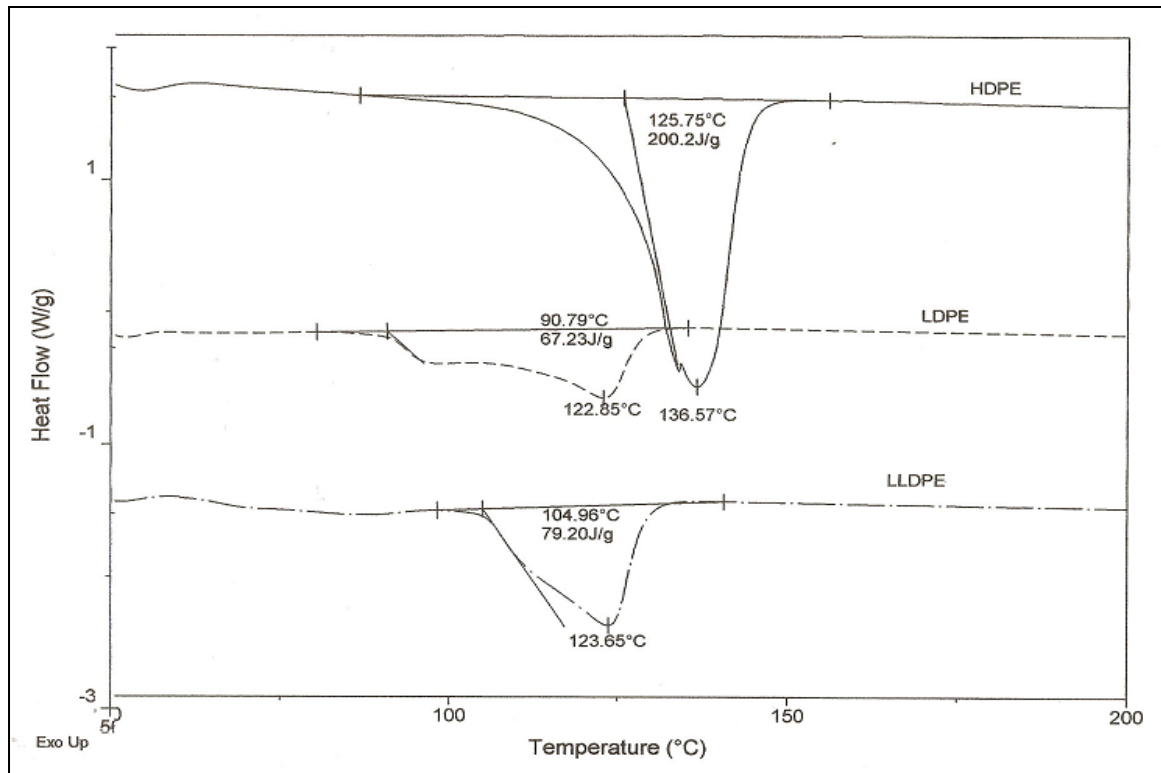


Figure 20: DSC Curves of HDPE, LDPE & LLDPE “as received”

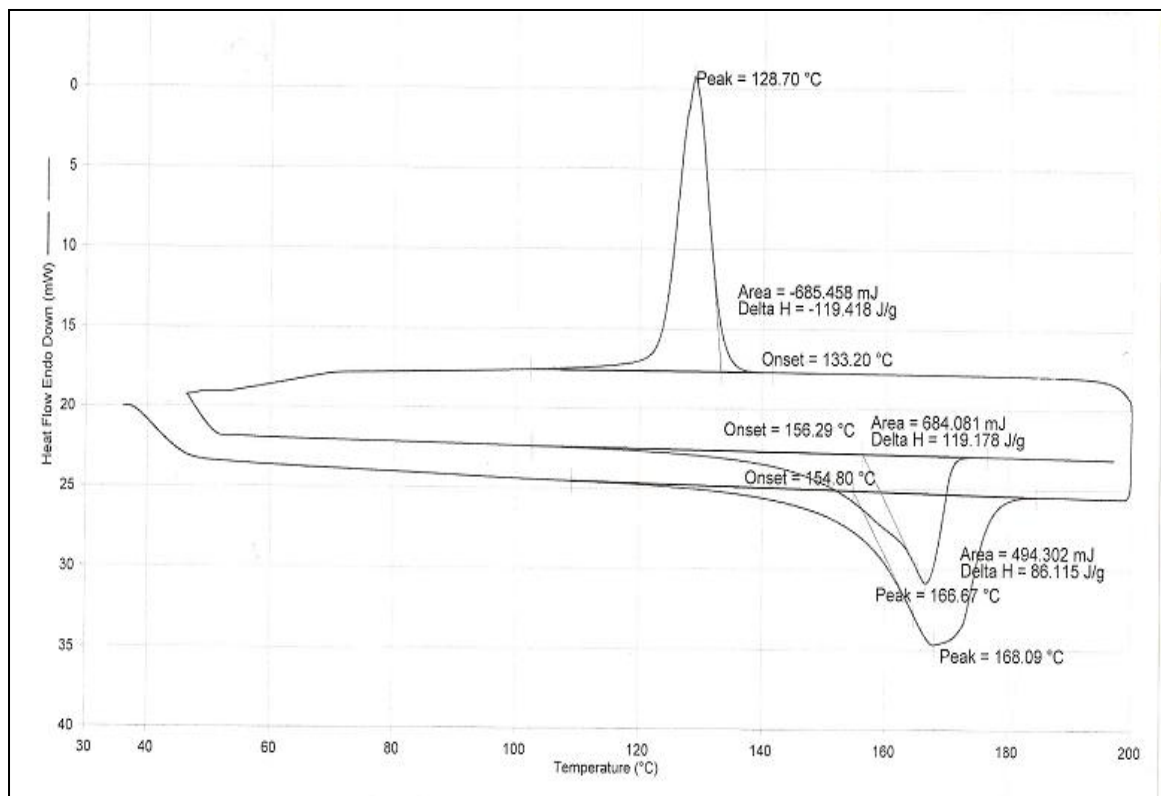


Figure 21: DSC Curve of PP-A “as received” & “after thermal treatment”

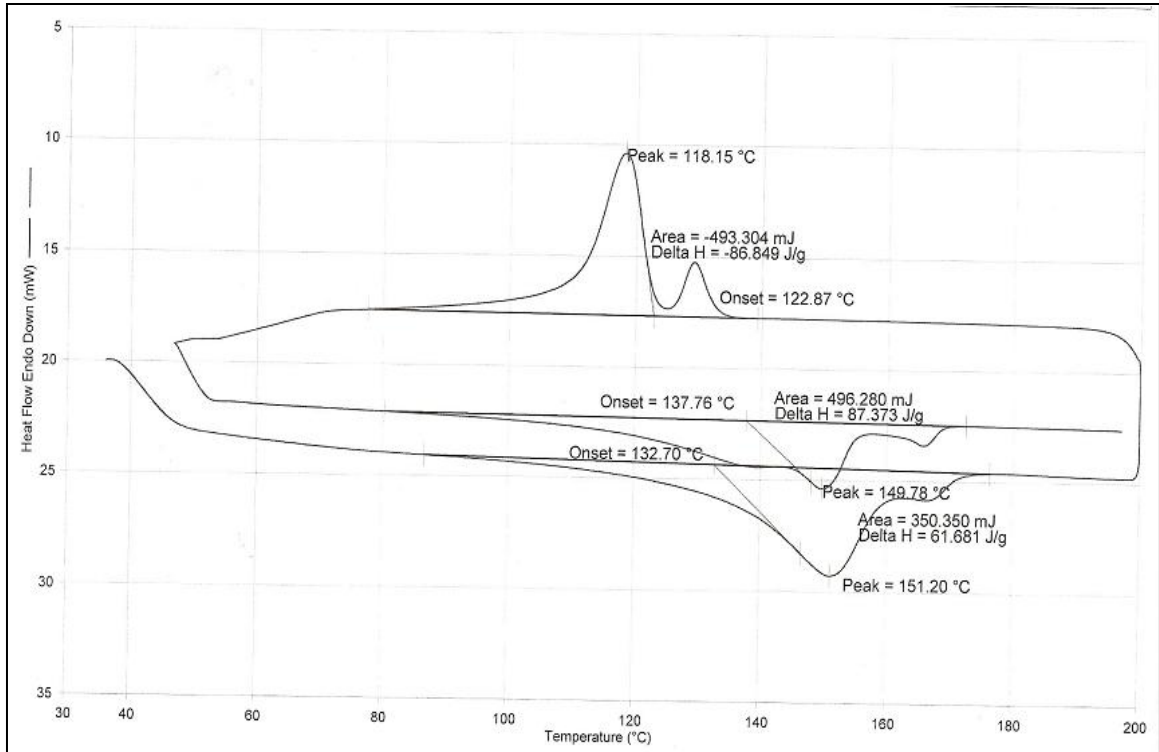


Figure 22: DSC Curve of PP-B “as received” & “after thermal treatment”

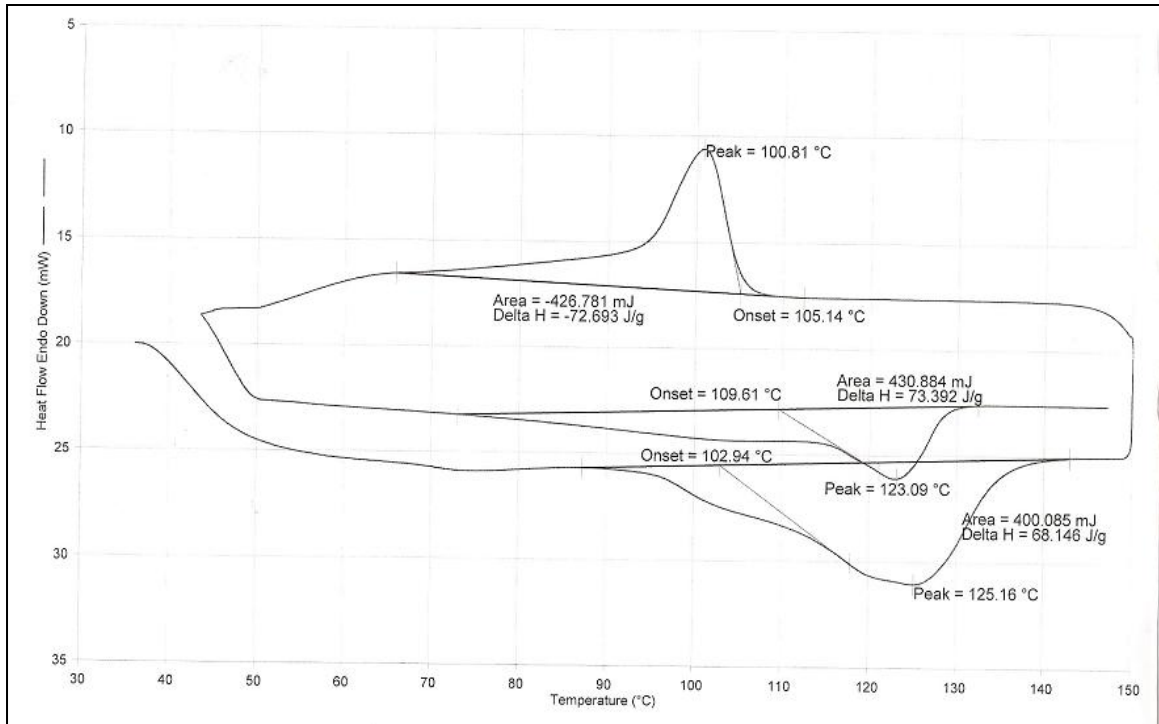


Figure 23: DSC Curve of LDPE “as received” & “after thermal treatment”

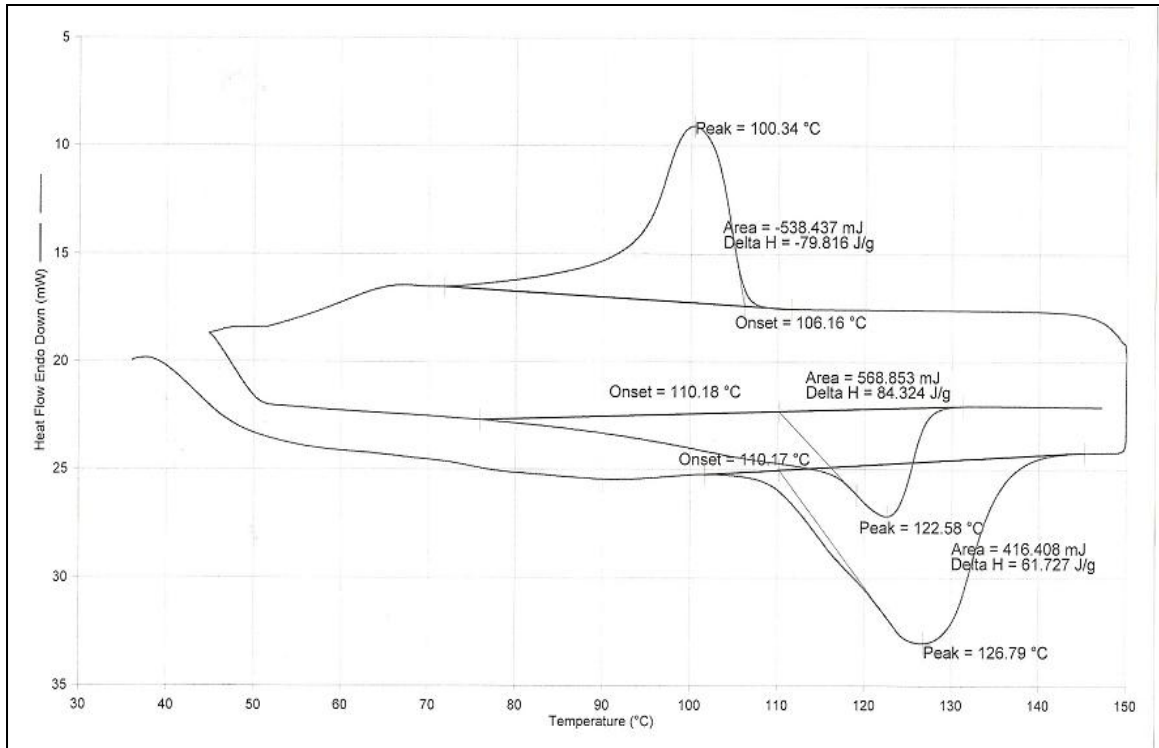


Figure 24: DSC Curve of LLDPE “as received” & “after thermal treatment”

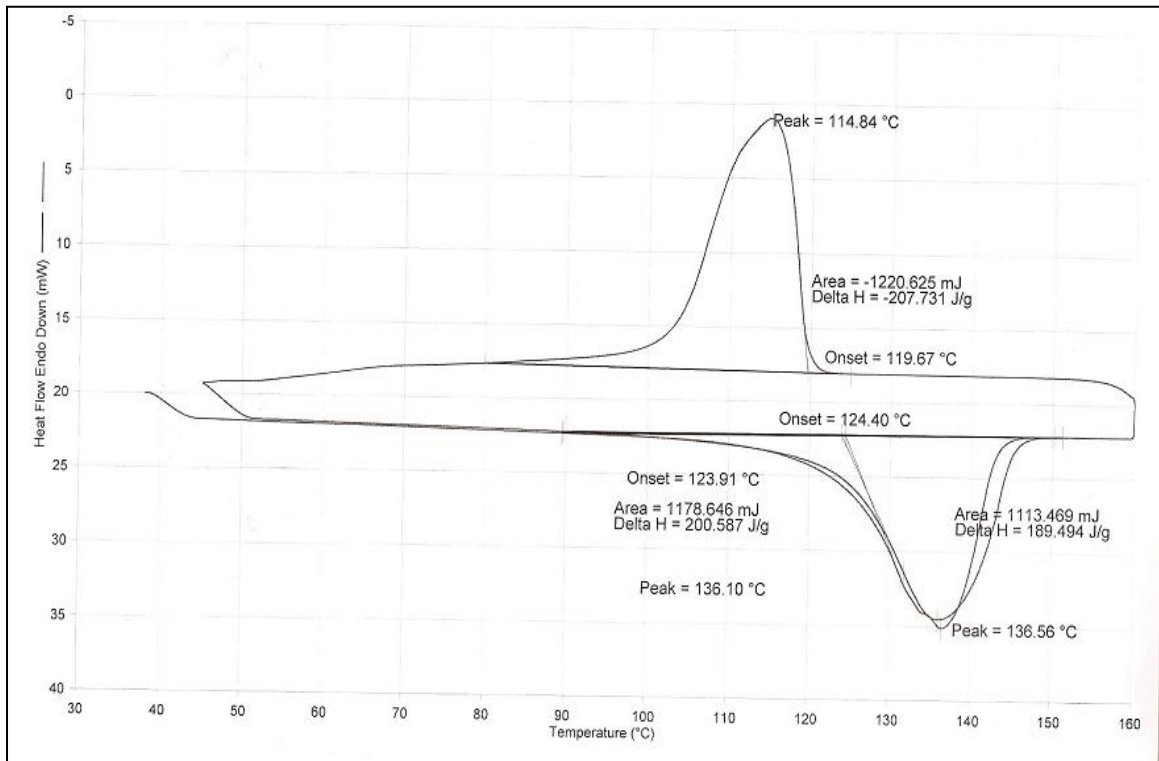


Figure 25: DSC Curve of HDPE “as received” & “after thermal treatment”

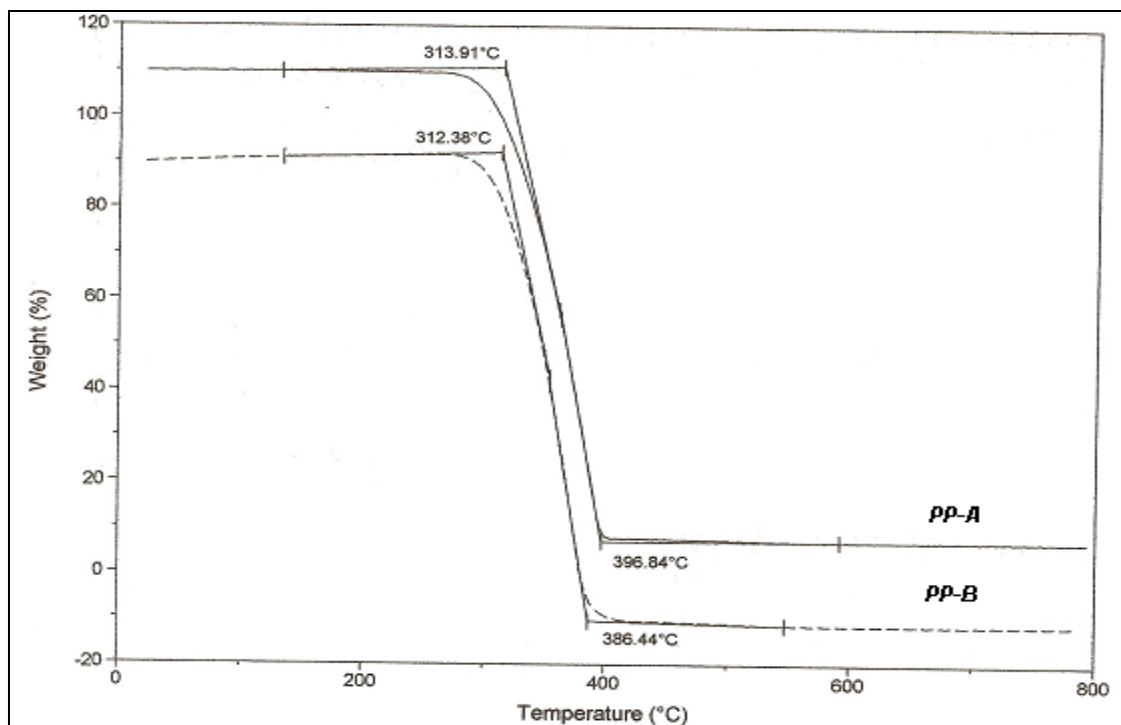


Figure 26: TG Curve of PP-A & PP-B in Air atmosphere

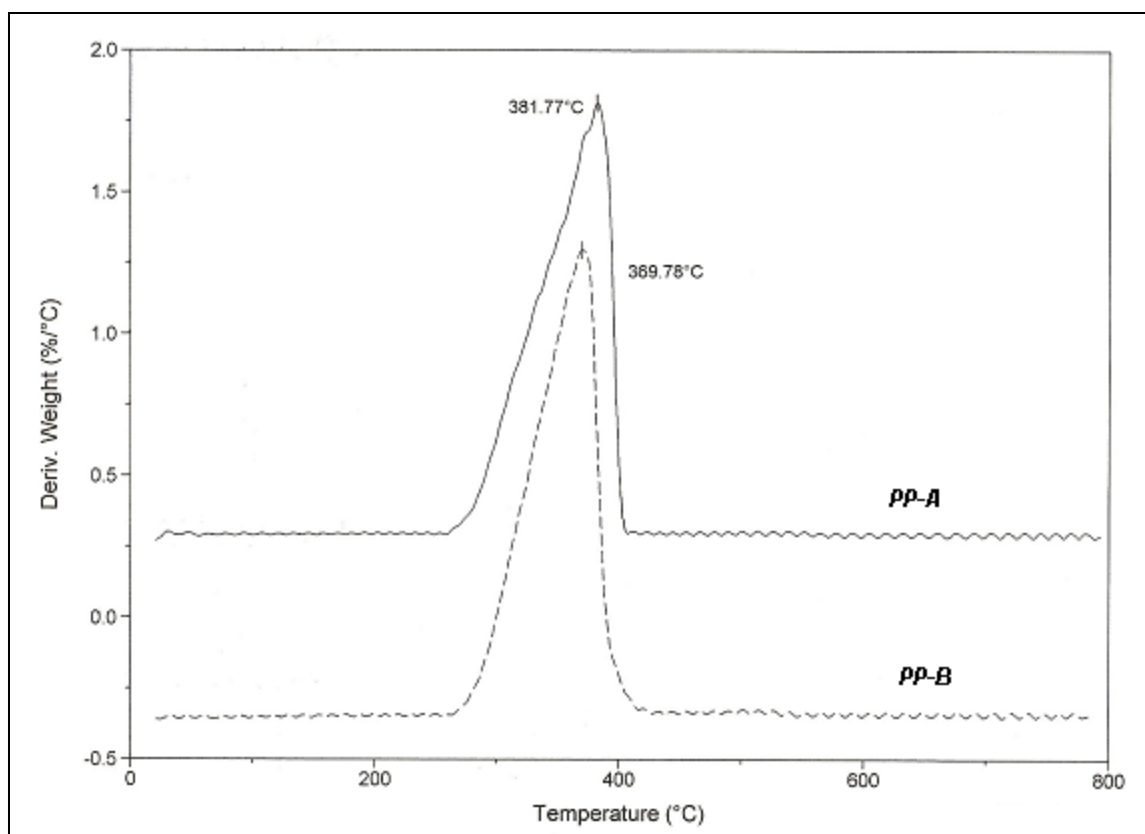


Figure 27: DTG Curve of PP-A & PP-B in Air atmosphere

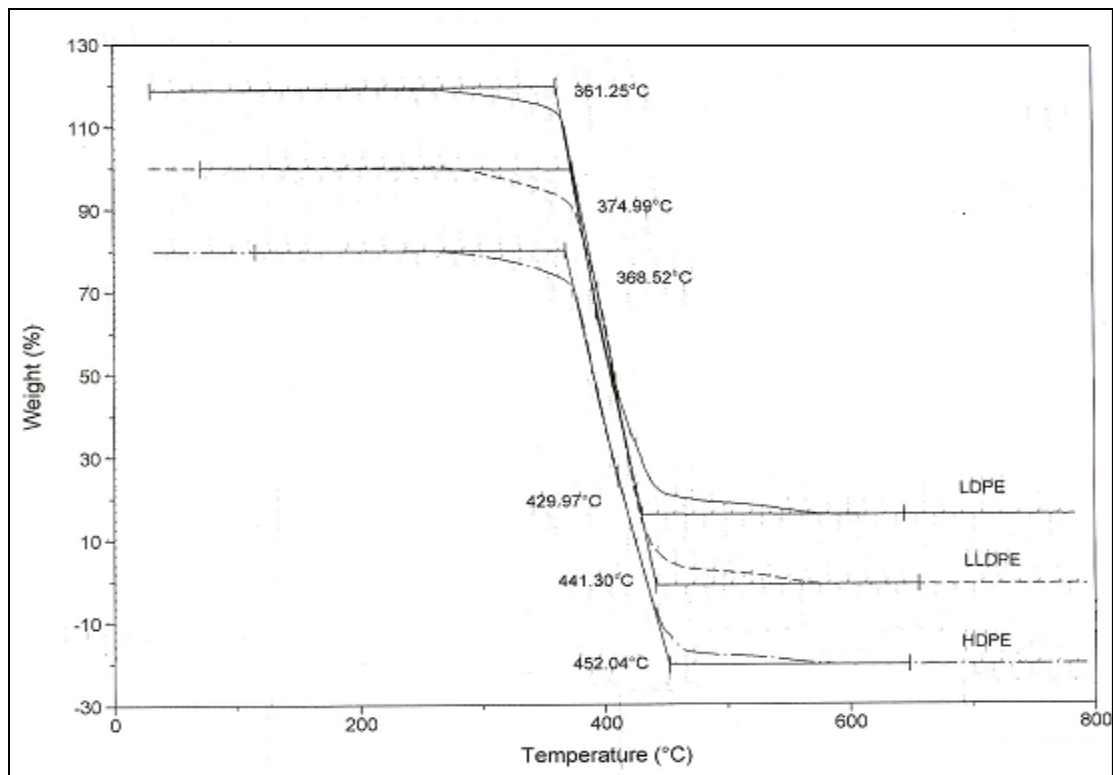


Figure 28: TG Curve of HDPE, LDPE & LLDPE in Air atmosphere

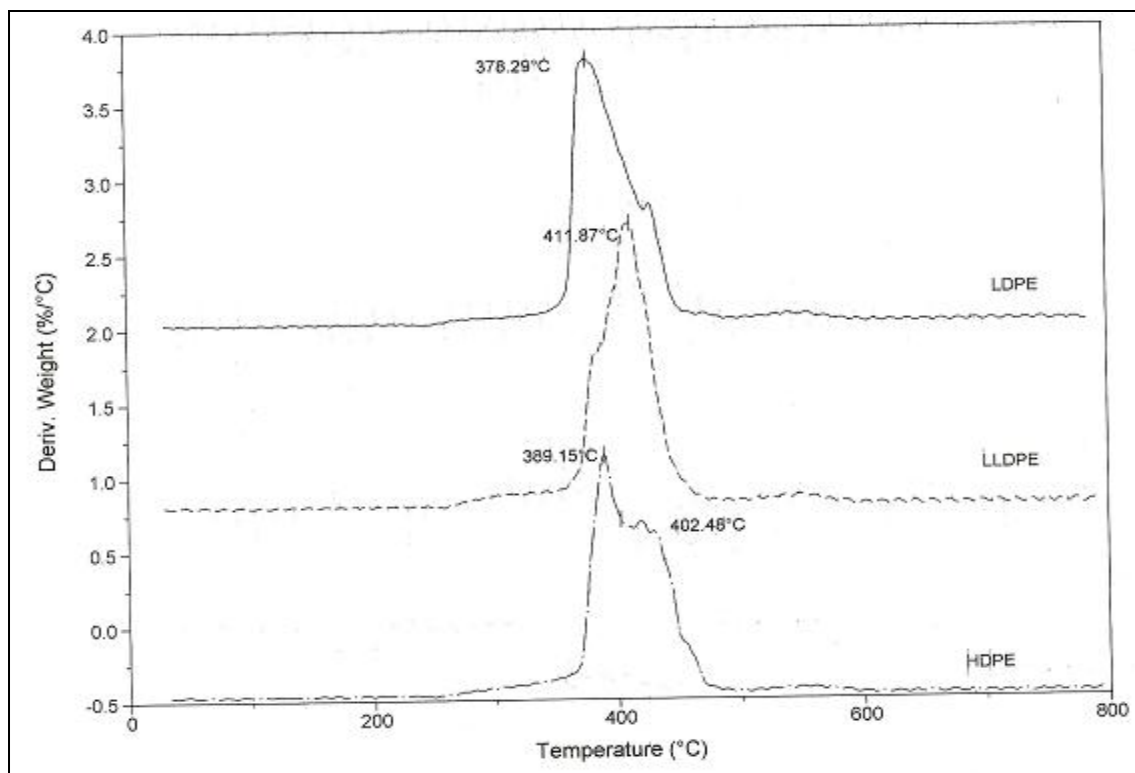


Figure 29: DTG Curve of HDPE, LDPE & LLDPE in Air atmosphere

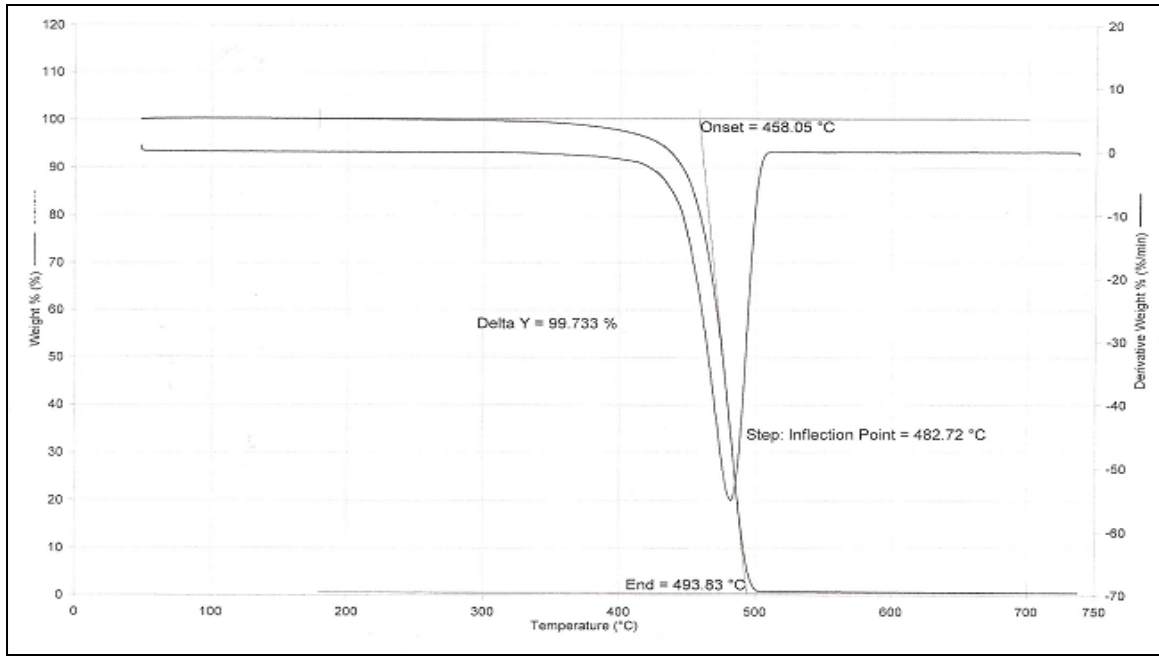


Figure 30: TG & DTG Curve of PP-A in N₂ atmosphere

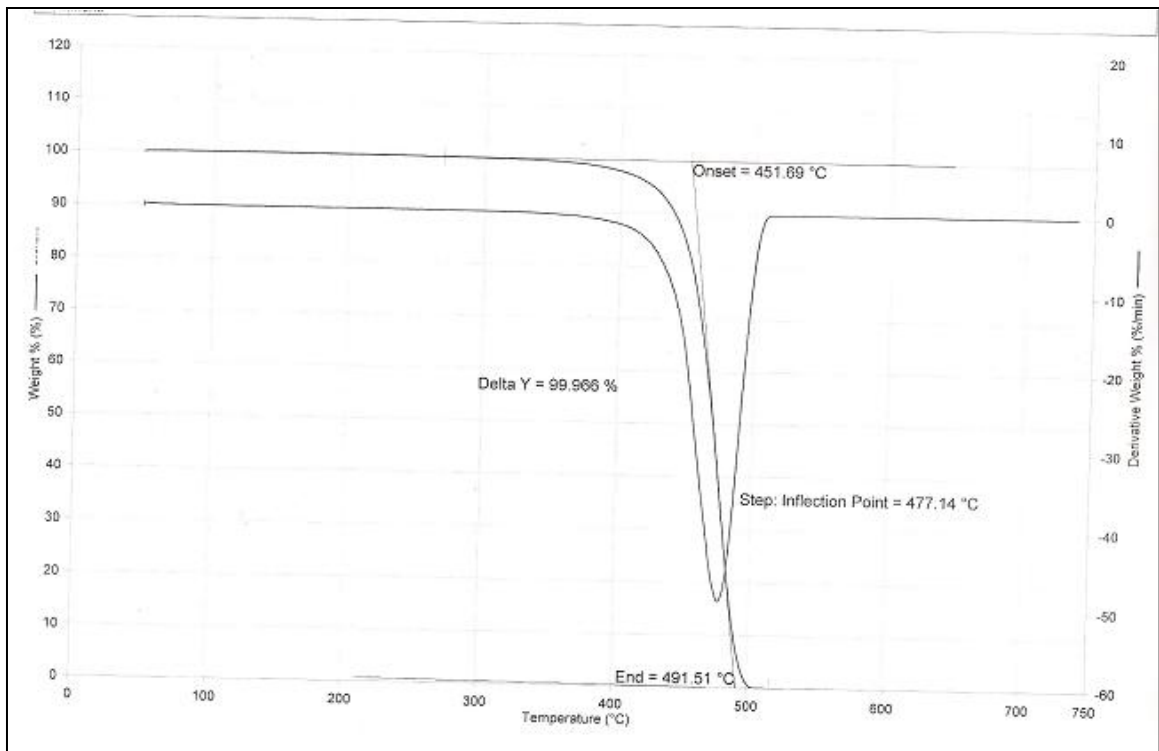


Figure 31: TG & DTG Curve of PP-B in N₂ atmosphere

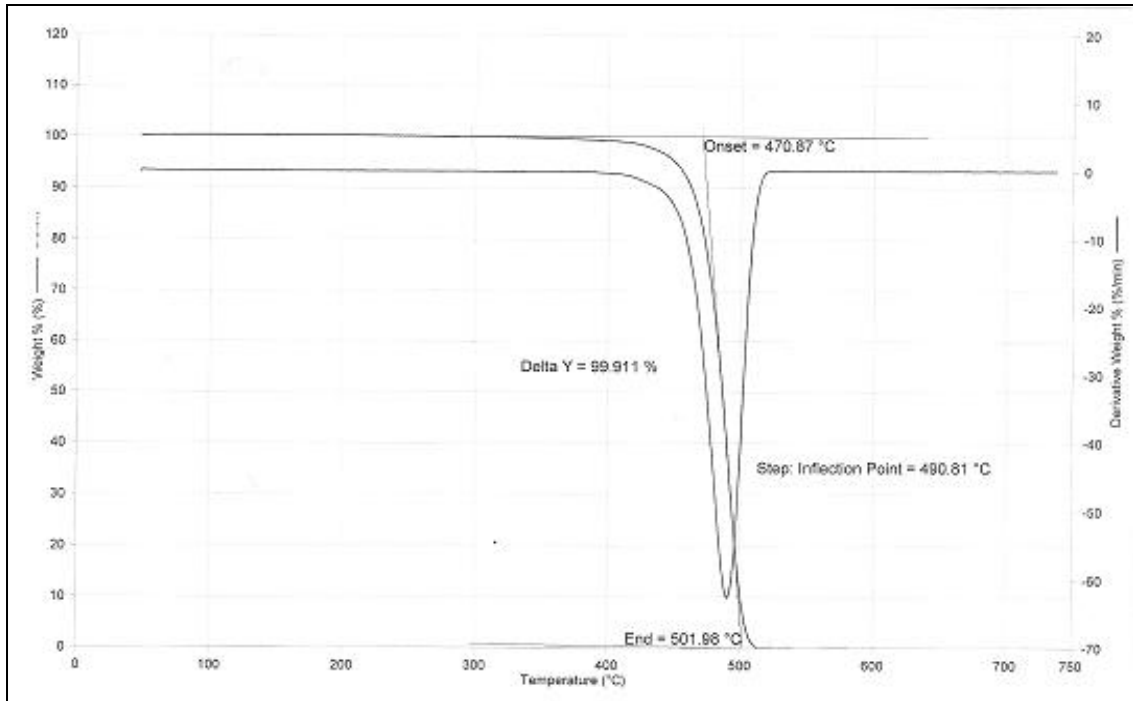


Figure 32: TG & DTG Curve of LDPE in N₂ atmosphere

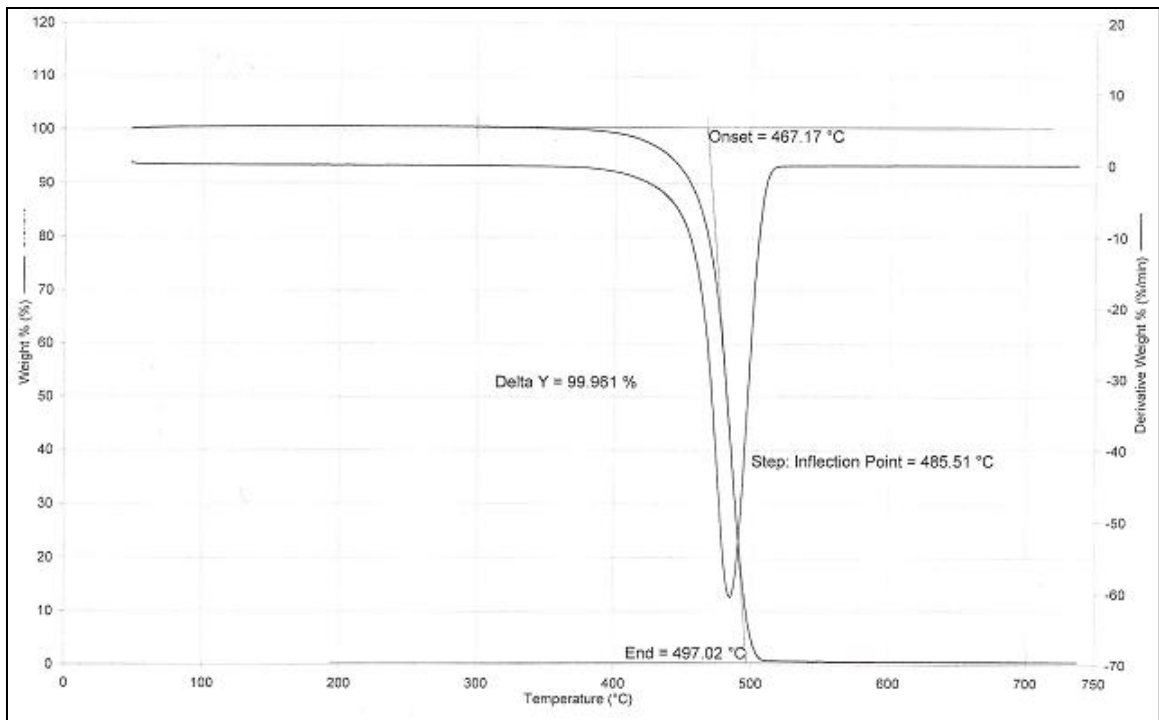


Figure 33: TG & DTG Curve of LLDPE in N₂ atmosphere

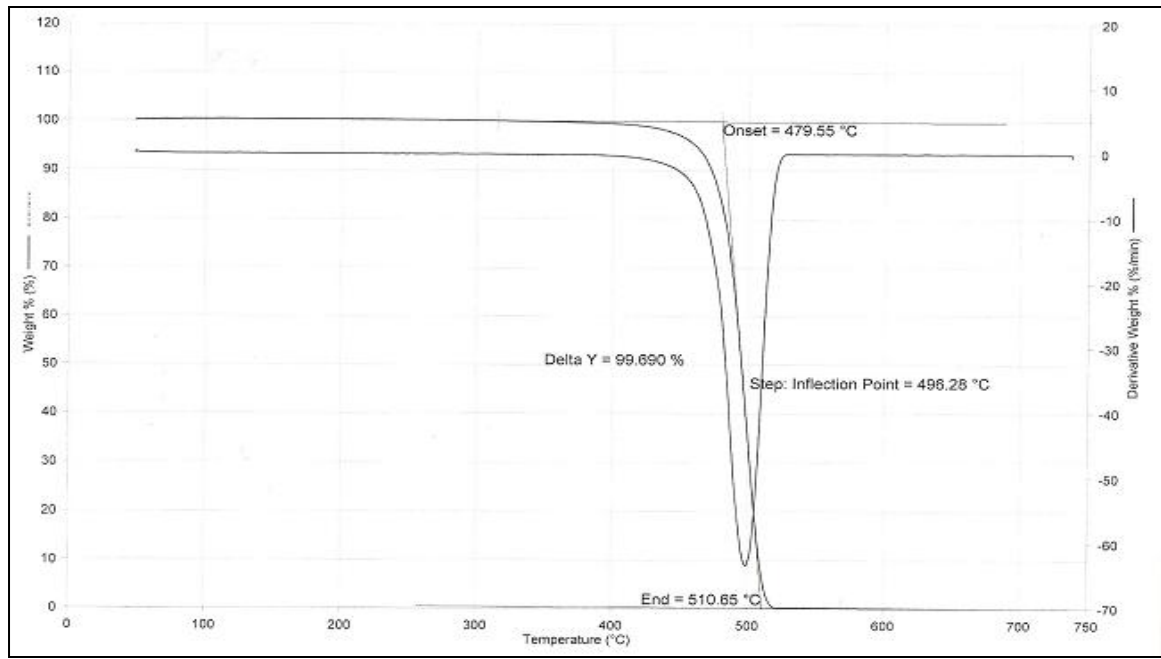


Figure 34: TG & DTG Curve of HDPE in N₂ atmosphere

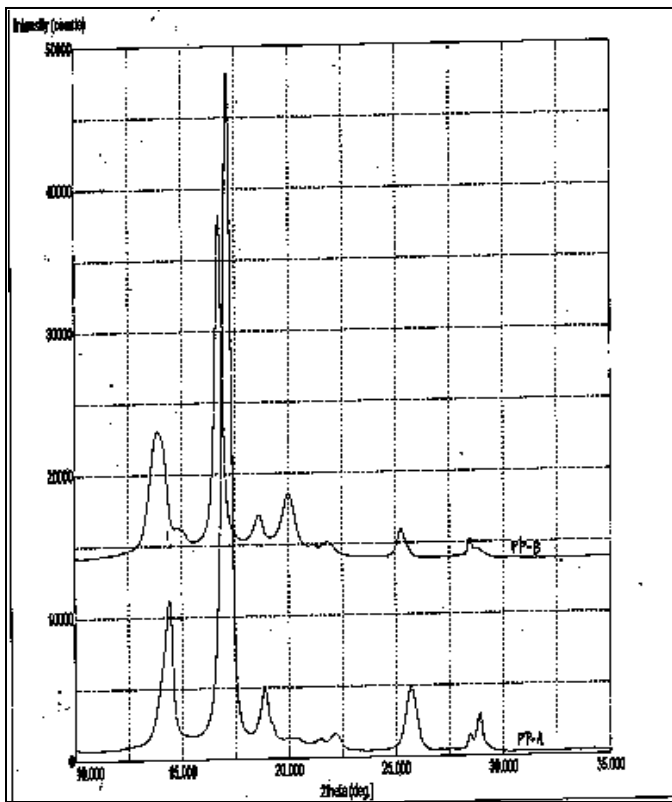


Figure 35: 1D XRD pattern of PP-A and PP-B

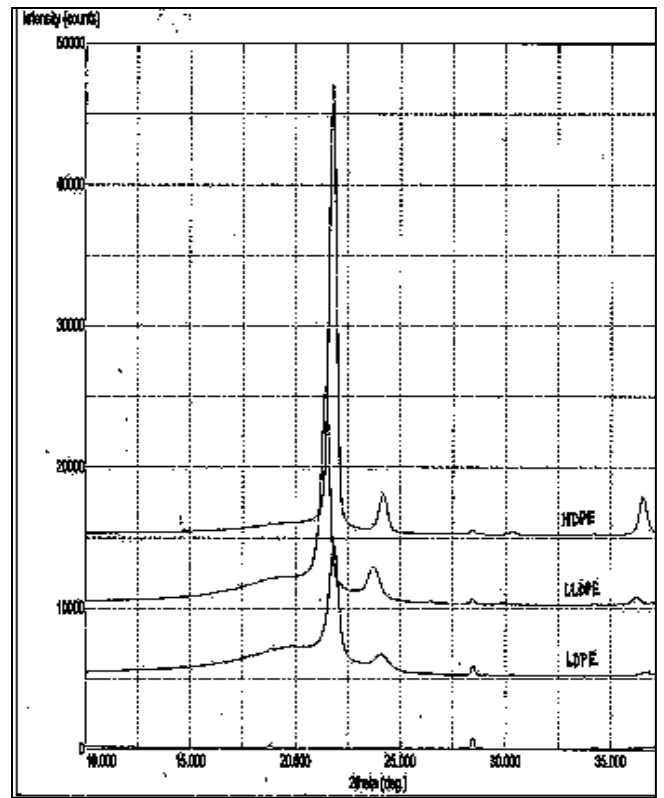


Figure 36: 1D XRD pattern of LDPE, LLDPE AND HDPE.

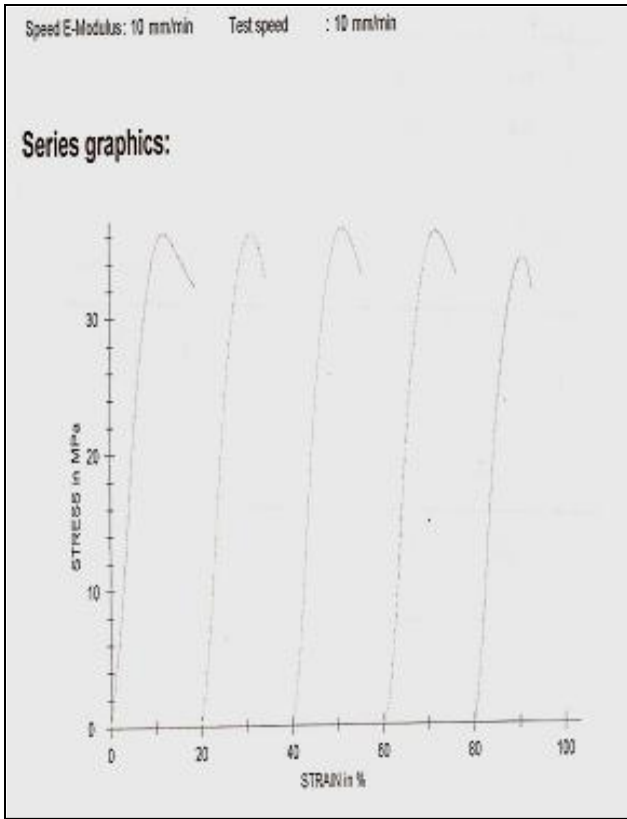


Figure 37: Stress-Strain Curve of PP-A

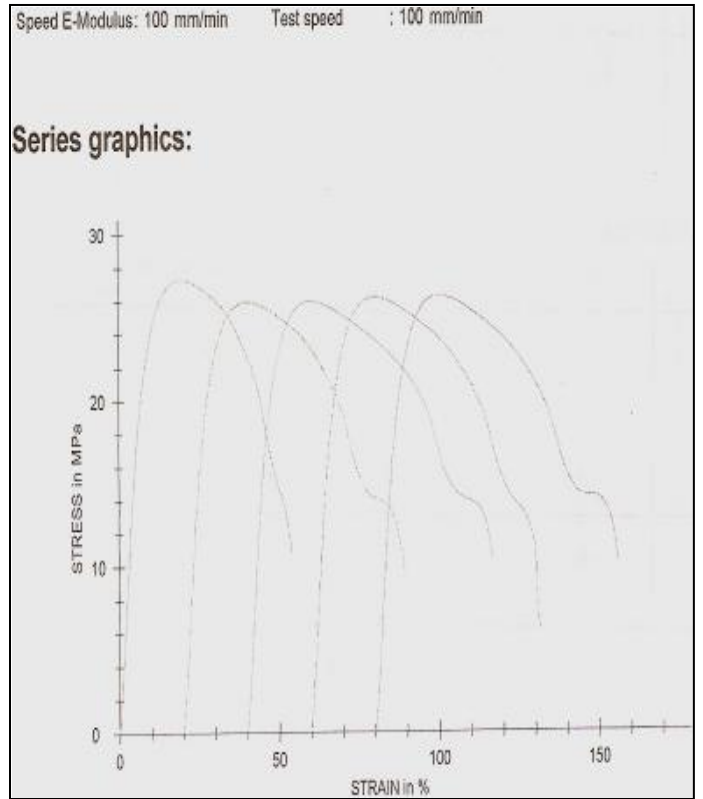


Figure 39: Stress-Strain Curve of HDPE

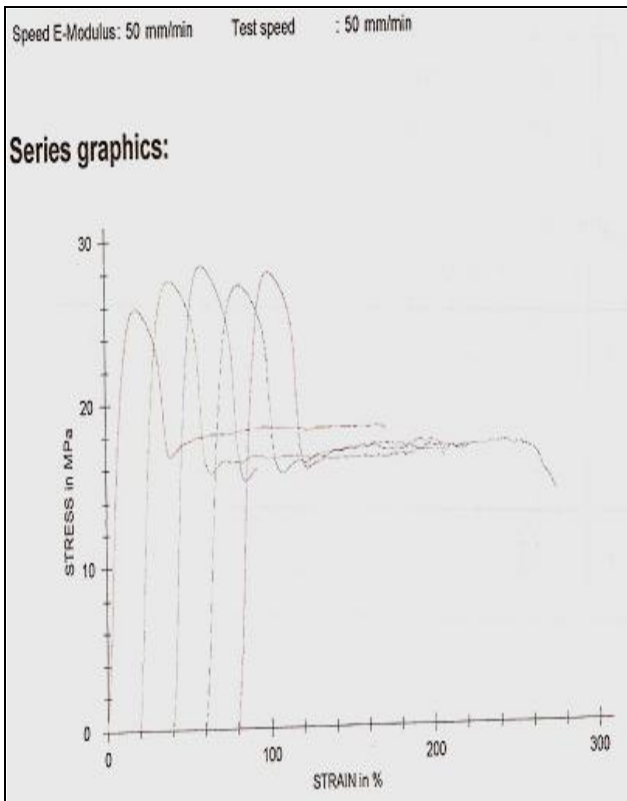


Figure 38: Stress-Strain Curve of PP-B

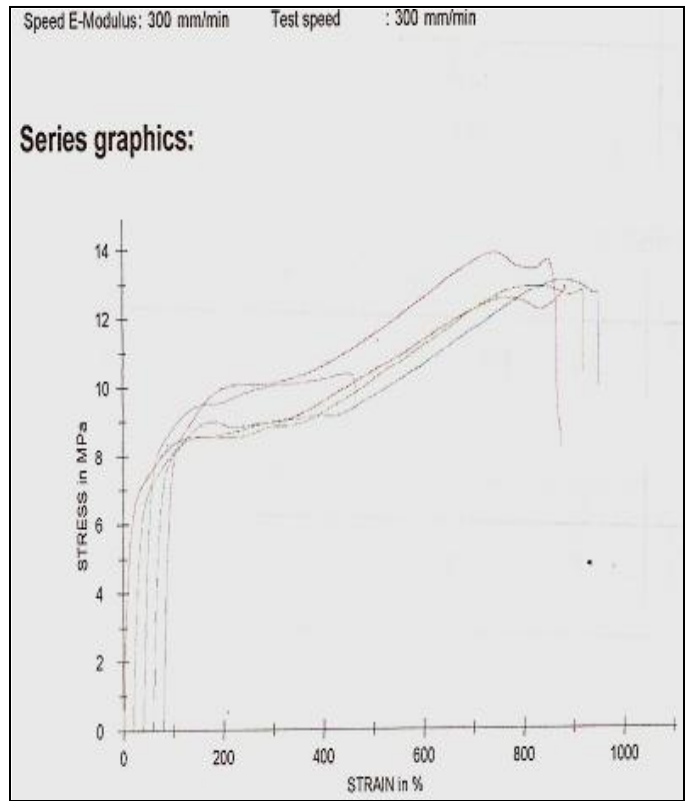


Figure 40: Stress-Strain Curve of LDPE

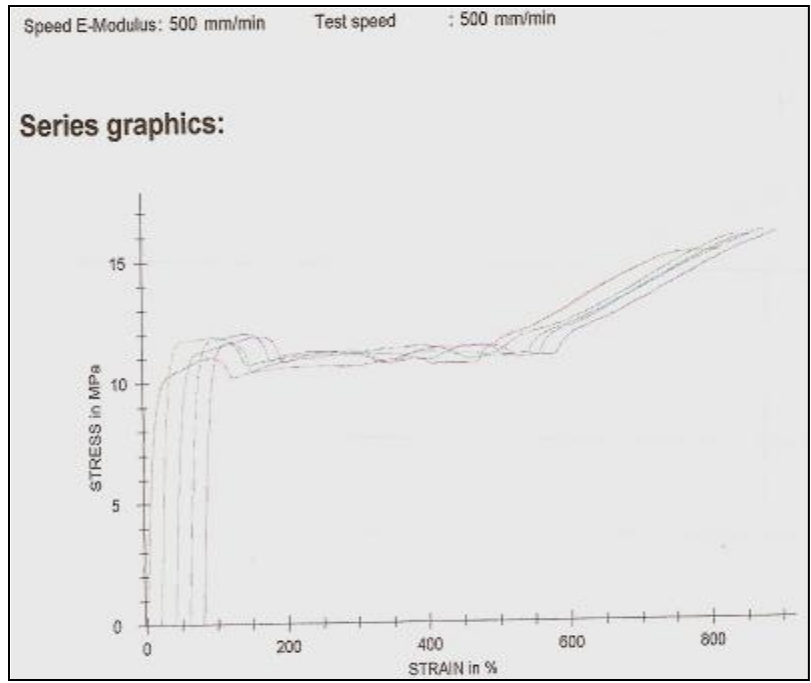


Figure 41: Stress-Strain Curve of LLDPE

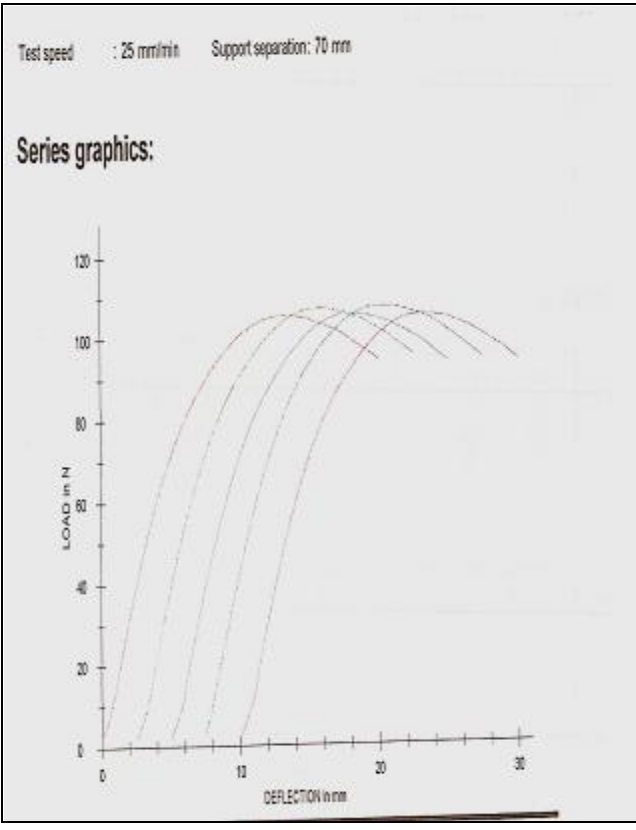
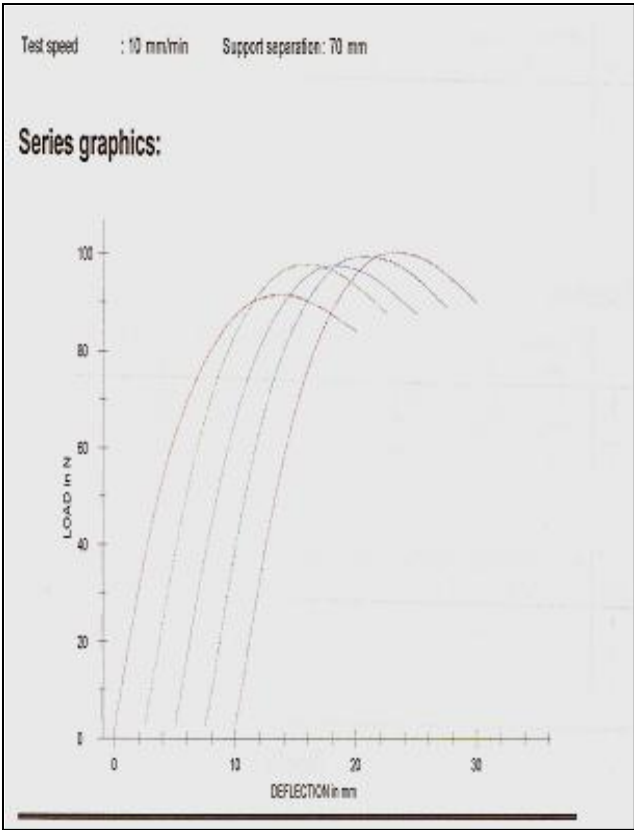


Figure 42: Load Vs Deformation Curve of PP-A

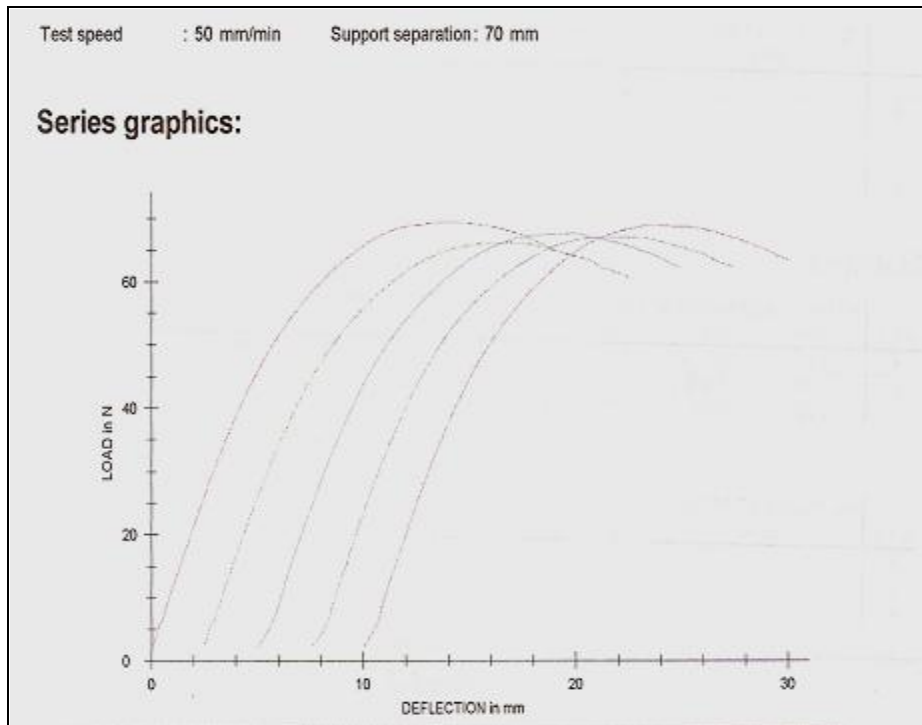


Figure 43: Load Vs Deformation Curve of PP-B

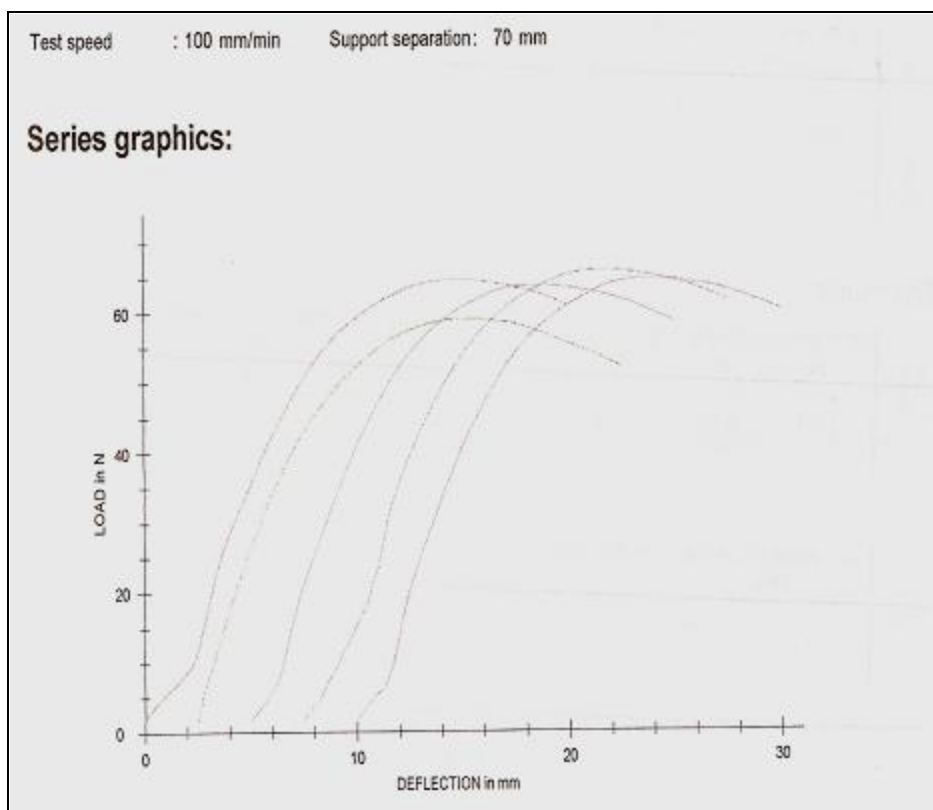


Figure 44: Load Vs Deformation Curve of HDPE

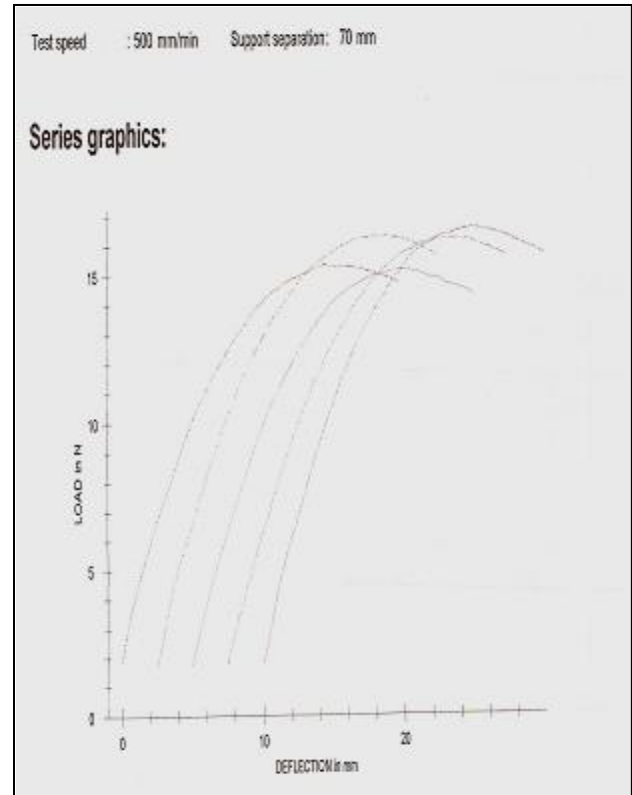
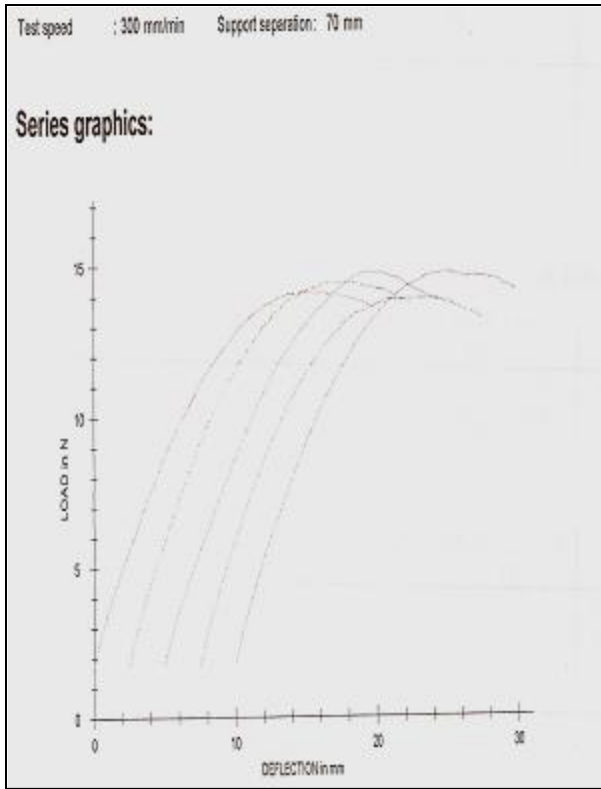


Figure 45: Load Vs Deformation Curve of LDPE

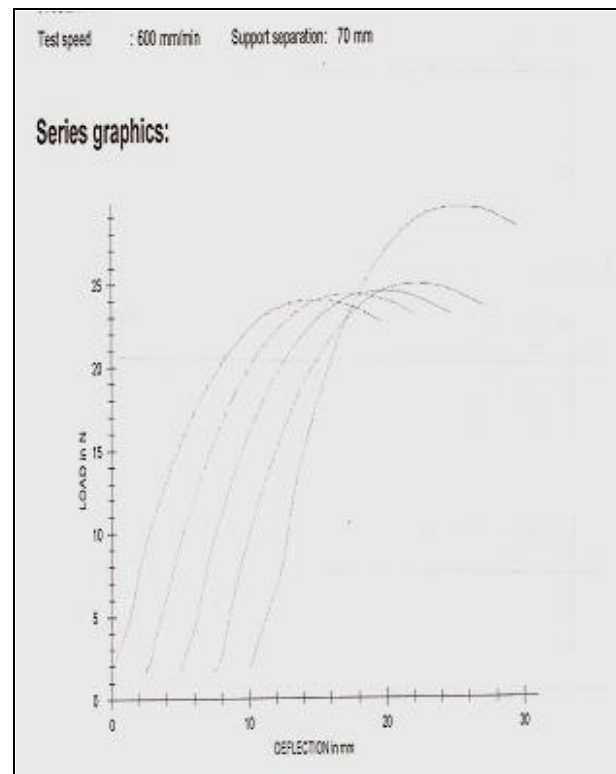
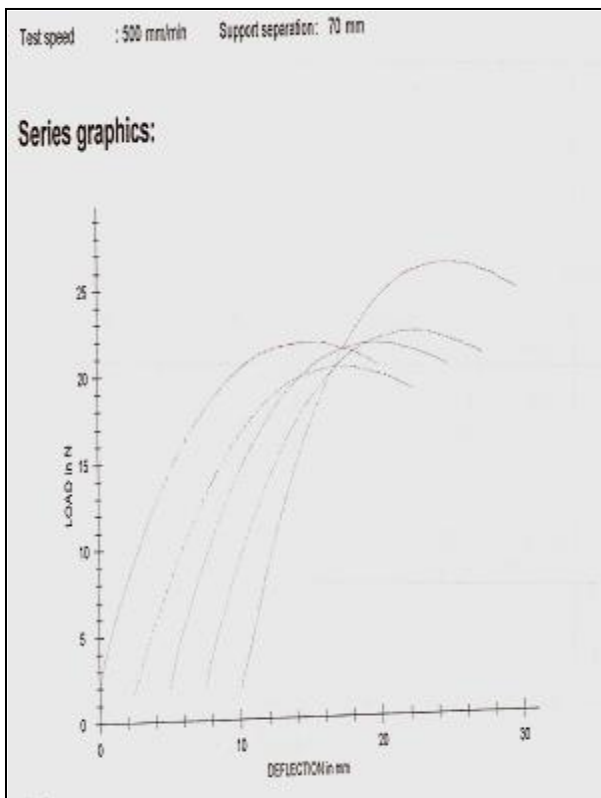
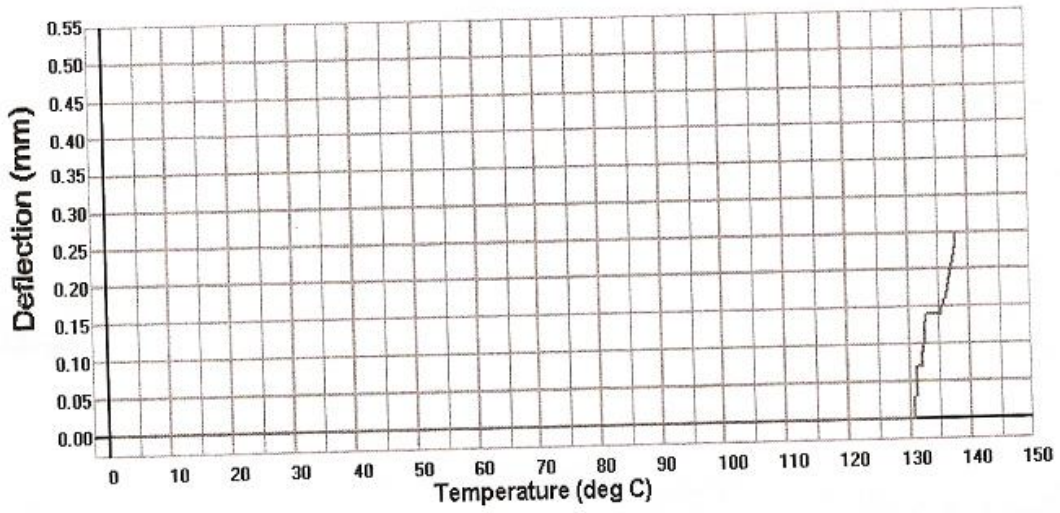


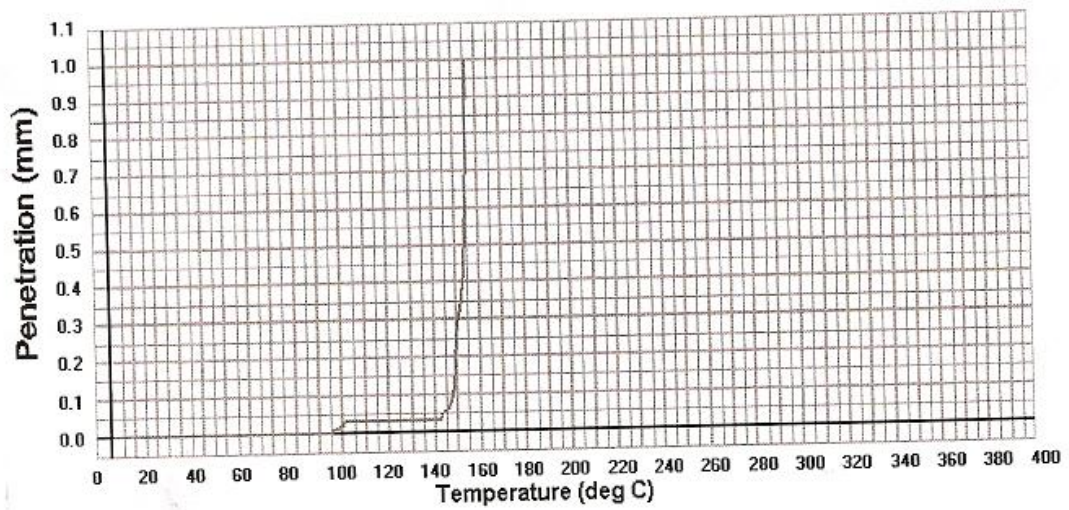
Figure 46: Load Vs Deformation Curve of LLDPE

HEAT DEFLECTION TEST



Remarks : The Heat Deflection Temperature is 137.9 deg C.

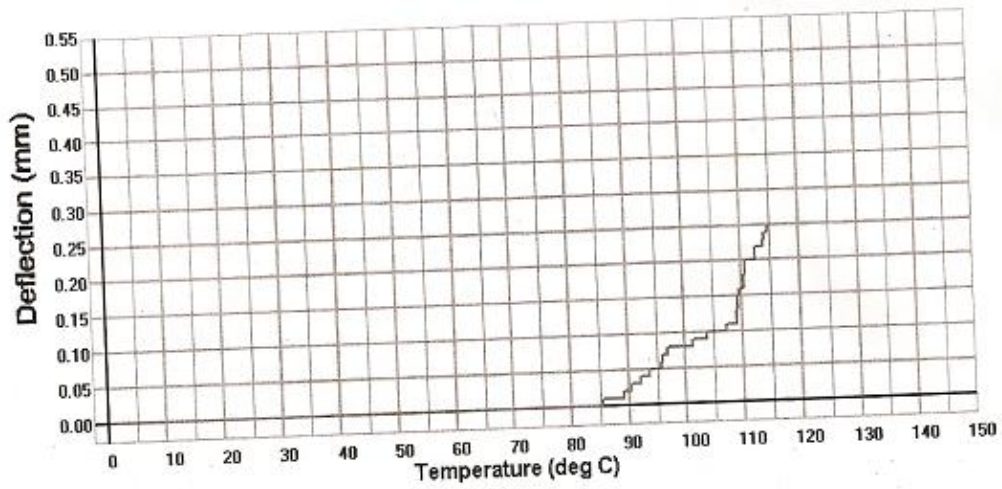
VICAT SOFTENING POINT TEST



Remarks : The Vicat Softening Point is 155.7 deg C.

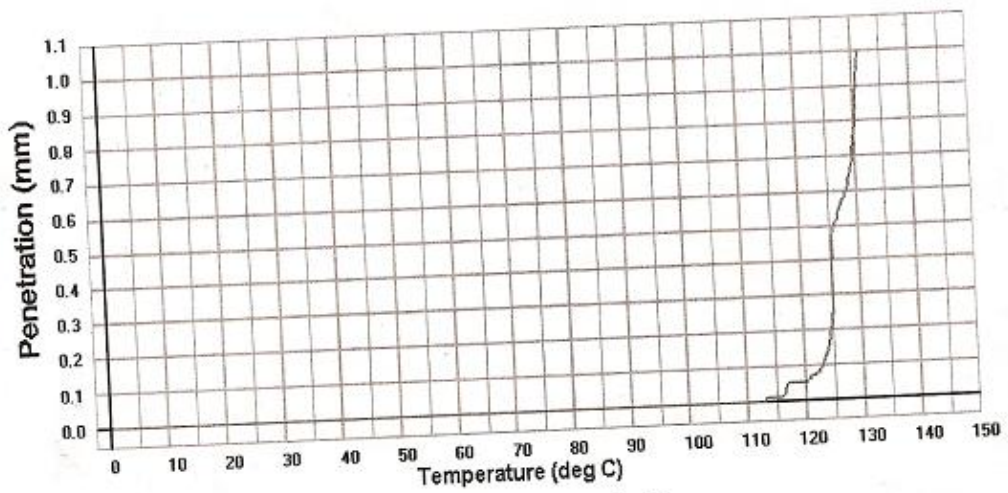
Figure 47: HDT and VSP Curves of PP-A

HEAT DEFLECTION TEST



Remarks : The Heat Deflection Temperature is 114.7 deg C.

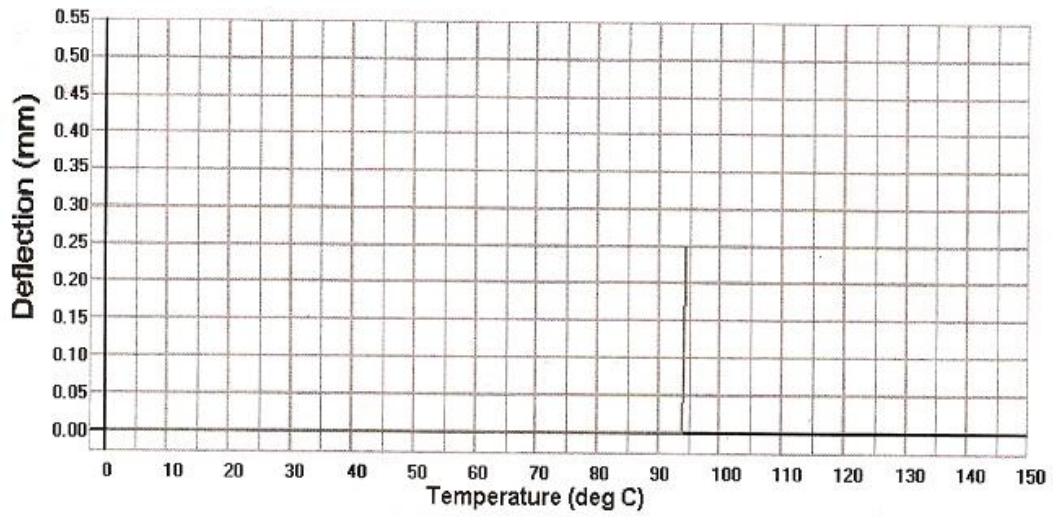
VICAT SOFTENING POINT TEST



Remarks : The Vicat Softening Point is 131.1 deg C.

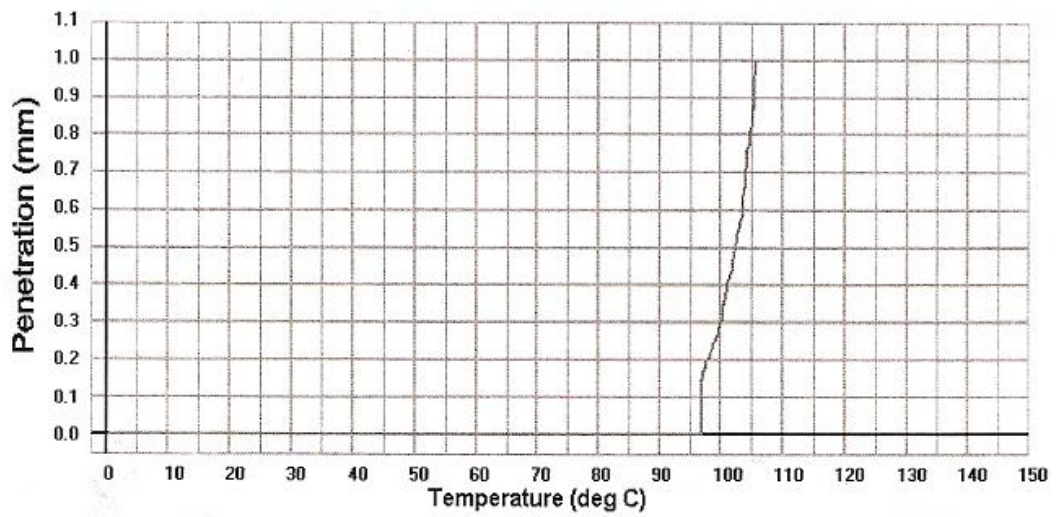
Figure 48: HDT and VSP Curves of PP-B

HEAT DEFLECTION TEST



Remarks : The Heat Deflection Temperature is 94.3 deg C.

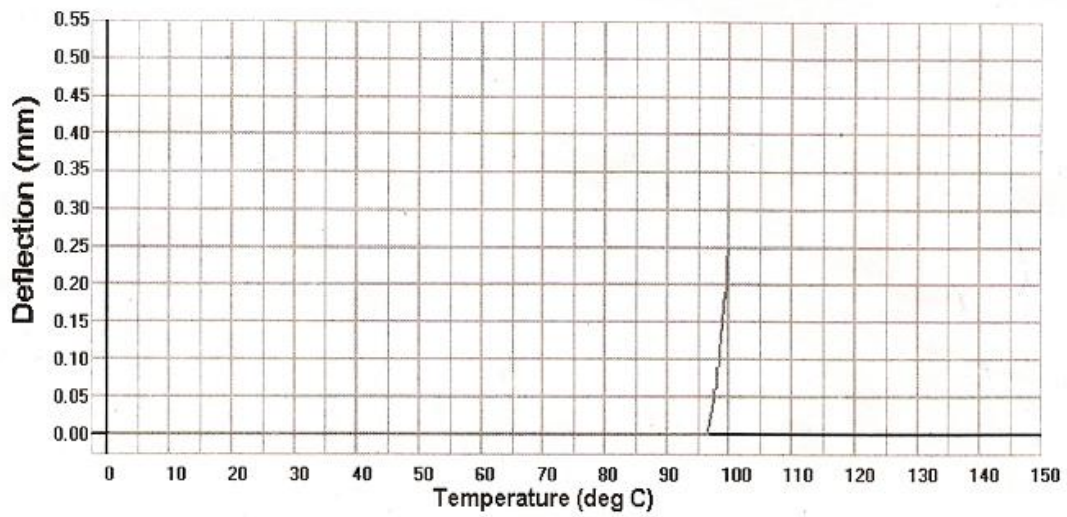
VICAT SOFTENING POINT TEST



Remarks : The Vicat Softening Point is 105.5 deg C.

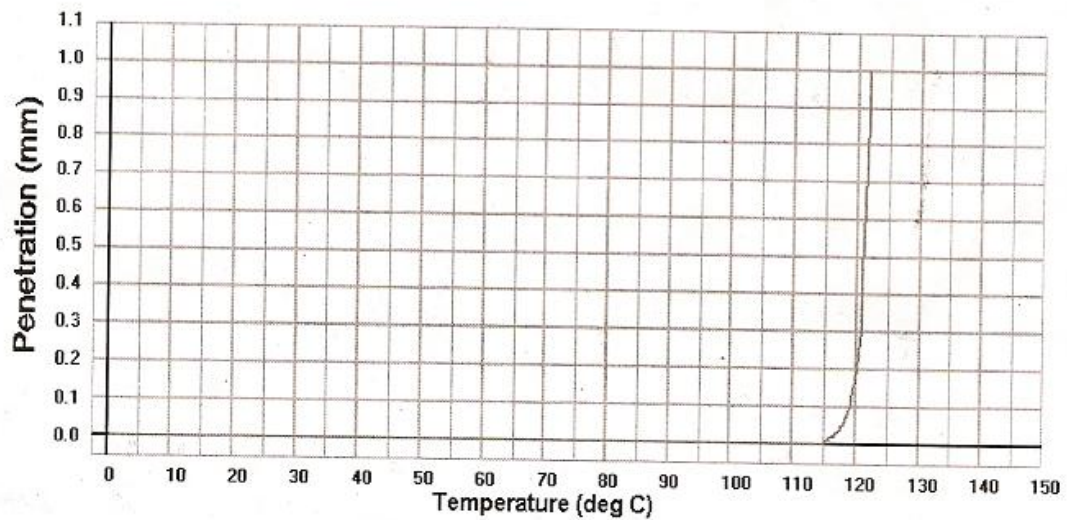
Figure 49: HDT and VSP Curves of LDPE

HEAT DEFLECTION TEST



Remarks : The Heat Deflection Temperature is 99.8 deg C.

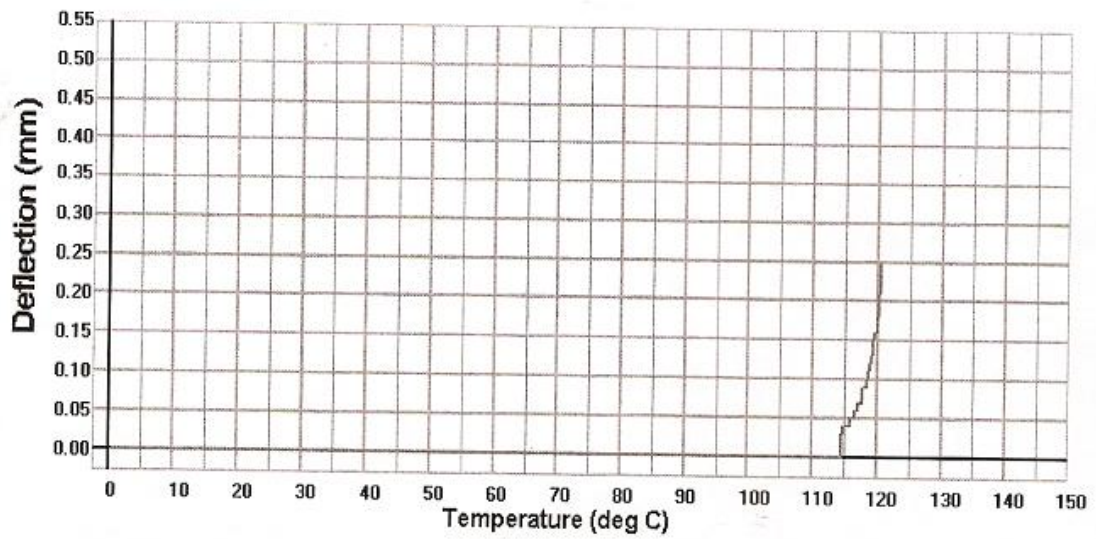
VICAT SOFTENING POINT TEST



Remarks : The Vicat Softening Point is 121.7 deg C.

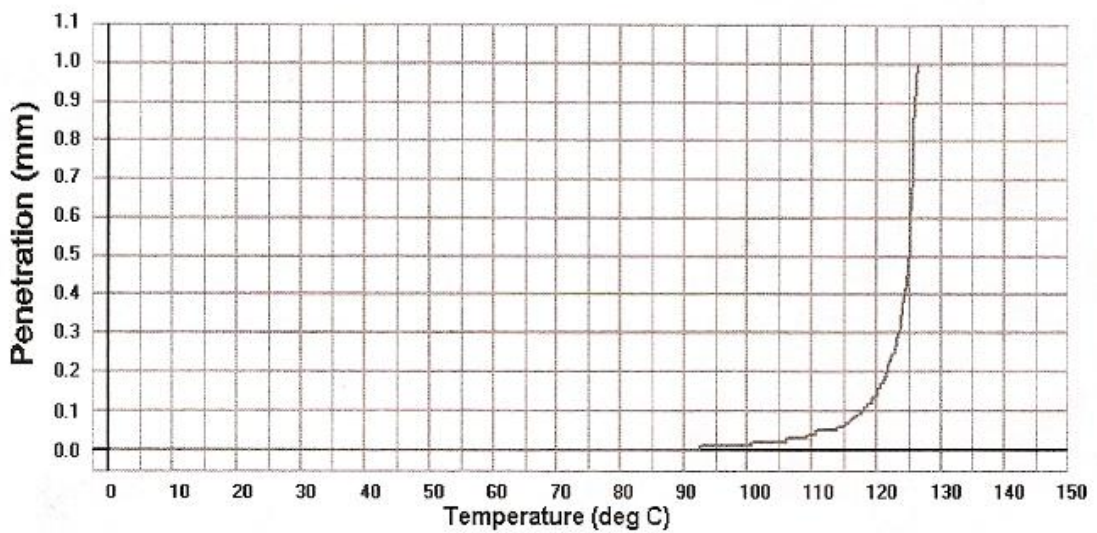
Figure 50: HDT and VSP Curves of LLDPE

HEAT DEFLECTION TEST



Remarks : The Heat Deflection Temperature is 120.5 deg C.

VICAT SOFTENING POINT TEST



Remarks : The Vicat Softening Point is 126.3 deg C.

Figure 51: HDT and VSP Curves of HDPE