Studies on Structure-Property-Performance-Relationship of Various Polyethylene Grades

A Major Project Report submitted towards partial fulfillment of the requirement for the degree

of

**MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY**

Submitted by

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CERTIFICATE

This is to certify that the M.E. major project entitled "Studies on Structure-Property-Performance-Relationship of various Polyethylene Grades" has been completed by MR. NAVEEN KUMAR, a student of M.E. (Polymer Technology) in the Department of Applied Chemistry, of Delhi College of Engineering, Delhi University. The original work has been carried out by him under our joint supervision and guidance for the partial fulfillment of the requirement of the M.E. Polymer Technology.

The project work has been carried out during the session 2010-2011.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENT

I would like to acknowledge all persons who have contributed directly or indirectly to the completion of my project and have seen its materialization in the form of this dissertation.

First and foremost I would like to thank the management of Indian Oil R&D Centre, Faridabad, for giving me this opportunity to carry out this project work in their esteemed R&D centre. I would like to express my gratitude to my mentor *Dr. G.S. Kapur (Chief Research Manager, Petrochemicals and Polymers, R&D center, IOCL)* for giving me an opportunity to complete my M.E. project-work under his selfless guidance. He not only proposed this project but also obliged me with his valuable suggestions at every step of the project. For me it was a privilege to work with his research team at the R&D Centre of IOCL, Faridabad. To him I owe more than I can say.

I would also like to thank *Dr. Shashikant (Deputy General Manager, R&D center, IOCL)* for not only providing me such an opportunity to work at the reputable R&D Centre but also for his rigorous and fruitful discussions on the interpretation of experimental data and results. Truly, I have learnt a lot from him. His contribution was remarkable and memorable.

I would also like to thank my Institutional guide *Dr. D. Kumar (Associate Professor)* & H.O.D. *Dr. G.L. Verma, Department of Applied Chemistry, Delhi College of Engineering, 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 would also like to thank *Mr. K.K. Vimal (Research Officer)* for his continuous guidance, advice, encouragement and most importantly for his patience. Without his consistent support this work wouldn't have been the same. I also appreciate the way he made me understand the physical meaning of each concept and I owe a great deal to him

providing me a genial and cozy environment that I could expedite my work independently.

I would also like to take this oppertunity of expressing my gratitude to Mr*. J.S. Dhaliwal (Senior Research officer), Dr. Vishal Goyal (Research officer), and Mr. M.S. Negi (Research officer)* for their valuable guidance and support during the course of my project work. I also like to thank *Dr. Anil Yadav (SRO-AD), Dr. Veena Bansal (SRM-AD) and Dr. Ravinder Singh (RO)* for their inputs in different experimental techniques. I also acknowledge and express my deepest gratitude to *Mr. S.M. Sanduja* (Training Manager) and *Mr. Sanjay Bhagat (Training Officer)* for providing me the most suitable environment during the period of my work.

Special thanks to *Mr. Anil Sharma, Mr. Ranbir Singh and Mr. Chander* for their kind co-operation during the experimental work.

Lastly, I desire to record here my sincere thanks to my colleagues for their friendly co-operation and co-ordination, and also to all those whose names I forgot to mention but who in different ways have helped and encouraged me.

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NAVEEN KUMAR

DEDICATED

TO

MY PARENTS

Executive Summary

The project work described in the dissertation consists of three parts.

1. HDPE Raffia Grade:

Total 7 HDPE raffia grades were collected from various manufacturers. Industrial trials for raffia tape manufacturing were done in one of the leading raffia manufacturing industry using different HDPE raffia grades. During the trials it was observed that HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades failed to perform well at higher line speeds of 300 Mt/min and many problems (like higher tape breakage, higher power consumption etc) were encountered while no such problems were encountered in HD/R/G grade which was able to run at a line speed 300 Mt/min. Some other established raffia grades HD/R/R-027, HD/R/R-067 and HD/R/H were also found to be performing well. Therefore, to ascertain the root cause of the problems encountered in case of HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades, structure-property-performance-relationship for HDPE raffia grades was studied. Various characterization techniques like MFI, MFR, Power Law curve, Parallel Plate Rheometer, High Temperature–Gel Permeation Chromatography, Dynamic Mechanical Analysis and Differential Scanning Calorimetry were used. It was found that HD/R/I-022 and HD/R/I-025 had higher melt viscosity than HD/R/G leading to higher power consumption. HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades had different concentration of very high molecular weight fractions and low molecular weight fractions as compared to HD/R/G. It was observed that even slight changes in these fractions, had resulted in widely different processing behaviours of the resins.

2. HDPE Large Blow Molding Grade:

Total 5 HDPE raffia grades were collected from various manufacturers. Processing trials were done in one of the leading manufacturing industry in INDIA with HDPE large blow molding grades HD/LBM1/024, HD/LBM1/111, HD/LBM1/121, HD/LBM1/125 and HD/LBM2/571 to produce primarily large capacity (220 litre) L-ring barrels. During the trails it was observed that HD/LBM2/571 grade was performing well with no difficulty and product quality was observed within the customer's requirement. But with HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and

HD/LBM1/125 grades various problems (like rough inner surface, decrease in product weight etc with HD/LBM1/024 and HD/LBM1/111 and uneven L-ring formation at the bottom of the barrel, short molding etc with HD/LBM1/121 and HD/LBM1/125) were observed during the process and in the product manufactured. Therefore, to ascertain the root cause of the problems encountered in case of HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades, structure-property-performance-relationship for HDPE large blow molding grades was studied. Various characterization techniques like MFI, MFR, Capillary Rheometer, Parallel Plate Rheometer, High Temperature–Gel Permeation Chromatography and Differential Scanning Calorimetry were used. Wide differences in extensional viscosity values for HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades as compared to HD/LBM2/571 were observed. It was found that HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades had lack of very high molecular weight fractions, varying low molecular fractions and absence of high extensional viscosity which plays an important role during large blow molding processes while HD/LBM2/571 had ideal set of properties for large blow molding process for manufacturing L-ring barells (220 litre).

3. LLDPE Blown Film Extrusion Grade:

Total 2 LLDPE (1-butene based) blown film extrusion grades were collected along with density, MFI, dart impact, tensile strength at break, % elongation at break and tear strength values. Both the grades had nearly similar MFI @ 2.16kg and density values. But there were appreciable differences in the properties of both the grades. Thus both the grades were tested by using various characterization techniques like High Temperature-Gel Permeation Chromatography, 13C-Nuclear Magnetic Resonance spectroscopy, Crystallization Analysis Fractionation and Differential Scanning Calorimetry, to ascertain the root cause for difference in properties and structure-property-relationship was studied for each LLDPE grade. It was found that different property values could be attributed to different concentration of the comonomer present and widely different comonomer composition distribution in polymer chains for both the grades.

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1.0 INTRODUCTION

1.1 <u>Raffia Grade (HDPE)</u>

Raffia was the name of natural fibres prepared from the leaves of palm (Named as Raffia plant) in the Cuba (Central Africa, Republic of Congo). People there weave the strips of leaf to make pieces of fabric, often called "Raffia Cloth", which reflect their social Status, age, marital status, and also the person's character. One of them is the Indigo which is the most popular fabrics of Africa and is considered to be a symbol of affluence and prosperity.

Woven sacks and oriented tapes are produced from High Density Polyethylene. The structure of woven sacks thus produced looks like mats that were made from leaves of palm (Named as Raffia Plant), that is why the grades which are used to produce these materials now a day are termed as "RAFFIA GRADES"[1].

1.1.1 <u>Raffia stretched tape and Mono-filament manufacturing process</u>[2,3]:

 The process mainly consists of the following steps

- **<u>Extrusion of film:</u>**

Extruders comprise of Hopper, Barrel/Screw and Dies. HDPE can be processed on conventional extruders with three zone screws viz. feed, compression and metering. The output obtained from extruder depends upon the L/D ratio (Length to Diameter Ratio). Higher the L/D ratio, higher will be the output per revolution of screw. The type of die used is referred to as a coat hanger die / T-die which provides a good streamlined flow. In coat hanger type of die, the design is of triangular pre-land section, which gives balanced pressure leading to uniform flow of the material. This minimizes the adjustment required to obtain uniform sheet thickness.
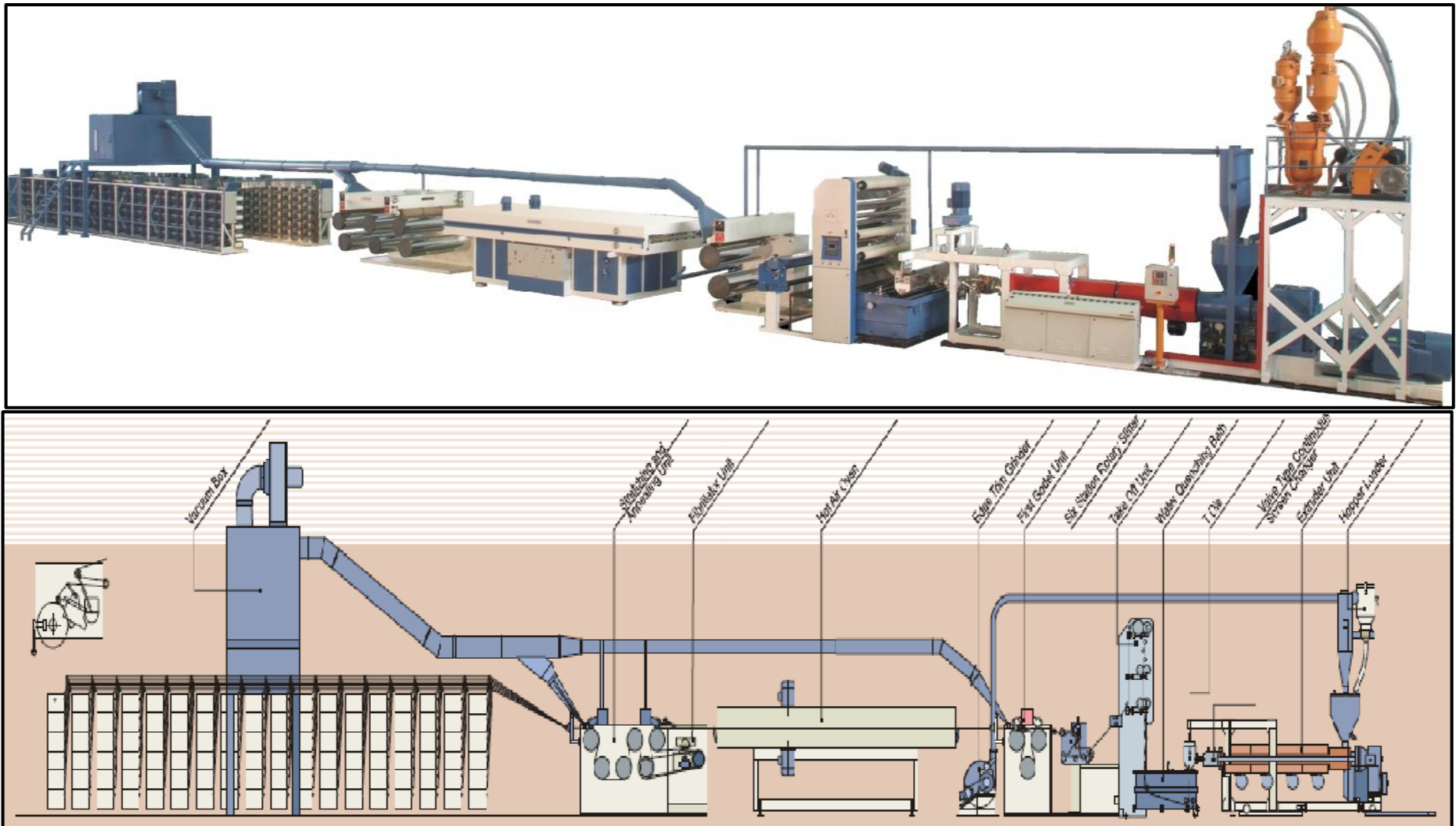
Figure 1.1: Extrusion Tape line [4]
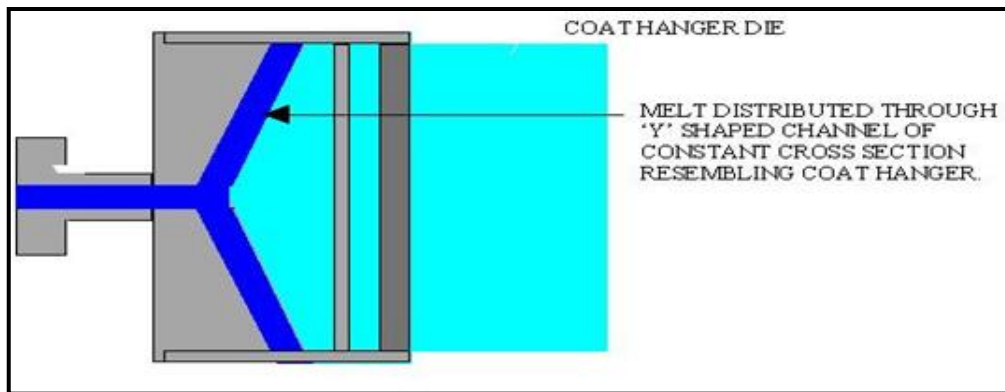
Figure 1.2: Coat Hanger Die [5]

- **Quenching of film:**

The polymer melt is partly oriented during extrusion through die. To prevent melt relaxation the melt is quenched rapidly after exiting from the die. Fast cooling promotes a finer crystalline structure of polymer in the film which in turn improves the performance of film during the stretching operation, apart from rendering better physicals.

In cast film, the cooling is done by quenching the film in a water tank. The film from the die is directly taken into the tank filled with water. Film quality and performance of the resulting tapes mainly depend on the quenching conditions. During quenching, the significant parameters which control the physicals of the tapes are die-water distance (air gap) and quench water temperature. Operation with a lower air gap will reduce the time for melt relaxation and result in films, with higher strength. A very fast rate of quench will result in a very fine crystal structure in the film, which will give higher clarity and strength, than a film which is quenched at slower rates. To achieve optimum strength and elongation, air gap of 12-25 mm and quench water temperature of 30-40°C is recommended.

Figure 1.3: Quenching Unit [(6)]

- **Slitting of film into tapes:**

The flat film after quenching is slit into tapes of specific width according to the end user requirements. The slitting tools generally used are industrial or surgical blades with sharp edges. Blunt blades produce poor cuts, which lead to problems in drawing, winding and weaving of tapes. The blades are equally placed on a bar using spacers and are set at an angle of 30° and 60° with the film. Initial tape width is adjusted by selecting appropriate spacer. Spacer width (SW), including blade thickness, is a function of stretch ratio (SR) and final tape width (A2) desired.

$$SW = \sqrt{SR} \times A2$$

Spacer width of 5.5-6.2 is recommended for HDPE cast film line.

Figure 1.4: Rotatory Slitter [(6)]

- **Orientation of tapes:**

Orientation is accomplished by stretching the tapes while passing them through a hot air oven or over a hot plate maintained at a temperature just below the melting temperature of HDPE ($<130^0$C). Stretching of tapes is done by passing them over two sets of rollers, called godet rollers, placed on either side of the hot air oven / hot plate and operating at different speeds. Ratio of speed of second set of rollers, operating at higher speed, to that of first set is termed as stretch ratio (SR). Stretching of tapes in presence of heat media results in molecular/chain orientation and thus greatly increases the mechanical strength of tapes. For HDPE SR of 5-6.8 and hot air oven temperature between 115-130^{0}C is recommended. Hot air oven length is often kept between 4-6m.

- **Annealing of tapes:**

Drawn tapes are "annealed" immediately after stretching operation. This helps to minimize tape shrinkage which may occur as a result of residual stresses in the oriented tapes. Annealing is done by heating the stretched tapes while they are passing over from second godet rollers to third godet rollers; the latter being maintained at a slightly lower speed (5% less) than the former. The annealing ratio is a function of second and third godet rollers. The annealing temperature is slightly lower (5-10°C) than the orientation temperature. For HDPE it is between 100-110°C. Alternatively, tapes can be annealed by using hot godet rolls, which are usually heated electrically or by circulating hot oil. Relaxation takes place over a short gap (the distance between the rolls).
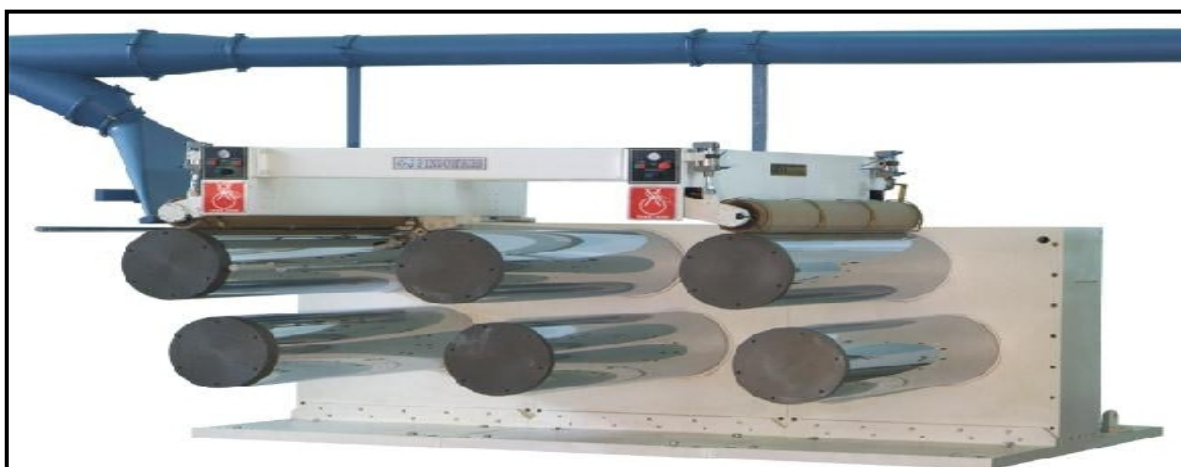
Figure 1.5: Annealing Godets [6]

- **Winding:**

After annealing process (after passing the final godet) the tapes pass to the winding strands where tapes are firmly wind with the help of bobbins.
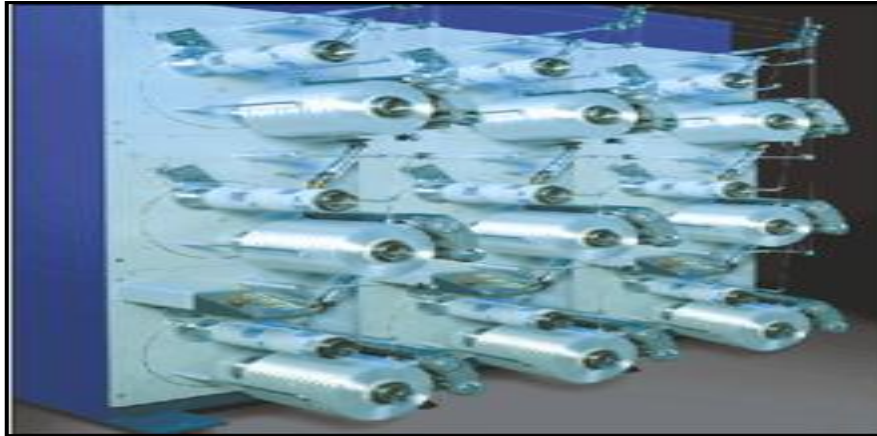
Figure 1.6: Winding Unit

1.1.2 Uses of HDPE raffia [2,3]:

(a) Tarpaulin:

Tarpaulin is HDPE raffia grade woven fabric laminated with LDPE/LLDPE on both the sides. It is mostly use as a protective covering for various applications in the monsoon season. This is widely used in transportation for covering trucks carrying goods, used as covering in godowns, fumigation of crops, mandaps of temporary sheds, out-door open storage and vehicles.

Advantages of tarpaulin:
- It is lighter in weight
- Handling is easier
- Water proof, does not get wet or soaked like canvas
- Can be manufactured in desired colours
- Printing is much more attractive

Figure 1.7: HDPE raffia grade made Tarpaulin

(b) Fertilizer bags:

In INDIA, HDPE Raffia grade is mostly used in the fertilizer industry bags manufacturing.

Figure 1.8: HDPE raffia grade made Fertilizer bags

(c) Ropes:

Ropes are manufactured from HDPE raffia grade are commonly used for domestic application like house hold, furniture & light fishing. Denier used for rope is ranges from 500-900 and tenacity ranges from 5.5 to 6grams/denier.

Figure 1.9: HDPE raffia grade made Ropes

1.1.3 General resin characteristics for HDPE raffia [3]:

- MFI around 0.9 @2.16kg, 190^0C
- Density (0.952 g/cc)
- Moderately broad molecular weight distribution
- Low water carry over in water bath quench
- Good orientation capabilities
- Excellent fibrillation resistance
- Good toughness & tenacity
- Minimum die lip build-up
- Good colour and processing stability

1.2 Large Blow Molding Grade (HDPE)

1.2.1 Blow Molding [7, 8, 9, 12]:

Blow molding is a versatile conversion process used to produce a wide variety of objects by inflating a molten tube of polymer inside a hollow mold.

The Blow Molding Process:

- A thermoplastic resin is heated to a molten state.
- It is then extruded through a die head to form a hollow tube called a parison.
- The parison is dropped between two mold halves, which close around it.
- The parison or preform is then inflated with high pressure air.
- The plastic solidifies as it is comes into contact with the chilled blow mold.
- The mold opens and the finished component is ejected.

Types of blow molding:

- (a) Extrusion blow molding - continuous or intermittent type
- (b) Injection blow molding
- (c) Extrusion stretch blow molding
- (d) Injection stretch blow molding

Extrusion blow molding is predominant in polyethylene molding. Common items fabricated by blow molding include bottles, drums, chemical storage tanks and toys.

1.2.2 Extrusion Blow Molding:

It is perhaps the simplest type of blow molding. A hot tube of plastic material is dropped from an extruder and captured in a water cooled mold. Once the molds are closed, air is injected through the top or the neck of the container; just as if one were blowing up a balloon. When the hot plastic material is blown up and touches the walls of the mold the material "freezes" and the container now maintains its rigid shape. This process produces a container with a blow chamber and tail scrap attached to the container. The blow chamber and tail must be removed from the container through a secondary process. After removal, the blow chamber and tail are
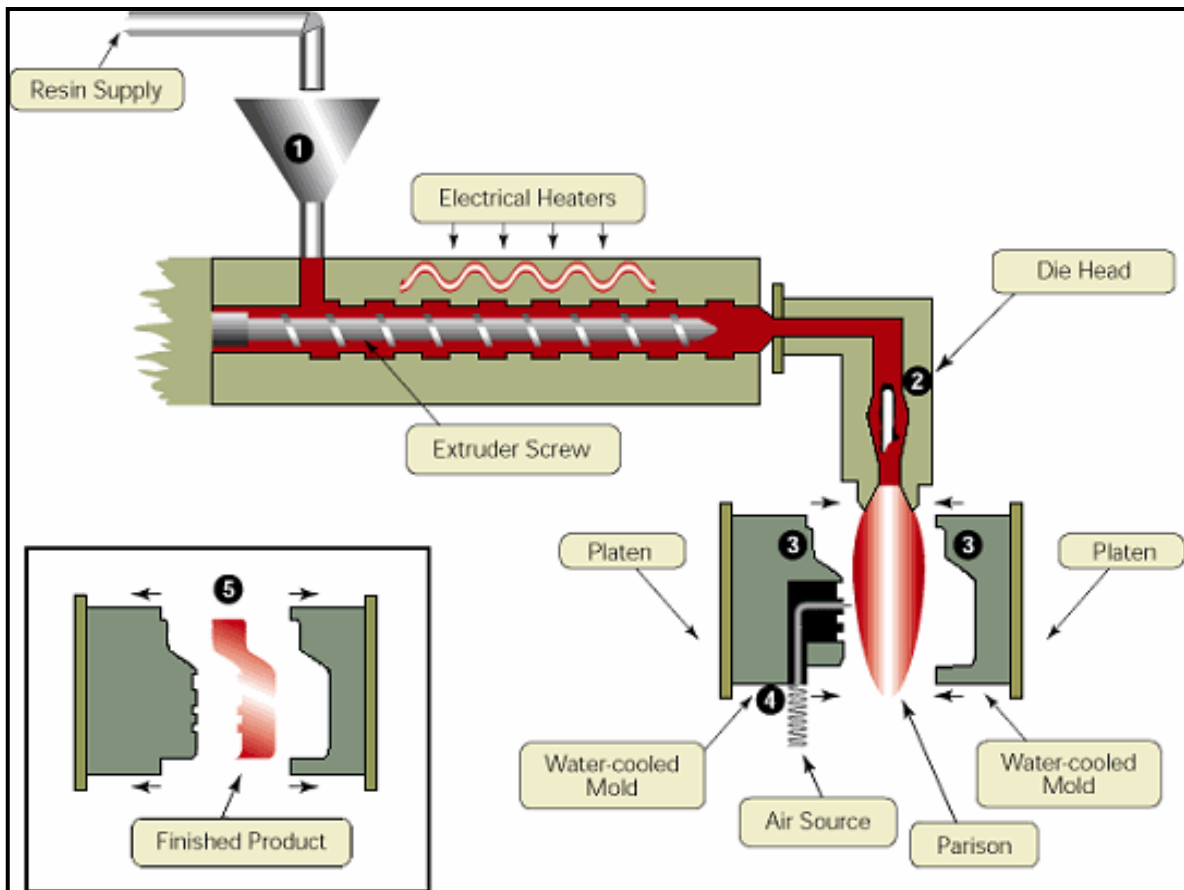
Figure1.10: General Extrusion Blow Molding Process Diagram [10]

ground into small particles referred to as regrind and are typically blended with virgin resin to manufacture new product. The general extrusion blow molding process diagram is shown in figure. Extrusion blow molding allows for a wide variety of container shapes, sizes and neck openings, as well as the production of handle ware. Extrusion blown containers can also have their gram weights adjusted over a fairly wide range by altering the extruder output. Extrusion blow molds are generally much less expensive than injection blow molds and can also be produced in a much shorter period of time.

There are two extrusion blow processes:

(i) Continuous extrusion blow molding
(ii) Intermittent blow molding

Continuous extrusion blow molding:

Continuous and intermittent are two variations of extrusion blow molding. In continuous extrusion blow molding the parison is extruded continuously and the individual parts are cut off by a suitable knife. Types of continuous extrusion blow molding equipment may be categorized as follows:

- Rotary wheel blow molding systems
- Shuttle machinery

Intermittent blow molding:

Intermittent extrusion may be also called shot extrusion. Parison shot extrusion is accomplished by means of a reciprocating screw almost identical to those used in injection molding machines. In Intermittent blow molding there are two processes: straight intermittent is similar to injection molding whereby the screw turns, then stops and pushes the melt out. With the accumulator method, an accumulator gathers melted plastic and when the previous mold has cooled and enough plastic has accumulated, a rod pushes the melted plastic and forms the parison. In this case the screw may turn continuously or intermittently. Types of intermittent extrusion blow molding equipment may be categorized as follows:

- Reciprocating screw machinery
- Accumulator head machinery

1.2.3 Uses of HDPE Blow molding [11]:

More than 90% of all blow-molded polyethylene products are made from high density resins. The majority are bottles that are consumed domestically, such as those used for milk, household chemicals, and cosmetic products. Other major products include chemical transportation drums, pails, and fuel tanks. Milk, fruit juice, vinegar, and water bottles are all blown from similar grades of high molecular weight, high density polyethylene resin. Some of the HDPE blow molded products are shown below in figure1.11.

Figure 1.11: HDPE blow molded products

1.2.4 General Resin characteristics for large blow moulding [(12)]:

Blow moulding requires resins with higher melt strength for parison formation and good process ability during extrusion. Consistent melt swell is also important. Product requirements usually include stiffness, impact strength and good environmental stress crack resistance (ESCR).

The three important factors which determine the properties of polyethylene are

- Molecular weight
- Molecular weight distribution
- Density

Higher the density, better is the chemical resistance, gas barrier, stiffness and hardness however toughness and ESCR decrease.A lower melt flow index (MFI) gives better mechanical properties, ESCR and melt strength. A broader molecular

weight distribution gives better swell, process ability & ESCR but poorer surface gloss.

HDPE blow moulding grades have broad MWD's with optimum combination of stiffness and stress crack resistance. This can be achieved with a low MFI and appropriate density. A higher density grade would give lower ESCR but higher stiffness.

During the blow molding process for manufacturing products like drums of higher capacity; polymer resin swell characteristics, parison sagging and melt strength of the resin are the important parameter for product to be manufactured properly.

Swelling Characteristics) [11, 13, 14]:

Die swell, also known as extrudate swell, is a common phenomenon in blow polymer processing. Die swell occurs in instances of polymer extrusion, in which a stream of polymeric material is forced through a die. Die swell is an instance where a polymer stream is compressed by entrance into a die, and is followed by a partial recovery or "swell" back to the former shape and volume of the polymer after exiting the die, hence the term die swell. Die swell is a phenomenon directly related to entropy and the relaxation of the polymer within the flow stream. Initially, a flow stream has a constant rate before entering the die, and the polymers within the stream occupy a roughly spherical conformation, minimizing entropy. Extrusion through the die causes an increase in flow rate through the polymer flow stream. As the polymer spends time inside the die and is subject to the much increased flow rate, the polymers lose the spherical shape, becoming longer due to the increased flow rate. Physical entanglements may relax, if the time scale of the polymer within the die is long enough. When the polymer stream leaves the die, the remaining physical entanglements cause the polymers in the die stream to regain a portion of its former shape and spherical volume, in order to return to the roughly spherical conformation that minimizes entropy.

HDPE resins comprise of long and medium chain molecules, which in the molten state have complex motions, with themselves and with each other, forming a coiled mass of molecules. When extruded through the die, they are forced to uncoil and stretch in the flow direction on emergence these relax to their random orientation. HDPE resins manufactured by different processes differ in their swelling

characteristics. For HDPE swelling is largely affected by the presence of long chain branching and very high molecular weight fractions in the resin. HDPE manufactured using ZN-catalyst don't contain any long chain branching, thus it high molecular fractions in the resin that controls the die swell characteristics.

Swells are of 2 types

- Diameter Swell
- Thickness Swell (Weight Swell)

Parison sagging[14]:

Parison sagging is the drawdown of the melt from the extruder die due to the effects of gravity. The sagging increases with time during extrusion, due to increasing mass of parison. After extrusion stops, the sagging further accelerates due to the parison cross-section at the die becoming smaller, as sagging takes place, increasing the stress at the die lips. Sagging often results in the parison thickness tapering down towards the die. The elastic recovery and sagging have opposing effects on the deformation of the parison. Sagging will be more if the melt strength of the resin is less. Higher the melt strength at low extensional rate will result in lower parison sagging.

Melt Strength[11, 13, 14]:

Melt strength is one of the most important properties that control the blow molding process of the polymer resin. Melt strength is directly related to the extensional behaviour of the polymer. Greater the extensional viscosity of the resin greater is the melt strength. Melt strength of the resin is improved by the presence of high molecular weight tail or long chain branches. Melt strength is directly proportional to the zero shear viscosity of the resin. Resins with higher zero shear viscosity shows higher melt strength and lower parison sagging.

1.3 Blown Film Extrusion Grade (LLDPE)

1.3.1 Blown Film Extrusion [15]:

Blown film extrusion is the process by which most commodity and specialized plastic films are made for the packaging industry. The film blowing process basically consists of extruding a tube of molten thermoplastic and continuously inflating it, up to several times initial diameter, to form a thin tubular product that can be used directly or slit to form a flat film.

The Process:

Plastic melt is extruded through an annular slit die, usually vertically, to form a thin walled tube. Air is introduced via a hole in the centre of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of film then continues upwards, continually cooling, until it passes through nip rolls where the tube is flattened to create what is known as 'lay-flat' tube of film. This lay-flat or collapsed tube is then taken back down the extrusion 'tower' via more rollers. On higher output lines, the air inside the bubble is also exchanged. This is known as IBS (Internal Bubble Cooling).

The lay-flat film is then either kept as such or the edges of the lay-flat are slit off to produce two flat film sheets and wound up onto reels. If kept as lay-flat, the tube of film is made into bags by sealing across the width of film and cutting or perforating to make each bag. This is done either in line with the blown film process or at a later stage.

Typically, the expansion ratio between die and blown tube of film would be 1.5 to 4 times the die diameter. The drawdown between the melt wall thickness and the cooled film thickness occurs in both radial and longitudinal directions and is easily controlled by changing the volume of air inside the bubble and by altering the haul off speed. This gives blown film a better balance of properties than traditional cast or extruded film which is drawn down along the extrusion direction only.
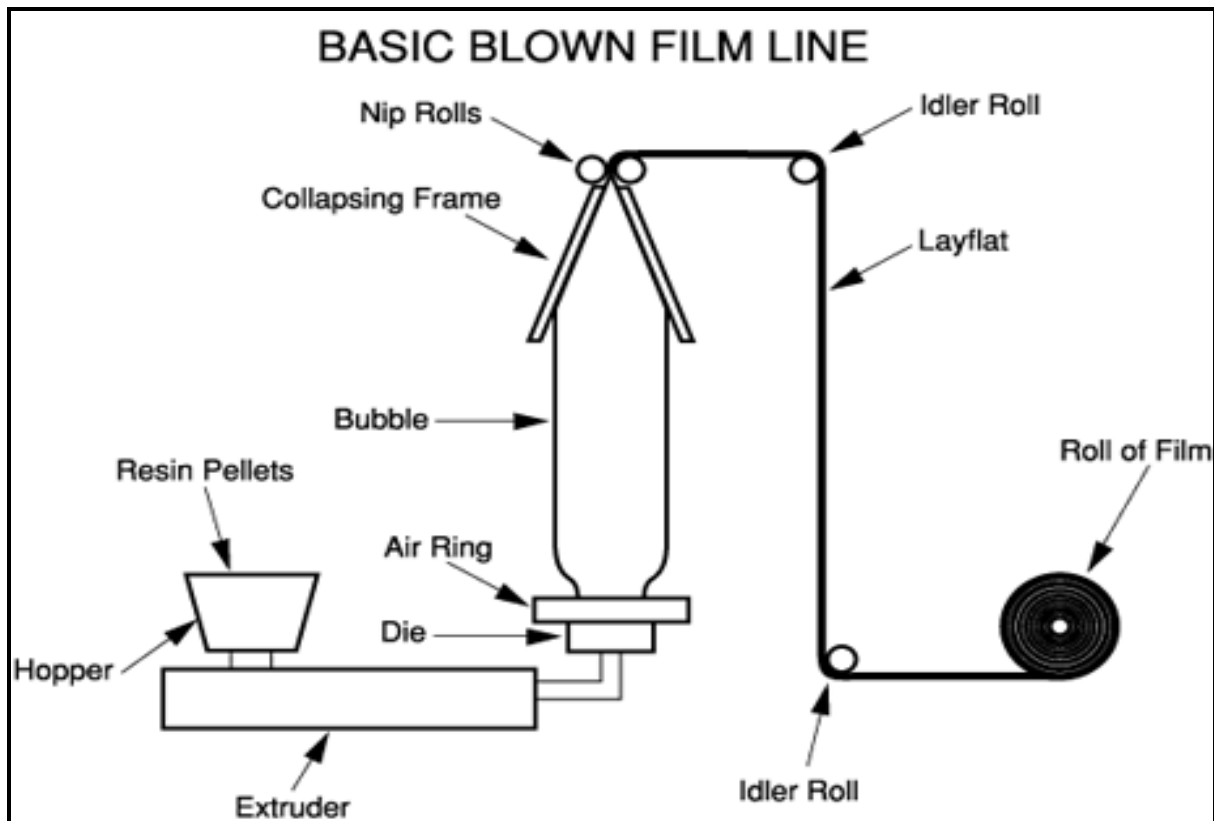
Figure1.12: Blown Film Extrusion Line Diagram

Advantages of Blown Film Extrusion Process:

- Produce tubing (both flat and gusseted) in a single operation
- Regulation of film width and thickness by control of the volume of air in the bubble, the output of the extruder and the speed of the haul-off
- Eliminate end effects such as edge bead trim and non uniform temperature that can result from flat die film extrusion
- Very high productivity
- Blown film due to its biaxial orientation gives balanced properties of the film in Machine & Transverse direction

Application of LLDPE Blown Film Extrusion grade:

LLDPE Blown Film Extrusion grade is used for general purpose, heavy duty and liquid packaging in laminated / non-laminated film applications.

2.0 TECHNICAL BACKGROUND

2.1 <u>HDPE RAFFIA GRADE</u>

7 HDPE raffia grades (manufactured using Zeigler Natta catalyst system) were collected from various manufacturers across INDIA.

Table 2.1: HDPE Raffia Grade Details

S. No.	Grade
1	HD/R/I-018
2	HD/R/I-022
3	HD/R/I-025
4	HD/R/R-027
5	HD/R/R-067
6	HD/R/G
7	HD/R/H

Processing trials were done in one of the leading raffia manufacturing industry in northern INDIA with HDPE raffia grades HD/R/G, HD/R/I-018, HD/R/I-022 and HD/R/I-025 for raffia tape production. During the trials it was observed that HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades failed to perform well at higher line speeds of 300 Mt/min and many problems were encountered while no problems were encountered in HD/R/G grade which was able to run at a line speed 300 Mt/min. Following were the problems observed during the trials.

❖ Dispersion of Anti-fibrilant was non-uniform / improper melting for HD/R/I-018 grade.

❖ Non-uniform thickness of the web coming out of T-die for HD/R/I-018 grade.

❖ Tape breakages were higher at line speed (> 150 Mt/min) for HD/R/I-018 grade.

- ❖ High tape breakage was observed above line speed of 250Mt/Min for HD/R/I-022 and HD/R/I-025 grades whereas normal lines speed of 300Mt/Min with HD/R/G grade.

- ❖ Due to higher tape breakage wastage increased from 0.6% for HD/R/G to 6% for HD/R/I-022 and HD/R/I-025 grades.

- ❖ Tape elongation was lower in HD/R/I-022 and HD/R/I-025 grades as compared to HD/R/G.

- ❖ Power consumption was increased by 3-4 Amps with HD/R/I-022 and HD/R/I-025 grades as compared to HD/R/G.

- ❖ Melt Pressure fluctuations, higher melt pressure and few carbon deposits at the die exit for HD/R/I-022 and HD/R/I-025 grades, thus requiring frequent screen pack cleaning as compared to HD/R/G.

HD/R/R-027, HD/R/R-067 and HD/R/H were already established raffia grades and found to be performing well for raffia tape manufacturing.

HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades were found performing inferior as compared to HD/R/G grade. While with HD/R/G grade, line speed up to 300Mt/min was easily achievable; other three grades (HD/R/I-018, HD/R/I-022 and HD/R/I-025) were not able to run properly on line speed of 300Mt/min. Hence HD/R/G grade had been chosen as a reference grade. HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades were compared against HD/R/G. Other established raffia grades HD/R/R-027, HD/R/R-067 and HD/R/H were also compared with HD/R/G and structure-property-performance relationship for each raffia grade was studied.

2.2 HDPE LARGE BLOW MOLDING GRADE

5 HDPE large blow molding grades were collected from various manufacturers.

Table 2.2: HDPE Large Blow Molding Grade Details

S. No.	Grade
1	HD/LBM1/024
2	HD/LBM1/111
3	HD/LBM1/121
4	HD/LBM1/125
5	HD/LBM2/571

Processing trials were done in one of the leading manufacturing industry in INDIA with HDPE large blow molding grades HD/LBM1/024, HD/LBM1/111, HD/LBM1/121, HD/LBM1/125 and HD/LBM2/571 to produce primarily large capacity (220 litre) L-ring barrels. During the trails it was observed that HD/LBM2/571 grade was performing well with no difficulty and product quality was observed within the customer's requirement. But with HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades various problems were observed during the process and in the product manufactured. Following were the problems observed during the trials.

- ❖ Rouge inner surface and higher cycle time for HD/LBM1/024 and HD/LBM1/111 as compared to HD/LBM2/571 grade.
- ❖ Decrease in product weight for HD/LBM1/024 and HD/LBM1/111 as compared to HD/LBM2/571 grade.
- ❖ Presence of burnt material like odour and fumes while ejecting parison for HD/LBM1/024 and HD/LBM1/111 grades as compared to HD/LBM2/571.
- ❖ Uneven L-Ring formation at the bottom of the drum made from HD/LBM1/121 and HD/LBM1/125 grades.
- ❖ Bulging was observed at the top of the drum made from HD/LBM1/121 and HD/LBM1/125 grades.

- ❖ Short molding was observed at the bottom of the drum made from HD/LBM1/121 and HD/LBM1/125 grades.
- ❖ Weight of the L-Ring barrel was decreased for HD/LBM1/121 and HD/LBM1/125 grades as compared to HD/LBM2/571.
- ❖ Decrease in parison formation time was also observed for HD/LBM1/121 and HD/LBM1/125 grades as compared to HD/LBM2/571.

HD/LBM2/571 grade had performed well without any difficulties and product manufactured had quality within the customer requirements. Hence HD/LBM2/571 had been chosen as a reference grade. HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades were compared against HD/LBM2/571 and structure-property-performance relationship for each grade was studied.

2.3 LLDPE BLOWN FILM EXTRUSION GRADE

2 LLDPE (1-butene based) blown film extrusion grades were collected along with density, MFI, dart impact, tensile strength at break, % elongation at break and tear strength values.

Table 2.3: LLDPE Blown Film Extrusion Grade Details

S. No.	Grade
1	LLDPE-1
2	LLDPE-2

Table 2.4: Density and MFI @ 2.16 values for LLDPE-1 and LLDPE-2 grades

S. No.	Grade	Density (g/cc) (23^{0}C) ASTM D 1505	MFI (g/10min) @2.16,190^{0}C ASTM D 1238
1	LLDPE-1	0.918	0.9
2	LLDPE-2	0.920	1.0

Table 2.5: Properties for LLDPE-1 and LLDPE-2 grades

S. No.	Grade	Dart Impact(F-50) g/µm	Tensile Strength at break (MD/TD) MPa	Elongation at break (MD/TD) %	Tear Strength (MD/TD) g/µm
		ASTM D 1709/A	ASTM D 882	ASTM D 882	ASTM D 1922
1	LLDPE-1	3.4	38.0/30.0	700/800	3.0/10.0
2	LLDPE-2	4.1	30.0/21.0	650/850	4.8/17.6

Both the grades had nearly similar MFI @ 2.16kg and density values (table 2.3.2). But there were appreciable differences in the properties of both the grades (table 2.3.3). Thus both the grades were tested by using various characterization techniques to determine the possible cause for difference in properties and structure-property-relationship was studied for each LLDPE grade.

3.0 EXPERIMENTAL TECHNIQUES

3.1 GRADE DETAILS:

3.1.1 HDPE RAFFIA GRADE:

Table 3.1: HDPE Raffia Grade Details

S. No.	Grade
1	HD/R/I-018
2	HD/R/I-022
3	HD/R/I-025
4	HD/R/R-027
5	HD/R/R-067
6	HD/R/G
7	HD/R/H

3.1.2 HDPE LARGE BLOW MOLDING GRADE:

Table 3.2: HDPE Large Blow Molding Grade Details

S. No.	Grade
1	HD/LBM1/024
2	HD/LBM1/111
3	HD/LBM1/121
4	HD/LBM1/125
5	HD/LBM2/571

3.1.3 <u>LLDPE BLOWN FILM EXTRUSION GRADE</u>:

Table 3.3: LLDPE Blown Film Extrusion Grade Details

S. No.	Grade
1	LLDPE-1
2	LLDPE-2

All the characterization studies were carried out as per ASTM standards wherever applicable.

3.2 <u>Density Determination</u>:

Density for PE is a very important parameter for characterization of different types PE resins. Density of different resins can be used as one factor to help predict their relative properties. The relationship between certain mechanical properties and the density of a sample arises from the semi crystalline nature of polyethylene. The higher the proportion of crystalline phases, the higher the density.

Density was measured by using Density Gradient Column technique. **Davenport two column density measuring apparatus** was used. Density gradient column for range from 0.940 to 0.980 g/cm^3 was prepared by mixing the following solutions.

Solution A: (Low density ~0.925 g/cc)

Water = 475ml

Isopropanol = 425ml

5% Sodium Acetate solution = 100ml

Total volume = 1000ml

Solution B: (High density ~0.995 g/cc)

Water = 760ml

Isopropanol = 140ml

5% Sodium Acetate solution = 100ml

Total volume = 1000ml

Gradient column was placed inside the water bath maintained at 23^{0}C. In the mixing apparatus of the gradient column, the heavier liquid was connected to lighter liquid and the lighter liquid is connected to the density gradient column through a Siphon tube. The density gradient obtained was determined by introducing a set of nine accurately calibrated marked glass floats whose densities cover the desired range of the column at equal density intervals. The height of each float was measured after attaining stability. A calibration curve was plotted between height verses density for the glass floats.

HDPE (Raffia grade and Large Blow molding grade) extruded specimens in the form of pallets were used (three specimen for each grade) for density determination. Height of each specimen in the column was recorded and value of density was determined using the calibration curve obtained between heights Vs density obtained earlier.

3.3 Melt Flow Index (MFI):

The melt flow index of a PE resin is the weight in grams of polymer that extrudes in 10 min from a standard capillary die under a fixed load, measured according to ASTM D 1238.

Melt flow index is a measure of the ability of the material's melt to flow under pressure. It is inversely proportional to viscosity of the melt at the conditions of the test. The MFI of a PE resin depends on its molecular characteristics, primarily average molecular weight, molecular weight distribution, and branching characteristics, and distribution. MFI of the PE resin made from similar process and same catalyst type; is inversely proportional to the weight-average molecular weight [11].

MFI of HDPE granules was carried out as per ASTM D 1238 on **CEAST (Model 7026) melt flow indexer** at different loads (@2.16kg, 5kg, 10.96kg, 20.6kg for HDPE raffia grades and @5kg, 10.0kg, 21.6kg for HDPE large blow molding grades) at 190 ^{0}C. The polymer granules were preheated for 240 seconds without load and a constant load was applied at a constant temp of 190 ^{0}C. Then the polymer was

allowed to flow through an annular die of 2.0955mm diameter and 8mm length (as per ASTM D 1238 standard). The extrudate was cut at a predetermined length (10mm) and weight was taken to calculate MFI of the grade. The shear rate and melt viscosity were also measured along with MFI.

3.3.1 Melt Flow Ratio (MFR):

MFR is the ratio of the MFI calculated at two different loads. MFR was calculated using MFI data collected from Melt flow tester. MFR for PE resin represent the resins propensity to undergo shear thinning. Higher the MFR value greater is the shear thinning in the resin. It is also used as a measure of the broadness of the MWD. Greater the value of MFR greater will be the broadness of the polymer.

MFR was evaluated for HDPE raffia grades at loads 5kg, 10.96kg, 20.6kg.
E.g. MFR at 5.0 kg load for HDPE raffia grades was calculated as

$$MFR\ 5.0Kg = \frac{MFI\ 5.0\ Kg}{MFI\ 2.16\ Kg}$$

MFR for HDPE large blow molding grades at 10.0kg and 21.6kg load were calculated.
E.g. MFR at 10.0 kg load for HDPE large blow molding grade was calculated as

$$MFR\ 10.0Kg = \frac{MFI\ 10.0\ Kg}{MFI\ 5.0\ Kg}$$

3.3.2 Shear Viscosity vs. Shear rate from Power Law, using MFI/MFR data:

The shear thinning behaviour of polymers is frequently expressed by the Power-Law Model [16].

$$\eta = m \times shear\ rate^{(n-1)}$$

Where n is Power Law Exponent, whose values were calculated using the formula

.

$$n = \frac{log(20.6) - log(2.16)}{log(MFI20.6) - log(MFI2.16)}$$

& m is known as consistency index, whose values were calculated using the formula.

$$m = \frac{[8982 \times 2.16]}{\left[1838 \times \frac{MFI2.16}{\rho}\right]^n}$$

Where ρ represent melt density at 2.16 kg weight.

Smaller the value of n more is the shear-thinning behavior of the polymer. Power-Law model gives a good fit of viscosity data at high shear rates but not at very low shear rates (because as shear rate goes near to zero, the viscosity goes near to infinity). Shear viscosity values obtained from the Power law give good idea about the polymer flow ability at higher shear rates.

Shear Viscosity Vs Shear rate curve were obtained for HDPE raffia grades.

3.4 Capillary Rheometer Analysis [17, 18]:

Capillary Rheometer is mainly used to evaluate the rheological response of molten PE resins to a wide range of shear rates. Primarily it is used to investigate the properties of melts under conditions of high shear akin to those found during processing. It is also useful in establishing the conditions under which melt instability (sharkskin, melt fracture, etc.) occurs. This information is valuable in determining the relative process ability of resins.

In Capillary Rheometer, the shear stress is determined from the pressure applied by a piston. The shear rate is determined from the flow rate.

$$Shear\ Stress\ (\tau_w) = \frac{R}{2}\left(\frac{\Delta P\ cap}{L}\right)$$

$$Apparent\ shear\ rate\ (\dot{\gamma}_a) = \frac{4Q}{\Pi R^3}$$

Where ΔP is capillary pressure drop, L is capillary length; R is radius of capillary, and Q is the volume flow rate.

The apparent shear rate corresponds to Newtonian behaviour (constant viscosity fluids). A correction is necessary (Rabinowitsch correction) for shear thinning fluids. For the Power-Law model, the true (Rabinowitsch corrected) shear rate becomes

$$Corrected\ Shear\ Rate\ (\dot{\gamma}_w) = \frac{3n+1}{4n}\dot{\gamma}_a$$

Where 'n' is Power law index

When capillaries are relatively short (L/R < 50), the Bagley correction is necessary to account for the excess pressure drop (ΔP_e) at the capillary entry. The Bagley correction factor is usually expressed as

$$n_B = \frac{\Delta P_e}{2\tau_w}$$

The Bagley corrected shear stress becomes

$$\tau_w = \frac{\Delta Pcap + \Delta P_e}{2\left(\frac{L}{R} + n_B\right)}$$

To apply the Bagley correction, measurements with at least two capillaries of same diameter and different length are needed.

The Shear Viscosity calculated:

$$Shear\ Viscosity\ (\boldsymbol{\eta}) = \frac{\tau_w}{\dot{\gamma}_w}$$

3.4.1 Extensional Viscosity [(16, 18, 19)]:

Extensional viscosity (also known as elongation viscosity) is a viscosity coefficient when applied stress is extensional stress. Extensional Viscosity and "Melt Strength" are related to the performance of polymers in processes involving stretching, such as film blowing, sheet extrusion, fiber spinning, blow molding and thermoforming. In these processes high melt strength/high extensional viscosity is desirable to ensure that the melt can be stretched without rupturing.

Extensional viscosity can be measured using Dual Bore Capillary Rheometer. Extensional viscosity is related to the entrance pressure drop inside a capillary Rheometer.

Cogswell Method for measurement of extensional viscosity (η_e) from excess pressure drop ΔP_e (i.e., the Bagley correction):

$$Extensional\ Viscosity\ (\boldsymbol{\eta_e}) = \frac{9(n+1)^2(\Delta P_e)^2}{32\eta\dot{\gamma}_a{}^2}$$

At

$$Extensional\ Rate\ \dot{\varepsilon} = \frac{4\eta\dot{\gamma}}{3(n+1)\Delta P_e}$$

Dual Bore Capillary Rheometer instrument from **Malvern (Model- Rosand RH-7)** was used for obtaining Shear viscosity and Extensional Viscosity Data.

Die Used: Capillary Die (1.0×1.6×180-15) & Zero Length Die (1.0×0.25×180-15)

Nitrogen gas was used during the experiment for creating inert atmosphere and to avoid oxidative degradation of the polymer melt.

For HDPE Raffia Grades; the experiments were done at 190^0C. Preheat time of 4 min was used. Shear rate from $100s^{-1}$ to $5000s^{-1}$ was applied.

For HDPE Large Blow Molding Grades; the experiments were done at 230^0C. Preheat time of 5 min was used. Shear rate from $20s^{-1}$ to $250s^{-1}$ was used.

Using Rosand Flow Master Analysis software Shear rate Vs Corrected Shear Viscosity curves were obtained for HDPE raffia and HDPE large blow molding grades. Extensional Viscosity Vs Extensional rate curves were also obtained for HDPE Large Blow Molding Grades using the same software.

3.5 HT-GPC (High Temperature Gel-Permeation Chromatography):

Gel Permeation Chromatography, also referred to as Size Exclusion Chromatography, is a mode of Liquid Chromatography in which the components of a mixture are separated on the basis of size or hydrodynamic volume. It is an important tool for the analysis of polymers. The essential results are molecular weight data and molecular weight distribution chromatogram. There is no upper limit in the molecular weight; even polymer analysis with molecular weight of several millions is possible.

GPC-Separation Mechanism:

- Polymer molecules dissolve in solvent (1, 2, 4-Tricholro Benzene) to form spherical coils with size dependent on molecular weight.
- Polymer coils introduced to the eluent (1, 2, 4-Tricholro Benzene) flowing through a column packed with porous gel beads.
- Smaller molecules pass through and around the beads while larger molecules excluded from all but the largest pores.
- Size separation converted to molecular weight separation by use of a calibration curve constructed by the use of polymer standards (Polystyrene Beads).

Procedure:

Highly crystalline polymers such as PE are soluble only at high temperature. This is because elevated temperatures are required to break-down the ordered crystalline structure and on cooling the material will re-crystallize and precipitate from solution. For these applications, high temperature is required throughout the entire analysis to ensure that the samples remain in solution.

Instrument used: **Polymer Laboratories' (PL-GPC 220)**

Temperature: 140^0 C (throughout the experiment)

Column Selection:

Column selection must be appropriate for the application in terms of molecular weight resolving range and efficiency of separation. The chromatographic columns were used are two PL gel MIXED-B columns. Packed with 13 µm particles for maximum resolution with minimal polymer shear, the column also can operate up to 220^0C for the analysis of highly crystalline materials. The columns with 13µm particle size also give good efficiency. In addition, the 13µm particles size ensures no shear degradation

> ➤ The solvent used for PE was 1, 2, 4-Trichloro benzene and the samples were prepared at a concentration of 1-2 mg/ml in 1, 2, 4-Trichloro benzene.
> ➤ Elevated temperature was needed for the dissolution, typically at 140°C for 5hrs.
> ➤ The volume injected into the column was 200µl at a flow rate of 1ml/min.

The molecular weight distribution chromatograms were obtained by using conventional calibration (GPC-RI System).

3.6 Dynamic Rotational Rheometer analysis [20, 21, 22]:

The standard practice for rheological experiments is to carry out experiments at 50^0C or more above the melting temperature of the polymer. At elevated temperatures, movements of polymer chains can be more easily observed. In addition, high temperatures are needed in order to avoid any possible strain induced crystallization in the polymer melt. High density polyethylene generally has its melting point around 130~135^0C, therefore we chose to conduct our experiments at 190^0C. At elevated temperatures, the thermal stability of the polymer is a key requirement therefore use of nitrogen gas to create inert atmosphere and to avoid oxidative degradation of PE was used.

In dynamic oscillatory shear experiments, a stress or strain is applied to the sample at a specific frequency (ω) and the response of the material is recorded. The stress and strain curves have the shape of a sine wave (figure 3.1), with the amplitude of

the curves being σ_0 and γ_0. The stress and strain curves differ from each other by a phase angle difference δ.

$$\sigma(t) = \sigma_0 sin\omega t$$

$$\gamma(t) = \gamma_0 \sin(\omega t - \delta)$$

σ -stress, σ_0 -stress at t = 0, ω –frequency, t -time

γ -strain, γ_0 -strain at t = 0, δ -phase angle
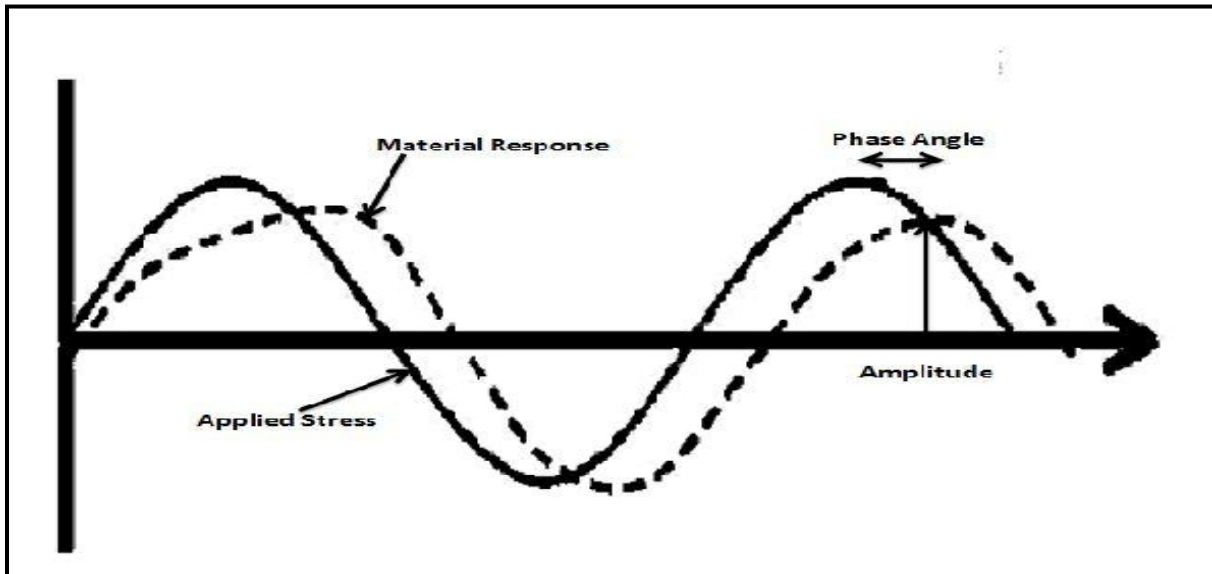
Figure 3.1: Schematic representation of stress and strain curves in an oscillatory shear experiment [23]

Based on structural mechanics, stress and strain are related through the modulus. The shear modulus in oscillatory shear analysis is called the complex modulus (G*). G* consists of a storage (G') and a loss modulus (*G*"). G' is a measure of the ability of the material to store energy (for a perfectly viscous fluid G'= 0). On the other hand, G" is a measure of its ability to dissipate energy (for a completely elastic material G"= 0). The ratio of the moduli is called damping, represented by tanδ. From the store and loss modulus, other material properties such as compliance (J*) and complex viscosity (η*) can be calculated.

$$G^* = G' + iG''$$

$$tan\delta = \frac{G''}{G'}$$

Dynamic testing has the advantage of being able to measure material response over a range of temperatures (temperature sweep) and frequencies (frequency sweep) in

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one single experiment. In temperature sweep experiments, by keeping the frequency constant and varying the temperature at a specific rate, the modulus over a range of temperatures can be determined. On the other hand, by holding the temperature constant and varying the frequency, the modulus of a material over a frequency range can be obtained.

There are many test geometries available for dynamic oscillatory shear experiments, such as the cone and plate geometry and the parallel plate geometry. The parallel plate geometry has an uneven strain field across the plate, where the material at the centre of the plate is strained very little, while the material at the edge of the plate is strained a lot. Therefore the obtained strain value from this geometry is an average value. Comparing to other geometries, the parallel plate geometry is more straightforward, and hence was selected for our experiments.

Instrument Used- **Anton Paar (Model- Physica MCR 301)**
HDPE grades were tested using the 25mm steel plate parallel plate geometry with a gap of 1mm. Experiments were carried out at 190°C under a nitrogen atmosphere to prevent oxidative degradation. Strain sweeps (from 0.01% to 100% strain) were carried out to determine the linear response region of grades at 190^0C at 1Hz frequency. Linear viscoelastic region was found at about 3% strain.

For HDPE Raffia Grades
Temperature – 190^0C
Preheat Time – 4 min
Strain – 3%
Frequency Sweep – 0.01-50 Hz

For HDPE Large Blow Molding Grades
Temperature – 190^0C
Preheat Time – 4 min
Strain – 3%
Frequency Sweep – 0.01-100 Hz

G', G'' and complex viscosity values over the range of frequencies used were obtained.

A typical response for a polymer melt was to exhibit elastic dominated behavior at high frequencies and viscous dominated behavior at low frequencies. This means that there is a critical frequency at which the two responses are equal. This is obviously a well defined point and conveniently this "cross-over" frequency and modulus (Gc) has been shown to depend on the molecular weight and molecular weight distribution of linear polymers.
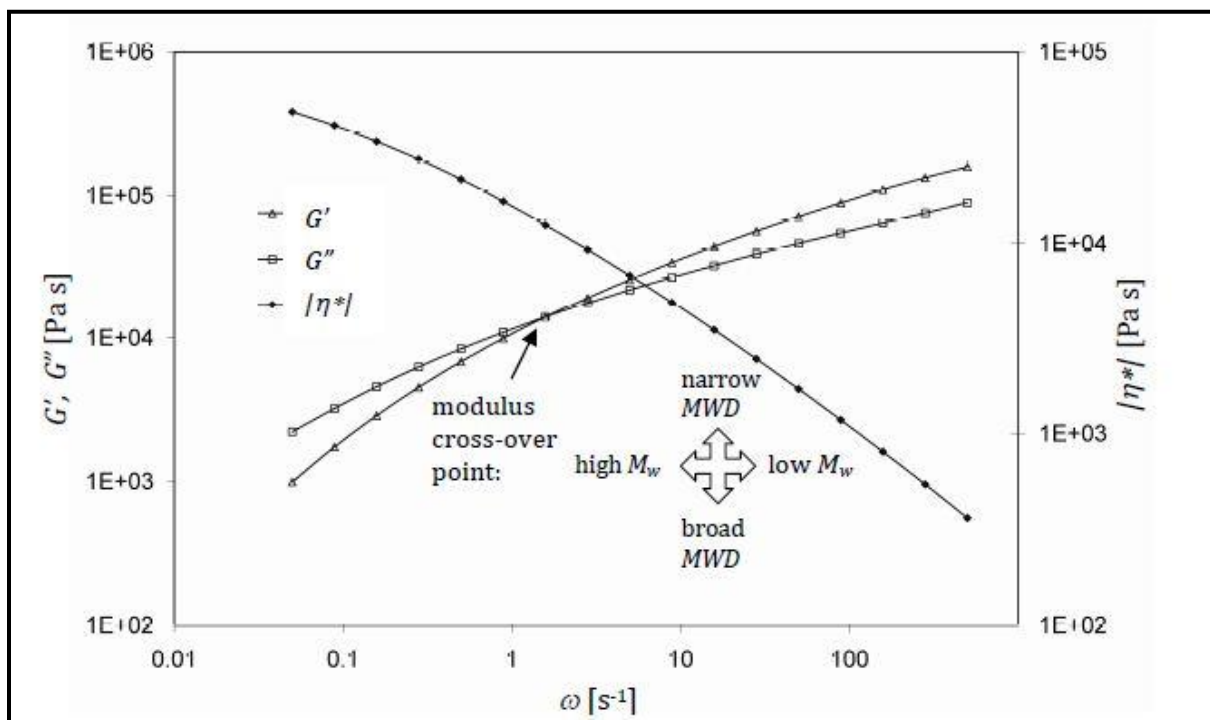
Figure 3.2: Relationship between Cross-over point location with Molecular Weight and MWD [25]

3.7 Dynamic Mechanical Analysis [22]:

Dynamic mechanical analysis (DMA) experiments utilize the same dynamic test principles described for Dynamic Rotational Rheometer experiments. The main difference between DMA and Dynamic Rotational Rheometer described in section 3.6 is that the former is done on polymer in the solid state, whereas the latter on polymer in the melt state.

The complex modulus for a viscoelastic material is defined as:

$$E^* = E' + iE''$$

Where, E' is the storage modulus relating to the energy stored by the sample in one cycle as potential energy and E" is the loss modulus which represents the energy dissipated in one cycle as heat during deformation. The ratio of the energy lost to the energy stored per cycle is defined as tan δ.

In general PE exhibit three transitions/relaxations prior to melting. These have been designated α, β and γ in order of decreasing temperature.

'α'- relaxation [26-31]:

The 'α' relaxation is due to motions of chain units which lie within the crystalline portion of the polymer. It is now well documented that, during a relaxation the chains in the crystal are mobilized (chain rotation, translation and twist) and it seems to be a very complex process associated not only with the crystalline phase but also with the amorphous phase. Sinnott demonstrated that 'α' relaxation is due to the motion of the chain folds at the crystal surfaces. Boyd has shown that the motion occurs in the amorphous phase but requires mobility of the crystals. It was also found that there exists a relation between crystal thickness and intensity of the 'α' relaxation, confirming that this process is affected by the chain mobility of the crystals and, therefore, it takes place at higher temperatures as the crystallite thickness increases. In general, its position and intensity have been related to the crystal thickness and crystallinity. The 'α' relaxation is usually observed in the temperature range 20-100°C, depending on the grade of PE.

'β'- relaxation [29, 31,32 , 34]:

The β-relaxation usually occurs between -30 and 20°C depending upon the grade of PE. The molecular origin of the β-relaxation is still unresolved but is commonly attributed to amorphous phase. Single crystals of linear PE do not exhibit a β-relaxation. Khanna et al. proposed that the enhanced intensity of the β- peak in LDPE is due to an increased amorphous volume as a consequence of branching rather than the branches themselves. Mandelkern et al. consider that it results from the motion of disordered chain units associated with the interfacial regions of semi-crystalline polymers and copolymers. In HDPE no significant 'β' relaxation has been observed.

'γ'- relaxation [(29, 31,32 , 34)]**:**

The γ-relaxation of linear and branched PE occurs between -120 and -90°C. The intensity of the γ-peak tends to decrease with increasing density indicating that it is mostly associated with the amorphous phase. Illers has shown that the γ-peak is due to the amorphous fraction while Sinnott and Hoffman attribute it to defects in the crystalline phase. They attribute the γ-transition to the association of chain end defects in the polymer crystal. Khanna et al. proposed, however, that the best model for the transition involves a crankshaft motion of short polymer chain segments involving a minimum of three to four CH_2 units in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions. The peak temperature at which γ-relaxation occurs is usually associated with the T_g (Glass Transition temperature) of PE.

HDPE raffia grades were tested on DMA instrument. Samples for testing on DMA were prepared using **Micro Injection Molding Machine (Thermo Scientific, Haake, Mini jet)**. Following conditions were used during the sample preparation.

Cylinder Temperature – 195^0C
Mold Temperature – 50^0C
Injection Pressure/Injection Time – 950 Psi/5 sec
Post Injection Pressure/Hold Time – 700 Psi/10sec
Samples thus prepared were conditioned in conditioning chamber (at 20^0C & 50% relative humidity) for 48hrs.

Instrument Used – **Dynamic Mechanical Analyser (TA Instruments, TA Q800)**
Assembly used for test – 3 point bending clamp
First linear viscoelastic region had been determined using the amplitude/strain sweep from 1-200 µm at 25^0C & using 1 Hz frequency. Linear visco-elastic region had been found at around 50 µm.
Temperature sweep experiment were conducted using conditions (frequency 1 Hz, amplitude 50µm, ramp @5^0C/min, preload force 0.03N and force track 150%), from -145^0C to 110^0C. Storage modulus, loss modulus and tan delta values were obtained against temperature.

3.8 Differential Scanning Calorimetry (DSC):

Differential Scanning Calorimeter is widely used for the determination of the melting and crystallization behavior of the polymers. It is also used for the determination of % crystallinity value of the polymer.

DSC studies were carried out on **METTLER TOLEDO DSC1** instrument to get the heat flow pattern of the polyethylene samples. The equipment was calibrated for enthalpy and onset temperature using Indium and Zinc sample as recommended by the instrument manufacturer.

Polyethylene (HDPE raffia, large blow molding grades and LLDPE blown film extrusion grades) sample amount about 5 - 10 mg for each of the grade was taken in the aluminum pan (40 μl capacity) and sealed properly.

Nitrogen gas at flow rate of 30 ml/min throughout the experiment was used in the furnace to create an inert atmosphere and to avoid oxidative degradation of the sample.

For HDPE raffia grades and LLDPE blown film extrusion grades

First the sample was heated from 30^0C up to a temperature of 170^0C @ 30^0C/min and kept at this temperature for a period of 5 min. The samples were heated beyond the melting point to remove thermal history.

Now the sample was cooled from 170^0C down to 30^0C @ 10^0C/min and kept at this temperature for 3 min.

The cooled sample was again heated from 30^0C up to 170^0C @ 10^0C/min.

For HDPE large blow molding grades

First the sample was heated from 30^0C up to a temperature of 170^0C @ 30^0C/min and kept at this temperature for a period of 5 min. The samples were heated beyond the melting point to remove thermal history.

Now the sample was cooled from 170^0C down to 30^0C @ 10^0C/min and kept at this temperature for 3 min.

The cooled sample was again heated from 30^0C up to 170^0C @ 2^0C/min.

Crystallization and subsequent melting curve (during 2nd melting stage) were obtained. Star-e software, provided by the METTLER, was used to determine the peak melting and peak crystallization temperature. Area under the melting curve was also evaluated and the area obtained (ΔH, heat of melting) was used to calculate % crystallinity by using the following formula.

$$\% \ Crystallinity = \frac{\Delta H}{\Delta H_{100\%}}$$

ΔH (j/g) corresponds to heat of melting, amount of energy which is consumed for melting and corresponding area in the thermogram.

$\Delta H_{100\%}$ (j/g) which is heat of fusion of 100% crystalline PE and its value for PE is 290j/g [35].

3.9 ^{13}C – Nuclear Magnetic Resonance Spectroscopy [24]:

Carbon-13 nuclear magnetic resonance spectroscopy (13C NMR) is a type of NMR used for study of organic compounds. When a polymer sample is placed in a magnetic field and excited by electromagnetic radiation, carbon-13 and other NMR active nuclei 'flip' from one energy level to the next, thus generating the nuclear magnetic resonance spectrum. The energy absorbed by each type of nuclei is characteristic at a specific resonance frequency. Hence identification of different types of chemical compounds is possible by comparing sample NMR spectra to a reference spectrum. Different structures of the same type of nuclei also generate a slight difference in resonance frequency, called the chemical shift. The intensity of NMR spectrum peaks gives an indication of the amount of each type of nuclei present. In 13C NMR the chemical shift can be used to identify different types of branching structures in polyethylene and to calculate average no of branching/1000C.

For LLDPE blown film extrusion grades, 0.20-0.25 gm. of sample had been dissolved in 1,2,4-trichlorobenzene to prepare a concentration of ~20 wt./vol.% of polymer solution. After swelling of polymers at 130^{0}C for 1 h, deuterated solvents such as

1,1,2,2-tetrachloroethane-d2 had been added as lock solvent. 13C-NMR spectra were acquired at 130^{0}C on a **Bruker AV 300 spectrometer** at 75.0 MHz for 13C nuclei with 90° pulse angle and 3000 transients. Power gated pulse sequence was applied to ensure equal NOE throughout the NMR spectrum.

The internal standard most often used in high-temperature NMR studies of polymers in solution is Hexamethyldisiloxane (HMDS). 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 has been established independently. The chemical shifts were also referenced internally to the major backbone methylene carbon resonance, taken as 30.0 ppm from TMS.

Instrument Parameters:

Pulse program, Zgig/Zgpg

Pulse angle, 90o

Pulse width, 8.4 μs

Pulse repletion, 10 s

Data size, 32 k

Sweep width, 200 ppm

Temperature, 398-403 deg K (120-130 deg C)

Number of scan, 3000-4000

3.10 Crystallization Analysis Fractionation (CRYSTAF) [36]:

Crystallization Analysis Fractionation, CRYSTAF, is a technique for the analysis of the comonomer distribution in semi-crystalline polymers and more specifically for the analysis of short chain branching distribution in LLDPE. In CRYSTAF the analysis is carried out by monitoring the polymer solution concentration during crystallization by a concentration detector. In fact the whole process is similar to a classical stepwise fractionation by precipitation with the exception that in this approach no attention is paid to the polymer precipitated but to the polymer which remains in solution.

In CRYTAF during experiment the first data points, taken at temperature above any crystallization, provide a constant concentration equal to the initial polymer solution concentration (zone 1 in figure3.3); as temperature goes down the most crystalline fractions , composed of molecules with zero or very few branches will precipitate first, resulting in a steep decrease in solution concentration (zone 2). This is followed by the precipitation of fractions of increasing branch content as temperature continues to decrease (zone 3). The last data point, corresponding to the lowest temperature of the crystallization cycle represents the fraction which has not crystallized (mainly highly branched material) which we refer as soluble fraction.
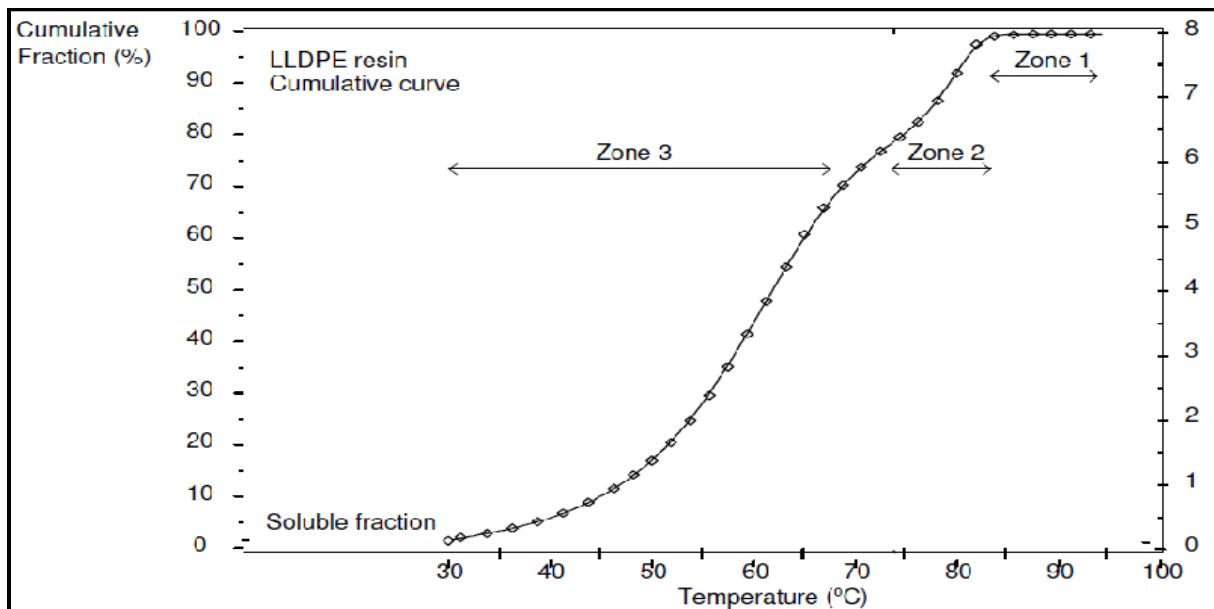
Figure 3.3: General LLDPE CRYSTAF cumulative curve [(36)]

The first derivative of this curve can be associated with the short chain branching distribution as shown in figure.
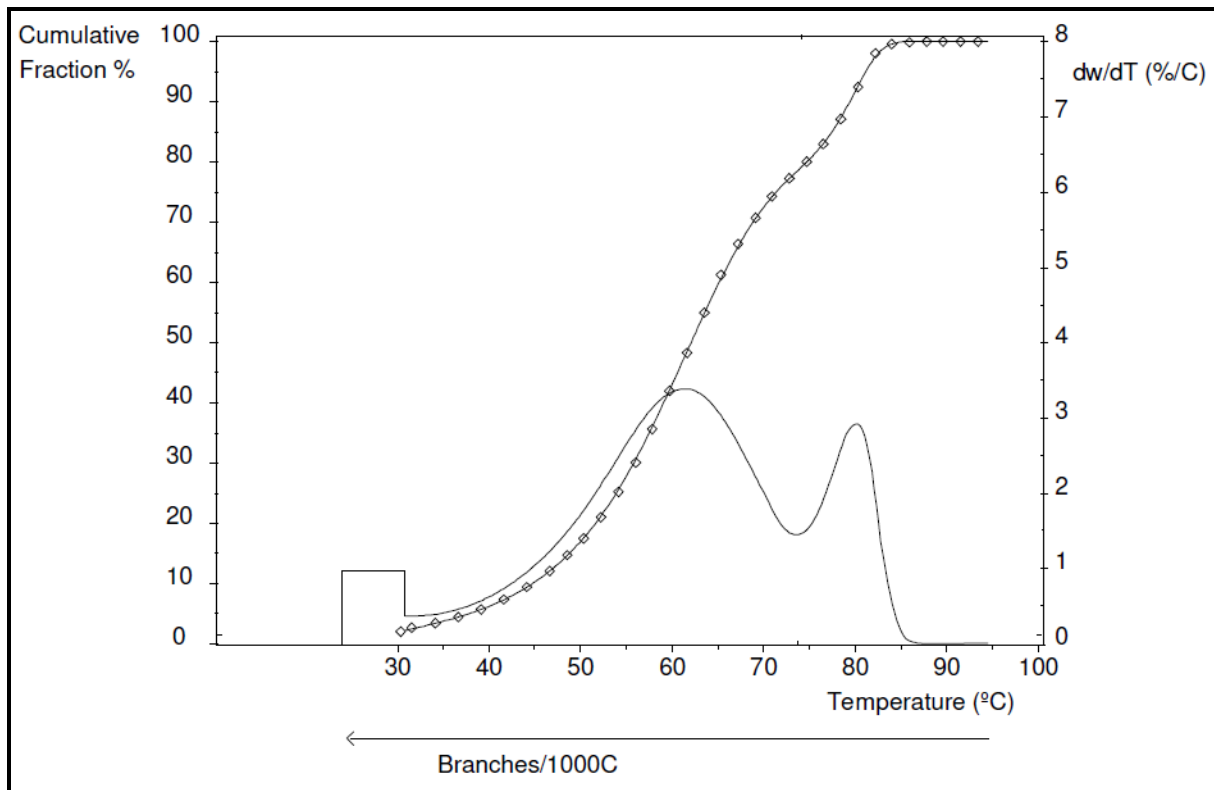
Figure 3.4: General LLDPE resin CRYSTAF cumulative and first derivative curves [36]

CRYSTAF analysis, for LLDPE grades, was carried out on CRYSTAF instrument (Polymer Char). About 40 mg of sample was dissolved in 40 ml of 1,2,4-trichlorobenzene (containing 300ppm antioxidant). The solution was first heated up to a temperature of 160^0C @ 30^0C/min and kept for 60 min. Then it was cooled back to 95^0C @30^0C and solution was stabilized for 45 min at his temperature. Now the solution was cooled from 95-35^0C @ 0.2^oC/min and then kept at 35^0C for 10 min.

4.0 RESULT AND DISCUSSION

4.1 HDPE RAFFIA GRADE

GRADE DETAILS:

Table 4.1: HDPE Raffia Grade Details

S. No.	Grade
1	HD/R/I-018
2	HD/R/I-022
3	HD/R/I-025
4	HD/R/R-027
5	HD/R/R-067
6	HD/R/G
7	HD/R/H

4.1.1 Density:

The value of density for each grade was calculated by using Density Gradient Column technique and given in table 4.2.

Table 4.2: Density values for HDPE Raffia Grades

S. No.	Grade	Density (g/cc)
1	HD/R/I-018	0.9501
2	HD/R/I-022	0.9498
3	HD/R/I-025	0.9503
4	HD/R/R-027	0.9547
5	HD/R/R-067	0.9521
6	HD/R/G	0.9503
7	HD/R/H	0.9495

Density for grades HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/G and HD/R/H was found to be almost similar. But the value for HD/R/R-027 (0.955 g/cc) and HD/R/R-067 (0.952 g/cc) grades was higher as compared to all other grades.

4.1.2 Melt Flow Index and Melt Flow Ratio:

Melt flow index of HDPE raffia grades were done as per the ASTM D 1238 at four different weights (2.16, 5, 10.96 & 20.6 Kg) at the temperature of 190°C.
The MFI at 2.16kg load along with shear rate and melt viscosity are given below in table 4.3.

Table 4.3: MFI and melt viscosity @2.16 values for HDPE Raffia Grades

S. No.	Grade	Weight(kg) /temp.(^{0} C)	MFI (g/10min)	Shear Rate (s^{-1})	Melt Viscosity (Pa.s)
1	HD/R/I-018	2.16kg/190^{0}C	0.9	2.1	9137
2	HD/R/I-022	2.16kg/190^{0}C	0.8	2.0	9869
3	HD/R/I-025	2.16kg/190^{0}C	0.77	1.9	10452
4	HD/R/R-027	2.16kg/190^{0}C	1.1	2.7	7239
5	HD/R/R-067	2.16kg/190^{0}C	0.9	2.1	9012
6	HD/R/G	2.16kg/190^{0}C	0.9	2.2	8650
7	HD/R/H	2.16kg/190^{0}C	1.1	2.6	7411

Above data shows that at 2.16kg load, HD/R/I-025 and HD/R/I-022 had lower MFI values and higher melt viscosity values as compared to all other grades.

The MFI values of HD/R/I-018, HD/R/G and HD/R/H were found to be same but HD/R/I-018 had higher melt viscosity than HD/R/G and HD/R/H.

HD/R/R-027 and HD/R/H grades had higher MFI and lower melt viscosity values as compared to all other grades.

HD/R/R-067 grade had higher MFI values and less melt viscosity than HD/R/I-025 and HD/R/I-022. HD/R/R-067 had same MFI value when compared to HD/R/G and HD/R/I-018 grades, and less MFI value than HD/R/H and HD/R/R-027 grades. HD/R/R-067 had higher melt viscosity than HD/R/R-027, HD/R/G and HD/R/H grades, but has slightly less melt viscosity when compared to HD/R/I-018 grade.

It was clear from above discussion that HD/R/I-025 and HD/R/I-022 had lower MFI than HD/R/G. The melt viscosities of HD/R/I-025, HD/R/I-022 and HD/R/I-018 were found to be on higher side when compared to the other raffia grades specially HD/R/G, which is the indication of presence of more high molecular weight fraction. Higher melt viscosity of HD/R/I-025 and HD/R/I-022 grades could be the reason for more power consumption than HD/R/G.

The values of MFI and MFR calculated at various loads and respective shear rates and melt viscosities are mentioned below in table 4.4.

Table 4.4: MFI and MFR values along with melt viscosity for HDPE Raffia grades at 5kg, 10.96kg and 20.6kg loads

Grade	MFI	MFR	Shear Rate (s^{-1})	Melt viscosity, (pa.s)
At 5.0 kg				
HD/R/I-018	3.1	3.4	7.3	6122
HD/R/I-022	2.6	3.3	6.5	6890
HD/R/I-025	2.6	3.4	6.5	6955
HD/R/R-027	3.2	2.9	8.0	5599
HD/R/R-067	3	3.3	7.3	6216
HD/R/G	3.1	3.4	7.9	5708
HD/R/H	2.9	2.6	7.2	6252
At 10.96 kg				
HD/R/I-018	9.5	10.6	23.2	4241
HD/R/I-022	8.7	10.9	21.4	4584
HD/R/I-025	8.5	11.1	20.7	4744
HD/R/R-027	8.8	8.0	21.8	4499
HD/R/R-067	9.6	10.7	23.5	4196

HD/R/G	9.8	10.9	24.0	4058
HD/R/H	7.8	7.1	19.0	5160
At 20.6				
HD/R/I-018	33.6	37.3	82.2	2245
HD/R/I-022	30.9	38.6	75.7	2438
HD/R/I-025	29.8	38.8	73.3	2519
HD/R/R-027	25.2	23.0	61.9	2985
HD/R/R-067	34.4	38.2	84.5	2184
HD/R/G	36.2	40.2	88.7	2081
HD/R/H	21.6	19.6	53	3486

At 5kg load

At 5kg load too HD/R/I-025 and HD/R/I-022 grades had lower MFI values and high melt viscosity values when compared to HD/R/G; however HD/R/I-018 had same MFI at 5kg load but higher melt viscosity than HD/R/G grade. MFR values at 5kg load for HD/R/G, HD/R/I-025, HD/R/I-022 and HD/R/I-018 grades were found to be nearly similar.

HD/R/I-025 and HD/R/I-022 grades shows very high melt viscosity at 5kg load when compared to all other grades.

HD/R/H had higher MFI value at 5kg load when compared to HD/R/I-025 and HD/R/I-022 grades but had less MFI value than HD/R/I-018 and HD/R/G grades.

HD/R/R-027 had highest MFI and lowest melt density value at 5kg load as compared to all other grades but had lower MFR values than all other grades except HD/R/H.

HD/R/R-067 had nearly similar value of MFI at 5kg load when compared to HD/R/I-018, HD/R/G and HD/R/H grades but had higher MFI value when compared to HD/R/I-025 and HD/R/I-022 .HD/R/R-067 had nearly similar MFR values at 5kg load as compared to all the grades except HD/R/R-067 and HD/R/H grades, which had lower MFR than HD/R/R-067.

At 10.96kg load

At 10.96kg load HD/R/G had highest MFI values when compared to HD/R/I-025, HD/R/I-022, HD/R/R-027 and HD/R/H grades; and had nearly the similar value of MFI as compared to HD/R/I-018 and HD/R/R-067. HD/R/G has comparable value of MFR at 10.96kg load when compared to other grades except HD/R/R-027and HD/R/H grades which had lower MFR value than HD/R/G. When compared, melt viscosity at 10.96kg load it was found that HD/R/G had lower value when compared to all other grades.

HD/R/H had lowest MFI and MFR value at 10.96kg load when compared to other grades, and had highest melt viscosity at this load than all other grades.

HD/R/I-025 and HD/R/I-022 had lower MFI values and higher melt viscosity than HD/R/G, HD/R/R-067, HD/R/R-027 and HD/R/I-018 grades, & had lower melt viscosity when compared to HD/R/H.

At 20.6kg load

At 20.6kg load, HD/R/G had highest MFI, highest MFR and lowest melt viscosity value when compared to all other grades.

HD/R/I-025 and HD/R/I-022 had nearly similar MFI and MFR values and comparable melt viscosity at 20.6kg load. Both these grades had lower MFI values when compared to HD/R/G, HD/R/R-067 and HD/R/I-018; but had higher MFI value when compared to HD/R/R-027 and HD/R/H.

HD/R/H had lowest MFI and MFR value at 20.6kg load and highest melt viscosity than all other grades.

HD/R/R-027 had lower MFI and MFR value, and higher melt viscosity value as compared to all other grades except HD/R/H grade.

From the above MFI & MFR data, it was found that HD/R/G has higher MFI values and lesser melt viscosity at each load (2.16, 5.0, 10.96 & 20.6kg) when compared to HD/R/I-025 , HD/R/I-022. This clearly indicated that HD/R/G grade had better flow ability relative to HD/R/I-025 and HD/R/I-022 grades, and could

be related to less power consumption than HD/R/I-025 and HD/R/I-022 during the trials.

HD/R/G had comparable MFI and MFR values at each load (2.16, 5.0, 10.96 & 20.6kg) when compared to HD/R/I-018 but had lower melt viscosity values at each load.

HD/R/G had nearly similar MFR values at each load (5.0, 10.96 & 20.6kg) when compared to HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/R-067 which indicated towards the almost similar broadness of molecular weight distribution.

HD/R/R-027 had lower MFR values at each load (5.0, 10.96 & 20.6kg) when compared to all other grades except HD/R/H, which indicated toward the narrow broadness of the molecular weight distribution than all grades except HD/R/H.

HD/R/H at loads (5.0, 10.96 & 20.6kg) had least MFR value when compared to all other grades which indicated that HD/R/H had narrowest molecular weight distribution.

4.1.3 Shear viscosity data using Power law model:

The Power law constants n and m were calculated, using formula given in section 3.3.2, for HDPE raffia grades.

Table 4.5: Power law constants (n and m) values for HDPE Raffia grades

S. No	Grade	Power law exponent (n)	Consistency index (m)
1	HD/R/I-018	0.62	159.1
2	HD/R/I-022	0.62	178.5
3	HD/R/I-025	0.62	186.6
4	HD/R/R-027	0.72	64.2
5	HD/R/R-067	0.62	165.3
6	HD/R/G	0.61	176.3
7	HD/R/H	0.76	48.2

The Power law exponent values for all the grades were found to be similar except for HD/R/R-027 and HD/R/H grades, for which the value of n was much higher and these higher value indicate towards the less shear thinning behaviour of these grades. The consistency index value for HD/R/R-027 and HD/R/H grades was exceptionally low as compared to all other grades.

From the values of n and m obtained above and using Power-law equation, the shear viscosity values at shear rates from 100-1000s^{-1} for each grade were calculated. The curves had been plotted for shear rate vs. shear viscosity on log scale for all grades.
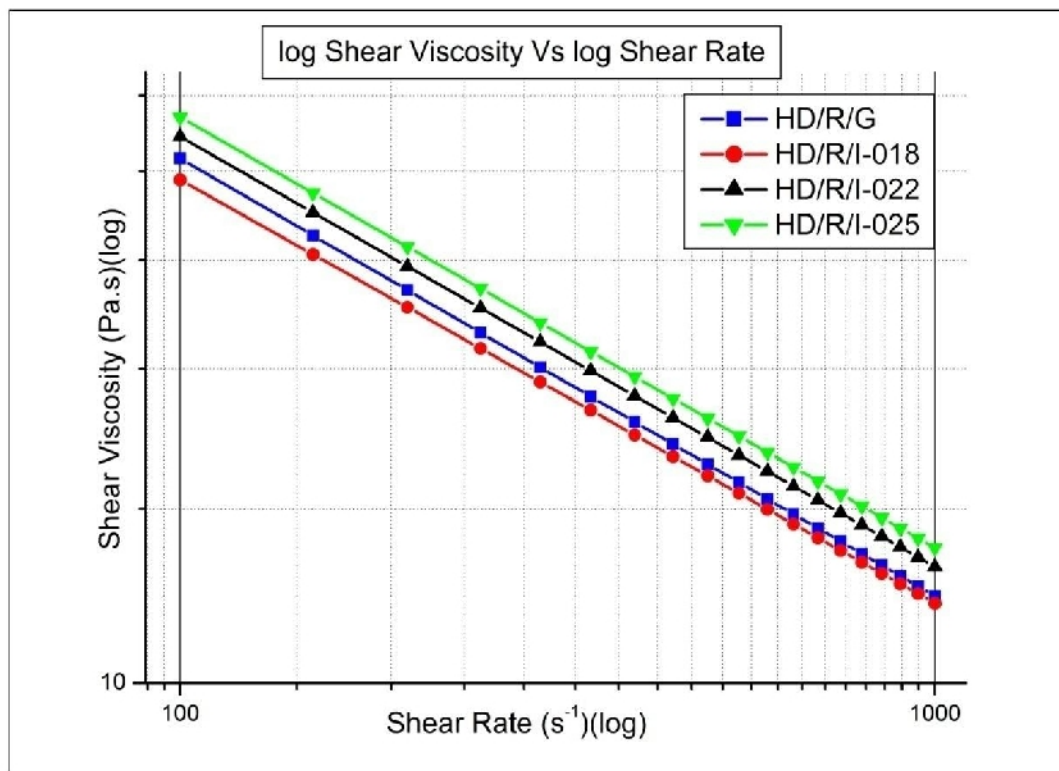
Figure 4.1: log shear rate Vs log shear viscosity for HD/R/G, HD/R/I-025, HD/R/I-022 and HD/R/I-018 grades

It was clearly visible from the figure 4.1 that HD/R/I-025 had higher shear viscosity over the whole range of shear rate with respect to other grades HD/R/I-022, HD/R/I-018 and HD/R/G, which indicated towards the higher power consumption in the trials conducted. Similar pattern was obtained for HD/R/I-022 which had higher shear

viscosity than HD/R/G over the entire range of shear rate which directly indicated towards the higher power consumption during trials compared to HD/R/G.

HD/R/I-018 had lower shear viscosity values over the entire range of shear rate when compared to HD/R/I-025, HD/R/I-022 and HD/R/G.
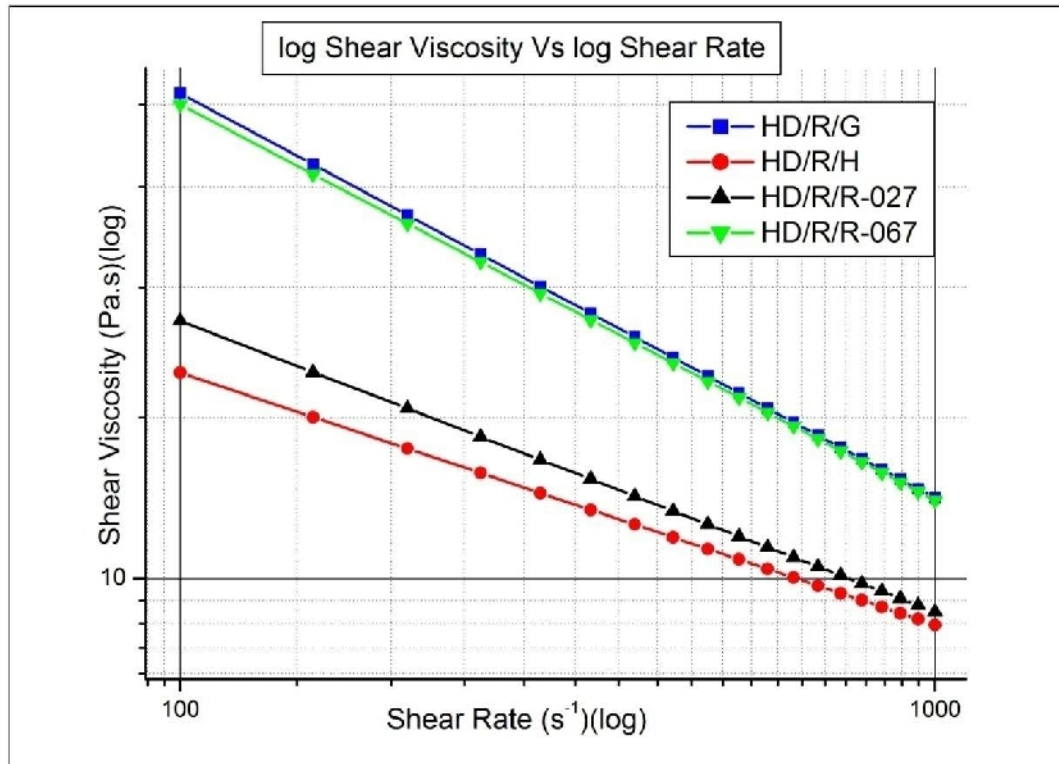
Figure 4.2: log shear rate(s^{-1}) Vs log shear viscosity (Pa.s) curve for HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H

From the figure 4.2 it was clear that HD/R/G and HD/R/R-067 had nearly similar shear viscosity over the entire range of shear rate. HD/R/H had low shear viscosity over the entire range of shear rate as compared to HD/R/G, HD/R/R-067 and HD/R/R-027. Thus HD/R/R-027, HD/R/G and HD/R/R-067 may have higher high molecular weight chain tail as compared to HD/R/H grade. HD/R/R-027 had low shear viscosity over the entire range of shear rate as compared to HD/R/R-067 and HD/R/G but had higher shear viscosity value than HD/R/H over the entire shear rate range.

To visualize the effect of shear rate on viscosity, a common graph for all grades was plotted.
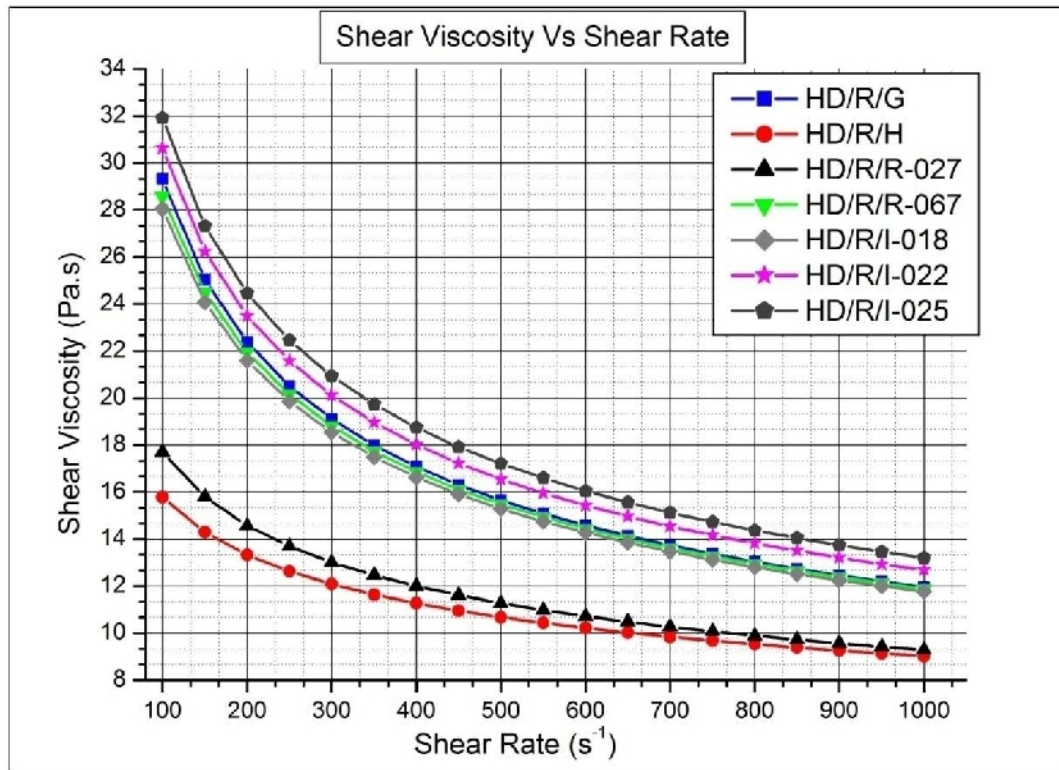
Figure 4.3: shear rate(s^{-1}) Vs shear viscosity (Pa.s) curve for HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H grades

It was thus found that HD/R/I-025 and HD/R/I-022 grades have higher shear viscosity over entire range of shear rate as compared to HD/R/G grade. This higher shear viscosity can be related to the higher power consumption by HD/R/I-025 and HD/R/I-022 grade as compared to HD/R/G grade.

4.1.4 Capillary Rheometer analysis:

Shear viscosity Vs corrected shear rate values were obtained from Capillary Rheometer and plotted against each other for all the grades.
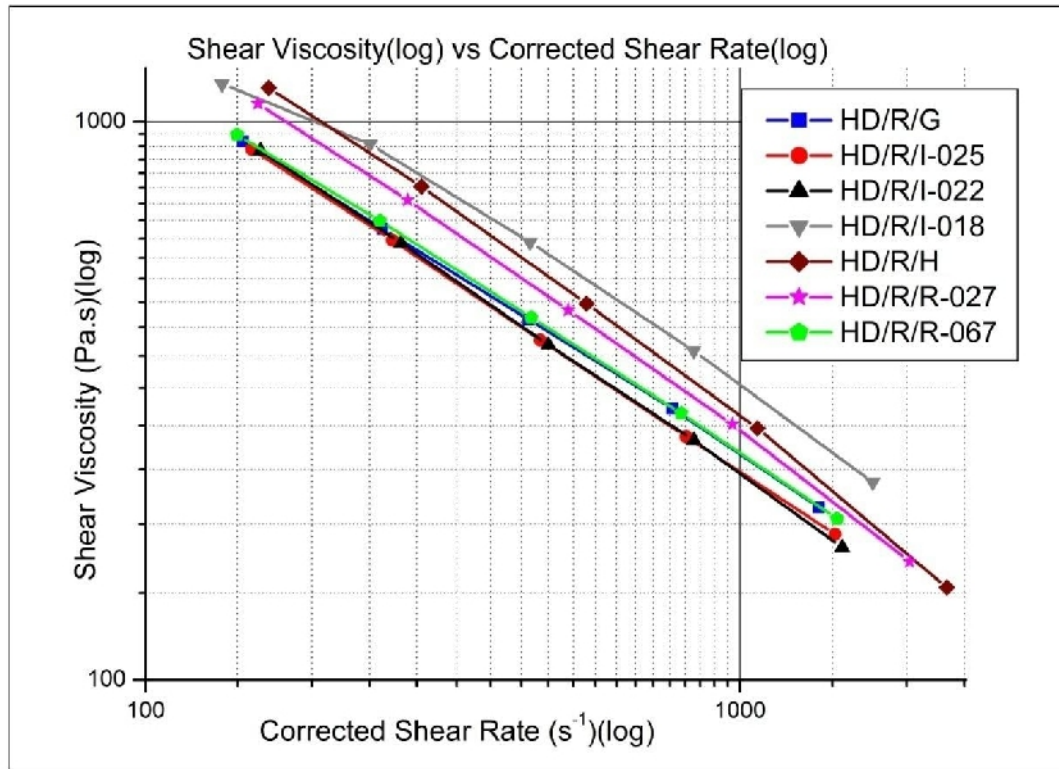
Figure 4.4: Shear Viscosity Vs Corrected Shear Rate curve (on log scale) for HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H grades

From the above figure it was found that HD/R/G, HD/R/R-067, HD/R/I-022 and HD/R/I-025 had almost identical profile of shear viscosity over the entire range of corrected shear rate. The values of shear viscosity at different shear rate for grades HD/R/R-027, HD/R/H and HD/R/I-018 were found to be on higher side as compared to HD/R/G.

4.1.5 <u>Dynamic Rotational Rheometer and High Temperature GPC analysis:</u>

Complex viscosity Vs Angular frequency curve for HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H was plotted from the data obtained from Parallel Plate Rheometer.
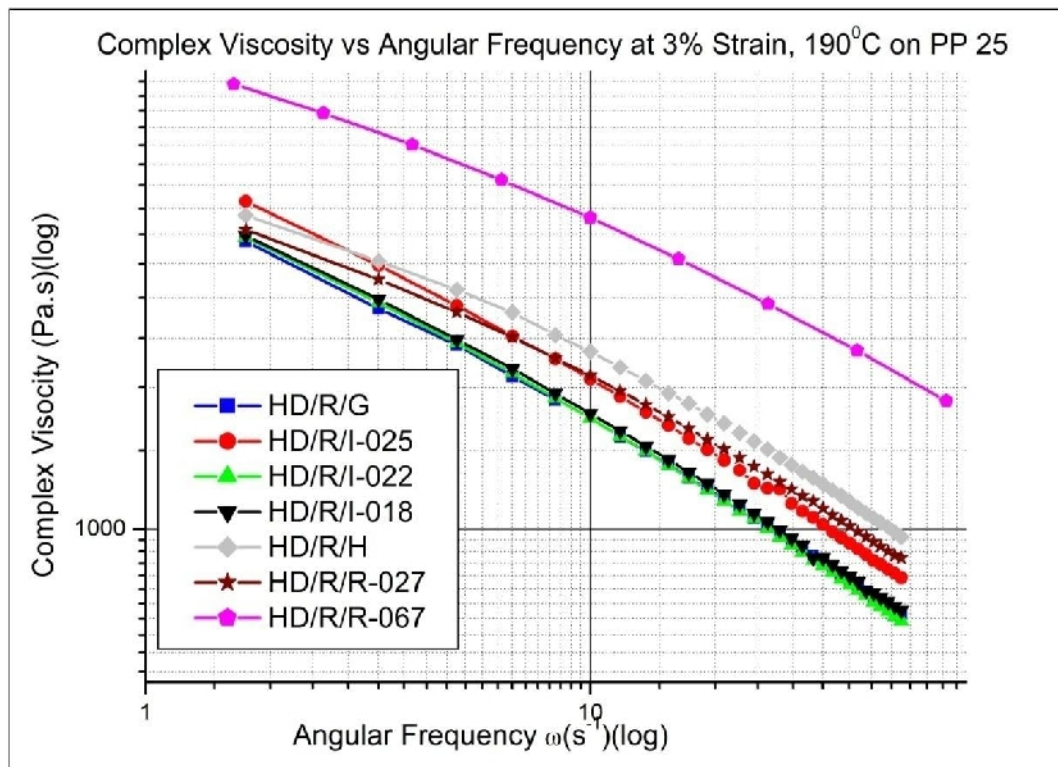
Figure 4.5: Complex Viscosity Vs Angular Frequency curve for HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H grades

The above figure 4.5 clearly indicated that HD/R/G, HD/R/I-022 and HD/R/I-018 had nearly similar complex viscosities over entire range of angular frequencies. HD/R/I-025, HD/R/R-027 and HD/R/H had higher complex viscosity over all angular frequencies when compared to HD/R/G. HD/R/R-067 had highest value of complex viscosity over the entire range of angular frequencies used.

HD/R/G Vs HD/R/I-025:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/R/G and HD/R/I-025 grades.
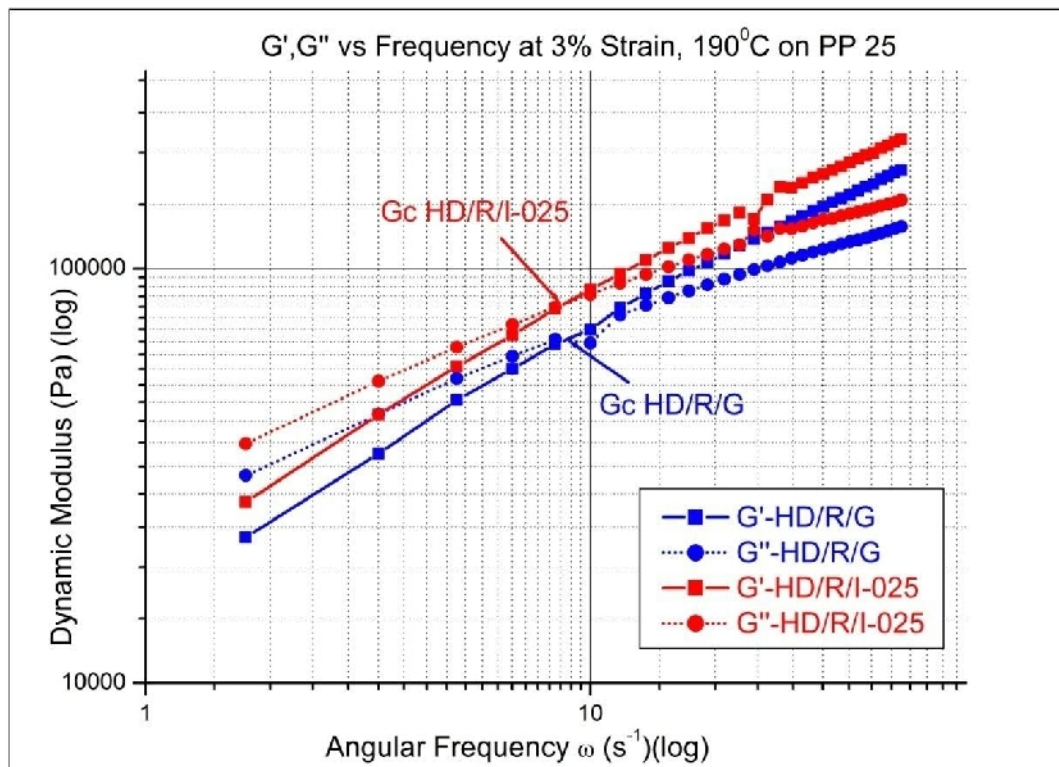
Figure 4.6: G', G'' vs. angular frequency curve for HD/R/I-025 and HD/R/G grades

Molecular Weight Distribution chromatogram for HD/R/G and HD/R/I-025 obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.

Figure 4.7: MWD chromatogram for HD/R/I-025 and HD/R/G grades

Figure 4.8: MWD Chromatogram (low molecular weight fraction and high molecular weight fraction zoom) for HD/R/G, HD/R/I-025, HD/R/I-022 and HD/R/I-018 grades

From figure 4.7, it was clear that HD/R/I-025 had higher complex viscosity value than HD/R/G over the entire range of angular frequencies used. When G' and G'' values were compared (figure 4.6) between HD/R/G and HD/R/I-025, it was found that HD/R/I-025 had higher values of G' and G'' than HD/R/G over entire frequency range. The value of cross over modulus (Gc) for HD/R/I-025 had higher value than HD/R/G. On comparing the broadness of MWD chromatogram (figure 4.7) for both the grades it was found to be the almost similar but HD/R/I-025 grade had the MWD chromatogram shifted slightly towards right (higher molecular weight fraction side) indicating high molecular weight of HD/R/I-025 than HD/R/G. The same was evident from the complex viscosity graph, that HD/R/I-025 had higher complex viscosity than HD/R/G. When we looked at the high molecular weight tail (figure 4.8) there was hardly any difference between the two grades but when we looked at the low molecular weight tail (figure 4.8), we found that HD/R/G had higher low molecular weight tail as compared to HD/R/I-025.

Thus from above discussion it was found that HD/R/I-025 had higher G', G'' and complex viscosity values than HD/R/G grade which can be related to the shift of HD/R/I-025 MWD chromatogram slightly towards the right than HD/R/G's MWD chromatogram. From MWD chromatogram (figure 4.8), it was evident that HD/R/I-025 had lower fraction of low molecular wt. tail than HD/R/G grade.

HD/R/G Vs HD/R/I-022:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/R/G and HD/R/I-022 grades.
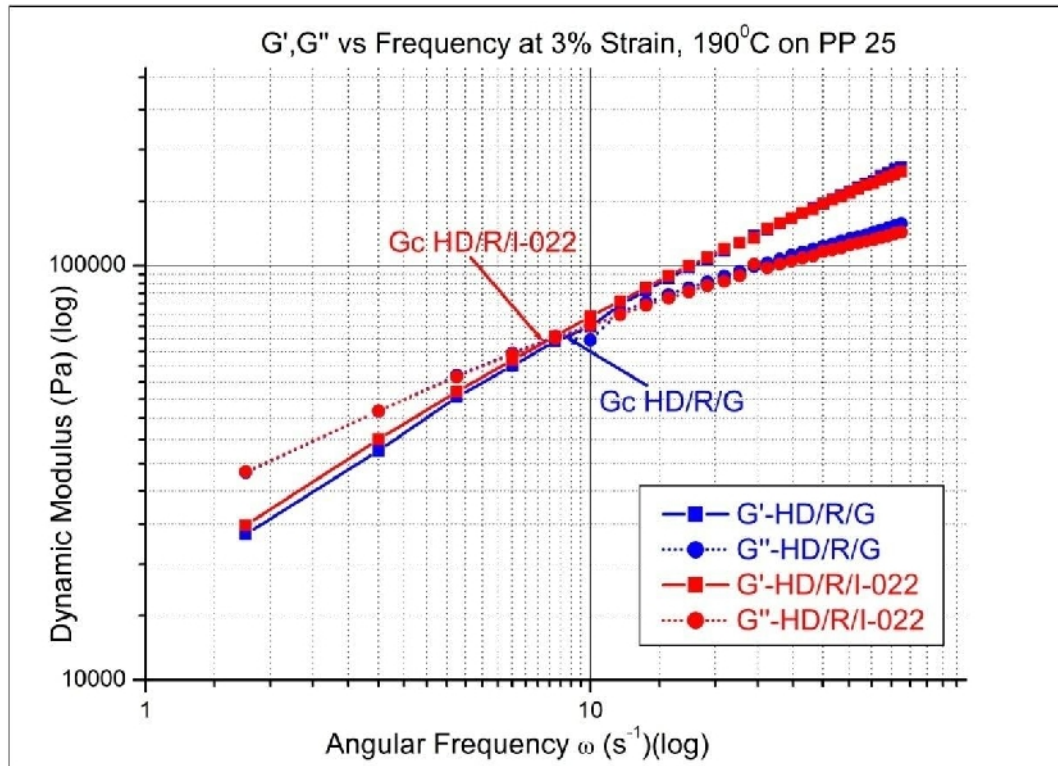
Figure 4.9: G', G'' vs. angular frequency curve for HD/R/I-022 and HD/R/G

From figure 4.5, it was found that HD/R/G and HD/R/I-022 had nearly similar complex viscosity over the entire range of angular frequencies. From figure 4.9, it was clearly visible that both grades had nearly similar G' and G'' values over whole range of frequencies. The values of cross-over modulus were also found to be nearly identical.

Molecular Weight Distribution chromatogram for HD/R/G and HD/R/I-025 obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
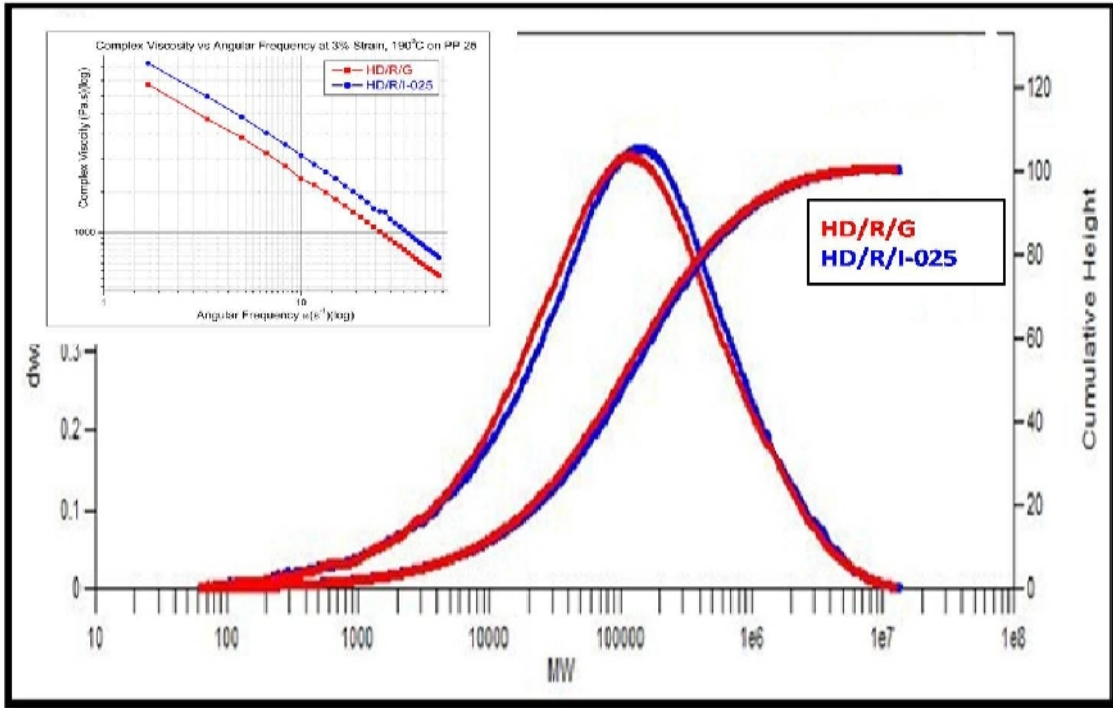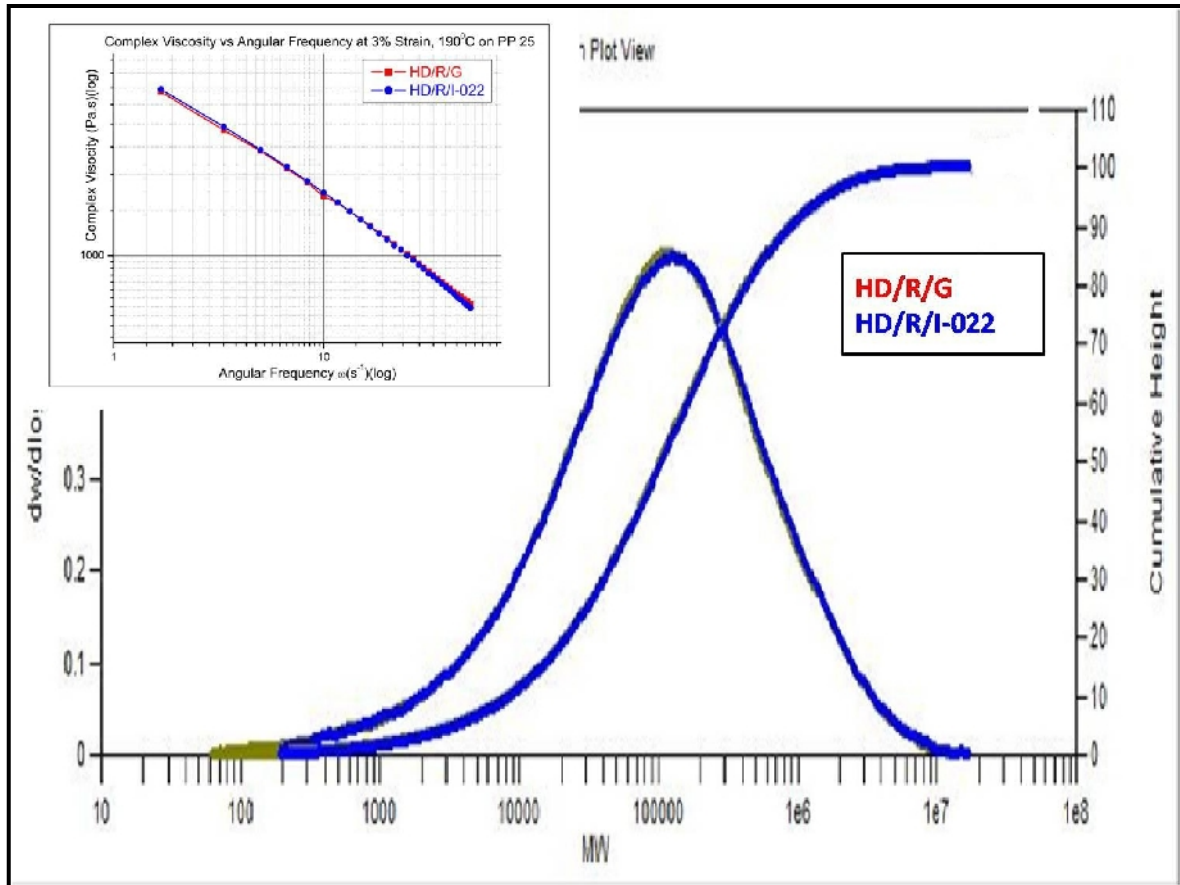
Figure 4.10: MWD chromatogram for HD/R/I-022 and HD/R/G grades

From the above MWD distribution curve (figure 4.10) obtained from HT-GPC we found that both grades had nearly the same broadness of MWD but in HD/R/G grade there was slight less high molecular weight tail when compared to HD/R/I-022 grade (figure 4.8) due to which HD/R/I-022 grade had little higher molecular weight value than HD/R/G. HD/R/G had higher low molecular weight tail (figure 4.8) than HD/R/I-022, which could be helpful during stretching at higher line speed.

Thus from above discussion it was found that HD/R/I-022 grade had lower fraction of low molecular wt. chain tail as compared to HD/R/G grade; and had slightly higher fraction of high molecular wt. tail than HD/R/G grade while the loss modulus, storage modulus and complex viscosity values were nearly identical.

HD/R/G Vs HD/R/I-018:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/R/G and HD/R/I-018 grades.
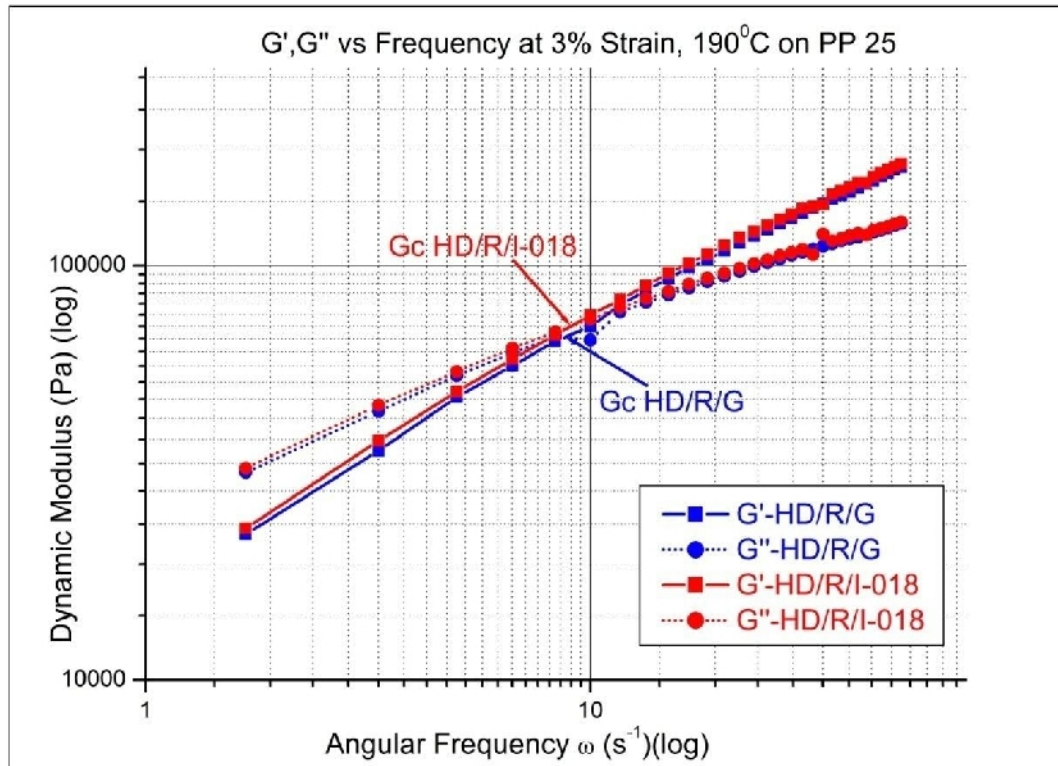
Figure 4.11: G', G'' vs. angular frequency curve for HD/R/I-018 and HD/R/G

From figure 4.5, we found that HD/R/I-018 and HD/R/G had nearly similar complex viscosity values over the entire range of angular frequencies. G' and G'' values (figure 4.11) were also found to be nearly identical (HD/R/I-018 had slight higher values of G', G'' than HD/R/G) over the entire range of angular frequencies and moreover the value of cross-over modulus for both grades were found to be nearly similar.

Molecular Weight Distribution chromatogram for HD/R/G and HD/R/I-025 obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
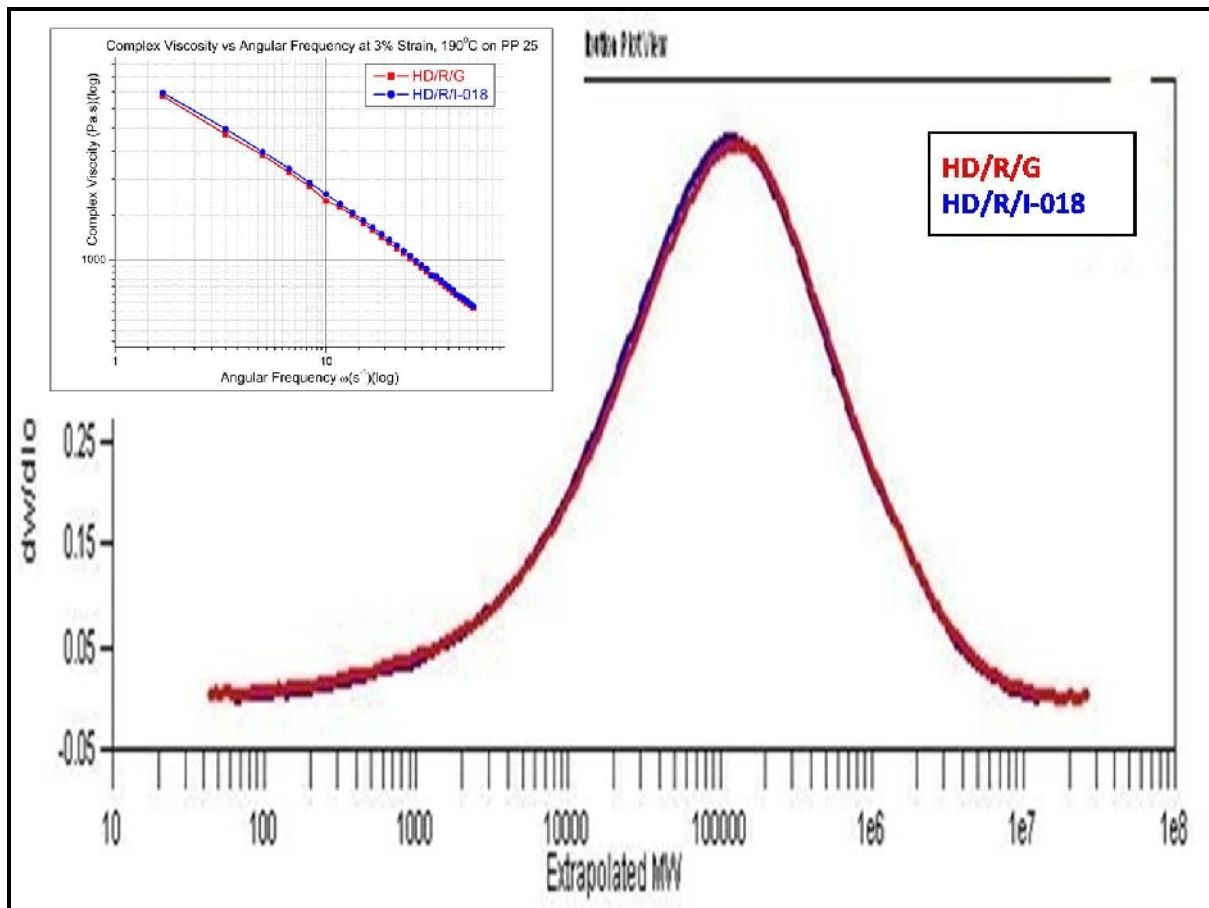
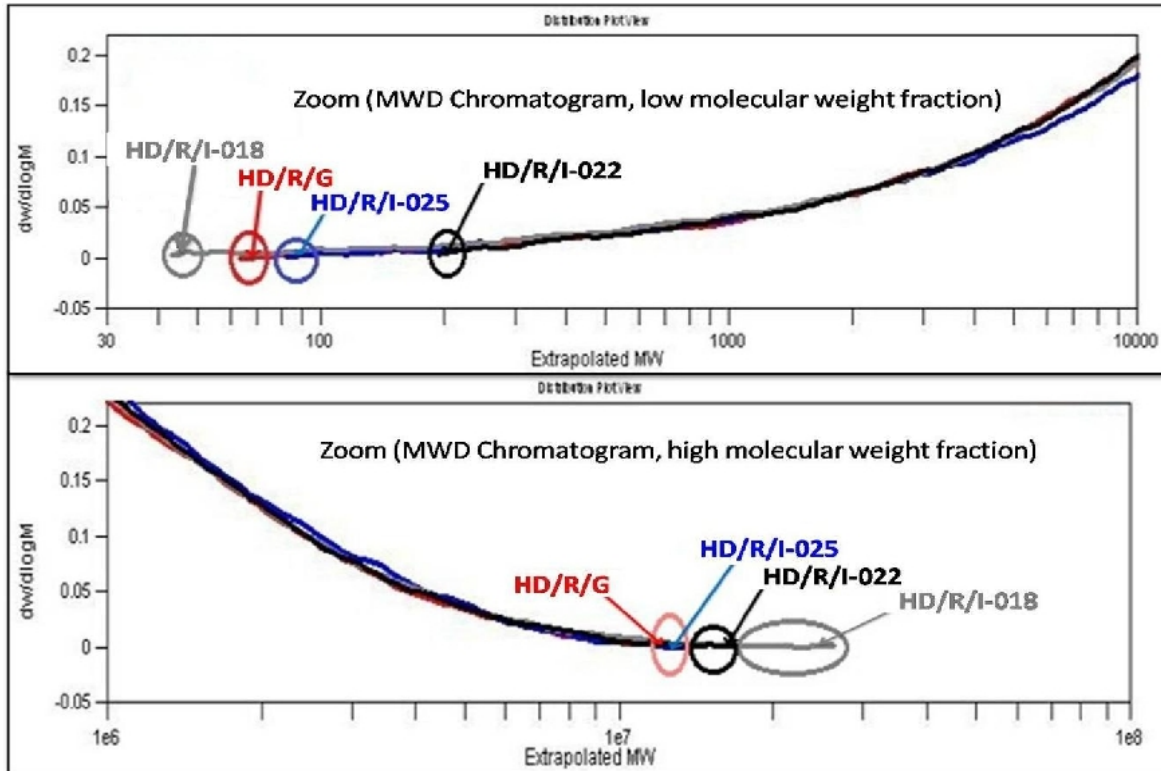**Figure 4.12: MWD chromatogram for HD/R/I-018 and HD/R/G grades**

From the above MWD distribution chromatogram (figure 4.12) obtained from HT-GPC we found that both grades had nearly the same broadness and overlapping each other but HD/R/I-018 grade has slightly higher concentration of high molecular weight tail (figure 4.8) as well as higher concentration of low molecular weight tail (figure 4.8) as compared to HD/R/G. As high molecular weight tail was complemented by low molecular weight tail in HD/R/I-018, but still the HD/R/I-018 had higher molecular weight value than HD/R/G which was also visible in G' and G'' values (HD/R/I-018 had slight higher values of G', G'' than HD/R/G).

Thus from above discussion it was found that HD/R/I-018 grade had higher fraction of high molecular weight tail as well as higher fraction of low molecular weight tail as compared to HD/R/G while both the grades had nearly similar loss modulus, storage modulus and complex viscosity values.

HD/R/G Vs HD/R/R-067 Vs HD/R/H:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/R/G, HD/R/R-067 and HD/R/H grades.

Figure 4.13: G', G'' vs. Angular Frequency curve for HD/R/G and HD/R/H
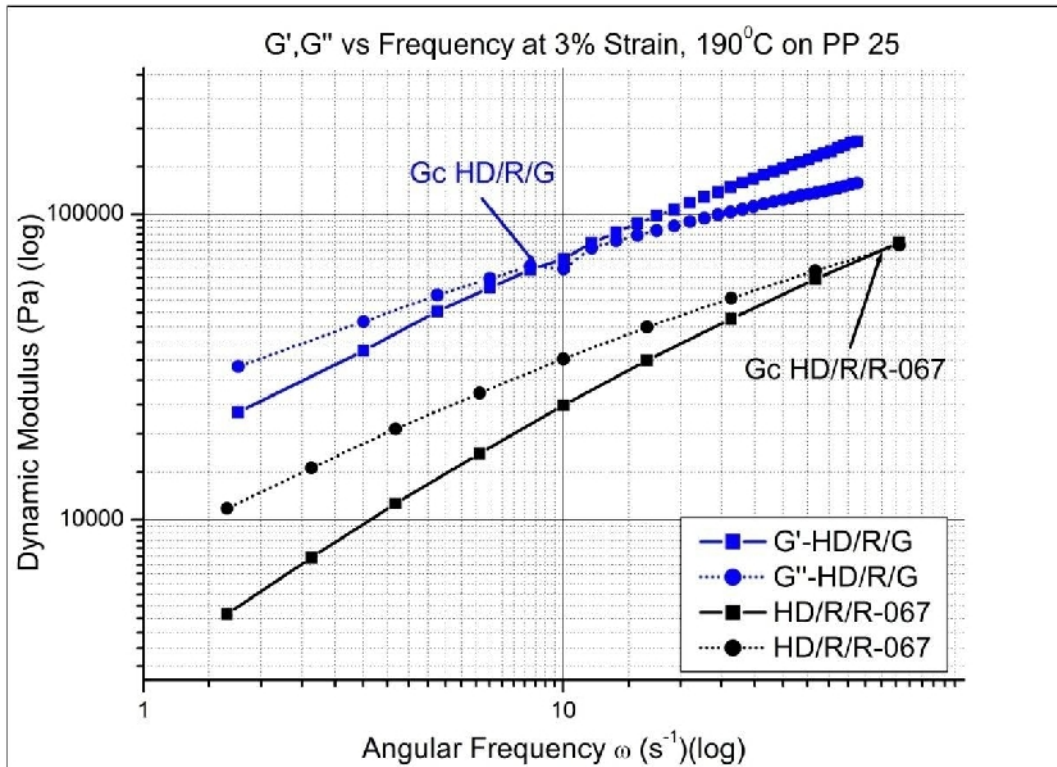
Figure 4.14: G', G" vs. Angular Frequency curve for HD/R/G and HD/R/R-067

Molecular Weight Distribution chromatogram for HD/R/G, HD/R/R-067 and HD/R/H obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
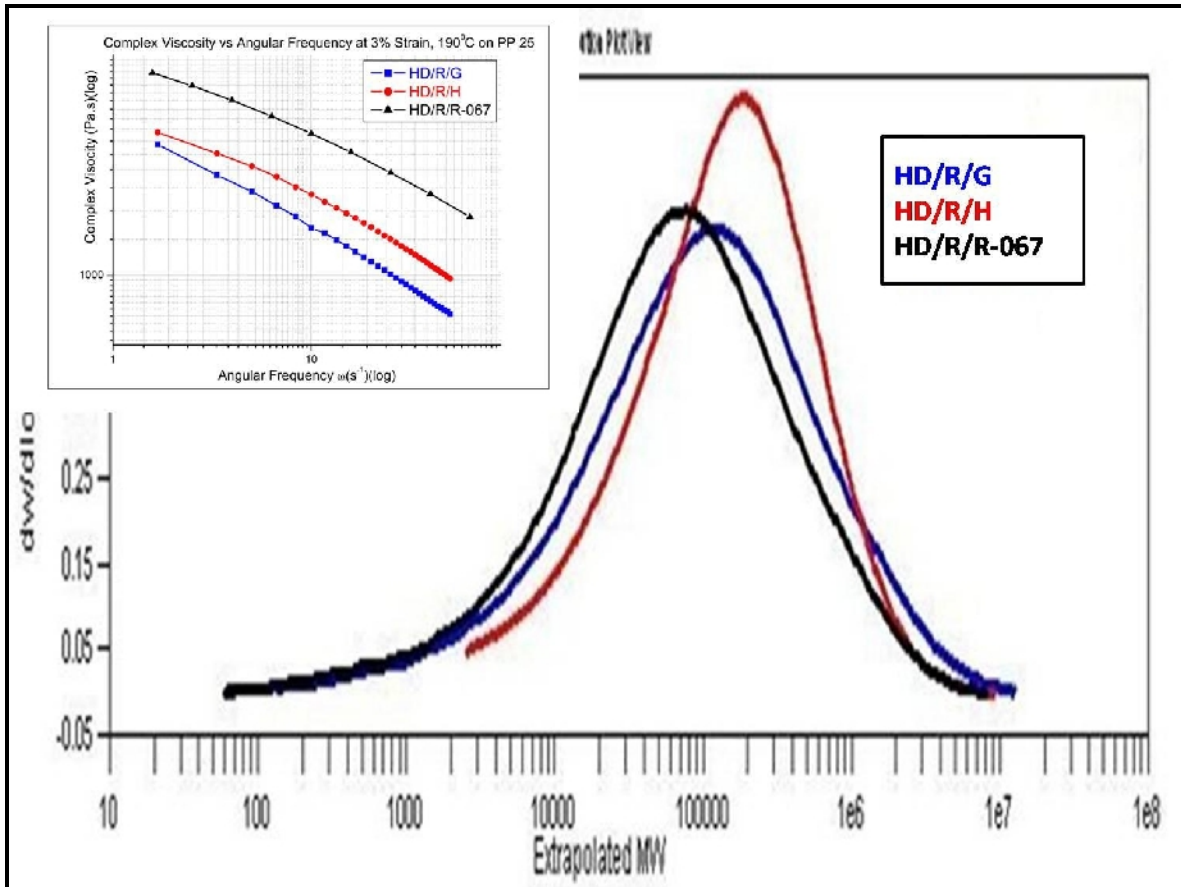
Figure 4.15: MWD chromatogram for HD/R/G, HD/R/R-067 and HD/R/H grades

From figure 4.5 it was clear that HD/R/H and HD/R/R-067 had much higher complex viscosity values over the entire range of angular frequencies as compared to HD/R/G.

From figure 4.13, it was found that at very low angular frequencies HD/R/H had lower G' values than HD/R/G but as the angular frequency increases, the G' values became much higher as compared to HD/R/G. HD/R/H had higher G'' values over the entire range of angular frequencies as compared to HD/R/G. The value of cross over modulus for HD/R/H was found to be much higher than HD/R/G which indicated towards the narrow molecular weight distribution of HD/R/H as compared to HD/R/G.

For HD/R/R-067 grade, (figure4.14) it was found that it had lower values of G' and G'' as compared to HD/R/G over the entire range of frequencies. The value of cross-over modulus for both HD/R/R-067 and HD/R/G grades were found to be similar but the cross-over frequency value for HD/R/R-067 was much higher than for HD/R/G,

which indicated towards the lower molecular weight value for the HD/R/R-067 grade as compared to HD/R/G.

MWD chromatogram (from figure 4.15) obtained from HT-GPC showed that HD/R/H don't contain any low molecular weight tail as present in HD/R/G, and HD/R/H had less high molecular wt. chain tail as compared to HD/R/G. Thus HD/R/H grade had narrow MWD as compared to HD/R/G which was also indicated by the higher cross-over modulus value for the HD/R/H grade. The peak of MWD chromatogram for HD/R/H was also much higher than HD/R/G.

Between HD/R/R-067 and HD/R/G grades (figure 4.15), it was found that both had nearly the same broadness of the MWD. Both the grades showed overlapping low molecular weight fraction in MWD chromatogram but the MWD chromatogram for HD/R/G had shifted towards more towards high molecular weight side which resulted in the higher molecular weight value for HD/R/G grade as compared to HD/R/R-067 and was supported by shift of cross-over modulus frequency towards the left side for HD/R/G grade as compared to HD/R/R-067(figure 4.14).

Thus from above discussion it was found that HD/R/H had high complex viscosity and modulus values than HD/R/G. HD/R/G grade had much broader MWD than HD/R/H grade. HD/R/H didn't contain any low molecular weight chain tail as present in HD/R/G and also had lower fraction of higher molecular weight tail as compared to HD/R/G.

HD/R/R-067 had lower higher molecular weight fraction as compared to HD/R/G. HD/R/G MWD chromatogram had shifted towards higher molecular weight side resulted in higher molecular weight value as compared to HD/R/R-067.

HD/R/G Vs HD/R/R-027:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/R/G, HD/R/R-067 and HD/R/H grades.
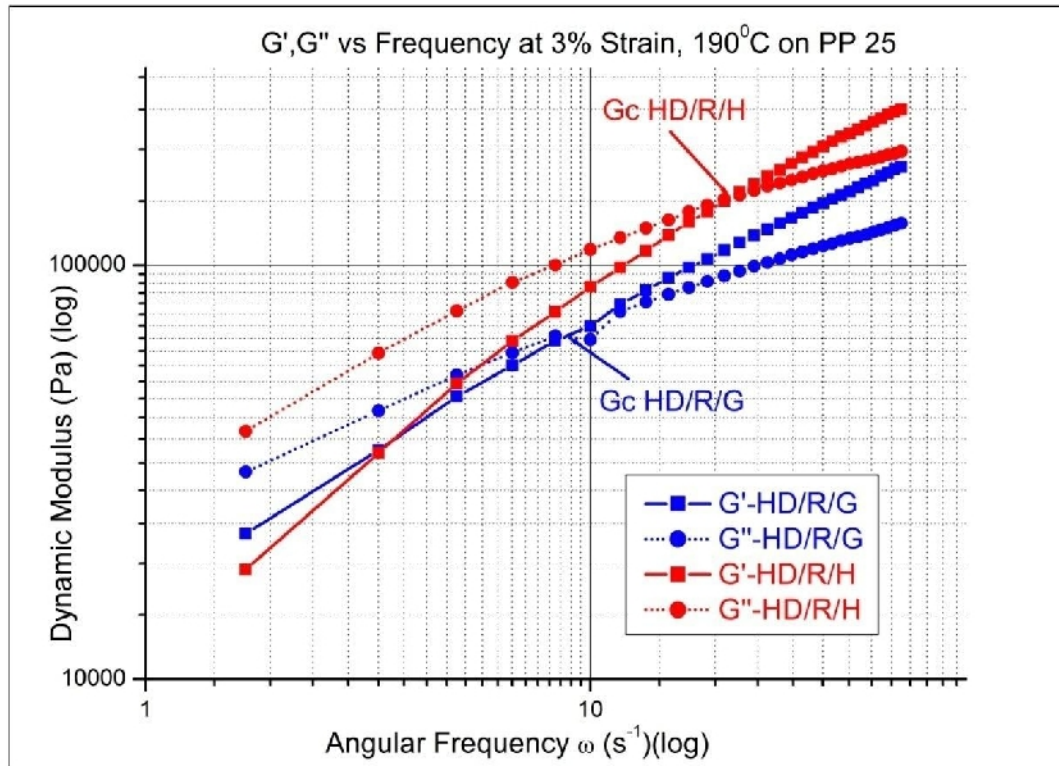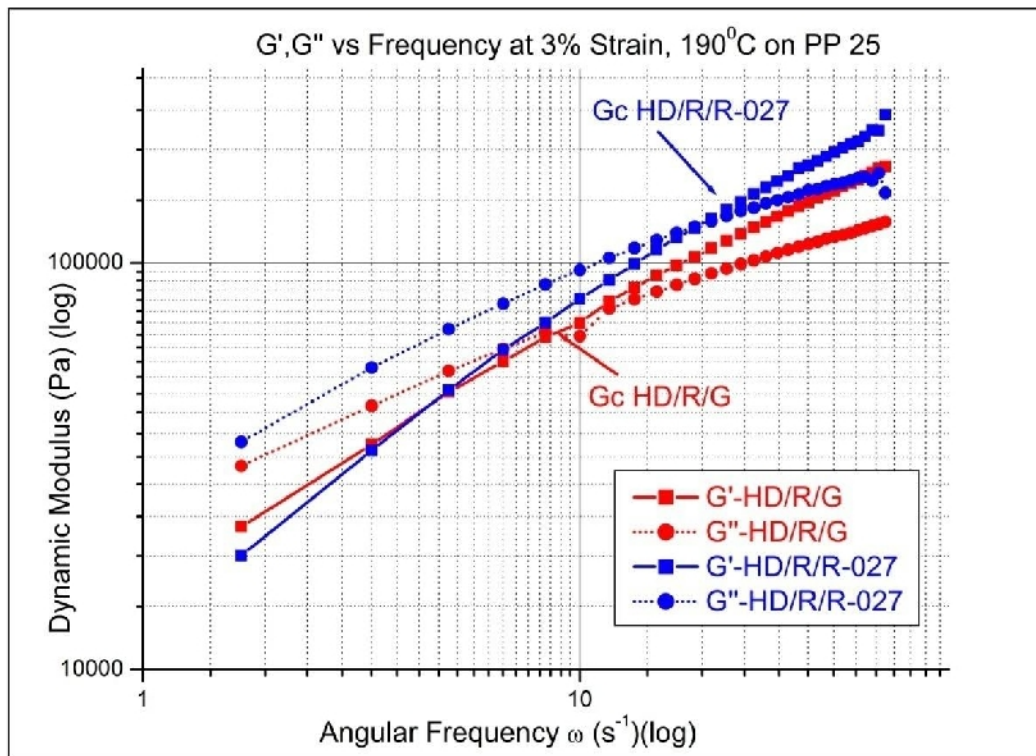

Figure 4.16: G', G'' vs. Angular Frequency curve for HD/R/G and HD/R/R-027

From figure 4.5, it was clear that HD/R/R-027 had higher complex viscosity values over the entire range of angular frequencies as compared to HD/R/G.

From figure 4.16, it was found that at very low angular frequencies HD/R/R-027 had lower G' values than HD/R/G but as the angular frequency increases, the G' values became higher as compared to HD/R/G. HD/R/R-027 had higher G'' values over the entire range of angular frequencies. The value of cross over modulus for HD/R/R-027 was also found to be much higher than HD/R/G which indicated towards the narrow molecular weight distribution of HD/R/R-027 as compared to HD/R/G.

Molecular Weight Distribution chromatogram for HD/R/G and HD/R/R-027 obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
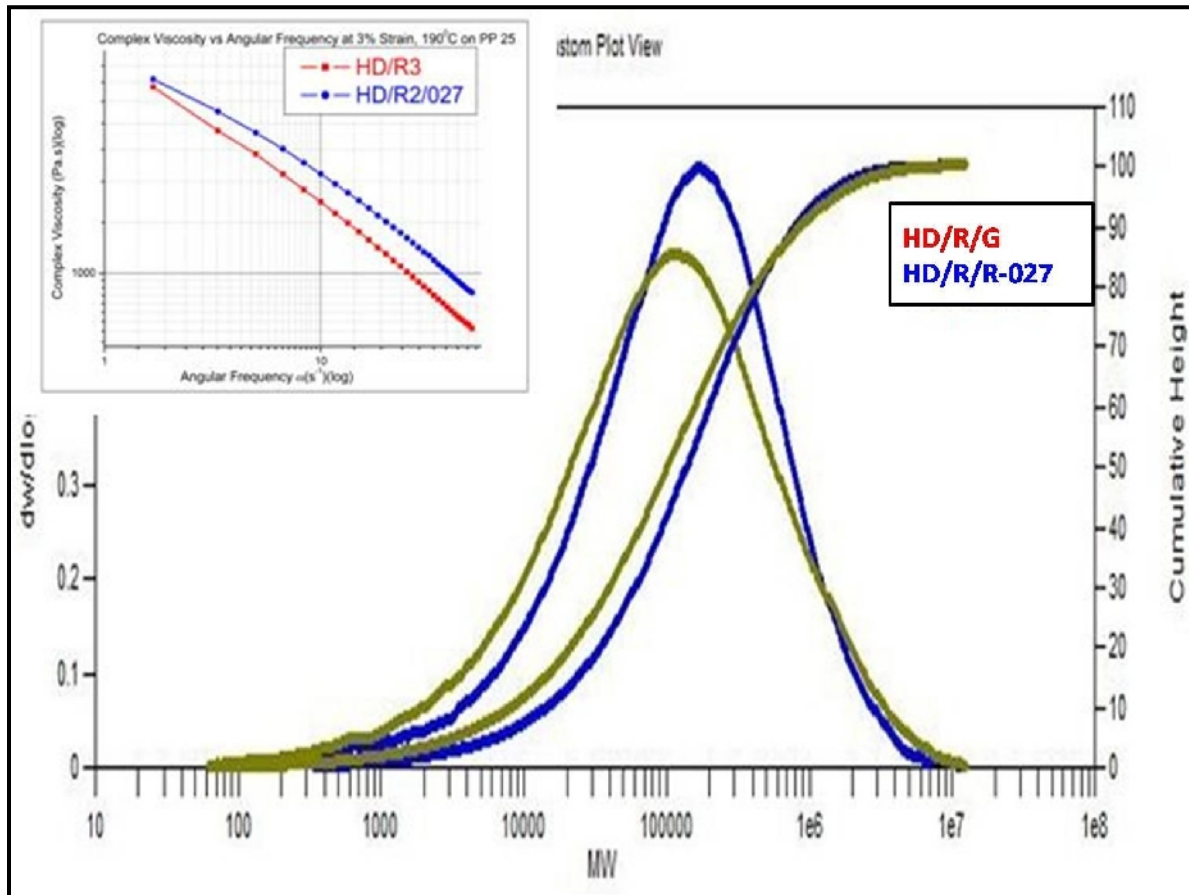
Figure 4.17: MWD chromatogram for HD/R/G and HD/R/R-027 grades

MWD curve (from figure 4.17) obtained from HT-GPC showed that HD/R/R-027 had lower amount of low molecular weight tail as present in HD/R/G and HD/R/R-027 had slight less very high molecular wt. chain tail as compared to HD/R/G. Thus HD/R/R-027 grade had narrow MWD as compared to HD/R/G which was also indicated by the higher cross-over modulus value for the HD/R/R-027 grade. The peak of MWD curve was also found to be much higher for HD/R/R-027 as compared to HD/R/G.

Thus from above discussion it was found that HD/R/R-027 had higher complex viscosity and higher G', G" values than HD/R/G. HD/R/G grade had much broader MWD than HD/R/R-027 grade. HD/R/R-027 had very less low molecular weight fraction as compared to HD/R/G.

4.1.6 Dynamic Mechanical Analysis:

Storage modulus (E'), loss modulus (E'') and tan delta as a function of temperature curve obtained from DMA for HD/R/I-018, HD/R/I-022, HD/R/I-025, HD/R/R-027, HD/R/G and HD/R/H grades. The β-relaxation was not observed in any of the grade. The α-relaxation and γ-relaxations were observed as a function of decreasing temperature.

Table 4.6: α-relaxation peak temperature and γ-relaxation peak temperature values for HDPE raffia grades

S. No.	Grade	α-relaxation peak temperature (^{0}C)	γ-relaxations peak temperature (^{0}C)
1	HD/R/I-018	38.85	115.54
2	HD/R/I-022	39.80	115.39
3	HD/R/I-025	40.49	115.75
4	HD/R/R-027	46.87	115.25
5	HD/R/G	40.47	116.43
6	HD/R/H	42.11	116.04

It was observed that HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G grade had nearly the same storage modulus and loss modulus values over the entire temperature range. The α-relaxation peak (between 38.85-40.49^{0}C) and γ-relaxations peak (between 115.39-116.43^{0}C) were also found to be nearly equal.

Both HD/R/G and HD/R/R-027 grades had nearly identical γ-relaxations peak value but for HD/R/R-027 grade α-relaxation peak value and intensity (modulus value at peak) was higher as compared to HD/R/G which indicated that HD/R/R-027 had higher crystalline thickness and higher % crystallinity value. At lower temperature range both had identical modulus profiles but as temperature increased HD/R/R-027 had higher modulus values as compared to HD/R/G.

HD/R/H had almost identical values of γ-relaxations peak and α-relaxation peak as compared to HD/R/G, but the intensity of α-relaxation for HD/R/H grade was little less as compared to HD/R/G. When compared modulus values it was observed that

HD/R/H had slight lower values of HD/R/G up to temperature of around $50^{0}C$ and had nearly equal values of modulus beyond this temperature.

Thus from above discussion it was observed that HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G had identical relaxation peaks with identical E' and E'' values over the entire temperature range. HD/R/R-027, HD/R/G and HD/R/H grades had similar γ-relaxations peak value. HD/R/R-027 had higher α-relaxation intensity and peak value as compared to HD/R/G and higher modulus values at higher temperatures. HD/R/H had almost identical α-relaxation peak but with low intensity as compared to HD/R/G. HD/R/H had slight lower modulus values at low temperatures, but had nearly similar values at higher temperatures.

4.1.7 Thermal analysis:

The values of peak melting point temperature (T_m), peak crystallization temperature (T_c), onset temperature of melting curve and total area under the melting thermo gram was obtained and % crystallinity was calculated. Melting thermogram for each grade was given in Appendix.

Table 4.7: Peak temperatures, enthalpy values and % crystallinity value for HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G grades

S. No	Grade	T_c (^{0}C)	T_m (^{0}C)	Onset T_m(^{0}C)	ΔH_1(j/g) Area up to T_m(^{0}C)	ΔH_2(j/g) Area after T_m(^{0}C)	ΔH(J/g)= ΔH_1(j/g)+ ΔH_2(j/g)	Crystallinity (%)
1	HD/R/I-018	111.9	132.5	121.3	124.1	68.6	192.8	66.5
2	HD/R/I-022	113.6	132.6	120.7	144.8	49.0	193.8	66.8
3	HD/R/I-025	112.8	134.2	122.0	138.7	55.5	194.2	67.0
4	HD/R/G	113.4	133.1	120.6	141.5	65.3	206.7	71.3

Single melting peaks were observed in all grades mentioned above. Peak crystallization temperature, Onset and peak melting temperatures for HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G were comparable with each other. However ΔH_1 value for HD/R/G and HD/R/I-022 were found on higher side as compared to HD/R/I-018 & HD/R/I-025. Higher value of ΔH_1 was desirable in running plant since as it is an added advantage over working range.

ΔH value of HD/R/I-018, HD/R/I-022 and HD/R/I-025 was close to each other but when compared to HD/R/G, it was found that HD/R/G had higher value of ΔH thus higher %crystallinity. Higher crystallinity is better for superior mechanical strength of a polymer to withstand line speed & stretching.

Table 4.8: Peak temperatures, enthalpy values and % crystallinity value for HD/R/R-027, HD/R/R-067, HD/R/G and HD/R/H grades

S. No	Grade	$T_c(^0C)$	$T_m(^0C)$	Onset $T_m(^0C)$	$\Delta H_1 (j/g)$ Area up to $T_m(^0C)$	$\Delta H_2(j/g)$ Area after $T_m (^0C)$	$\Delta H(J/g)=$ $\Delta H_1(j/g)+ \Delta H_2(j/g)$	Crystallinity (%)
1	HD/R/R-027	114.0	135.4	126.4	138.0.	76.5	211.9	73.1
2	HD/R/R-067	112.4	135.4	122.6	132.5	65.2	197.7	68.2
3	HD/R/G	113.4	133.1	120.6	141.5	65.3	206.7	71.3
4	HD/R/H	114.8	136.4	124.1	132.4	61.2	193.5	66.7

Table above indicated that peak melting temperature value of HD/R/H, HD/R/R-067 and HD/R/R-027 grades were comparable with each other and slightly higher than HD/R/G peak melting temperature value. HD/R/G had highest ΔH_1 value (141.5 j/g) as compared to HD/R/R-067 (132.4 j/g), HD/R/H (132.5 j/g) and HD/R/R-027 (138 j/g) grades. ΔH value of HD/R/G (206.7 j/g) was found to be higher than HD/R/R-067 (197.7 j/g) and HD/R/H (193.3 j/g) but had lower value than HD/R/R-027 (211.9 j/g).

It was observed that $T_{m\ onset}$ and peak melting temperatures (T_m) for HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G grades were comparable with each other, which was observed around 120 ^{0}C and 130 ^{0}C. Single melting peaks were observed for all the grades, indicating uniform lamellar thickness. ΔH values of HD/R/I-018, HD/R/I-022, and HD/R/I-025 grades were found less as compared to HD/R/G, therefore the corresponding crystallinity and mechanical strength at higher line speed for HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades was less as compared to HD/R/G.

RESULT AND DISCUSSION

4.2 HDPE LARGE BLOW MOLDING GRADE

GRADE DETAILS:

Table 4.9: HDPE Large Blow Molding Grade Details

S. No.	Grade
1	HD/LBM1/024
2	HD/LBM1/111
3	HD/LBM1/121
4	HD/LBM1/125
5	HD/LBM2/571

4.2.1 Density:

The value of density for each HDPE large blow molding grade was calculated by using Density Gradient Column technique and given in table 4.10..

Table 4.10: Density values for HDPE Large Blow Molding grades

S. No.	Grade	Density (g/cc)
1	HD/LBM1/024	0.9503
2	HD/LBM1/111	0.9497
3	HD/LBM1/121	0.9547
4	HD/LBM1/125	0.9555
5	HD/LBM2/571	0.9527

Density of HD/LBM2/571 was higher than grades HD/LBM1/024 and HD/LBM1/111 but had lower value than HD/LBM1/121 and HD/LBM1/125.

4.2.2 Melt Flow Index and Melt Flow Ratio:

Melt flow index of HDPE large blow molding grades were done as per the ASTM D 1238 at three different loads (5, 10 & 21.6 Kg) at the temperature of 190°C.

Table 4.11: MFI and MFR values for HDPE Large Blow Molding grades

S. No.	Grade	MFI@5kg/ 190^{0}C	MFI@10kg/ 190^{0}C	MFI@21.6kg/ 190^{0}C	MFR@ 21.6kg/ 5kg	MFR@ 21.6kg /10kg
1	HD/LBM1/024	0.09	0.4	1.8	20.0	5.0
2	HD/LBM1/111	0.08	0.3	1.6	20.0	5.2
3	HD/LBM1/121	0.13	0.5	3.3	25.6	7.0
4	HD/LBM1/125	0.11	0.5	3.2	29.3	6.7
5	HD/LBM2/571	0.07	0.3	1.9	27.1	5.9

At 5.0 kg load:

At 5kg load it was found that HD/LBM1/024 and HD/LBM1/111 had higher MFI value compared to HD/LBM2/571 but had lower MFI value as compared to HD/LBM1/121 and HD/LBM1/125. HD/LBM2/571 had the lowest MFI at 5kg load.

At 10.0 kg load:

At 10kg load HD/LBM1/111 and HD/LBM2/571 had similar MFI values but had less MFI value as compared to HD/LBM1/024. HD/LBM1/121 and HD/LBM1/125 grades were found to have the highest value of MFI at 10kg load as compared to all other grades.

At 21.6 kg load:

At 21.6 kg load HD/LBM2/571 had higher value of MFI as compared to HD/LBM1/024 and HD/LBM1/111 but had lower value of MFI as compared to HD/LBM1/121 and HD/LBM1/125 grades.

When compared MFR (@21.6kg/5kg) values it was found that HD/LBM2/571 had higher value as compared to HD/LBM1/024, HD/LBM1/111 and HD/LBM1/121 grades but had lower value as compared to HD/LBM1/125. At MFR (@21.6/10kg), it was observed that HD/LBM2/571 had higher value as compared to HD/LBM1/024 and HD/LBM1/111 but had lower value as compared to HD/LBM1/121 and HD/LBM1/125 grades.

From above discussion it was found that HD/LBM2/571 had lower MFI value (which will give better mechanical properties, ESCR and melt strength) and higher value of MFR (@21.6/5.0kg) which means higher shear thinning behaviour resulting in better process ability as compared to all other grades.

4.2.3 <u>Capillary Rheometer analysis:</u>

<u>Shear viscosity Vs corrected shear rate:</u>

Shear viscosity Vs corrected shear rate values were obtained from Capillary Rheometer analysis and curve was plotted for each grade.

Curve was plotted for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades between shear viscosity and corrected shear rate.
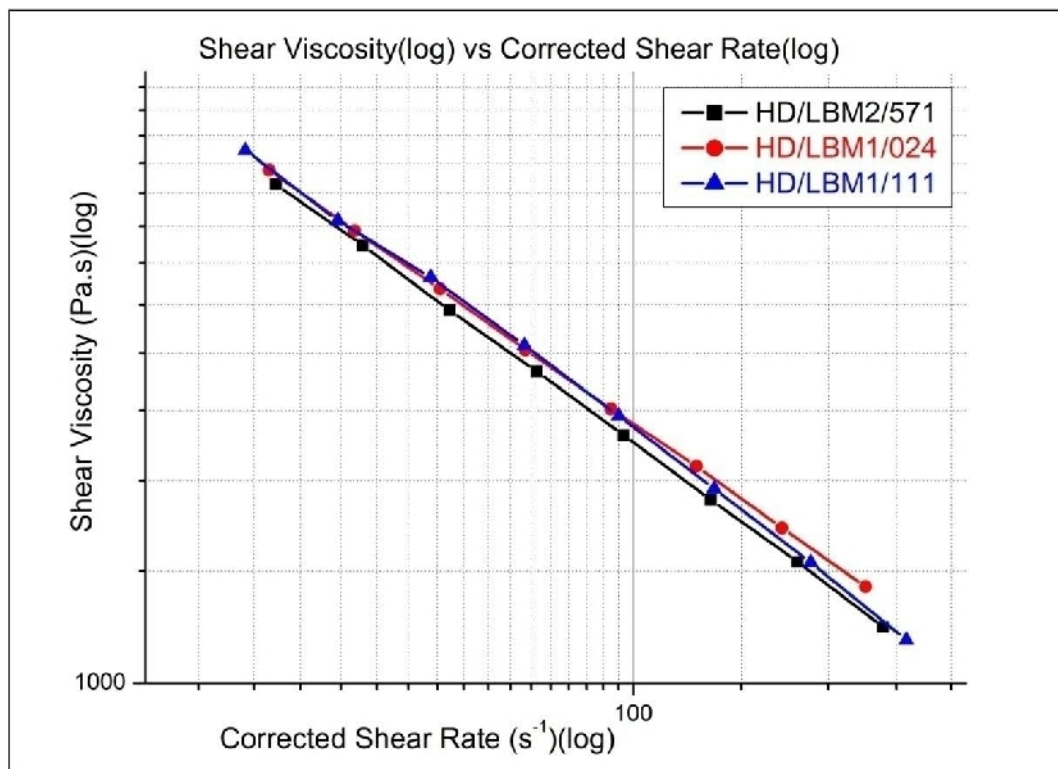
Figure 4.18: Shear viscosity Vs corrected shear rate (on log scale) for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades

From above figure 4.18, it was found that HD/LBM2/571 had the lower melt viscosity values as compared to HD/LBM1/024 and HD/LBM1/111 which means that HD/LBM2/571 had better process ability as compared to HD/LBM1/024 and HD/LBM1/111 grades.

Shear viscosity Vs corrected shear rate curve was plotted for the grade HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades.
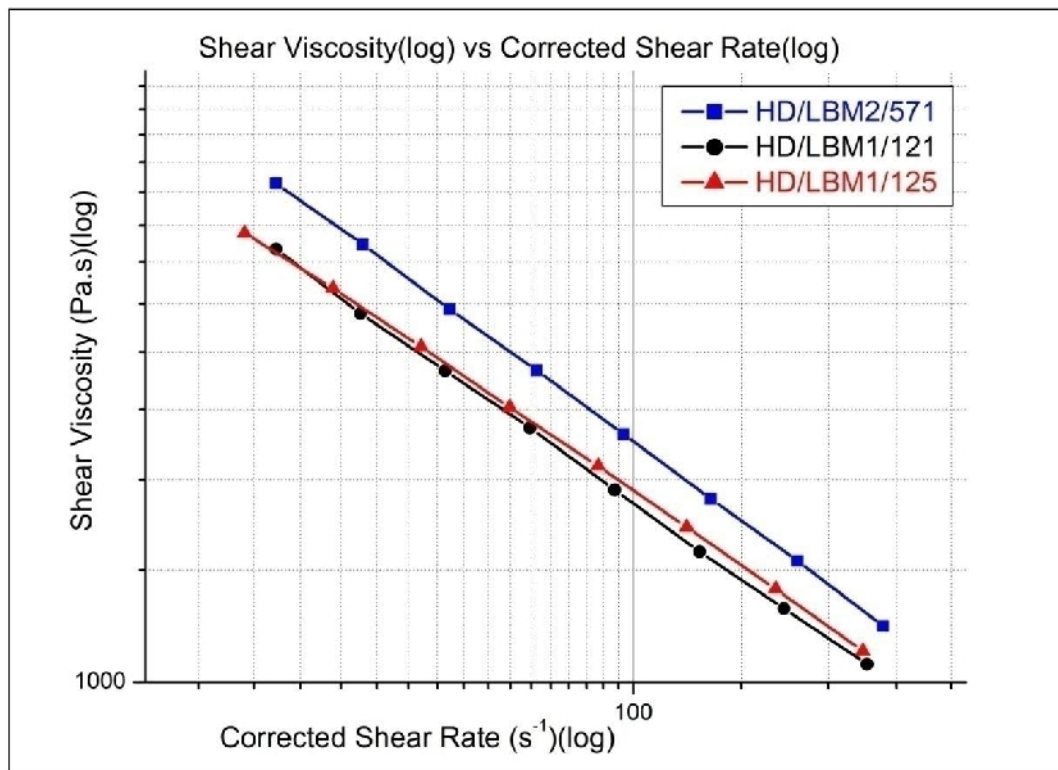
Figure 4.19: Shear viscosity Vs corrected shear rate curve (log scale) for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades

From the above figure 4.19, it was observed that HD/LBM2/571 had higher value of shear viscosity as compared to HD/LBM1/121 and HD/LBM1/125 grades. Lower shear viscosity values for HD/LBM1/121 and HD/LBM1/125 grades than HD/LBM2/571 were also supported by the higher MFI values for HD/LBM1/121 and HD/LBM1/125 grades at different loads.

Thus from above discussion it was found that HD/LBM2/571 had lower melt viscosity as compared to HD/LBM1/024 and HD/LBM1/111 at varying shear rates which resulted in better/easy process ability of HD/LBM2/571. HD/LBM1/121 and HD/LBM1/125 had lower melt viscosity value at varying shear rates as compared to HD/LBM2/571.

Extensional Viscosity Vs Extensional Rate:

Extensional viscosity plays very important role during blow molding processes. Extensional viscosity represents the behaviour of the melt under extension. During blow molding process larger extensional viscosity values at extensional rates would result in better melt strength and less sagging of the parison.

Extensional Viscosity Vs Extensional Rate curve were plotted using the data obtained from Capillary Rheometer analysis.
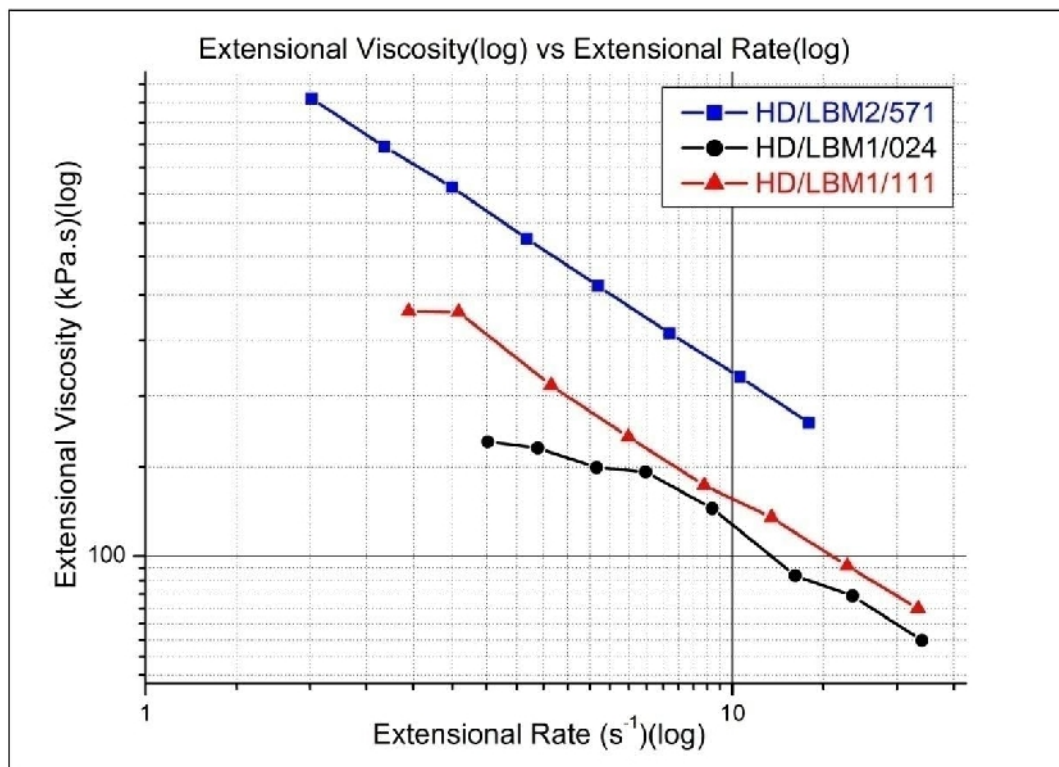
Figure 4.20: Extensional Viscosity (log) Vs Extensional Rate (log) curve for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades

From the above figure 4.20, it was found that HD/LBM2/571 had higher value of extensional viscosity at different extensional rates as compared to HD/LBM1/024 and HD/LBM1/111. The decrease in extensional viscosity with extension rate for HD/LBM2/571 was linear and uniform as compared to HD/LBM1/024 and HD/LBM1/111 grades, which had nonlinear response of extensional viscosity with extensional rate. Lower extensional viscosity values for HD/LBM1/024 and

HD/LBM1/111 as compared to HD/LBM2/571, resulted in lower melt strength and higher parison sagging.
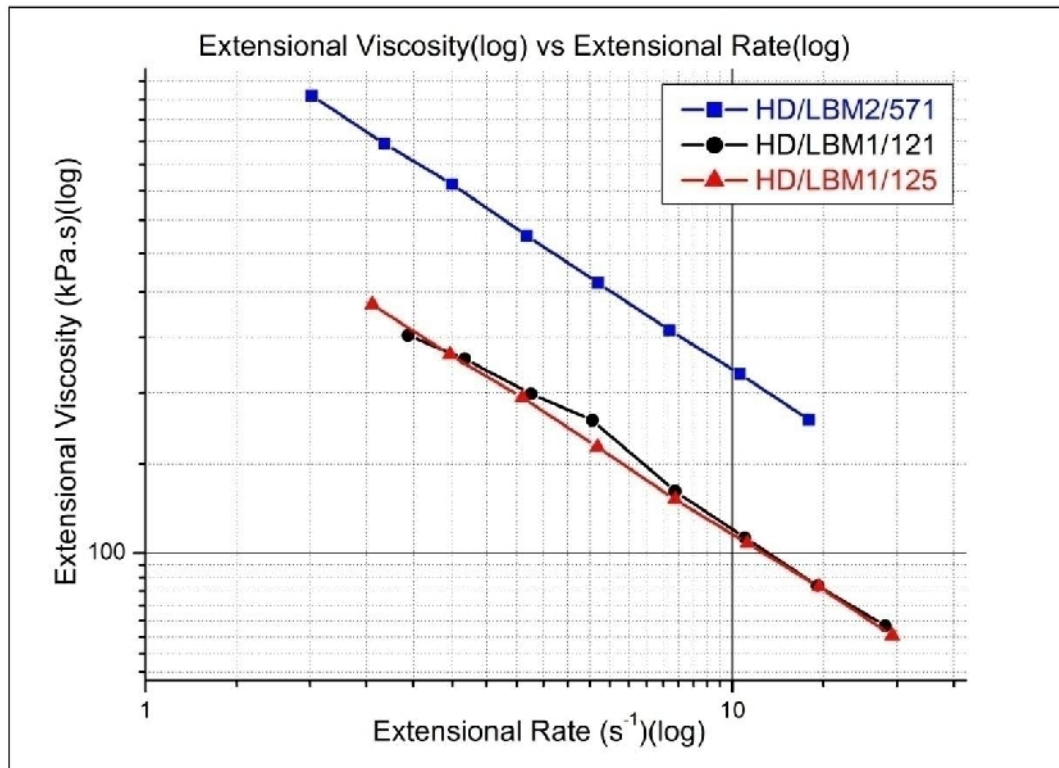
Figure 4.21: Extensional Viscosity (log) Vs Extensional Rate (log) curve for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades

From above figure 4.21, it was found that HD/LBM1/121 and HD/LBM1/125 had lower extensional viscosity as compared to HD/LBM2/571 grades at various extensional rates. Due to lower values of extensional viscosity, HD/LBM1/121 and HD/LBM1/125 grades had low melt strength and higher sagging of parison resulted in short molding observed during processing.
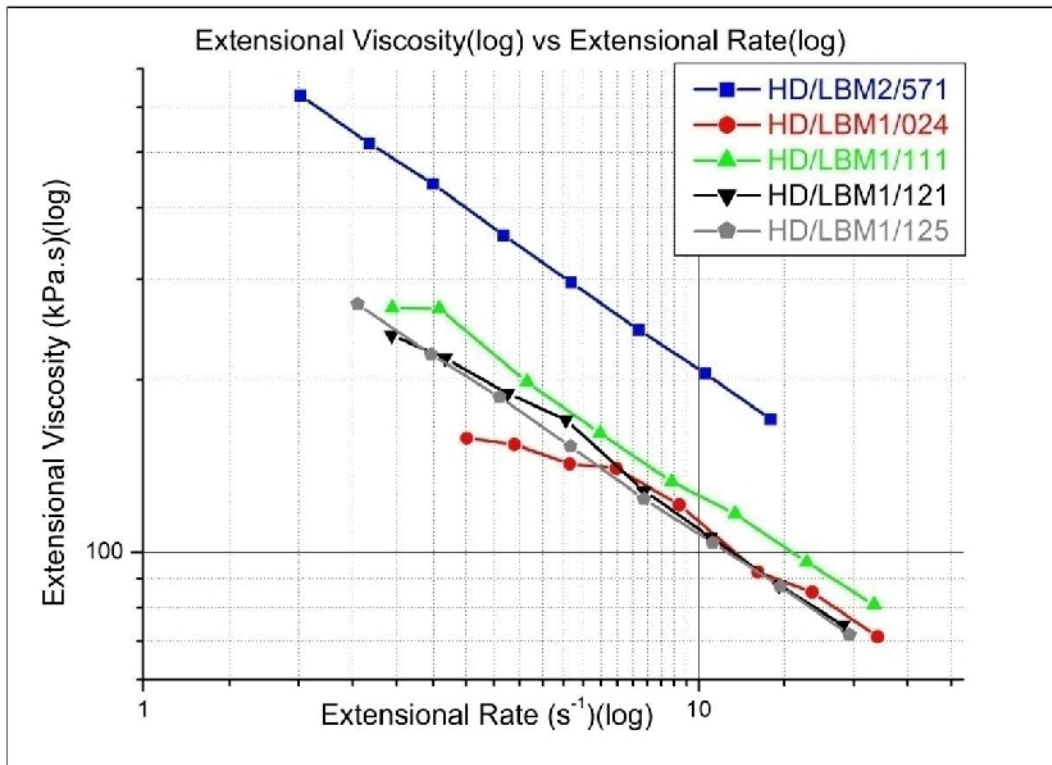
Figure 4.22: Extensional Viscosity (log) Vs Extensional Rate (log) curve for HD/LBM2/571, HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades

From figure 4.22, it was cleared that HD/LBM2/571 had very high value of extensional viscosity at various extensional rates as compared to all other grades.

Thus from above discussion it was found that extensional viscosity which is very important parameter in controlling blow molding processes varies widely between HD/LBM2/571 and other grades. As high value of extensional viscosity were required for better melt strength, lower parison sagging and for higher die swell. Among all grades HD/LBM2/571 only had higher value of extensional viscosity at varying extensional rates. All grades except HD/LBM2/571 had much lower values of extensional viscosity resulting in lower melt strength, lower die swell and higher parison sagging during processing, ultimately affecting the product manufactured as short molding and less total product weight was observed.

4.2.4 Dynamic Rotational Rheometer and High Temperature GPC analysis

Complex viscosity Vs Angular frequency curve for HD/LBM1/024, HD/LBM1/111, HD/LBM1/121, HD/LBM1/125 and HD/LBM2/571 was plotted from the data obtained from Parallel Plate Rheometer.
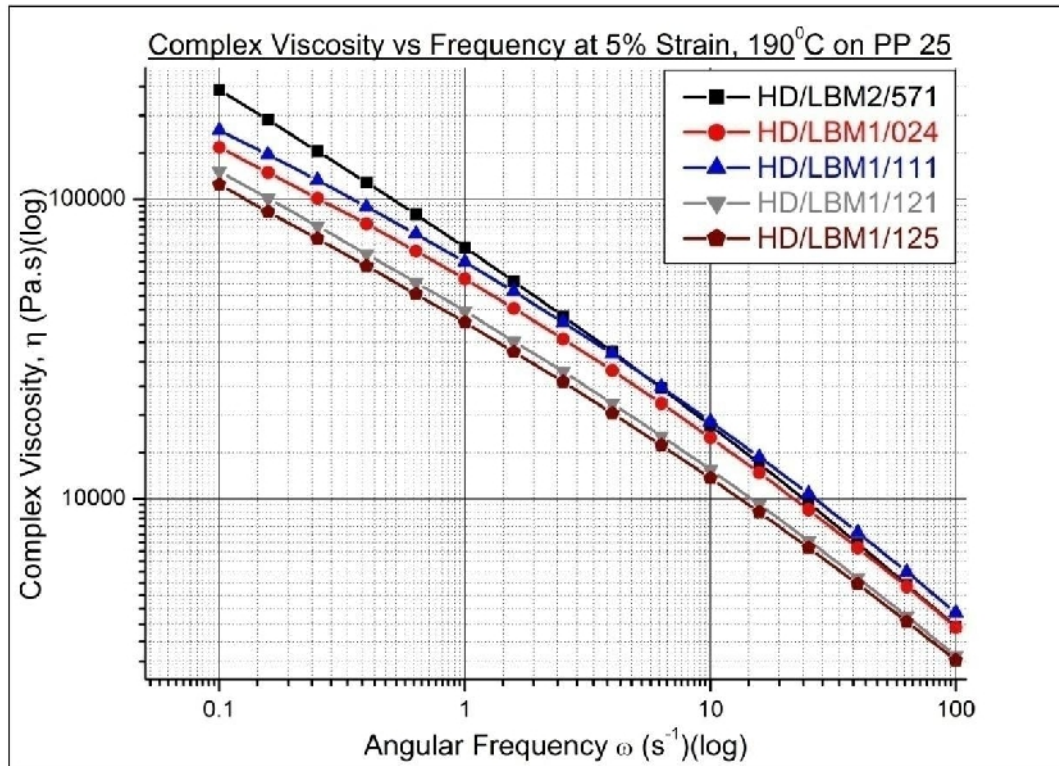
Figure 4.23: Complex Viscosity Vs Angular Frequency curve for HD/LBM1/024, HD/LBM1/111, HD/LBM1/121, HD/LBM1/125 and HD/LBM2/571 grades

From the above figure 4.23, it was found that HD/LBM2/571 had highest complex viscosity at low angular frequencies as compared to all other grades. Viscosity profile decreases more sharply for HD/LBM2/571 relative to other grades which clearly indicated towards the more shear thinning behaviour of HD/LBM2/571 and better process ability.

HD/LBM2/571 Vs HD/LBM1/024 Vs HD/LBM1/111:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades.
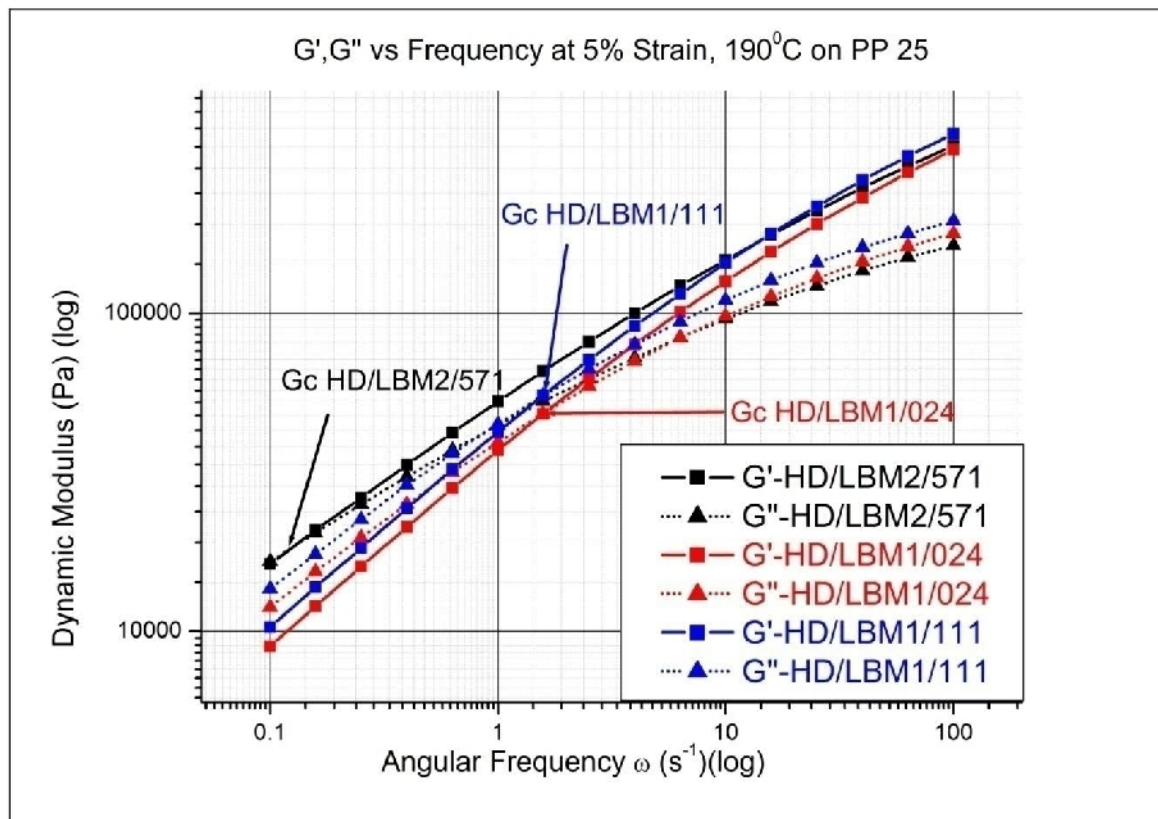
Figure 4.24: G', G'' vs. angular frequency curve for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades

Molecular Weight Distribution chromatogram for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
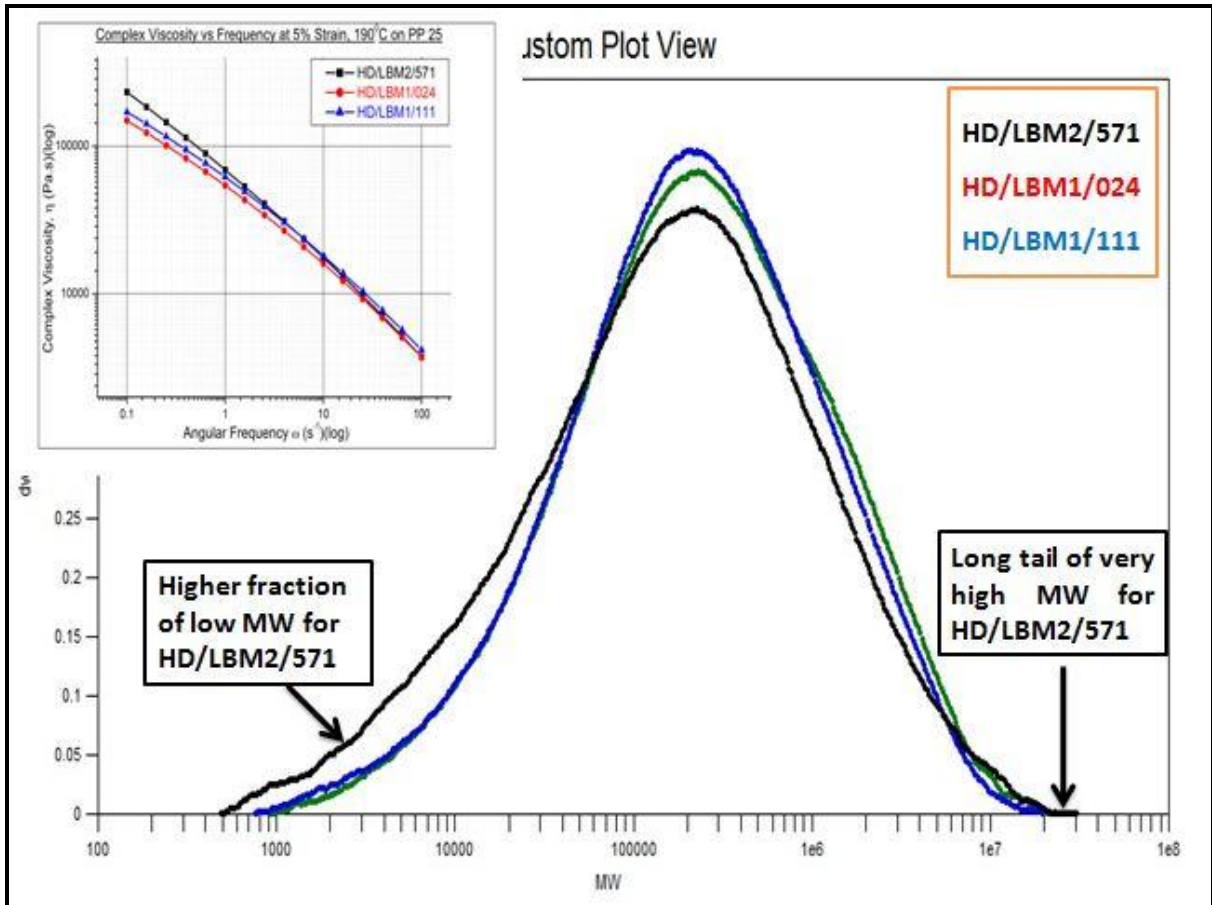
Figure 4.25: MWD chromatogram for HD/LBM2/571, HD/LBM1/024 and HD/LBM1/111 grades

From figure 4.24, it was found that HD/LBM2/571 had higher value of storage modulus values at very low frequencies as compared to HD/LBM1/024 and HD/LBM1/111 grades which indicated that HD/LBM2/571 had higher high molecular weight fraction tail as compared to HD/LBM1/024 and HD/LBM1/111. When compared the cross over values, it was found that HD/LBM2/571 had much lower value of cross over modulus value occurring at much lower cross over frequency as compared to HD/LBM1/024 and HD/LBM1/111, indicating towards the broader molecular weight distribution for HD/LBM2/571. Among HD/LBM1/024 and HD/LBM1/111 grades, later had little higher G', G'' values as well as had slightly higher cross over modulus value with same cross over frequency value as HD/LBM1/024.

From figure 4.23, it was found that HD/LBM2/571 had much higher value of complex viscosity at very low frequency as compared to HD/LBM1/024 and HD/LBM1/111

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grades indicated towards the higher zero shear viscosity values for HD/LBM2/571 grade and ultimately higher melt strength. From MWD chromatogram 4.25, it was found that HD/LBM2/571 had higher amount of high molecular weight tail as compared to HD/LBM1/024 and HD/LBM1/111 which indicate towards the higher melt strength and higher die swell for the HD/LBM2/571. HD/LBM2/571 also had higher fraction of low molecular weight chain as compared to HD/LBM1/024 and HD/LBM1/111 grades indicated towards the higher shear thinning behaviour resulting in easier processing.

The MWD chromatogram for HD/LBM1/024 and HD/LBM1/111 grades had shifted towards the high molecular weight fraction resulting in higher melt viscosity values as compared to HD/LBM2/571 grade.

Among the HD/LBM1/024 and HD/LBM1/111 grades, it was found that the former one had slight higher fraction of high molecular weight tail resulting in little higher die swell and melt strength as compared to HD/LBM1/111 and had slight broader MWD as also indicated by the lower cross over modulus value for HD/LBM1/024.

Thus from above discussion it was cleared that HD/LBM2/571 had higher fraction of high molecular weight tail, higher lower molecular weight fraction, higher complex viscosity value at low angular frequency and had broader molecular weight distribution as compared to HD/LBM1/024 and HD/LBM1/111 grades which resulted in higher die swell, higher melt strength and more shear thinning for HD/LBM2/571.

HD/LBM2/571 Vs HD/LBM1/121 Vs HD/LBM1/125:

Curve was plotted between G', G'' Vs angular frequency from the Dynamic Rotational (Parallel Plate) Rheometer data for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades.
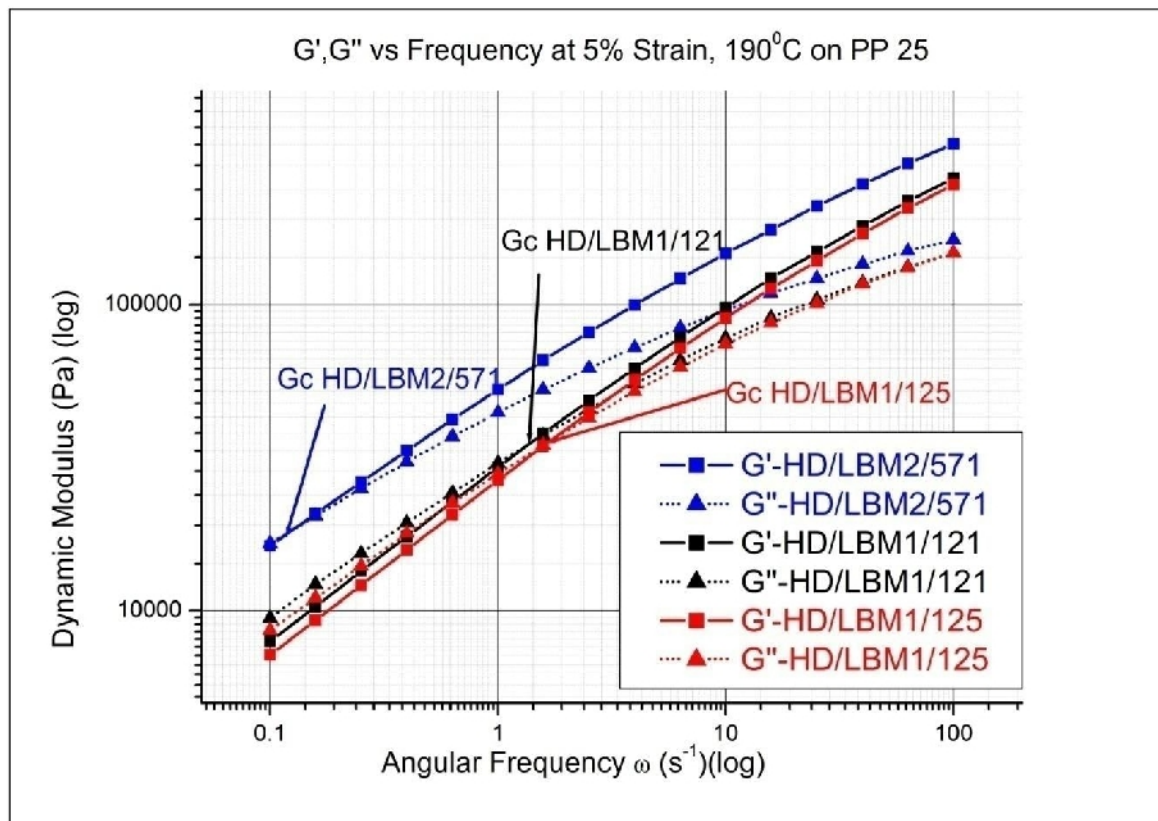
Figure 4.26: G', G'' vs. angular frequency curve for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125

Molecular Weight Distribution chromatogram for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades obtained from HT-GPC analysis and plotted along with complex viscosity Vs angular frequency curve obtained from Dynamic Rotational (Parallel Plate) Rheometer data.
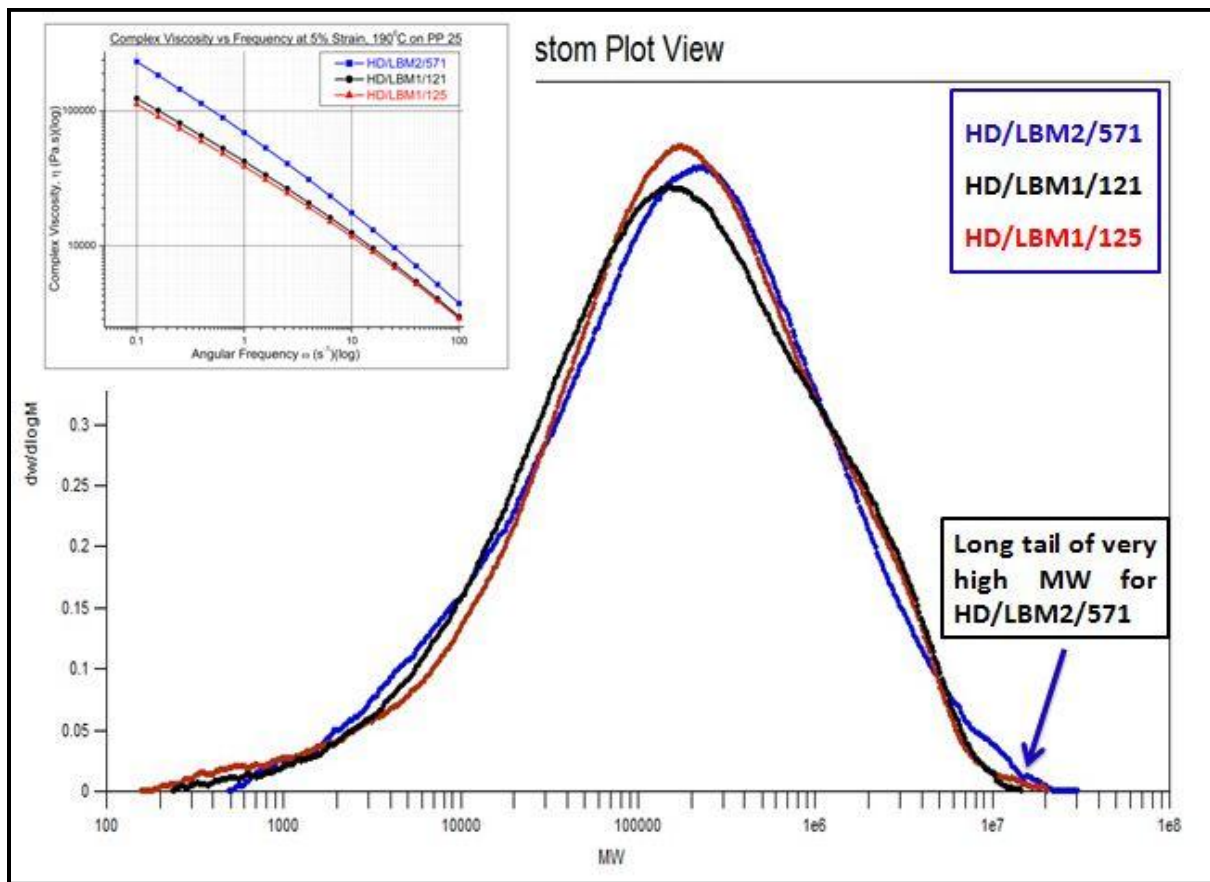
Figure 4.27: MWD chromatogram for HD/LBM2/571, HD/LBM1/121 and HD/LBM1/125 grades

From figure 4.26, it was found that HD/LBM2/571 had higher value of storage modulus values at very low frequencies as compared to HD/LBM1/121 and HD/LBM1/125 grades which indicated that HD/LBM2/571 had higher fraction of high molecular weight fraction tail as compared to HD/LBM1/121 and HD/LBM1/125 grades.

HD/LBM2/571 had lower cross over modulus value as compared to HD/LBM1/121 and HD/LBM1/125 grades. Among the HD/LBM1/121 and HD/LBM1/125 grades, both had similar value of cross over modulus, with HD/LBM1/121 having slight higher storage modulus values as compared to HD/LBM1/125.

From MWD chromatogram figure 4.27, it was clear that HD/LBM2/571 had higher fraction of high molecular weight tail as compared to HD/LBM1/121 and HD/LBM1/125 resulting in higher melt strength and higher die swell. HD/LBM1/121

and HD/LBM1/125 grades had long tail of very low molecular weight fraction as compared to HD/LBM2/571 indicated towards the higher MFI values for both grades which was also supported by the MFI values obtained earlier. Moreover, MWD chromatogram for HD/LBM2/571 grade had better uniformity as compared to HD/LBM1/121 and HD/LBM1/125 grades.

Thus from above discussion it was found that HD/LBM2/571 had higher fraction of very high molecular weight tail, higher complex viscosity value at very low shear rate as compared to HD/LBM1/121 and HD/LBM1/125 which resulted in better melt strength and higher die swell. HD/LBM1/121 and HD/LBM1/125 had long tail of very low molecular weight fraction as compared to HD/LBM2/571 resulting in higher MFI at low shear rates as confirmed from MFI values calculated earlier.

Cross over modulus and frequency values for each grade was calculated from Parallel Plate Rheometer data and value of ratio of M_z/M_w was calculated using the following equation [37].

$$Gc = 3.1 \times \left(\frac{M_z}{M_w}\right)^{-3.1}$$

Table 4.12: Cross over modulus, cross over frequency and M_z/M_w values for HDPE large blow molding grades

S. No.	Grade	Cross over modulus, Gc (Pa)	Cross over Frequency, (Hz)	M_z/M_w
1	HD/LBM1/024	49064.5	1.63	3.81
2	HD/LBM1/111	53866.9	1.52	3.70
3	HD/LBM1/121	34670.3	1.35	4.26
4	HD/LBM1/125	35997.6	1.72	4.21
5	HD/LBM2/571	18228.8	0.13	5.24

From the above table it was cleared that HD/LBM2/571 had the lowest cross over modulus and highest M_z/M_w value as compared to all other grades which was also supported by the MWD chromatograms discussed earlier.

4.2.5 Thermal analysis:

The values of peak melting point temperature (T_m), peak crystallization temperature (T_c), onset temperature of melting curve and total area under the melting curve was obtained and % crystallinity was calculated using the equation. Melting thermo gram for each grade was given in Appendix.

Table 4.13: Peak temperatures, enthalpy values and % crystallinity value for HDPE Large Blow Molding grades

S. No	Grade	T_c (^{0}C)	T_m (^{0}C)	Onset T_m(^{0}C)	ΔH_1 (j/g) Area up to T_m(^{0}C)	$\Delta H2$(j/g) Area after Tm(^{0}C)	ΔH(J/g)= $\Delta H1$(j/g)+ $\Delta H2$(j/g)	Crystallinity (%)
1	HD/LBM1/024	115.95	133.69	125.19	148.6	38.18	186.78	64.4
2	HD/LBM1/111	115.58	133.80	124.87	143.8	36.37	180.17	62.1
3	HD/LBM1/121	119.1	131.82	123.85	149.8	43.94	193.74	66.8
4	HD/LBM1/125	121	133.17	125.25	160.9	36.71	197.61	68.1
5	HD/LBM2/571	118.57	132.41	124.18	147.5	41.06	188.56	65.0

One to one comparison of HD/LBM2/571 with other grades was not feasible as HD/LBM2/571 was hexane based HDPE (as found through material technical data sheet) and all other grades were butane based HDPE.

Among HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades, HD/LBM1/111 had the lowest % crystallinity value which was also evident from density value as it had the lowest density among all the grades. % Crystallinity had increased with increase in density of the grades. HD/LBM1/125 had highest density as well as highest value of % crystallinity.

RESULT AND DISCUSSION

4.3 LLDPE BLOWN FILM EXTRUSION GRADE

GRADE DETAILS:

Table 4.14: LLDPE Blown Film Extrusion Grade Details

S. No.	Grade
1	LLDPE-1
2	LLDPE-2

Density and MFI @2.16kg values for both the LLDPE grades as received.

Table 4.15: Density and MFI @ 2.16 values for LLDPE-1 and LLDPE-2 grades

S. No.	Grade	Density (g/cc) (23^0C) ASTM D 1505	MFI (g/10min) @2.16,190^0C ASTM D 1238
1	LLDPE-1	0.918	0.9
2	LLDPE-2	0.920	1.0

Among LLDPE-1 and LLDPE-2 grades, LLDPE-2 had the slight higher MFI @2.16kg and density values (table 4.15) as compared to LLDPE-1.

Table 4.16: Properties for LLDPE-1 and LLDPE-2 grades as received

S. No.	Grade	Dart Impact(F-50) g/µm	Tensile Strength at break (MD/TD) MPa	Elongation at break (MD/TD) %	Tear Strength (MD/TD) g/µm
		ASTM D 1709/A	ASTM D 882	ASTM D 882	ASTM D 1922
1	LLDPE-1	3.4	38.0/30.0	700/800	3.0/10.0
2	LLDPE-2	4.1	30.0/21.0	650/850	4.8/17.6

4.3.1 <u>High Temperature GPC analysis</u>:

MWD chromatogram for both the grades was obtained from HT-GPC analysis.
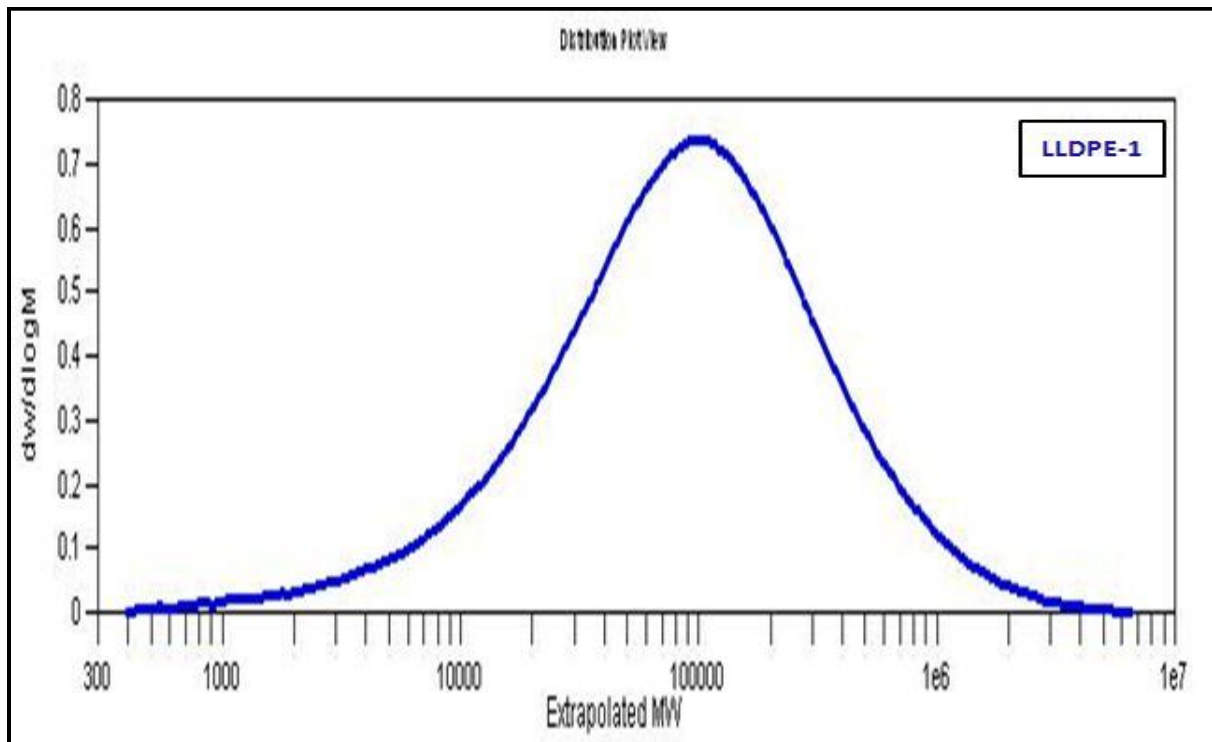
Figure 4.28: Molecular Weight Distribution chromatogram for LLDPE-1 grade
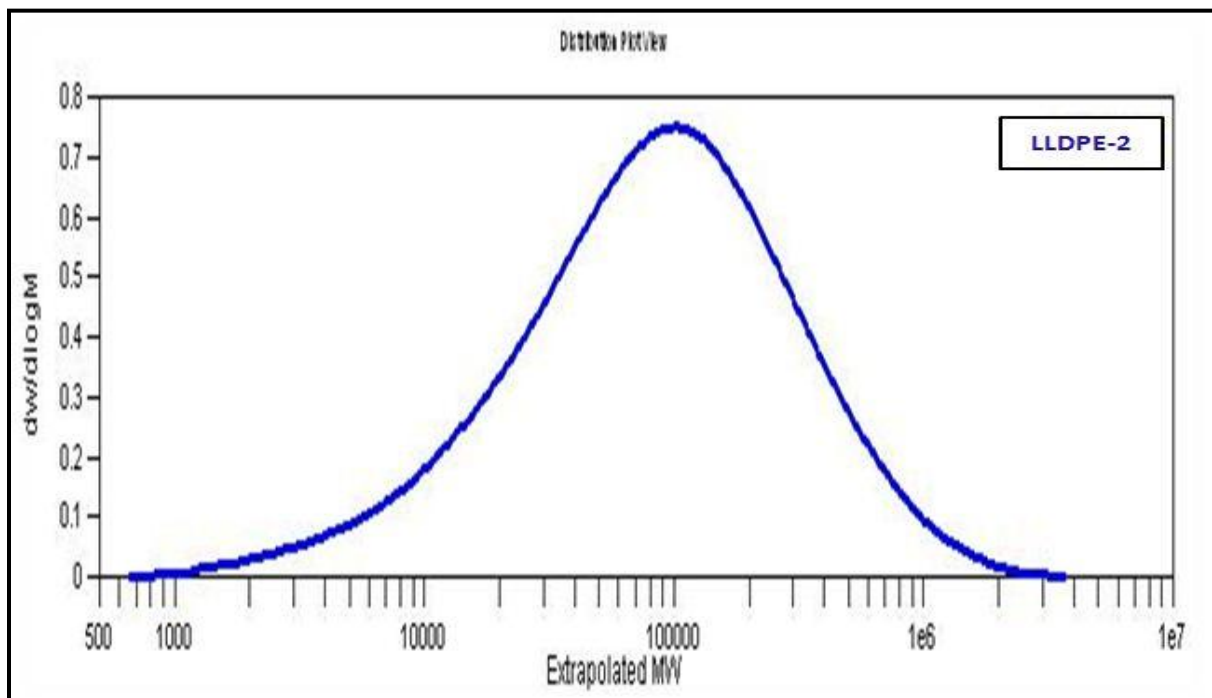
Figure 4.29: Molecular Weight Distribution chromatogram for LLDPE-2 grade

From figure (4.28 & 4.29), it was found that both the grades LLDPE-1 and LLDPE-2 had almost similar broadness of molecular weight distribution. LLDPE-1 had slight higher fraction of very high molecular weight tail as compared to LLDPE-2 grade, which will result in higher molecular weight value for LLDPE-1. For LLDPE, higher molecular weight value will result in low MFI and increase in tensile properties [38]. Thus from above discussion it was found that LLDPE-1 had lower MFI and higher tensile strength at break value than LLDPE-2 due to higher molecular weight for LLDPE-1.

4.3.2 ^{13}C-Nuclear Magnetic Resonance Spectroscopy analysis:

Short chain branching content (branching per 1000 C) and mole% of 1-butene was calculated from the NMR spectra obtained from ^{13}C-NMR analysis and values are given below.

Table 4.17: Mole % 1-butene and Short chain branching content for LLDPE-1 and LLDPE-2 grades

S. No.	Grade	1-butene Mole %	Branching /1000C
1	LLDPE-1	2.2	10.9
2	LLDPE-2	3.3	16.0

From the above table 4.17, it was cleared that despite having almost similar densities, short chain branching content was higher in LLDPE-2 (16 branching/1000C) than LLDPE-1 (10.9 branching/1000C). LLDPE-2 had higher 1-butene (3.3, mole %) content as compared to LLDPE-1 (2.2, mole %). For LLDPE, increase in comonomer content will result in decrease in tensile strength at break and %elongation at break values [11]. Thus decrease in tensile strength at break and % elongation at break for LLDPE-2 grade as compared to LLDPE-1 can be related with the higher amount of comonomer present in the LLDPE-2 grade.

4.3.3 Crystallization Analysis Fractionation (CRYSTAF) analysis:

CRYSTAF curves (comonomer composition distribution curve) for both the grades were obtained using CRYSTAF analysis.

:
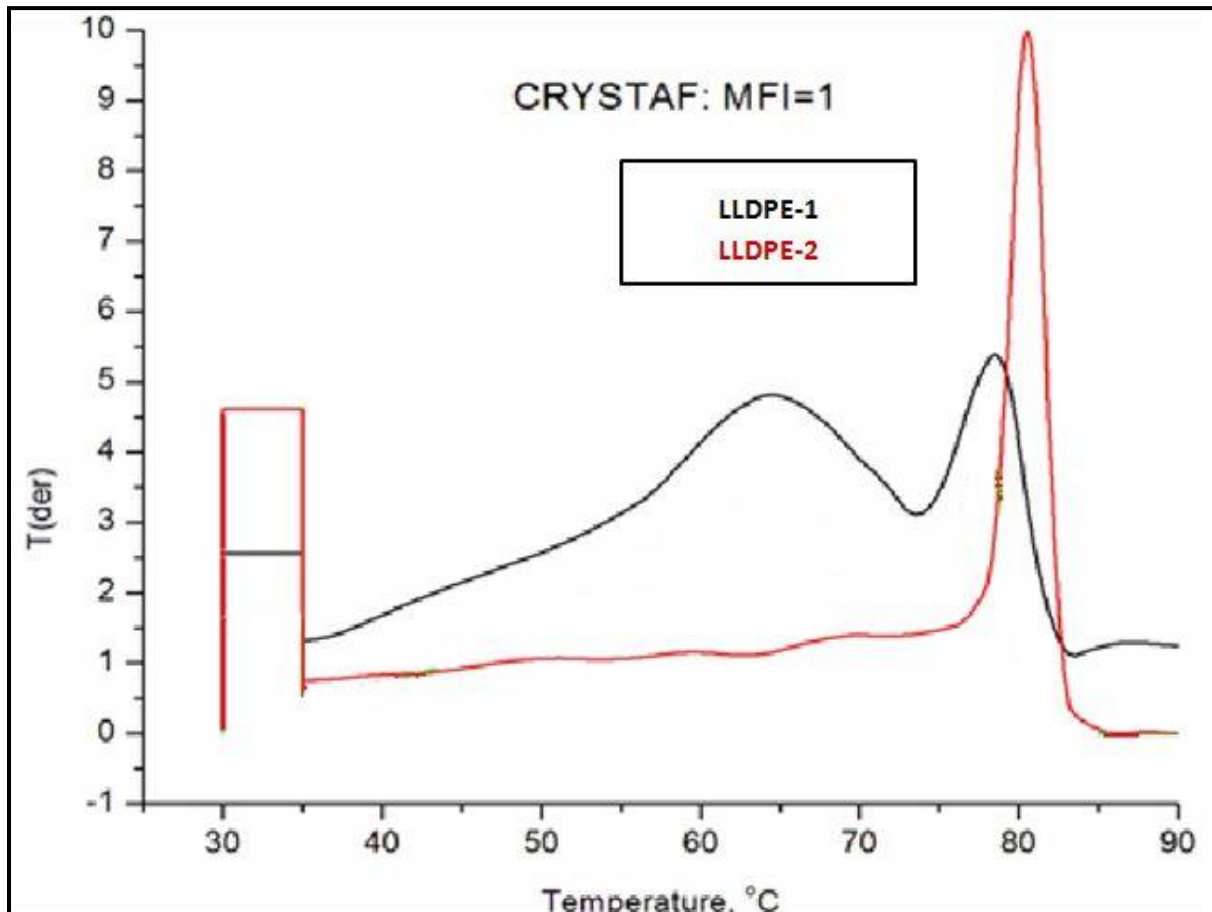
Figure 4.30: Comonomer composition distribution curve for LLDPE-1 and LLDPE-2 grade obtained by CRYSTAF analysis

From figure 4.30, it was found that both the grades had bimodal comonomer distribution. The bimodality in the LLDPE's could be attributed to multiple active sites present in the Ziegler Natta catalyst system used during resin manufacturing. Both the grades LLDPE-1 and LLDPE-2 had different comonomer composition distribution pattern within the polymer chains.

Table 4.18: Comonomer distribution in LLDPE-1 and LLDPE-2 by CRYSTAF

S. No.	Grade	Peak 1 (80.0-85.0^{0}C)	Peak 2 (70.0-80.0^{0}C)	Peak 3 (50.0-65.0^{0}C)	Peak 4 Soluble Fraction (<35^{0}C)
		Area (%)	Area (%)	Area (%)	Area (%)
1	LLDPE-1	-	22.8	70.5	6.6
2	LLDPE-2	38.2	11.5	17.2	23.1

The above table 4.18 represent the distribution of comonomer present within the polymer chains in both the LLDPE grades.

It is well known that the peak at the higher temperature (>80^{0}C) in CRYSTAF curve corresponds to mainly linear polyethylene/homo-polyethylene content i.e. linear polymer chains with longer length with no branching, whereas the temperature is decreased, polymer chains with increasing comonomer/braching content will crystallize out. The soluble portion consists of the polymer chains having maximum number of short chain branching/comonomer [36].

It was found from table 4.18, LLDPE-2 had unique distribution pattern compared to LLDPE-1. LLDPE-2 had high linear PE content of around 38% while LLDPE-1 had nil linear polyethylene content. LLDPE-2 had 11.5% area in the 70-80^{0}C region (which represent long polymer chains with little branching) while LLDPE-1 had 22.8% area. It was also found that LLDPE-2 had very high soluble fraction around 23% as compared to LLDPE-1, which had only 6.6% soluble fraction.

LLDPE-2 had amorphous content almost 3 times doubled than LLDPE-1. In a semi-crystalline polymer a small region between different spherulites are amorphous trannstion regions. Polymer chains in the crystalline region extend in to amorphous region as tie chains. The high dart impact strength and high tear strength for LLDPE-2 could be because of the more number of tie chains [39].

Thus from the above discussion it was found that LLDPE-1 and LLDPE-2 both had different comonomer composition distribution curve. LLDPE-2 had high content of linear polyethylene as well as high content of soluble fraction as compared to LLDPE-1, which resulted in higher tie chain concentration for LLDPE-2 and higher value of dart impact and tear strength than LLDPE-1.

4.3.4 <u>Thermal analysis</u>:

The values of peak melting point temperature (T_m), onset temperature of melting thermo gram and total area under the melting thermo gram was obtained and % crystallinity was calculated. Melting curve for each grade was given in Appendix.

Table 4.19: Peak melting temperatures, enthalpy values and % crystallinity value for LLDPE-1 and LLDPE-2 grades

S. No	Grade	T_m (^{0}C)	Onset T_m(^{0}C)	ΔH_1(j/g) Area up to T_m(^{0}C)	$\Delta H2$(j/g) Area after Tm(0C)	ΔH(J/g)= $\Delta H1$(j/g)+ $\Delta H2$(j/g)	Crystallinity (%)
1	LLDPE-1	121.2	108.2	101.8	14.1	115.9	40.0
2	LLDPE-2	126.9	119.7	95.1	14.3	109.4	37.7

From the above table it was found that LLDPE-2 had lower % crystallinity value as compared to LLDPE-1 which was also supported by the higher soluble fraction (amorphous content) present in LLDPE-2 than LLDPE-1 as appeared in CRYSTAF curve. But LLDPE-2 despite having low % crystallinity had higher melting peak temperature than LLDPE-1. As peak temperature corresponds to the thickness of the lamellae formed during crystallization. Higher thickness lamellae are formed by the linear high molecular weight chains. From CRYSTAF curve it was found that LLDPE-2 had higher linear polyethylene region as compared to LLDPE-1 and thus had higher peak melting temperature than LLDPE-1.

It was well known that with increase in %crystallinity, the tear strength and impact strength decreases [11]. LLDPE-1 had higher %crystallinity as compared to LLDPE-2, thus had lower value of tear and dart impact strength values.

5.0 CONCLUSION

5.1 <u>HDPE RAFFIA GRADE</u>

Industrial trials for raffia tape manufacturing were done using HDPE raffia grades. HD/R/I-018, HD/R/I-022 and HD/R/I-025 failed to perform on higher line speed of 300 Mt/min and many problems were encountered (like higher tape breakage, higher power consumption etc) while HD/R/G was performed well at line speed of 300 Mt/min. Other established raffia grades HD/R/R-027, HD/R/R-067 and HD/R4 were also found to be performing well. Therefore, to ascertain the root cause of the problems encountered in case of HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades, structure-property-performance-relationship was studied. Various characterization techniques like MFI, MFR, Power Law curve, Parallel Plate Rheometer, High Temperature–Gel Permeation Chromatography, Dynamic Mechanical Analysis and Differential Scanning Calorimetry were used and following were the major outcomes.

⇒ **From the MFI & MFR data, it was found that HD/R/G had higher MFI values, indicating lower melt viscosity as compared to HD/R/I-022 and HD/R/I-025 grades. Due to this HD/R/G had better flow ability and process ability.**

⇒ **It was found by using Power law model equation that HD/R/I-022 and HD/R/I-025 grades had higher shear viscosity over entire range of shear rate as compared to HD/R/G, which can account for higher power consumption by HD/R/I-022 and HD/R/I-025 grades.**

⇒ **From Angular frequency v/s complex viscosity curves it was found that HD/R/G, HD/R/I-018 and HD/R/I-022 had nearly similar complex viscosities over entire range of angular frequencies. HD/R/I-025 had higher complex viscosity over entire range of angular frequencies when compared to HD/R/G.**

⇒ **From rheological studies done using Parallel Plate Rheometer it was found that HD/R/I-025 had higher storage and loss modulus values over the entire**

frequency range than HD/R/G which can be related to the shift of HD/R/I-025 grade's MWD chromatogram slightly towards the right than HD/R/G grade's MWD chromatogram.

$\Rightarrow$ From MWD chromatogram it was evident that HD/R/I-025 grade had lower fraction of low molecular wt. tail than HD/R/G grade.

$\Rightarrow$ From MWD chromatogram for HD/R/I-022 and HD/R/G grades; it was found that HD/R/I-022 grade had lower fraction of low molecular wt. chain tail as compared to HD/R/G; and had slightly higher fraction of high molecular wt. tail than HD/R/G, while the loss and storage modulus values were nearly identical as obtained from rheological measurements.

$\Rightarrow$ From MWD chromatogram for HD/R/I-018 and HD/R/G; it was found that HD/R/I-018 had higher fraction of high molecular weight tail as well as low molecular weight tail as compared to HD/R/G grade, while both the grades had nearly similar loss and storage modulus values as obtained from rheological measurements.

$\Rightarrow$ From DMA analysis, it was found that HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G grades had nearly identical relaxation peaks with similar modulus values over the entire temperature range.

$\Rightarrow$ It was observed that T_m onset and peak melting temperatures (T_m) for HD/R/I-018, HD/R/I-022, HD/R/I-025 and HD/R/G grades were comparable with each other, which was observed around 120^0C and 130^0C respectively. Single melting peaks were observed for all the grades, indicating uniform lamellar thickness. ΔH values of HD/R/I-018, HD/R/I-022, and HD/R/I-025 grades were found to be lower as compared to HD/R/G, therefore the corresponding crystallinity and mechanical strength at higher line speed for HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades was less as compared to HD/R/G.

It was observed that HD/R/G had ideal MWD distribution along with proper very high molecular weight and low molecular weight fractions. For raffia tape manufacturing process, the resins used must have appropriate MWD along with the right combination of very high molecular weight fraction tail and low molecular weight fraction tail. Even slight differences in these fractions would result in poor performance of the resin during processing.

5.2 <u>HDPE LARGE BLOW MOLDING GRADE:</u>

Industrial trials for L-ring barrel (220 litre) manufacturing were done using HDPE large blow molding grades. During the trails it was observed that HD/LBM2/571 grade was performing well with no difficulty and product quality was observed within the customer's requirement. But with HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades various problems (like rough inner surface, decrease in product weight etc with HD/LBM1/024 and HD/LBM1/111 and uneven L-ring formation at the bottom of the barrel, short molding etc with HD/LBM1/121 and HD/LBM1/125) were observed during the process and in the product manufactured. Therefore, to ascertain the root cause of the problems encountered in case of HD/LBM1/024, HD/LBM1/111, HD/LBM1/121 and HD/LBM1/125 grades, structure-property-performance-relationship for HDPE large blow molding grades was studied. Various characterization techniques like MFI, MFR, Capillary Rheometer, Parallel Plate Rheometer, High Temperature–Gel Permeation Chromatography and Differential Scanning Calorimetry were used and following were the major outcomes.

⇒ **Density of HD/LBM2/571 grade was higher than HD/LBM1/024 and HD/LBM1/111 grades, but had lower value than HD/LBM1/121 and HD/LBM1/125 grades.**

⇒ **From MFI and MFR values it was found that HD/LBM2/571 had lower MFI value (which will give better mechanical properties, ESCR and melt strength) and higher value of MFR (@21.6/5.0kg) which means higher shear thinning behaviour, resulting in better process ability and better flow ability as compared to all other grades.**

⇒ **From Capillary Rheometer shear viscosity curves it was found that HD/LBM2/571 had lower melt viscosity as compared to HD/LBM1/024 and HD/LBM1/111 at varying shear rates which resulted in better/easy process ability of HD/LBM2/571. HD/LBM1/121 and HD/LBM1/125 had low melt viscosity value at varying shear rates as compared to HD/LBM2/571.**

⇒ **From Extensional viscosity curves obtained from Capillary Rheometer it was clear that extensional viscosity which is very important parameter in controlling blow molding processes, varies widely between HD/LBM2/571**

and other grades. Among all grades, HD/LBM2/571 only had higher value of extensional viscosity at varying extensional rates. All grades except HD/LBM2/571 had much lower values of extensional viscosity resulting in lower melt strength, lower die swell and higher parison sagging during processing, ultimately affecting the product manufactured as short molding and less total product weight.

⇒ From MWD chromatogram obtained from HT-GPC and from the rheological data obtained from Parallel Plate Rheometer; it was found that HD/LBM2/571 had higher fraction of high molecular weight tail, higher lower molecular weight fraction, higher complex viscosity value at low angular frequency and had broader molecular weight distribution as compared to HD/LBM1/024 and HD/LBM1/111 grades, which resulted in higher die swell, higher melt strength and more shear thinning for HD/LBM2/571 grade.

⇒ From MWD chromatogram obtained from HT-GPC and from the rheological data obtained from Parallel Plate Rheometer; it was found that HD/LBM2/571 had higher fraction of very high molecular weight, higher complex viscosity value at very low shear rate as compared to HD/LBM1/121 and HD/LBM1/125, which resulted in better melt strength and higher die swell for HD/LBM2/571 grade. HD/LBM1/121 and HD/LBM1/125 had long tail of very low molecular weight fraction as compared to HD/LBM2/571 resulting in higher MFI at low shear rates as confirmed from MFI data.

Thus it was found that HD/LBM2/571 had ideal set of properties (like low MFI, high extensional viscosity, higher fraction of very high molecular weight tail and appropriate fraction of low molecular weight tail) for L-ring barrels (220 litre) manufacturing process. It was found that it were the extensional viscosity, very high molecular weight fraction tail and appropriate low molecular weight fraction of the resin which controls the large blow molding process and products manufactured from it. Even slight differences in any of the above property of the resins, would result in different processing behaviour during manufacturing process.

5.3 LLDPE BLOWN FILM EXTRUSION GRADE

2 LLDPE (1-butene based) grades were collected along with density, MFI, dart impact, tensile strength at break, % elongation at break and tear strength values. Both the grades had nearly similar MFI @ 2.16kg and density values. But there were appreciable differences in the properties of both the grades. Thus both the grades were tested by using various characterization techniques like High Temperature-Gel Permeation Chromatography, 13C-Nuclear Magnetic Resonance spectroscopy, Crystallization Analysis Fractionation and Differential Scanning Calorimetry, to ascertain the root cause for difference in properties and structure-property-relationship was studied for each LLDPE grade and following were the outcomes.

⇒ **Both LLDPE-1 and LLDPE-2 had similar MFI and nearly identical densities.**

⇒ **Both grades had similar broadness of MWD as obtained from HT-GPC analysis.**

⇒ **From ^{13}C-NMR analysis it was found that short chain branching content was higher in LLDPE-2 (16 branching/1000C) than LLDPE-1 (10.9 branching/1000C). LLDPE-2 had higher 1-butene (3.3, mole %) content as compared to LLDPE-1 (2.2, mole %). Thus decrease in tensile strength at break and % elongation at break for LLDPE-2 grade can be related with the higher amount of comonomer present in the grade.**

⇒ **From CRYSTAF analysis, it was found that LLDPE-1 and LLDPE-2 both had different comonomer composition distribution curve. LLDPE-2 had high content of linear polyethylene as well as high content of soluble fraction as compared to LLDPE-1, which resulted in higher tie chain concentration for LLDPE-2 and higher value of dart impact and tear strength than LLDPE-1.**

⇒ **From thermal analysis done using DSC, it was found that LLDPE-2 had lower % crystallinity value as compared to LLDPE-1 which was also supported by the higher soluble fraction (amorphous content) present in LLDPE-2 than LLDPE-1 as appeared in CRYSTAF curve. But LLDPE-2 despite having low % crystallinity had higher melting peak temperature than LLDPE-1. As peak temperature corresponds to the thickness of the lamellae formed during crystallization. Higher thickness lamellae are**

formed by the long linear high molecular weight chains. From CRYSTAF curve it was found that LLDPE-2 had higher linear polyethylene region as compared to LLDPE-1 and thus had higher peak melting temperature than LLDPE-1.

$\Rightarrow$ LLDPE-1 had higher %crystallinity as compared to LLDPE-2, thus had lower value of tear and dart impact strength values.

Thus it was observed that both LLDPE grades despite having similar MFI, density and identical MWD chromatogram had different property (dart impact, tensile strength at break, % elongation at break and tear strength) values, which could be attributed to different amount of the comonomer present in the grades and widely different comonomer composition distribution in polymer chains for both the grades.

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APPENDIX

Figure: E', E'' and tan delta Vs temperature curve for HD/R/G and HD/R/I-018 grade
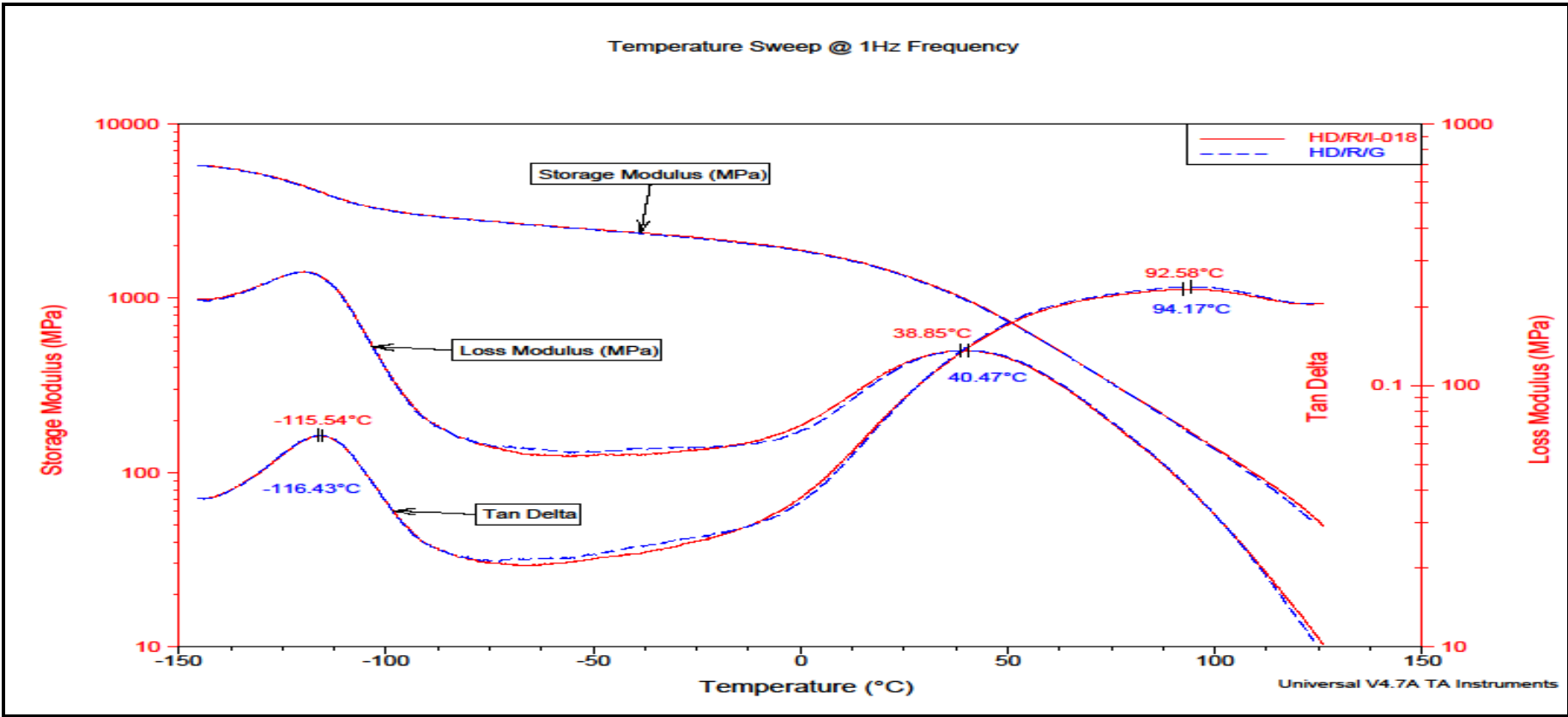
Figure: E', E" and tan delta Vs temperature curve for HD/R/G and HD/R/H grade
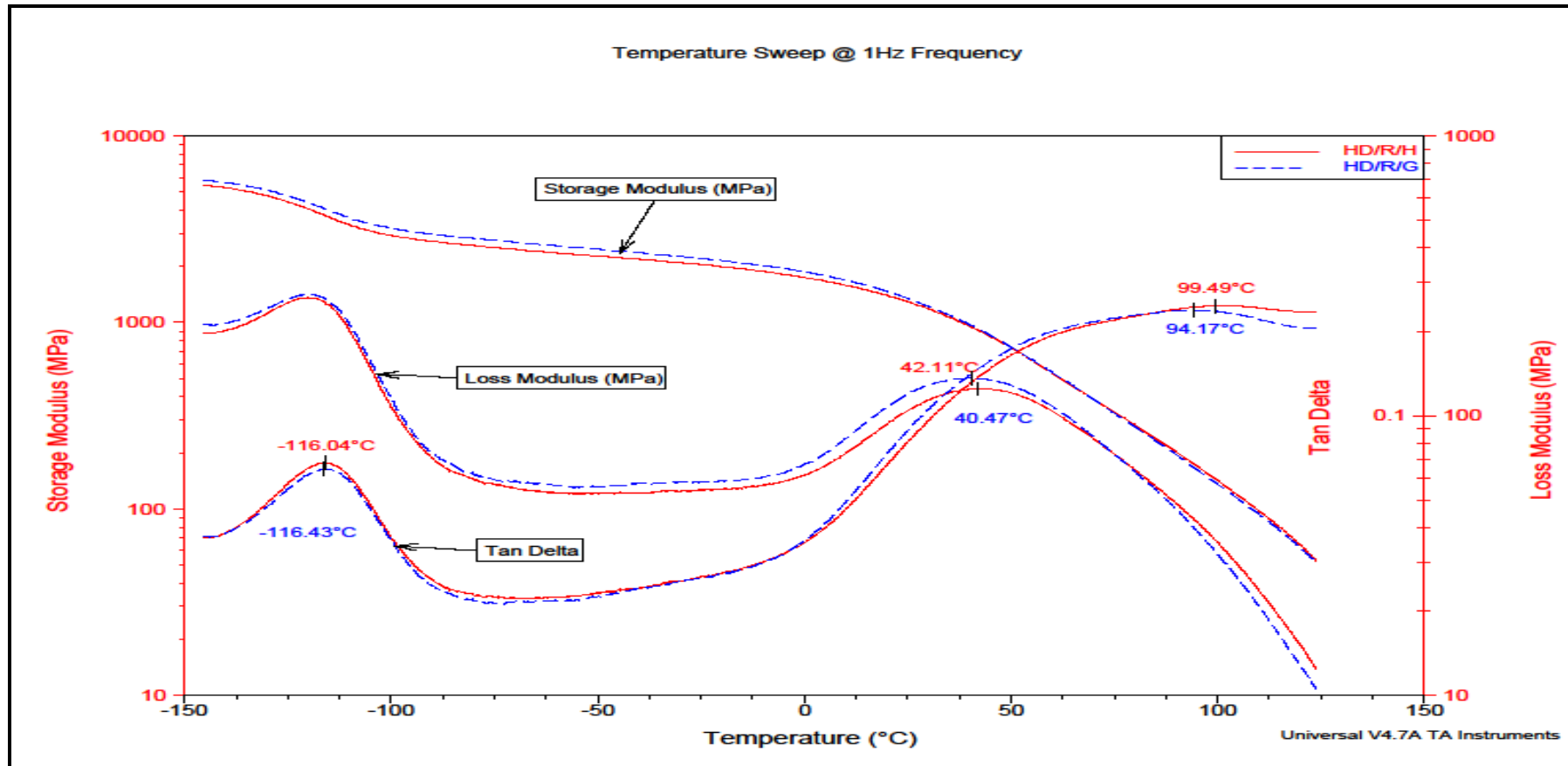
Figure: E', E" and tan delta Vs temperature curve for HD/R/G and HD/R/I-025 grade
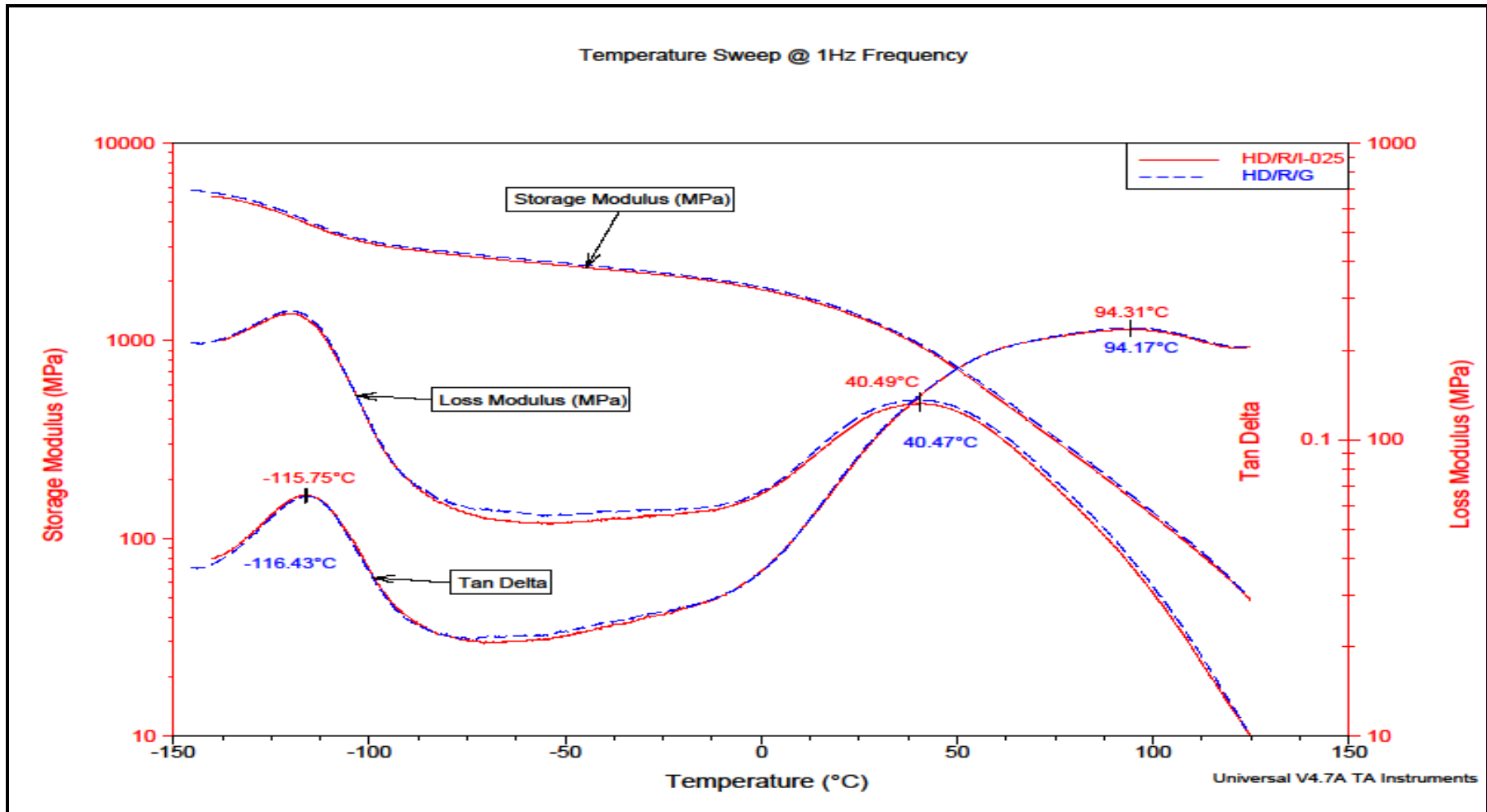
Figure: E', E'' and tan delta Vs temperature curve for HD/R/G and HD/R/I-022 grade
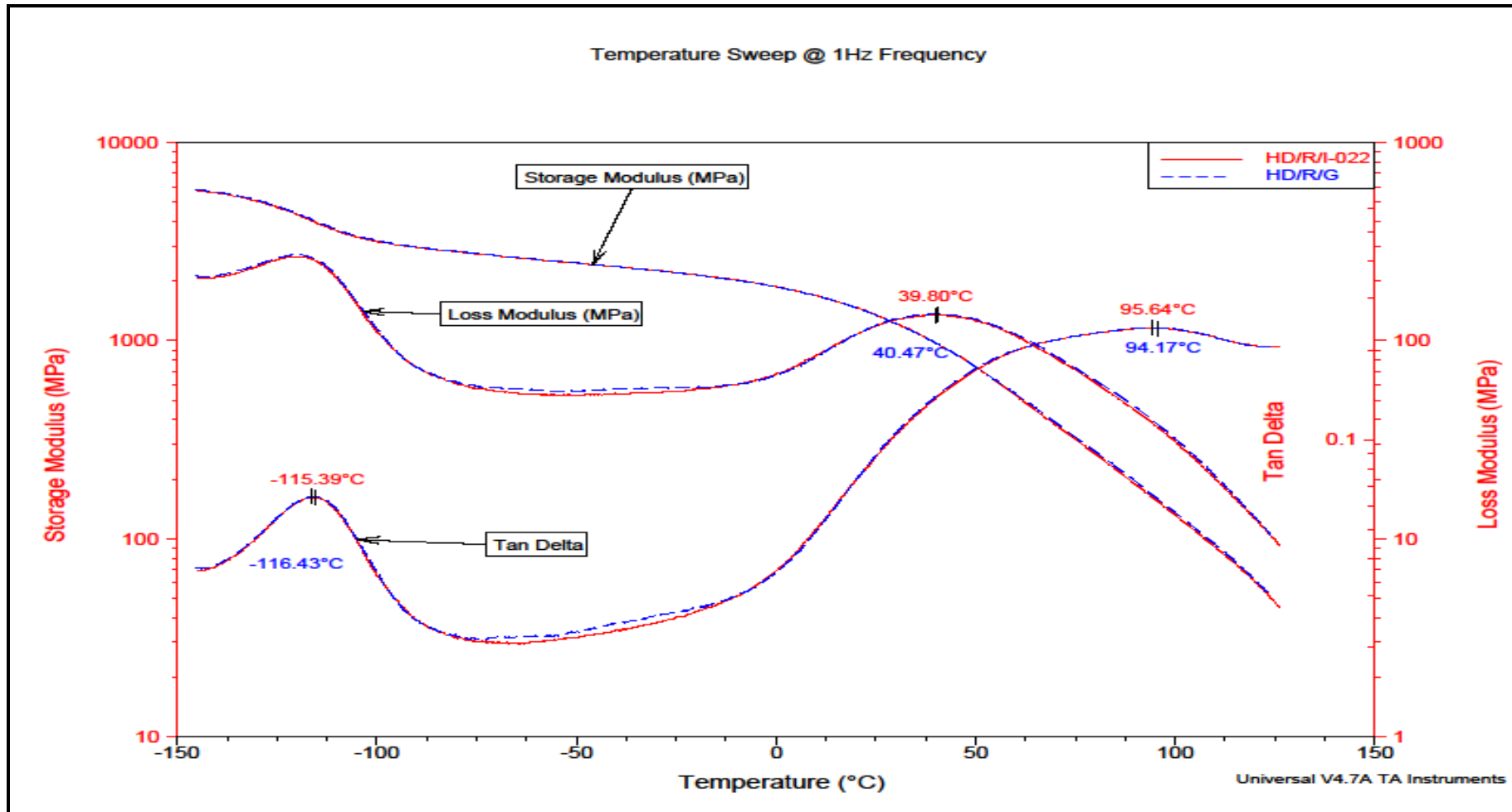
Figure: E', E" and tan delta Vs temperature curve for HD/R/G and HD/R/R-027grade
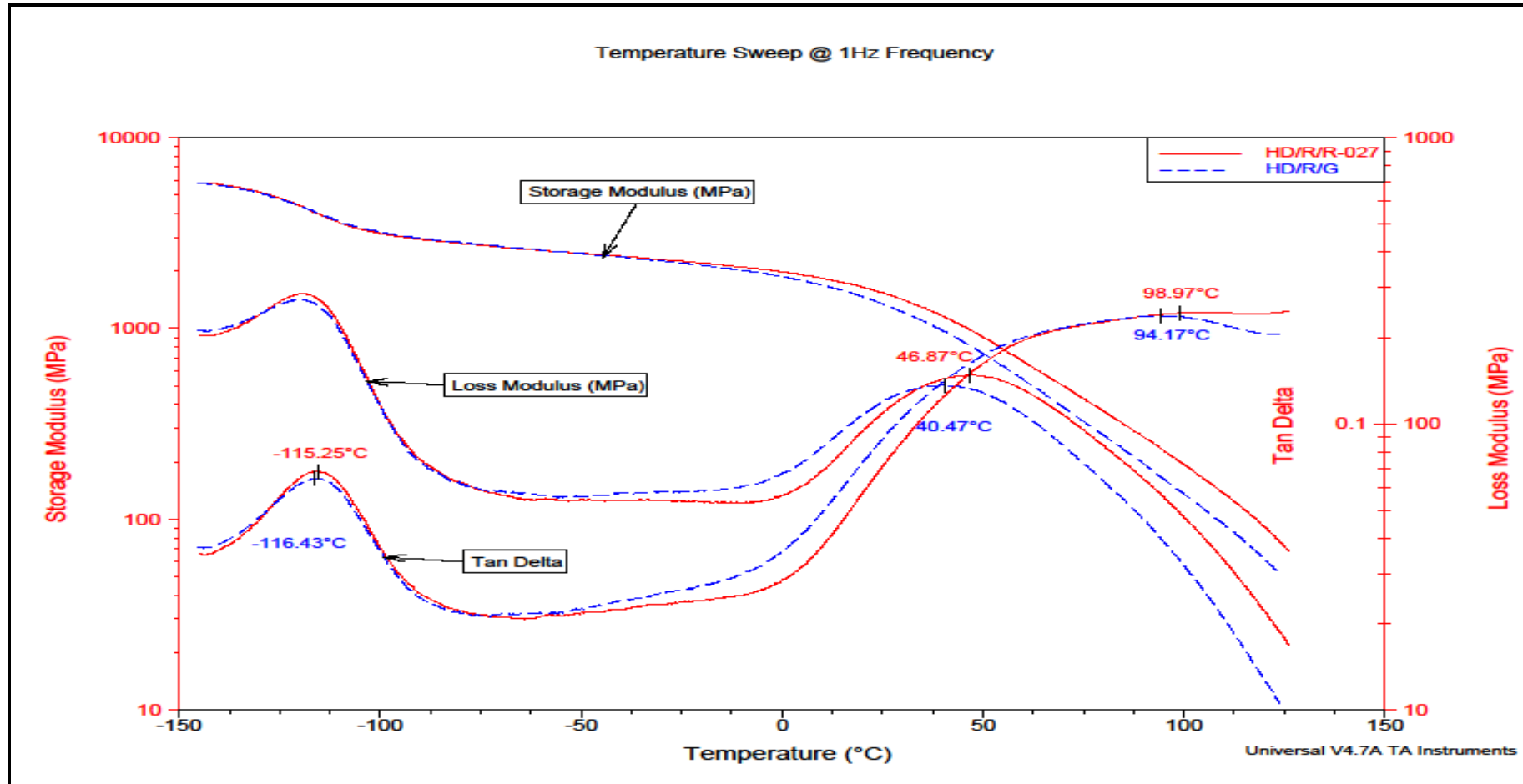
Figure: DSC 2nd heating melting thermo gram for HD/R/G, HD/R/I-018, HD/R/I-022 and HD/R/I-025 grades

HD/R/G

Integral	-1323.08 mJ	Integral	-905.42 mJ
normalized	-206.73 Jg^-1	normalized	-141.47 Jg^-1
Onset	120.63 °C	Onset	120.63 °C
Peak	133.13 °C	Peak	133.13 °C
Left Area	68.43 %		
Right Area	31.57 %		

HD/R/I-022

Integral	-1240.54 mJ	Integral	-926.76 mJ
normalized	-193.83 Jg^-1	normalized	-144.81 Jg^-1
Onset	120.74 °C	Onset	120.74 °C
Peak	132.62 °C	Peak	132.61 °C
Left Area	74.79 %		
Right Area	25.21 %		

HD/R/I-025

Integral	-1475.68 mJ	Integral	-1054.20 mJ
normalized	-194.17 Jg^-1	normalized	-138.71 Jg^-1
Onset	121.98 °C	Onset	121.98 °C
Peak	134.22 °C	Peak	134.22 °C
Left Area	71.43 %		
Right Area	28.57 %		

HD/R/I-018

Integral	-1600.08 mJ	Integral	-1030.31 mJ
normalized	-192.78 Jg^-1	normalized	-124.13 Jg^-1
Onset	121.32 °C	Onset	121.32 °C
Peak	132.54 °C	Peak	132.54 °C
Left Area	64.45 %		
Right Area	35.55 %		

50 mW

Figure: DSC 2nd heating melting thermo gram for HD/R/H, HD/R/R-027 and HD/R/R-067 grades

HD/R/R-067

Integral	-1166.23 mJ	Integral	-781.48 mJ
normalized	-197.67 Jg^-1	normalized	-132.45 Jg^-1
Onset	122.57 °C	Onset	122.57 °C
Peak	135.43 °C	Peak	135.43 °C
Left Area	67.01 %		
Right Area	32.99 %		

HD/R/R-027

Integral	-1462.10 mJ	Integral	-934.33 mJ
normalized	-211.90 Jg^-1	normalized	-135.41 Jg^-1
Onset	126.35 °C	Onset	67.99 °C
Peak	138.01 °C	Peak	138.00 °C
Left Area	63.92 %		
Right Area	36.08 %		

HD/R/H

Integral	-1432.21 mJ	Integral	-979.37 mJ
normalized	-193.54 Jg^-1	normalized	-132.35 Jg^-1
Onset	124.06 °C	Onset	71.77 °C
Peak	136.44 °C	Peak	136.44 °C
Left Area	68.37 %		
Right Area	31.63 %		

Figure: DSC thermo gram for HD/LBM2/571 grade

HD/LBM2/571

Integral	1129.24 mJ	Integral	864.13 mJ
normalized	205.32 Jg^-1	normalized	157.11 Jg^-1
Onset	121.78 °C	Onset	118.57 °C
Peak	118.57 °C	Peak	118.57 °C
Left Area	76.52 %		
Right Area	23.48 %		

Integral	-1037.10 mJ	Integral	-811.11 mJ
normalized	-188.56 Jg^-1	normalized	-147.47 Jg^-1
Onset	124.18 °C	Onset	124.18 °C
Peak	132.41 °C	Peak	132.41 °C
Left Area	78.21 %		
Right Area	21.79 %		

Figure: DSC thermo gram for HD/LBM1/024 grade

HD/LBM1/024

Integral	1088.18 mJ	Integral	699.49 mJ
normalized	201.51 Jg^-1	normalized	129.53 Jg^-1
Onset	122.14 °C	Onset	115.95 °C
Peak	115.95 °C	Peak	115.95 °C
Left Area	64.29 %		
Right Area	35.71 %		

Integral	-1008.59 mJ	Integral	-802.45 mJ
normalized	-186.78 Jg^-1	normalized	-148.60 Jg^-1
Onset	125.19 °C	Onset	101.07 °C
Peak	133.69 °C	Peak	133.69 °C
Left Area	79.56 %		
Right Area	20.44 %		

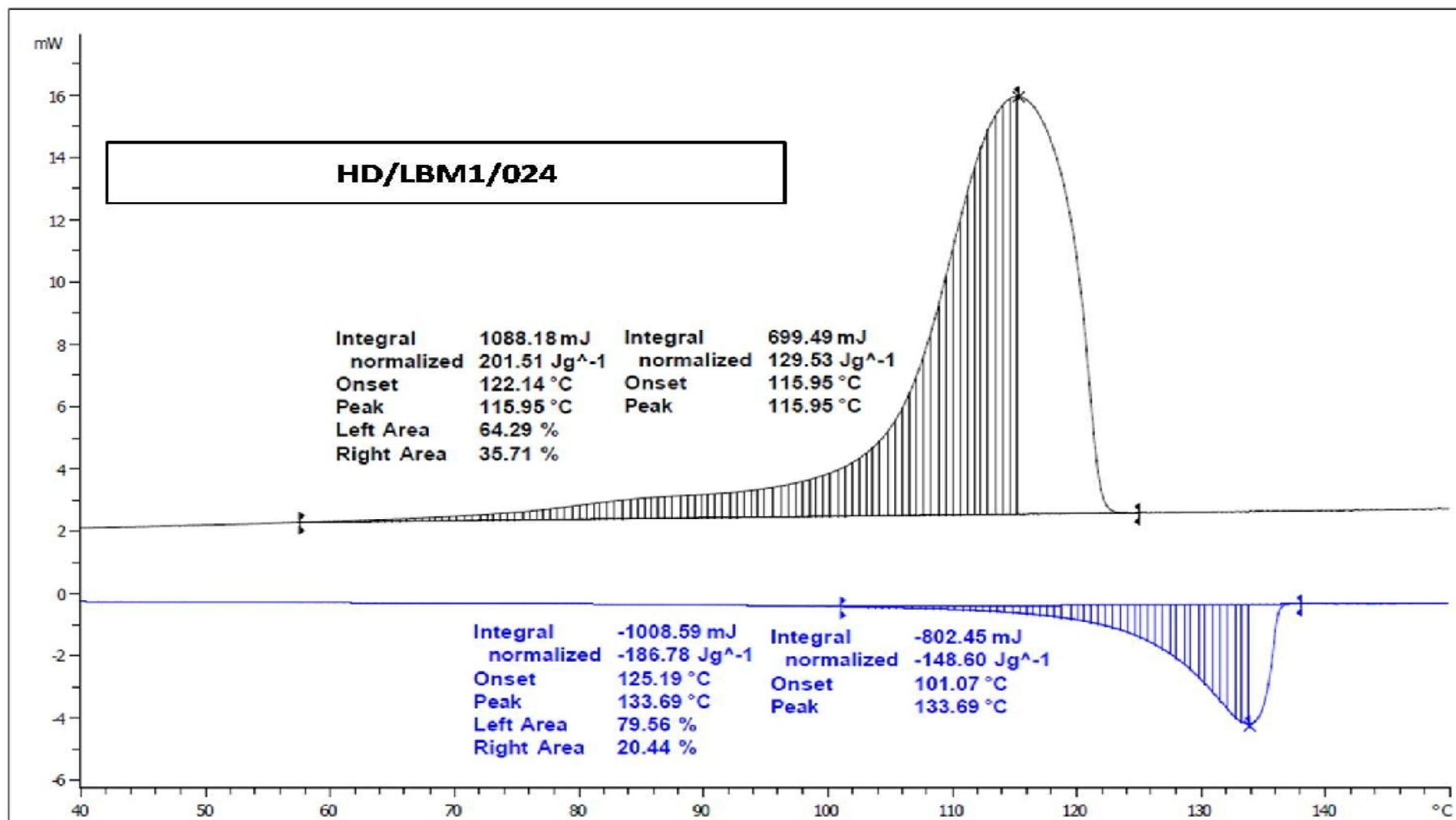**Figure: DSC thermo gram for HD/LBM1/111 grade**

Figure: DSC 2nd heating melting thermo gram for HD/LBM1/121 and HD/LBM1/125 grades

HD/LBM1/121

Integral	-1007.44 mJ	Integral	-778.87 mJ	
normalized	-193.74 Jg^-1	normalized	-149.78 Jg^-1	
Onset	123.85 °C	Onset	86.49 °C	
Peak	131.82 °C	Peak	131.82 °C	
Left Area	77.31 %			
Right Area	22.69 %			

HD/LBM1/125

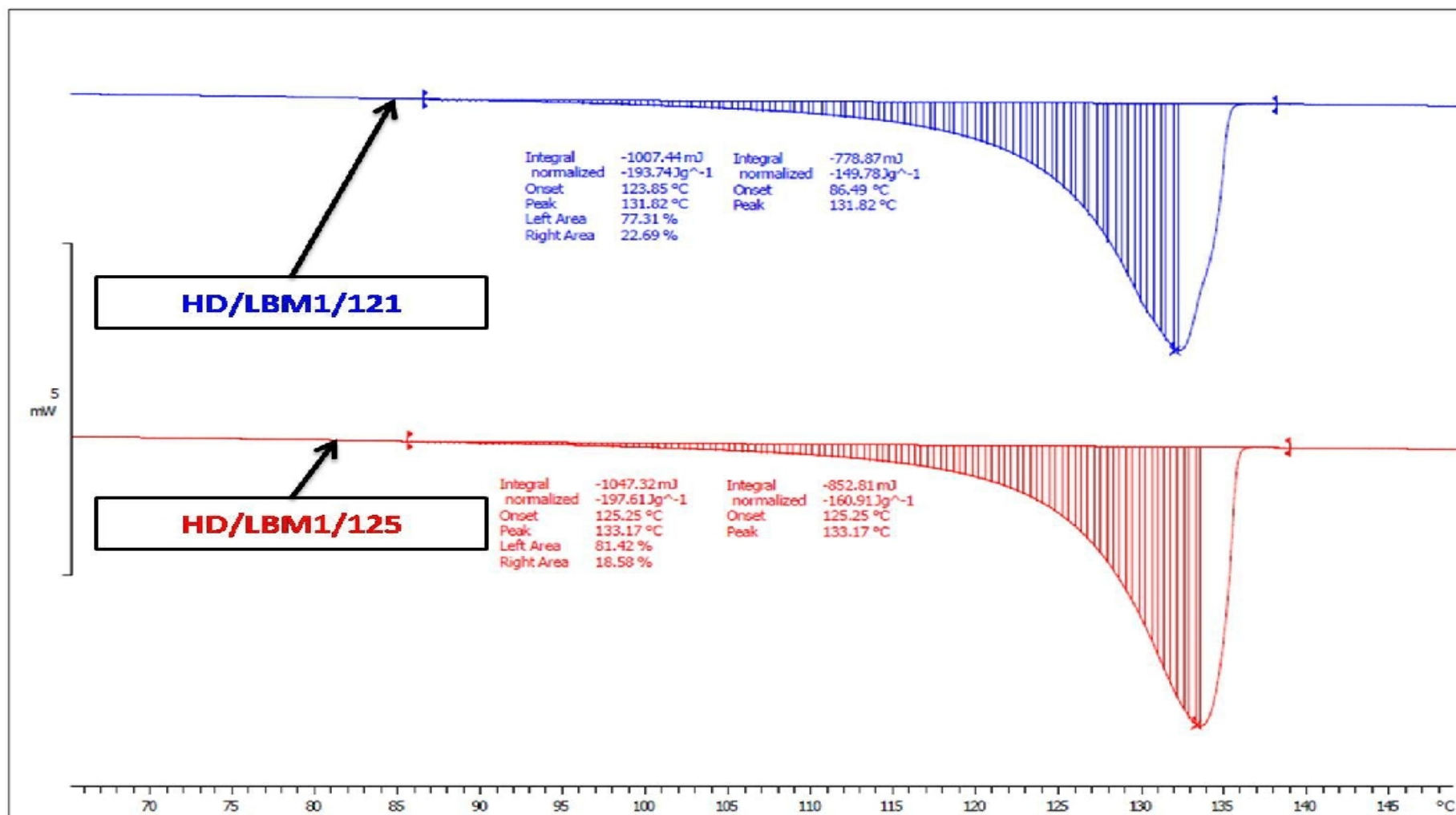|				
Integral	-1047.32 mJ	Integral	-852.81 mJ	
normalized	-197.61 Jg^-1	normalized	-160.91 Jg^-1	
Onset	125.25 °C	Onset	125.25 °C	
Peak	133.17 °C	Peak	133.17 °C	
Left Area	81.42 %			
Right Area	18.58 %			

5 mW

Figure: DSC 2nd heating melting thermo gram for LLDPE-1 and LLDPE-2 grades

10
mW

LLDPE-1

Integral   -718.48 mJ
  normalized -115.88 Jg^-1
Onset   108.22 °C
Peak   121.21 °C
Left Area   87.85 %
Right Area   12.15 %

LLDPE-2

Integral   -721.98 mJ
  normalized -109.39 Jg^-1
Onset   119.69 °C
Peak   126.93 °C
Left Area   86.90 %
Right Area   13.10 %

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