

Comparative Study for Melt Flow Index of Different Microstructure Polyethylene

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Abstract

This study focus on the rheological behavior of polyethylene. The effect of molecular weight for three different types of polyethylene were study; high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). To find the rheological behaviour of the polymer, melt flow indexer and capillary rheometer were used in this study. The shear stress and shear viscosity obtained from these three different polyethylene polymers were compared with the shear rate. It was observed that with the increase in shear rate, shear stress also increases. The behaviour of viscosity for HDPE, LLDPE and LDPE also discussed at the varying amount of shear rate. It was also found that viscosity of HDPE, LLDPE and LDPE decreases with increasing shear rate. The value of log shear stress of HDPE increases with an increase in log shear rate. The value of extension viscosity decreases from 8.295 to 1.606 KPa.s with a very high increase in extension rate of 23.5 s⁻¹ to 721 s⁻¹. Molecular mass and its distribution have a significant effect on the rheological behavior of polymers.

Key Words: Melt flow index, Polyethylene, Extension Rate, Shear Stress, Shear Viscosity

1. Introduction

From the past two decades, the plastic industry has grown significantly, lots of plastic are consuming millions of material every year. Nowadays all these are looking for various techniques of characterization in order to avoid batch to batch variation. The variation in properties during processing and the processing of polymer have very costly. For considering the batch to batch variation, one must know the polymerization process. In the polymerization process the monomer or mixture of monomer used in the reaction kettle in the presence of a catalyst, initiator or water. This will depend upon the type of polymerization. After the reaction, these monomer converts into the polymer. The distribution of the molecule in polymers vary significantly; it may be narrow distribution or broad distribution. Because of this variation, there is a need for material characterization test. There is a different way of material characterization, some of them are very simple and some are very complex. The most common test of material characterizations is melt index (flow rate), viscosity test, capillary rheometer test, gel permeation chromatography test and analytical test [1, 2].

Rheology is defined as the flow of fluids and deformation of solids under stresses and strain. The rheometer is the instrument used to measure a material's rheological properties. There are many types of Rheometer that are available

with versatile properties; these are controlled stress and strain Rheometer and capillary Rheometer. Rheology of the polymer melt is influenced by different parameters such as the design of equipment, the structure of the polymer and processing of the polymer. In the rheological measurement, the most important concepts are defined by shear stress, shear rate, viscosity elasticity and extensional viscosity [3]. The scope of the study is to compare the flow behavior of the different grades of Polyethylene.

2. Materials and Methods

“Polyethylene is light weight flexible, tough, chemical resistant polymer”. Concerning electrical insulation polyethylene exhibits outstanding properties. Because of these properties, Polyethylene is widely used in the packaging industry. The general empirical formula for Polyethylene is $[-CH_2 - CH_2 -]$ which shows ethylene unit of the polymer. The molecular structure depends upon the polymerization reaction condition [1, 2].

High density polyethylene is a linear structure polymer with little branching. Because of this structure, the polymer is highly crystalline and give the following advantages in comparison with Low density polyethylene. It increases stiffness, tensile strength and hardness. However, the impact strength and environmental stress crack are reduced because of the crystalline nature of HDPE

[4-6]. The HDPE form pellets have been purchased by Sigma Aldrich, Germany. The product grade is 547999, density 0.965 g/mL at 25 °C and high density average $M_w \sim 125,000$.

Low density polyethylene has a branched chain structure. Because of structural symmetry of molecules, the nature of polyethylene is partially crystalline." Complete crystallization is prevented since the highly branched regions of the polymers chain will not pack closely, leaving unordered regions in the molecule" [7-9]. The LDPE have been purchased by Sigma Aldrich, Germany. The product grade is 428043, density 0.925 g/mL at 25 °C and low density average $M_w \sim 847,00$.

Linear low density polyethylene has a linear structure with short side chains. The highly crystalline structure is formed because of these short side chains similar to high density polyethylene. Low density polyethylene gives advantages because of its short chain. It has a high tensile strength, high melting point, higher flexural modulus, better elongation, and better environmental stress crack resistance [10-12]. The LLDPE have been purchased by Sigma Aldrich, Germany. The product grade is 428078, density is 0.918 g/ml at 25 °C and linear low density average $M_w \sim 837,00$.

The shear stress and shear rate are determined by the Eq. (1) and (2) respectively [13].

$$\tau = \frac{F}{A} = \frac{mg}{2\pi rL} \quad (1)$$

$$\dot{\gamma} = \frac{4Q}{\pi r^3} \quad (2)$$

where; F is the force, A is the area, m is the mass, g is the gravitational constant, r is the radius and Q is the flow rate.

For the characterization of the above material the equipment used are melted flow indexer and capillary rheometer. The melt flow indexer (MFI)

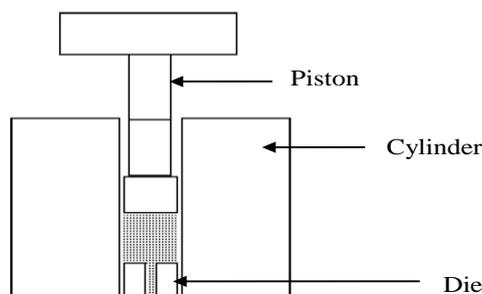


Fig. 1: Typical structure of melt flow indexer

is the equipment for evaluating melt flow properties in the plastics industries. MFI are easy to operate and usually economical. It required less of expertise to decipher the outcomes. The essential test utilizes a solitary dead weight to record the amount of material expelled over a settled timeframe. Thus, the MFI rapidly turned into the true standard in the plastics business [14, 15]. The melt index tests measure the rate of extrusion of thermoplastic material through a hole of a particular length and diameter across under endorsed states of temperature and pressure as appeared in Fig. 1. The significance of the MFI is; it characterize the behaviour of molten plastic, measures the uniformity in the flow, the grades of the polymers can be differentiated and used for quality control. It is used to determine the extent of degradation. Melt flow indexer consists of piston, cylinder, die and heater. The material is kept in the cylinder and heated with the help of heaters. After heating the molten material is pushed out from the die with the help of piston as shown in Fig. 2. The methodology of MFI is given in Fig. 3.

The rheometer is used to measure the rheological properties of a material. They can rapidly and effortlessly measure the flow properties of material over the full range of pressures, temperatures, forces, geometry and that are experienced in actual procedures. Capillary rheometer is a technique whereby a sample is extruded through a die of definite dimensions and the shear pressure drop across the die noted at set volumetric flow rates. Capillary rheometer comprised of a temperature-controlled barrel integrating at least one precision bores fixed with capillary dies at the exit as shown in Fig. 4. Pressure transducers are mounted quickly over the dies to record the pressure drop since the material tested is extruded over the dies [3, 12]. The methodology of capillary rheometer is given in Fig. 5.

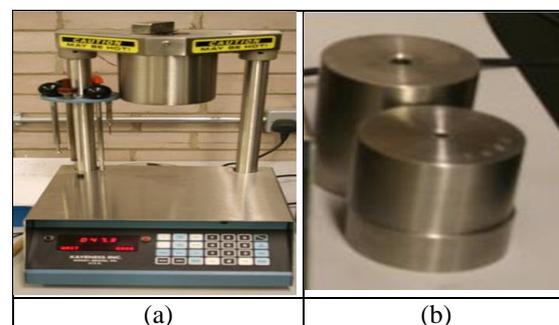


Fig. 2: (a) Kanyeness melt flow indexer used for the characterization of HDPE, LDPE and LLDPE (b) The dies used in melt flow indexer

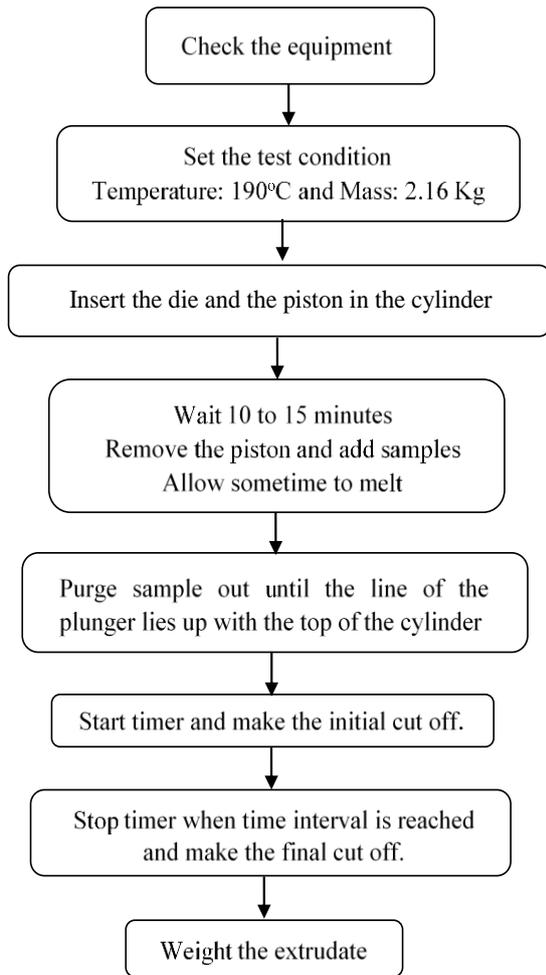


Fig. 3: Test procedure for melt flow indexer

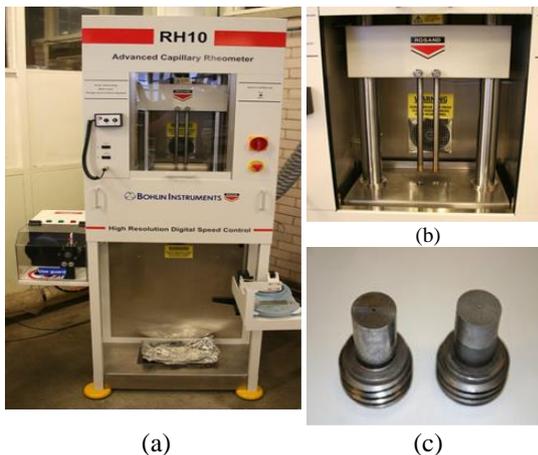


Fig. 4: (a) Bohun Instruments RH 10 advanced capillary rheometer (b) Closer view of capillary rheometer showing the pistons (c) View of capillary dies, the short die is used for an extension while the long die is used for Shear

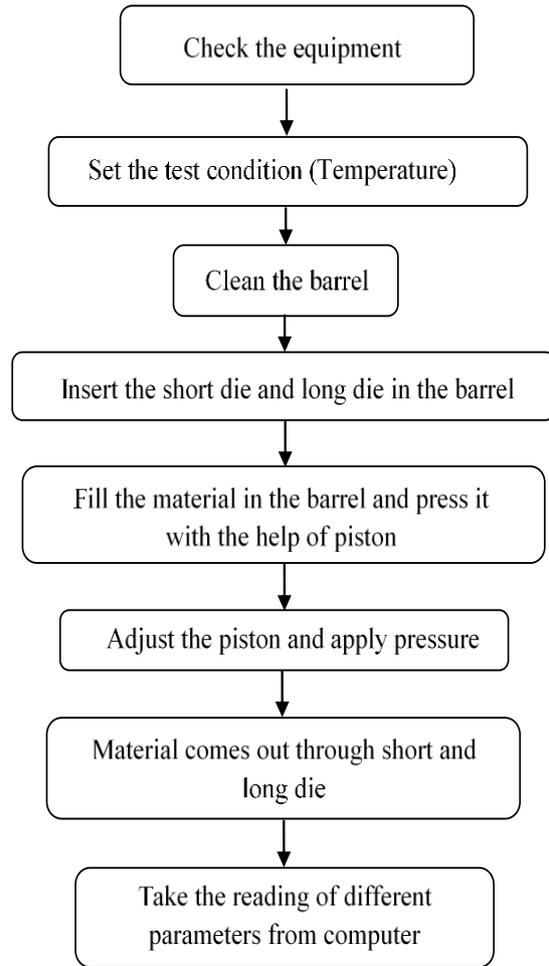


Fig. 5: Test procedure for capillary rheometer

3. Results

Fig. 6 shows the flow curve of LDPE, HDPE and LLDPE at 90°C obtained with the capillary dies of length 8.0×10^{-3} m. The plotted curve shows the viscoelastic curve of LDPE, HDPE and LLDPE at 190°C. The data indicated the effect of pressure on the viscosity of material as discussed in the literature [3].

During the first run to carry out the effect of pressure isothermally the results explains that with the increase in shear rate the shear stress increases in LDPE, HDPE and LLDPE. At the value of a very small shear rate (100s^{-1}) HDPE shows the stress value around 91.7 KPa which is lowest as compared to LDPE and LLDPE having a value of 178.64 KPa and 108.41 KPa respectively. This behaviour was studied by Mnekbi Cheima, which predict the viscosity-pressure dependency on HDPE due to increase in pressure as the shear rate increases [5].

Similar behaviour was shown by LDPE, where the value of shear stress is 108.41KPa at a shear rate of 100 s^{-1} . The behaviour was studied by Burghlea, explains at greater rate of deformation the maximum value is stress is observed however the deformation is inhomogeneous [15]. The summarized result for shear stress and shear rate of HDPE, LLDPE and LDPE are shown in Table 1. Analogous experiments were performed on LLDPE, but there lies an anomaly, the shear stress increases with increasing the shear strain from 178.64 KPa (at 100 s^{-1}) to a value of 350 KPa (at 750 s^{-1}). However, after this value, the stress decrease to 343 KPa and again raised till the value

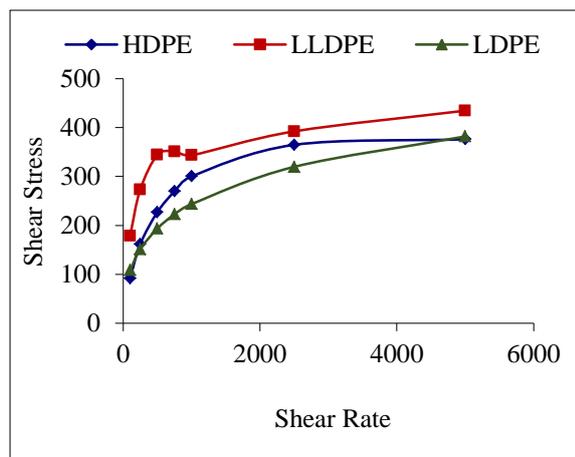


Fig. 6: Comparison between shear stress and shear rate of HDPE, LLDPE and LDPE

Table 1: Summarized result for shear stress and shear rate of HDPE, LLDPE and LDPE

HDPE		LLDPE		LDPE	
Shear rate (s ⁻¹)	Shear stress (kPa)	Shear rate (s ⁻¹)	Shear stress (kPa)	Shear rate (s ⁻¹)	Shear stress (kPa)
100	91.756	100	178.643	100	108.414
248.146	161.551	248.118	272.938	248.146	151.190
499.162	227.079	498.937	343.895	498.937	193.465
750.515	269.565	750.937	350.973	750.459	222.878
999.337	300.186	999.703	343.585	999.506	243.588
2499.693	364.647	2500.087	392.157	2499.159	319.640
5000.315	376.031	4999.781	434.486	5000.034	381.778

Fig. 7 depicts the behaviour of viscosity by varying the amount of shear rate. At shear rate 100 s^{-1} , HDPE shows the lowest value of viscosity (917 Pa.s) followed by LDPE with viscosity of 1084.14 Pa.s and LLDPE with the value of 1786.47 Pa.s HDPE confirm that with an increase in shear rate there is a decrease in viscosity of HDPE to the value of 75.20 Pa.s at 5000 s^{-1} . This is due to the chain branching significantly affect the viscosity of HDPE [6]. This decrease was also because of the flexible structure backbone and weak intermolecular forces. The most strength of

of 434 KPa at a strain of 5000 s^{-1} . The C-C bond flexibility leading low glass transition temperature. However, the T_g is related with the movement of moderately long segments in the amorphous region hence in a crystalline polymer there are few such portions the T_g has minimal physical importance [16].

The appearance of this hump was studied by Weon Jong, describes that the crosslinking density of LLDPE effect the thermal properties of the material [17].

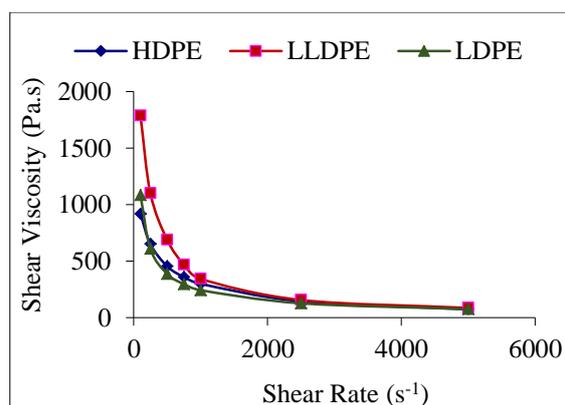


Fig. 7: Comparison between shear viscosity and shear rate of HDPE, LLDPE and LDPE (Capillary Rheometer)

the polymer is because, crystallization permits molecular packing very closer.

LDPE behaviour can also be studied in Fig. 2 demonstrates the same trend as of HDPE, although the value of viscosity varies from 1084 Pa.s to 76 Pa.s with share strain changing from 100 to 500 s^{-1} . This was reported by Peres Anderson explaining that at the low shear rate the chains are more resistive to deformation, however with an increase in the shear rate the deformation dominant [7]. Table 2 shows the summarized result for shear viscosity and shear rate of HDPE,

LLDPE and LDPE. The experimental results also show that in LLDPE the value of shear viscosity decreases from 1786 to 86 Pa.s with an increase in shear strain from 100 to 5000s⁻¹. The behaviour was explained by Weon Jong, that at constant temperature the increase in shear strain the viscosity decrease due to increase in crosslinking which results in greater value of viscosity among LDPE and HDPE at 5000s⁻¹ [17]. This changed behaviour is due to the variation in the degree of short and long chain branching in the polymer, molecular weight, impurities, the presence of some comonomer residues, and polymerization residues [18, 19].

Fig. 8 explains the log-log relationship among shear stress and shear strain HDPE, LDPE and LLDPE. The value of log shear stress of HDPE increases with an increase in log shear rate. The value varies from 1.92 to 2.572 for log shear rate of 2 and 3.69 respectively. Although LDPE shows very different behaviour as compared to HDPE. The curve indicates the value of log shear stress is 2.394. After this point, the trend of LDPE is similar to that of HDPE. The curve of LLDPE explain the similar trend with HDPE, the log value of shear stress is lowest (2.2519) at log shear strain of 2 and increases till 2.637 at the log shear stress of 3.69895, also present in Table 3.

Table 2: Summarized result for shear viscosity and shear rate of HDPE, LLDPE and LDPE

HDPE		LLDPE		LDPE	
Shear rate (s ⁻¹)	Shear viscosity (Pa.s)	Shear rate (s ⁻¹)	Shear viscosity (Pa.s)	Shear rate (s ⁻¹)	Shear viscosity (Pa.s)
100	917.564	100	1786.436	100	1084.145
248.146	651.030	248.118	1100.033	248.146	609.278
499.162	454.920	498.937	689.255	498.937	387.754
750.515	359.173	750.937	467.380	750.459	296.990
999.337	300.385	999.703	343.687	999.506	243.709
2499.693	145.876	2500.087	156.857	2499.159	127.899
5000.315	75.201	4999.781	86.901	5000.034	76.355

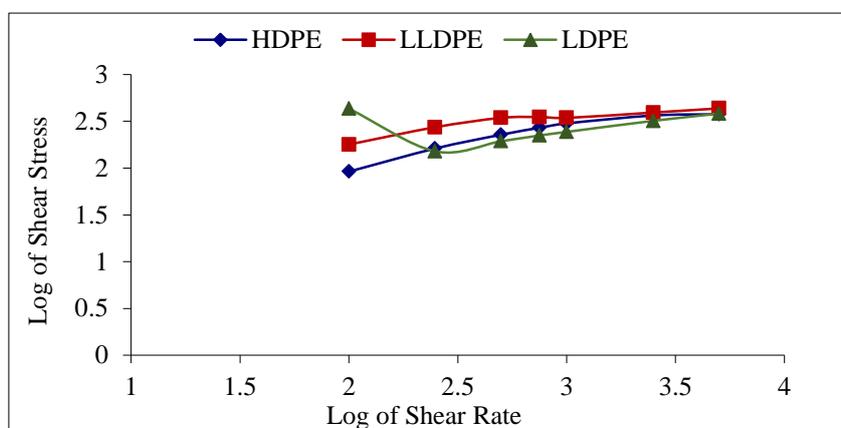


Fig. 8: Comparison between log shear stress and log shear rate of HDPE, LLDPE and LDPE

Table 3: Summarized result for log of shear viscosity and log of shear rate of HDPE, LLDPE and LDPE

HDPE		LLDPE		LDPE	
Log of shear stress	Log of shear rate	Log of shear stress	Log of shear rate	Log of shear stress	Log of shear rate
1.962	2	2.251	2	2.635	2
2.208	2.394	2.436	2.394	2.179	2.394
2.356	2.698	2.536	2.698	2.286	2.698
2.430	2.875	2.545	2.875	2.348	2.875
2.477	2.999	2.536	2.999	2.386	2.999
2.561	3.397	2.593	3.397	2.504	3.397
2.575	3.698	2.637	3.698	2.581	3.698

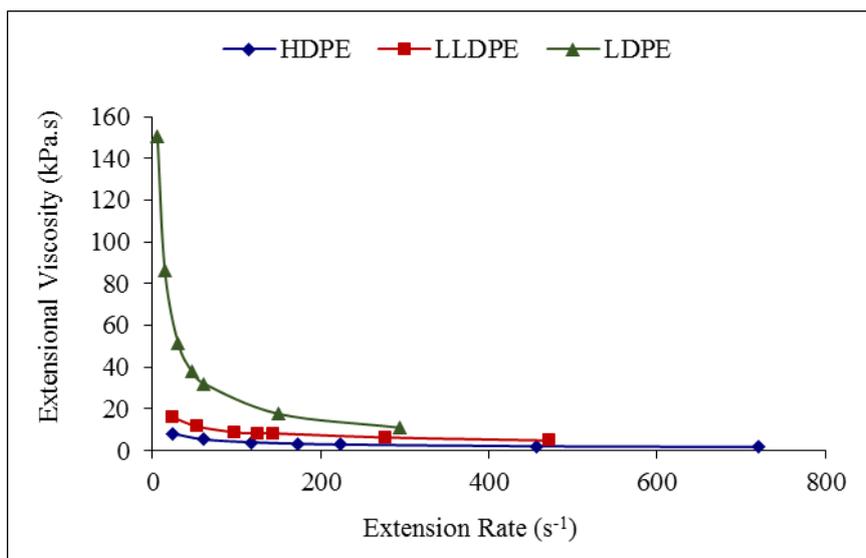


Fig. 9: Comparison between extensional viscosity and extensional rate of HDPE, LLDPE and LDPE

Table 4: Summarized result for extension rate and extension viscosity of HDPE, LLDPE and LDPE

HDPE		LLDPE		LDPE	
Extension rate (s ⁻¹)	Extensional viscosity (kPa.s)	Extension rate (s ⁻¹)	Extensional viscosity (kPa.s)	Extension rate (s ⁻¹)	Extensional viscosity (kPa.s)
23.516	8.295	23.572	16.074	5.998	150.638
60.352	5.502	54.032	11.598	14.7197	86.576
118.422	4.041	98.479	8.846	30.640	51.407
172.813	3.387	125.733	8.335	46.923	37.982
224.261	2.982	143.740	8.312	61.576	32.105
456.363	2.188	277.098	6.384	150.524	17.628
721.399	1.806	472.118	4.872	293.451	11.083

Table 5: MFI, shear stress and shear rate calculated of HDPE, LLDPE and LDPE

Polymers	MFI gm/10 min	mx10 ⁻⁶ kg/sec	Flow rate Qx10 ⁻⁹ m ³ /sec	Shear stress τ Pa	Shear rate γ̇ sec ⁻¹
HDPE	3.975	6.625	8.728	402449.92	9.6603
LLDPE	1.15	1.9166	2.2084	402461.538	2.44
LDPE	0.22	0.36667	0.39726	402453.89	0.44

The relation between extension viscosity and an extension rate of LDPE, HDPE and LLDPE. The experimental run for HDPE in Fig. 9 shows that with a significant increase in extension rate there is very less decrease in viscosity. The value of extension viscosity decreases from 8.295 to 1.606 KPa.s with a very high increase in extension rate of 23.5 s⁻¹ to 721 s⁻¹. Though LDPE shows a very drastic decline in extension viscosity from 150.63 to 86.57 KPa.s when extension rate decreases from 5.998 s⁻¹ to 14.716 s⁻¹ and this keep on reducing till the value of 0.11 KPa.s when the extension rate increase to 293.4551. Although the LLDPE curve shows the same behaviour as that of HDPE. Table 4 represents the summarized

result for extension rate and extension viscosity of HDPE, LLDPE and LDPE.

Table 5 represents the calculated values of MFI, shear stress and shear rate of HDPE, LLDPE and LDPE at temperature 190°C, mass 2.16 Kg, radius 1.048 x 10⁻³ m and length 8.0 x 10⁻³ m. The existence of these branch points is restrict to inhibit with the crystallization and this difference is clearly observed in the polymers. The high-pressure polymer has the low density (crystallization is reduced because of close packing), the minimum opacity and lower yield point, melting point and Young's modulus in tension (reliant on the crystallinity)[1, 2]. LLDPE

are almost comprised of short side chains (free of long chain branches) through copolymerizing ethylene with a little amount of a complex alkene (oct-1-ene). This branching inhibits with the capability to crystallize the polymer. Thus, the degree of crystallinity mainly affect the properties like; molecular weight differences and small solid displacement that involve large deformations such as melt viscosity, tensile strength, low-temperature brittle point and elongation at break [16, 17, 20]. LDPE has low melt shear sensitivity and strength [3, 8, 21]. The flow of LDPE may restrict due to large chain branches that's why its MFI is very low. Due to very short chain branches HDPE flows more easily that's why its melt flow rate is more than the flow rate of LDPE. LLDPE has average branches so it is showing average flow rate.

4. Conclusions

In polymer processing, it is very important to know the flow behavior of the material. By the characterization techniques, one can check the process ability, rheological and mechanical properties and performance. Melt flow indexer and capillary rheometer were used to study the rheological behaviour of the HDPE, LLDPE and LDPE polymers. Molecular weight and morphology of polymer have a significant effect on the process ability of the polymer through dynamic effects on their rheological properties. The flow rate was measured at single shear stress and shear rate performed at one set of temperature in MFI and the apparent viscosity is calculated while the capillary rheometer measure viscosity over an entire range of shear stress and shear rate. So, it is important to know the flow behavior of polymer in order to set good processing condition on actual processing equipment and avoid batch to batch variation.

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