PROCESSABILITY OF POLYETHYLENE HOMOPOLYMERS AND COPOLYMERS WITH RESPECT TO THEIR MOLECULAR STRUCTURE

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Abstract – The processability of commercial polyethylene homopolymers and copolymers, including both high and low density polyethylenes, was evaluated with respect to their molecular structure by measuring their melt rheological and thermodynamic properties. Short chain branching (SCB) mainly controls the density and thermodynamic properties, but it has little effect on the melt rheological properties. Long chain branching (LCB) has little effect on the density and the thermodynamic porperties, but it has drastic effects on the melt rheological properties. LCB increases the pseudoplasticity and the flow activation energy, reducing the viscosity in processing and thus improving the processability. Very small amounts of LCB in metallocene type low density polyethylenes very effectively reduce the viscosity and improve the flow stability in processing.

INTRODUCTION

1. Molecular Parameters-Physical Properties-Melt Viscosity Relationships

The properties of polymers in solid state and also in melt state depend on chemical composition, molecular structure, molecular weight (MW) and molecular weight distribution (MWD). The high strength of a polymer comes from its gigantic molecular size. Large polymer molecules are highly entangled each other effectively connecting all molecules, and the molecular entanglement greatly contributes to the high strength of polymers in solid state. For a given average MW, a broader MWD indicates greater amount of low MW molecules with low strength. Therefore, the strength of a polymer deteriorates with increasing MWD. High MW and narrow MWD are desirable to achieve good physical properties.

The viscosity of a fluid 'comes from the internal friction between the molecules, and it increases proportional to the MW for simple fluids. Since a gigantic polymer molecule is entangled with many neighboring molecules dragging them along with it as it flows, its effective size is greatly amplified in flow and it exhibits a greatly higher viscosity than the level expected for its MW [Bueche, 1952; Graessley, 1967]. Polymers have high viscosities and develop undesirably high melt temperatures, often limiting the production rates, in modern high speed processes. Some entanglements become disentangled in flow as the molecules are oriented along the flow direction. Thus, the viscosity of a polymer decreases with increasing shear rate as more entanglements become disentangled. The viscosity of linear polymers depends on the MW by a power of about 3.5 at extremely low shear rates near zero [Bueche, 1952], but the power decreases with increasing shear rate eventually to 1.0 at very high shear rates when all entanglements

are dissipated [Graessley, 1967]. Such pseudoplastic or shear thinning behavior becomes more pronounced with increasing MWD at a given average MW. Contrary to the requirements for good physical properties, low MW and broad MWD are desired to achieve low viscosities in processing.

Polymer melts exhibit elasticity as demonstrated by the well known swelling phenomenon of extrudates exiting from dies. This is due to the relaxation of molecules from the unstable oriented shapes in flow to the stable random coils upon removal of the applied stress. The elasticity causes various types of flow instability or melt fracture at high shear rates such as rough or fractured surface and distorted extrudate. Molecules with higher MWs can orient more in flow and contribute more to the elasticity and the flow instability.

The MW and MWD of a commercial polymer must be chosen as a compromise to achieve good physical properties and a good processability.

2. Molecular Structures of Different Polyethylene Homopolymers and Copolymers

Polyethylene (PE) molecules with a regular molecular structure crystallize upon cooling from molten state. A perfect PE crystal has a density of about 1.000 g/cc at 25°C and melts at about 141°C [Brandrup and Immergut, 1964]. The melting point decreases as the amount of crystal defects increases. Crystalline PE is a hard solid at room temperature (RT). Completely amorphous PE has a density of about 0.855 g/cc at 25°C without a melting point, and it behaves as a soft elastomer at RT. Real PE molecules cannot crystallize completely due to structural irregularities such as chain ends, short chain branches (SCB) and long chain branches (LCB). As the amount of SCB or LCB increases, the amount of crystal defects is increased resulting in a lower crystallinity with a lower melting point, density and modulus.

High density polyethylene (HDPE) used for bottles is a homopolymer produced by polymerizing only one monomer, ethy-
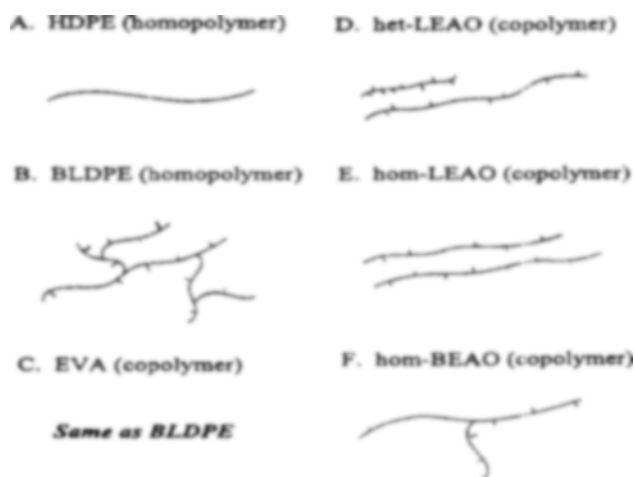

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Fig. 1. Molecular structures of various polyethylene homopolymers and copolymers.

Fig. 2. Molecules of various comonomers for polyethylene copolymers.

lene. HDPE has a linear molecular structure without SCB or LCB as shown in Fig. 1, and it can crystallize extensively to about 70 wt%, resulting in a high density around 0.960 g/cc.

High pressure low density PE, or branched low density PE (BLDPE), used for films is also a homopolymer of ethylene, but the molecules have a branched structure with LCB and SCB as shown in Fig. 1. Polymers with LCB are called branched polymers. Polymers with SCB, but without LCB, are usually classified as linear polymers. BLDPE can crystallize to only about 40 wt% mainly due to the large amount of SCB, resulting in a low density below 0.920 g/cc. It is well known that BLDPE, compared at the same density and melt index [MI] (ASTM), is much easier to process than HDPE, consuming less motor power and developing lower melt temperatures. Such a difference results from the LCB in BLDPE. LCB increases the temperature and shear sensitivities of viscosity, reducing very effectively the viscosity in processing [Tung, 1960; Boghetich and Kratz, 1965; Mendelson et al., 1970; Chung et al., 1972].

A controlled amount of SCB along PE molecules can be incorporated by polymerizing ethylene with a comonomer, such as vinyl acetate (VA), acrylic acid or various α-olefins (butene, hexene or octene, etc.) shown in Fig. 2. These comonomers become SCB upon polymerization. Poly(ethylene/vinyl acetate) (EVA) is a random copolymer of ethylene with a minor fraction of VA distributed randomly along the molecules. EVA is a branched polymer with LCB like BLDPE, and its viscosity also has a high temperature sensitivity and a high shear sensitivity.

The polymer commonly known as linear low density polyethylene (LLDPE) is a copolymer produced by polymerizing ethylene (E) with an α-olefin (AO) comonomer. It has a linear molecular structure without LCB like HDPE, but with lots of SCB. The α-olefin comonomers or the SCBs are distributed nonuniformly at different intervals along a molecule, and heterogeneously at different concentrations in different molecules as shown in Fig. 1. LLDPE is a heterogenous linear poly (ethylene/α-olefin) copolymer, and it will be called het-LEAO in this paper following the designation like EVA for a clear scientific comparison of molecular structure. It is well known that het-LEAO, compared with BLDPE at the same density
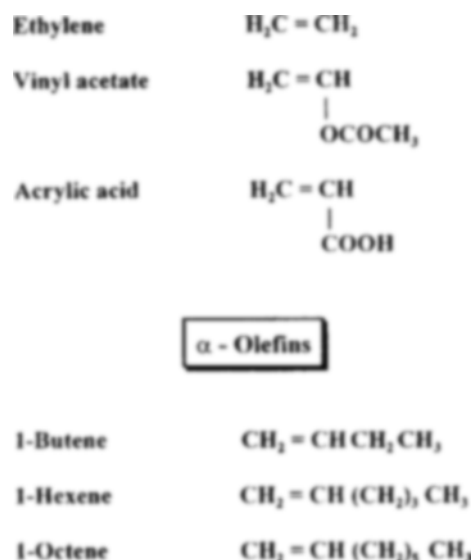
and [MI], draws more motor power and develops higher melt temperatures in processing.

A new type of LLDPE, produced by the single site catalyst technology including metallocene and other proprietary catalysts, has been introduced in recent years by Exxon [Speed et al., 1991] and others. The single site catalyst technology produces linear molecules with the comonomers distributed quite randomly and uniformly at relatively uniform intervals along a molecule, and homogeneously among the molecules with about the same concentration as shown in Fig. 1 as well as a very narrow MWD of weight average MW/number average MW= about 2. This polymer is a homogeneous linear poly(ethylene/α-olefin) copolymer (hom-LEAO) with a different molecular structure from het-LEAO with respect to the comonomer distribution. The same amount of comonomer content in hom-LEAO and het-LEAO leads to a lower density for hom-LEAO. Due to the very narrow MWD, hom-LEAO has better physical properties but a higher viscosity, and it is more difficult to process than het-LEAO.

The newest low density polyethylene is the resin from Dow produced by a proprietary constrained geometry catalyst technology called INSITE™ technology [Lai et al., 1994]. It is also a homogeneous poly(ethylene/α-olefin) copolymer (hom-EAO) with the same type of comonomer distribution as hom-LEAO, but it has a small amount of LCB as shown in Fig. 1. It is a homogeneous branched poly(ethylene/α-olefin) copolymer (hom-BEAO). The amount of LCB is usually less than one per molecule, but it is controllable over a wide range. Dow's IN-SITE technology can easily produce elastomeric resins with extremely low densities around 0.870 g/cc incorporating very high contents of α-olefin comonomer over 20 wt%.

All types of polyethylene homopolymers and copolymers discussed above are evaluated in this study for their processability with respect to their molecular composition and structure by measuring their melt rheological and thermodynamic properties, which are the two most important material properties controlling the processability. A polymer with a lower melting

point, heat of fusion and viscosity will by easier to process, resulting in a lower melt temperature and a higher output rate.

3. Long Chain Branching Characterization

The small amounts of LCB in Dow's hom-BEAO are difficult to measure by analytical means, but they can be conveniently represented by the Dow Rheology Index (DRI). DRI is basically a melt rheological index calculated using melt viscosity data as shown below [Lai et al., 1994].

$$DRI \text{ (dimensionless)} = \frac{1}{10}\left[A \cdot \left(\frac{\tau_0}{\eta_0}\right) - 1\right] \quad (1)$$

where $A = 3.65 \times 10^5$ Pa

τ_0 = characteristic relaxation time, s

η_0 = zero shear viscosity, Pa-s

τ_0 and η_0 are determined by fitting the measured melt viscosity data (η) over a range of shear rate ($\dot{\gamma}$) at a given temperature to a generalized Cross equation with three constants (τ_0, η_0, n);

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (\dot{\gamma} \cdot \tau_0)^n} \quad (2)$$

DRI is based on the finding that (τ_0/η_0) has a constant value equal to $(1/A)$ at any temperature for linear homogeneous polyethylene copolymers but (τ_0/η_0) increases with increasing LCB. Higher values of DRI indicate higher contents of LCB. DRI=0 indicates no LCB, and DRI value around 30 indicates about one LCB per molecule.

EXPERIMENTS

Table 1 lists all samples used in this study together with some pertinent data for the samples. The [MI] and the DRI are the measured values, but the density and the MWD are the nominal values reported by the producers. The MWD values for the three samples in D series were measured by a gel permeation chromatograph back to assure an accurate comparison. Some are commercial resins and others are experimental resins. The samples in A (HDPE), B (BLDPE), C (EVA) and D (het-LEAO) series are extrusion film grade resins well known to the industry. The samples in E (hom-LEAO) and F (hom-BEAO)

series are the new hom-EAOs produced by single site catalysts. Sample E1 from Exxon was produced by a metallocene catalyst, Sample E2 from Mitsui by another proprietary catalyst, and the samples in F series from Dow by the INSITE technology. Samples E2, F4 and F5 are elastomeric resins with an extremely low density of 0.870 g/cc.

Viscosity was measured using an Instron capillary rheometer. The capillary had a dimension of 1.27 mm (0.050 in) D × 76.2 mm (3 in) L with 90° entrance angle. Dut to the high L/D ratio of 60 and tapered entry of the capillary, Bagley correction for elasticity was not necessary. Rabinowitsch correction for non-Newtonian behavior was made. Several duplicate measurements were made at four temperatures, 170, 190, 220 and 250°C, and at six apparent shear rates from 3.52 to 1,174/s covering the usual shear rates in processing. The samples exhibited flow instability or melt fracture to different degrees, resulting in rough, fractured or distorted extruded strands. Since the onset of melt fracture was determined subjectively by visually examining the extruded strands, the reported shear rates at the onset of melt fracture are approximate values.

Specific heat (C_p), which is the amount of energy necessary to change the temperature of unit mass by unit degree at a constant pressure, was measured using a Perkin-Elmer differential scanning calorimeter (DSC). The C_p curve measured over a wide temperature range shows how much energy is required to process the polymer and also reveals the melting range of the polymer. A specimen of less than 10 mg, taken from a pellet, was heated at 10°C/min in the first heating cycle, quenched at the maximum cooling rate of about 200°C/min, and then reheated at 10°C/min in the second heating cycle. All data were taken from the second heating cycle to eliminate the effects of different thermo-mechanical histories of the pellets. N_2 gas was used for purging the specimen cell.

RESULTS AND DISCUSSION

1. Melt Rheological Properties

1-1. Viscosity as a Function of Temperature and Shear Rate

The measured viscosity data of all samples are presented in Fig. 3-15 as a function of shear rate at four temperatures. The viscosity (η) is a function of both temperature (T) and shear rate ($\dot{\gamma}$). The onset of melt fracture is indicated by an arrow.

Table 1. List of ethylene homo- and copolymer samples

ID	Name	Producer	Monomers	Density, g/cc	[MI]	MWD	DRI
A1	HDPE	Dow	ethylene	0.959	0.73	5.0	N/A
B1	BLDPE	Exxon	ethylene	0.920	0.85	-	N/A
C1	EVA	DuPont	ethylene with vinyl acetate	12 wt% VA	0.40	-	N/A
D1	het-LEAO	UCC	ethylene with butene	0.918	1.09	3.6	N/A
D2	het-LEAO	Exxon	ethylene with hexene	0.917	1.04	3.6	N/A
D3	het-LEAO	Dow	ethylene with octene	0.905	0.79	4.5	N/A
E1	hom-LEAO	Exxon	ethylene with butene	0.910	1.04	2.0	0.0
F1	hom-BEAO	Dow	ethylene with octene	0.908	1.04	2.0	1.1
F2	hom-BEAO	Dow	ethylene with octene	0.908	0.87	2.0	4.4
F3	hom-BEAO	Dow	ethylene with octene	0.908	0.69	2.0	14.0
E2	hom-LEAO	Mitsui	ethylene with propylene	0.870	0.93	2.0	0.0
F4	hom-BEAO	Dow	ethylene with octene	0.870	0.80	2.0	2.2
F5	hom-BEAO	Dow	ethylene with octene	0.870	0.94	2.0	3.8

N/A: Not Applicable

Fig. 3. Viscosity of high density polyethylene (Sample A1) as a function of temperature and shear rate.
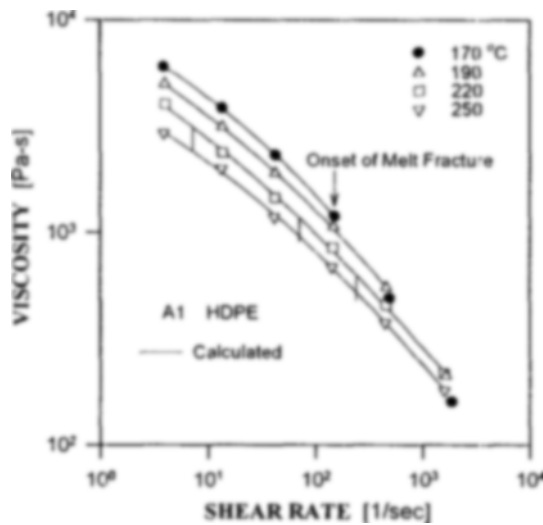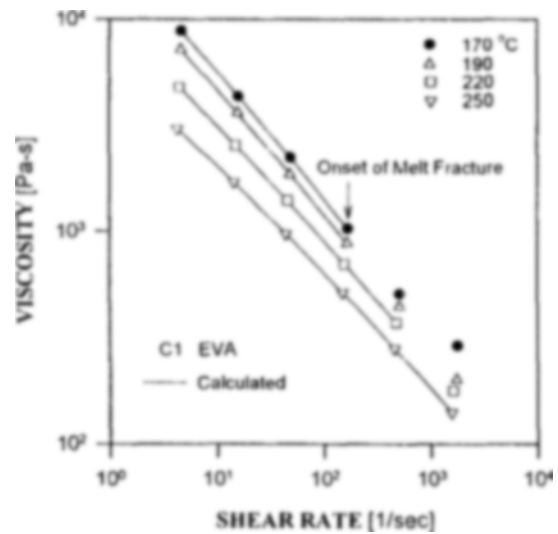

Fig. 4. Viscosity of branched low density polyethylene (Sample B1) as a function of temperature and shear rate.

Fig. 5. Viscosity of poly(ethylene/vinyl acetate) (Sample C1) as a function of temperature and shear rate.
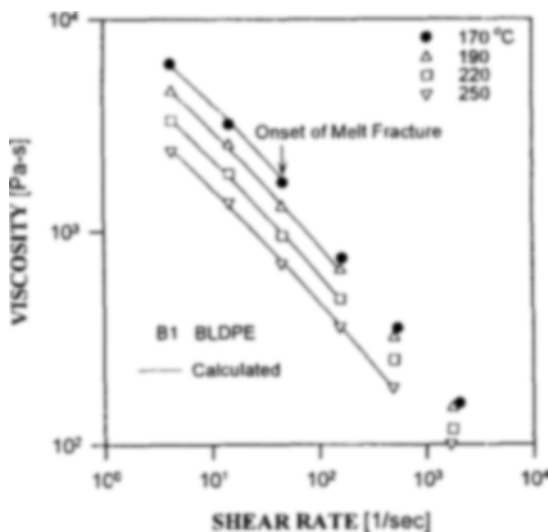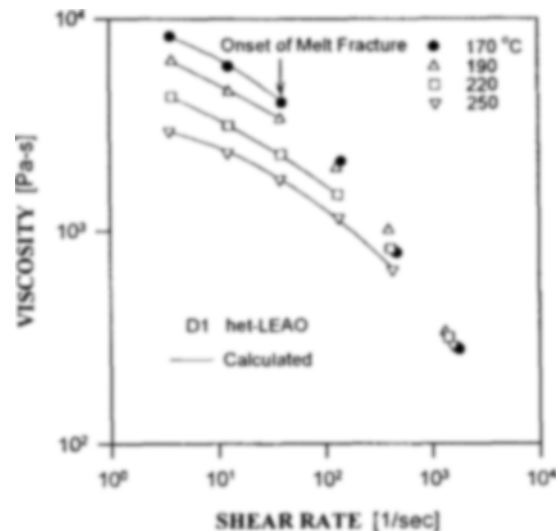

Fig. 6. Viscosity of heterogeneous linear poly(ethylene/α-olefin) copolymer (Sample D1) as a function of temperature and shear rate.

When melt fracture occurs, the flow becomes unstable making the viscosity data incorrect. Thus, only the data before the onset of melt fracture were used in fitting to equations throughout this paper.

The viscosity decreases with increasing shear rate. Such shear thinning or pseudoplastic behavior is often approximated by the power-law equation with two constants given below;

$$\eta(\dot{\gamma}) = N \cdot \dot{\gamma}^{n-1} \qquad (3)$$

where N is the viscosity at unit shear rate, representing the viscosity level. The power-law exponent, n, represents the shear sensitivity. For most polymers with pseudoplastic behavior, n is less than 1.0. A lower value of n indicates a greater viscosity reduction with increasing shear rate. The power-law equation is a straight line on log-log scale, and it is applicable only for a narrow range of shear rate. Although a straight line cannot fit the data over a wide range of shear rate, the simple power-law equation is widely used in mathematical analyses of

polymer processes because it can be easily differentiated and integrated yielding analytical solutions. The following quadratic equation with three constants can accurately describe the viscosity at a given temperature over a wide range of shear rate for most polymers;

$$\log\eta(\dot{\gamma}) = A_0 + A_1 \cdot (\log\dot{\gamma}) + A_2 \cdot (\log\dot{\gamma})^2 \qquad (4)$$

All three constants, A_0, A_1 and A_2, depend on temperature. A_0 is related to the viscosity at unit shear rate, representing the viscosity level. A_1 and A_2 are related to the shear sensitivity. The η vs. $\dot{\gamma}$ curves in Fig. 3-15 and all other figures are drawn by fitting the data to Eq. (4) at each temperature. Only the data up to the onset of melt fracture were used in fitting. The curves show an excellent fit to the data. The power-law exponent, n, in Eq. (3) changes with shear rate, and it can be obtained as a function of shear rate by differentiating log η in Eq.
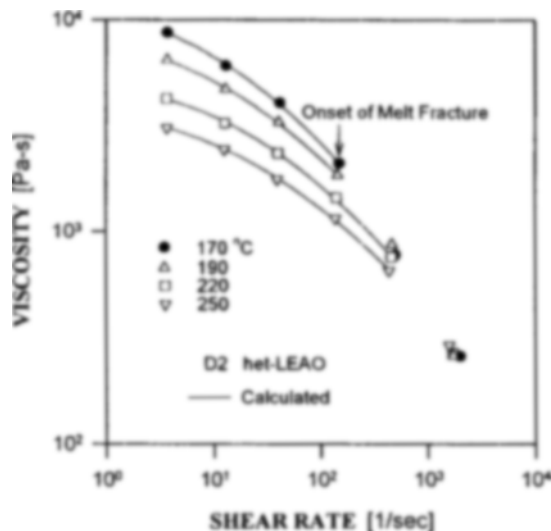
Fig. 7. Viscosity of heterogeneous linear poly(ethylene/α-olefin) copolymer (Sample D2) as a function of temperature and shear rate.
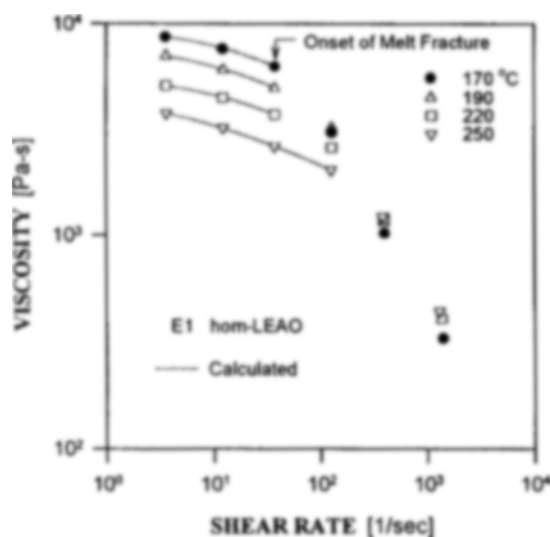

Fig. 9. Viscosity of homogeneous linear poly(ethylene/α-olefin) copolymer (Sample E1) as a function of temperature and shear rate.
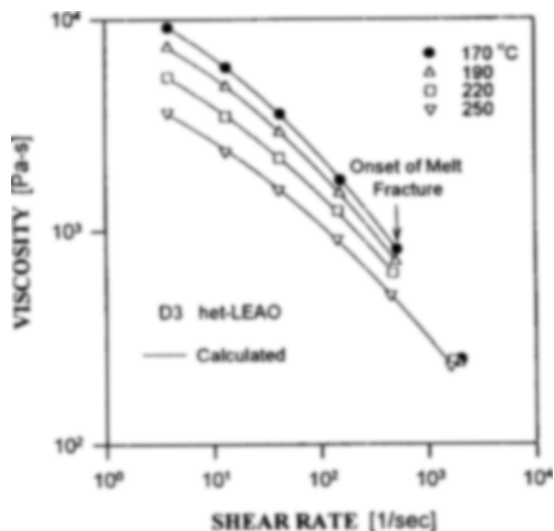

Fig. 8. Viscosity of heterogeneous linear poly(ethylene/α-olefin) copolymer (Sample D3) as a function of temperature and shear rate.
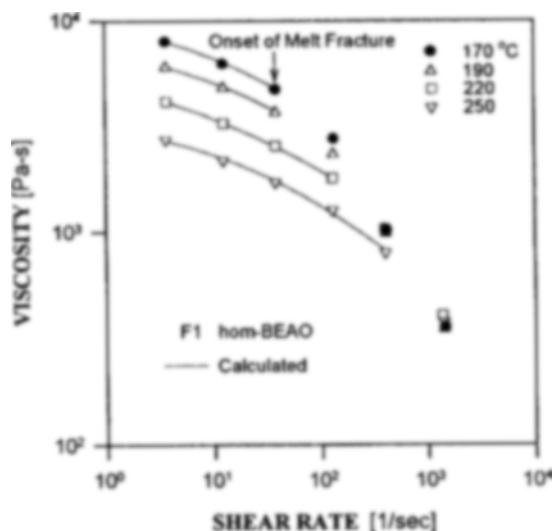

Fig. 10. Viscosity of homogeneous branched poly(ethylene/α-olefin) copolymer (Sample F1) as a function of temperature and shear rate.

(4) with respect to log γ as shown below;

$$n(\dot{\gamma}) = \left(\frac{d\log\eta}{d\log\dot{\gamma}} \right) + 1 = A_1 + 2 \cdot A_2 \cdot \log\gamma + 1 \tag{5}$$

Since A_1 and A_2 depend on T, n changes with both T and $\dot{\gamma}$. Two n values at 190°C, n_1 and n_2 listed in Table 2 were calculated using Eq. (5) at two shear rates of 10 and 100/s, respectively. These shear rates cover the usual shear rates inside an extruder screw channel.

The viscosity decreases sharply with increasing temperature, and the temperature dependence of viscosity in the processing temperature range far above the melting or glass transition temperature is expressed by the apparent flow activation energy (ΔE) in the Arrhenius equation given below;

$$\eta(T) = \eta(T_0) \cdot \exp\left[\frac{\Delta E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

or $\log\eta(T) = \log\eta(T_0) + \dfrac{\Delta E}{(2.3)R} \cdot \left(\dfrac{1}{T} - \dfrac{1}{T_0} \right)$ (6)

where R is the gas constant and $\eta(T_0)$ is the viscosity at the reference temperature T_0. Absolute temperature in degree kelvin must be used in Eq. (6). ΔE depends on the chemical composition and structure of a polymer, but it is virtually independent of MW or MWD. Higher ΔE indicates greater viscosity reduction with increasing temperature. ΔE is determined from the vertical distance between the curves measured at a constant $\dot{\gamma}$. The vertical distance between any two curves in Fig.
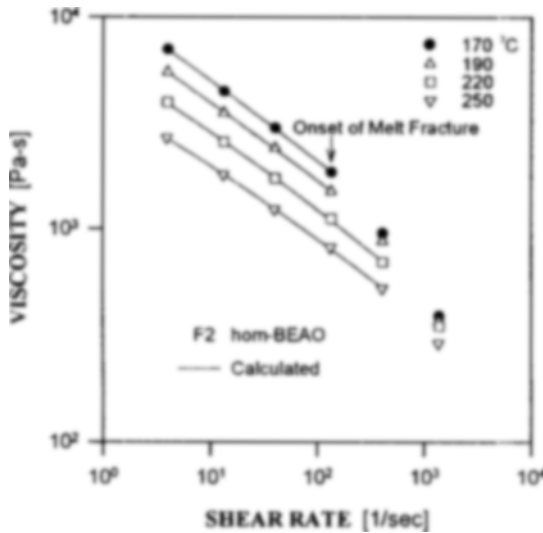
Fig. 11. Viscosity of homogeneous branched poly(ethylene/α-olefin) copolymer (Sample F2) as a function of temperature and shear rate.
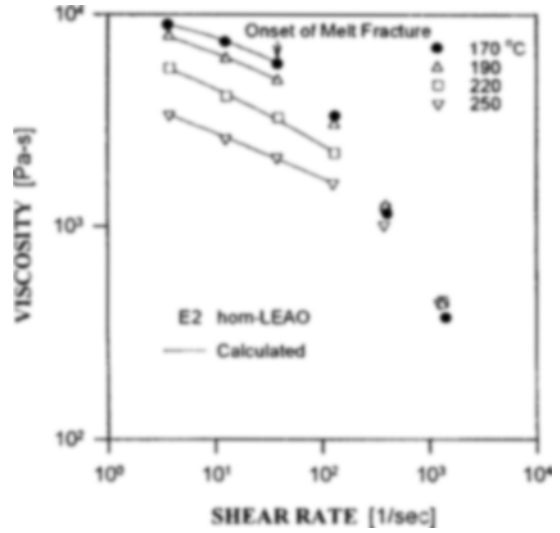

Fig. 13. Viscosity of homogeneous linear poly(ethylene/α-olefin) copolymer (Sample E2) as a function of temperature and shear rate.
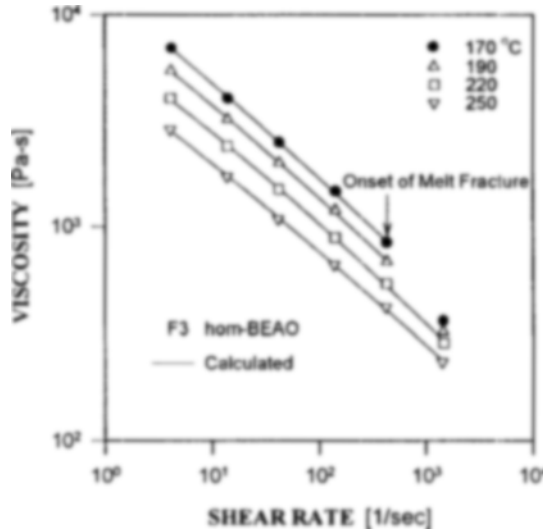

Fig. 12. Viscosity of homogeneous branched poly(ethylene/α-olefin) copolymer (Sample F3) as a function of temperature and shear rate.
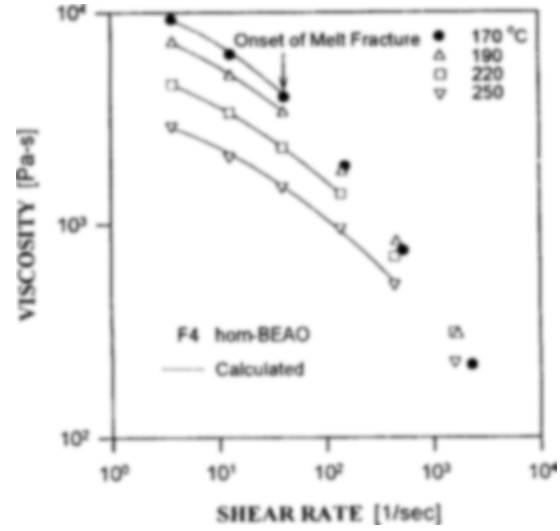

Fig. 14. Viscosity of homogeneous branched poly(ethylene/α-olefin) copolymer (Sample F4) as a function of temperature and shear rate.

Table 2. Summary of the viscosity measurements

ID	Rheological constants for viscosity in Pa-s at T_0=463 K :						Apparent shear rate (/s) at the onset of melt fracture at:			
	ΔE_τ	A_0	A_1	A_2	n_1	n_2	170°C	190°C	220°C	250°C
A1	28.5	3.885	0.280	0.055	0.610	0.499	352.2	1,174	none	none
B1	44.8	3.952	-0.431	-0.039	0.491	0.413	117.4	117.4	352.2	1,174
C1	46.8	4.218	-0.530	-0.021	0.429	0.387	352.2	352.2	352.2	1,174
D1	31.7	3.936	-0.221	-0.021	0.738	0.697	117.4	117.4	352.2	1,174
D2	30.0	3.889	-0.084	-0.095	0.727	0.537	352.2	352.2	1,174	1,174
D3	32.8	4.008	-0.192	-0.087	0.635	0.461	1,174	1,174	1,174	none
E1	25.0	3.877	0.016	-0.062	0.859	0.735	35.2	117.4	117.4	352.2
F1	32.6	3.837	-0.064	0.066	0.804	0.672	117.4	117.4	352.2	1,174
F2	33.0	3.942	-0.333	-0.012	0.642	0.617	352.2	352.2	1,174	1,174
F3	33.7	3.977	0.391	0.015	0.578	0.548	1,174	1,174	none	none
E2	31.5	3.981	-0.129	-0.035	0.800	0.729	35.2	117.4	352.2	352.2
F4	39.5	3.956	-0.125	0.086	0.703	0.531	117.4	117.4	352.2	1,174
F5	38.8	3.835	-0.160	-0.069	0.701	0.563	352.2	352.2	1,174	none

Rabinowitsch correction made.
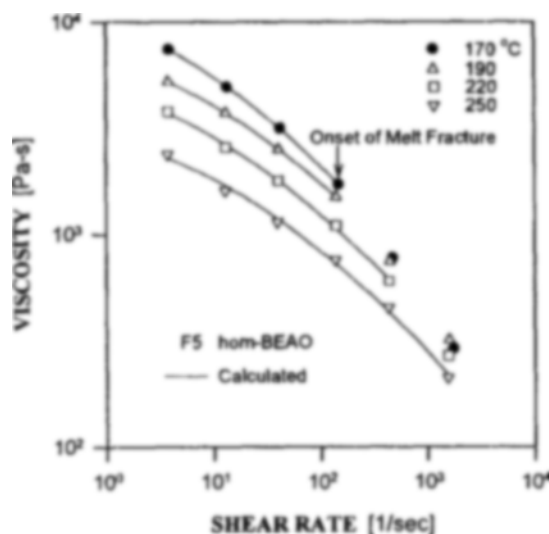
ΔE_τ in KJ/mol. n_1 at 10 /s and n_2 at 100 /s.

Fig. 15. Viscosity of homogeneous branched poly(ethylene/α-olefin) copolymer (sample F5) as a function of temperature and shear rate.

Fig. 16. Viscosity of various polyethylene homopolymers and copolymers as a function of shear rate at 190°C.

3 decreases with increasing $\dot{\gamma}$ as demonstrated by three vertical markers with a constant length. Thus, $\Delta E_{\dot{\gamma}}$ determined at a constant $\dot{\gamma}$ decreases with increasing $\dot{\gamma}$ and it is difficult to express the viscosity as a function of temperature using $\Delta E_{\dot{\gamma}}$.

Although the viscosity usually is drawn as a function of shear rate as in Fig. 3-15, the viscosity also can be drawn as a function of shear stress. The viscosity vs. shear stress curves at different temperatures are found to be vertically parallel, giving a constant ΔE_τ for a given polymer independent of shear stress level. ΔE_τ is considered as a better representation of the molecular mechanism controlling the temperature-dependent viscous behavior than $\Delta E_{\dot{\gamma}}$. The ΔE_τ values for all samples in Table 2 were determined by replotting the viscosity data in Fig. 3-15 as a function of shear stress [Kim et al., 1996].

A solid polymer is heated to melt, and then the melts is further heated from the melting point to the final melt temperature inside a processing equipment. Also, the melt is subjected to a wide range of shear rate inside a processing equipment. Therefore, the processability of a polymer is controlled by the entire viscosities over the wide range of temperature and shear rate encountered in processing. "The average viscosity" of a polymer in processing may be defined as the average value of the entire viscosities. At least three constants; viscosity level (A_o), apparent flow activation energy (ΔE) and shear sensitivity (n), are necessary to properly describe the average viscosity. The average viscosity will decrease with decreasing A_o, increasing ΔE and decreasing n.

1-2. Dependence of Flow Activation Energy on Molecular Structure and Composition

Referring to Table 2, comparison of the ΔE_τ values for Samples A1, B1, C1, D1 and E1 shows that the branched polymers with LCB (Samples B1 and C1) have a greatly higher flow activation energy than the linear polymers (Samples A1, D1 and E1) in agreement with the previous investigators [Tung, 1960; Boghetich and Kratz, 1965; Mendelson et al., 1970; Chung et al., 1972]. Thus, the viscosities of the branched polymers will decrease faster than those of the linear polymers as melt temperature increases in processing.
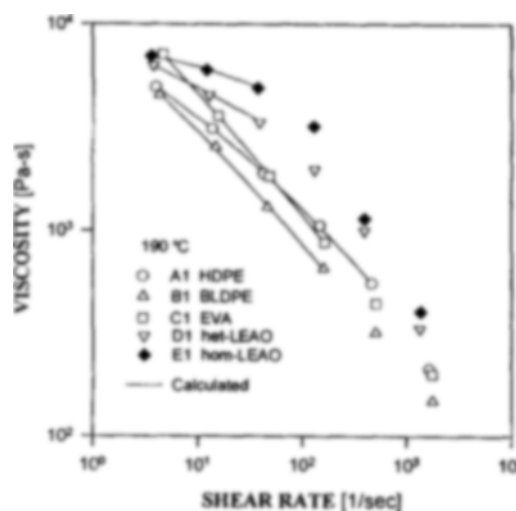
Comparison of the ΔE_τ values for Samples D1, D2 and D3 shows that the flow activation energy of het-LEAO is insensitive to the type of comonomer, i.e., up to hexyl (C_6) SCB. The ΔE_τ values of D series samples are only slightly higher than that of Sample A1, indicating that SCB has little influence on ΔE_τ. A previous study [Tung, 1960] reported that the apparent flow activation energy of HDPE was not affected by ethyl SCB incorporated using butene comonomer.

Comparisons of the ΔE_τ values for Samples E1, F1, F2 and F3, and also for Samples E2, F4 and F5, show that hom-BEAO due to the small amounts of LCB has a significantly higher flow activation energy than hom-LEAO.

1-3. Dependence of Shear Sensitivity and Flow Stability on Molecular Structure and Composition

[MI] is widely used by the industry to specify the processing behavior of polymers. It is the flow rate, expressed in g/10 min., measured at a specific temperature of $T_1=190°C$ and a very low shear stress of $\tau_1=1.966 \times 10^4$ Pa using a very short capillary of 2.0955 mm D. by 8 mm L. with L/D=3.8 and a flat entry according to Condition E of ASTM Method-1238. Noting that the melt density of PE is about 0.77 g/cc at 190°C, [MI] = 1 corresponds to an apparent shear rate of only about 2.4 /s and a viscosity of about $(1.966 \times 10^4$ Pa/2.4/s)=8,200 Pa-s. Although the [MI] value is supposed to represent the reciprocal of the particular viscosity measured at the [MI] condition of temperature and shear stress, it is strongly influenced by the elasticity of the polymer because of the short L/D ratio and flat entry of the capillary. Two polymers with the same [MI] can have very different viscosities, elasticities, shear sensitivities and temperature sensitivities. [MI] is an important parameter, but it alone cannot properly describe the processing behavior of a polymer.

Fig. 16 compares the viscosities of different polyethylene homopolymers and copolymers (Samples A1, B1, C1, D1 and E1) at 190°C. Except for Sample C1 (EVA), all other samples have a similar [MI] around 1.0 but they have very different shear sensitivities and viscosities. Sample C1 with the lowest [MI] has the highest viscosity at the [MI] condition, but it has the highest shear sensitivity resulting in a low average viscosity.
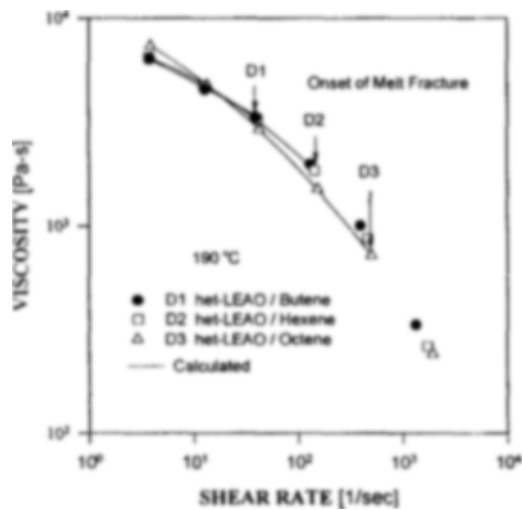
Fig. 17. Effects of the length of short chain branching on the viscosity and flow stability of heterogeneous linear poly (ethylene/α-olefin) copolymer with about 0.917 g/cc density at 190°C.
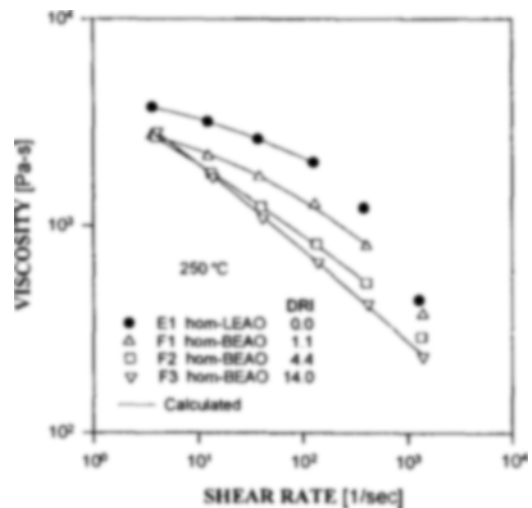

Fig. 19. Effects of long chain branching (expressed by DRI) on the viscosity and flow stability of homogeneous poly (ethylene/α-olefin) copolymer with about 0.908 g/cc density at 250°C.

Fig. 18. Effects of long chain branching (expressed by DRI) on the viscosity and flow stability of homogeneous poly (ethylene/α-olefin) copolymer with about 0.908 g/cc density at 190°C.

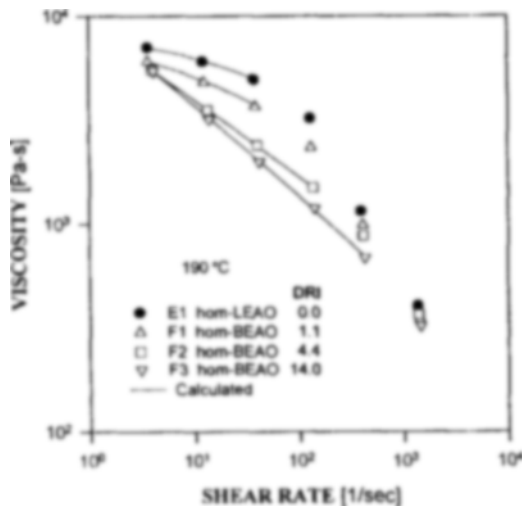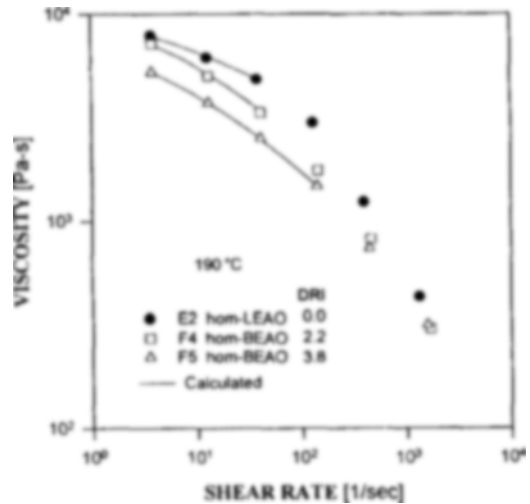**Fig. 20.** Effects of long chain branching (expressed by DRI) on the viscosity and flow stability of homogeneous poly (ethylene/α-olefin) copolymer with about 0.870 g/cc density at 190°C.

Sample B1 has the lowest average viscosity, followed by Samples A1, C1, D1 and finally E1. Sample E1 with a very narrow MWD has the lowest shear sensitivity and consequently the highest average viscosity. The processing difficulty of Sample E1 in comparison to Samples B1 and D1, drawing higher torque and developing higher melt temperatures, is certainly understandable. The branched polymers with LCB (Samples B1 and C1) have a greatly higher shear sensitivity than the linear polymers. The lower n values of the branched polymers in comparison to the linear polymers listed in Table 2 also lead to the same conclusion.

Fig. 17 compares the viscosities and flow stabilties of the het-LEAO samples D1, D2 and D3. The flow stability is greatly improved and the shear sensitivity is somewhat increased from Samples D1 to D2 D3. Although this appears to indicate improved processability with increasing SCB length, care must be

taken in the interpretation since Sample D3 has a broader MWD than the other samples and the observed effects may be due to the increased MWD.

Similar comparisons are made for two sets of hom-LEAO (E series) vs. hom-BEAO (F series) samples, each set with about the same density, to study the effects of small amounts of LCB in hom-EAO. The amount of LCB is represented by DRI in Table 1. For one set with about 0.910 g/cc density, Sample E1 is compared with Samples F1-F3 in Fig. 18 at 190°C and in Fig. 19 at 250°C. For the other set with about 0.870 g/cc density, Sample E2 is compared with Samples F4 and F5 in Fig. 20 at 190°C. Fig. 18-20 and also the n values in Table 2 clearly show that the shear sensitivity of hom-EAO increases very effectively with increasing DRI, greatly decreasing the average viscosity in processing. The viscosity curve of Sample F3 comes very close to that of Sample A1. Extreme dependence of the melt temperature in extrusion on shear sensitivity was re-
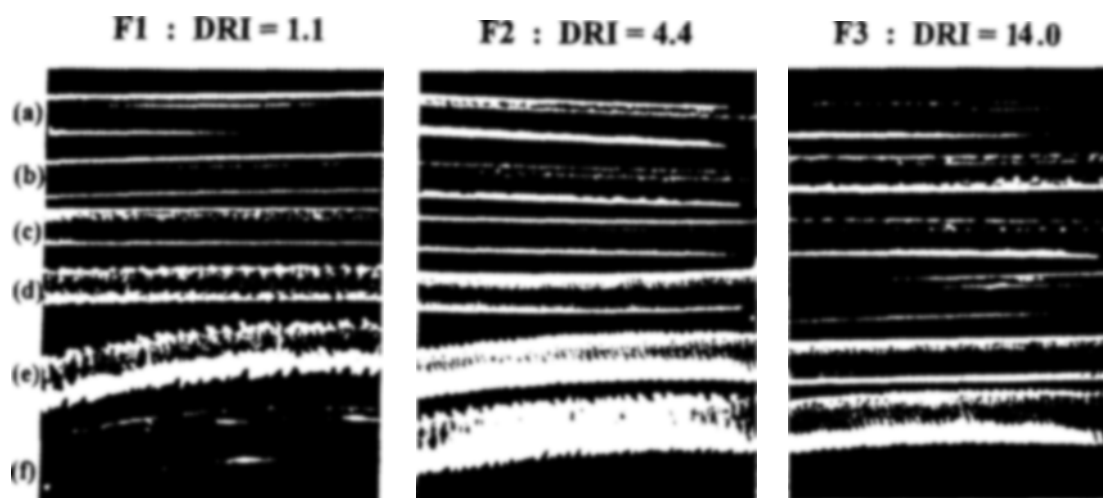
Fig. 21. Photographs of the capillary strands of homogeneous branched poly(ethylene/α-olefin) copolymer with about 0.908 g/cc density (sample F1, F2 and F3) at 170°C and six apparent shear rates,/s.
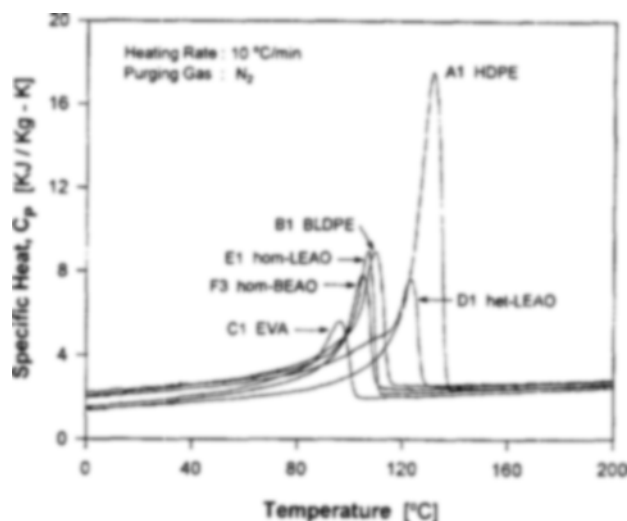(a) 3.52, (b) 11.74, (c) 35.2, (d) 117.4, (e) 352.2 and (f) 1,174

Fig. 22. Differential scanning calorimeter thermograms of various polyethylene homopolymers and copolymers.

Table 3. Summary of the thermodynamic properties
Measured by differential scanning calorimeter. Data taken from the second heating cycle. Heating rate = 10°C/min: Cooling rate = quenching : Purging gas = nitrogen

ID	Density g/cc	Melting peak, °C: Start	Peak	End	Heat of fusion KJ/Kg	Crystallinity* weight %
A1	0.959	62.4	131.5	140.2	206.2	70.3
B1	0.920	23.7	109.4	116.8	118.9	40.5
C1	12 wt% VA	6.0	96.1	106.2	85.4	29.1
D1	0.918	33.7	123.2	130.2	114.1	38.9
D2	0.917	27.7	121.8	128.2	112.9	38.5
D3	0.905	10.0	121.2	129.5	93.0	31.7
E1	0.910	15.1	106.8	113.2	108.5	37.0
F1	0.908	15.1	103.8	114.2	92.3	31.5
F2	0.908	12.7	104.8	112.5	97.6	33.3
F3	0.908	17.7	104.8	112.8	96.7	33.0
E2	0.870	− 22.3	42.4	66.1	46.9	16.0
F4	0.870	− 25.7	55.4	80.8	46.9	16.0
F5	0.870	− 24.3	61.4	84.8	48.5	16.6

*: Weight % crystallinity was calculated by dividing the measured heat of fusion by the reference value of 293 KJ/Kg for perfect PE crystal.

ported recently for het-LEAO [Christensen and Cheng, 1991]. The melt temperature of one sample with a higher shear sensitivity was as much as 40°C lower than that of another sample with the same [MI] in an extrusion experiment using a 114.3 mm (4.5 in.) D. with L/D=24 extruder running at 75 RPM.

The onset of melt fracture was noted by visual examination in this study and it is not expected to be an accurate determination of flow instability. Fig. 18-20 and Table 2 clearly show that melt fracture occurs at higher shear rates as DRI increases. Fig. 21 is the photograph of the strands of Samples F1, F2 and F3 extruded at six apparent shear rates at 170°C. As shear rate is increased, the strand of Sample F1 starts to show a rough surface at 35.2/s and a fractured surface at 117.4/s, progressing to a badly fractured surface at 352.2/s, and then to a relatively smooth surface but with a long range wave at 1,174/ s. As LCB (indicated by DRI) increases from Samples F1 to F2 to F3, the flow stability is improved and melt fracture occurs at higher shear rates.

2. Thermodynamic Properties

Examples of the DSC results are shown in Fig. 22 for Samples A1, B1, C1, D1, E1 and F3, comparing different polyethylene homopolymers and copolymers. The important values obtained from the DSC measurements are reported in Table 3 for all samples. The heat of fusion was obtained from the total area of the melting peak including the initial broad region. The weight crystallinity was calculated by dividing the measured heat of fusion by the reference value for perfect PE crystal [Kroschwitz, 1985].

Referring to Table 3 and Fig. 22, Sample A1 (HDPE) with about 0.959 g/cc density has 70 wt% crystallinity with a melting peak at 131.5°C. Sample B1 (BLDPE) with about 0.920 g/ cc density has 41 wt% crystallinity with a melting peak at 109.4 °C. Sample D1 (het-LEAO) has about the same density and crys-

tallinity as Sample B1, but it starts to melt as a significantly higher temperature with a melting peak at 123.2°C than that of Sample B1. The length of SCB in het-LEAO has virtually no effect on the thermodynamic properties. The hom-EAO samples with about 0.910 g/cc density, Samples E1 (hom-LEAO) and F1-F3 (hom-BEAO), have a melting peak around 105°C, somewhat lower than the melting peak of Sample B1. The DSC melting curves of these hom-EAO samples are quite similar to that of a BLDPE with a similar density. Comparison of the data for Samples F1-F3 shows that small amounts of LCB do not influence the density or the thermodynamic properties. Samples E2, F4 and F5 have an elastomeric behavior and a high transparency due to their very low density of about 0.870 g/cc corresponding to only about 16 wt% crystallinity. They start to melt below room temperature at about − 24°C with a melting peak around 55°C. The elastomeric behavior of these samples was explained by their particular fringed micelle crystalline structure [Chum et al., 1965].

CONCLUSION

The melt rheological and thermodynamic properties of polyethylene homopolymers and copolymers depend on various molecular structural attributes such as LCB, SCB and the distribution of SCB as well as molecular composition, MW and MWD. The MWD and molecular structure of a polymer depend on the particular catalyst and polymerization process. Some differences in MWD and molecular structure are expected even for the samples listed in the same structural category in Table 1 since they were obtained from different producers. Thus, care should be taken in comparing the experimental results of these samples.

The densities of polyethylene homopolymers and copolymers are mainly affected by the large amounts of SCB, and they are not affected by the small amounts of LCB. Within the same structural category, a sample with a lower density starts to melt at a lower temperature with a corresponding lower melting peak. Compared at a similar density, het-LEAO has a melting peak at a significantly higher temperature than BLDPE but both hom-LEAO and hom-BEAO have a melting peak close to that of BLDPE. The length of SCB in het-LEAO has no effect on the melting peak. The small amounts of LCB in hom-EAO do not affect the density and the melting peak.

Compared at the same [MI], hom-LEAO has the lowest shear sensitivity due to the very narrow MWD, making the average viscosity in processing highest among all samples. Small amounts of LCB in hom-EAO drastically increase the pseudoplasticity, significantly increase the flow activation energy and greatly improve the flow stability. The average viscosity of hom-EAO in processing can be very effectively decreased by small amounts of LCB.

Hom-EAOs in processing draw higher torque and develop higher melt temperatures than het-LEAO due to their higher average viscosities. Since they melt faster than het-LEAO due to their lower melting points and higher average viscosities, screws with deeper channel can be used to lower the melt temperatures.

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