Melt Rheological and Thermodynamic Properties of Polyethylene Homopolymers and Poly(ethylene/α-olefin) Copolymers with Respect to Molecular Composition and Structure

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SYNOPSIS

Various types of polyethylene homopolymers and copolymers, including linear high-density polyethylene (HDPE), branched low-density polyethylene (BLDPE), poly(ethylene vinyl acetate) copolymer (EVA), heterogeneous linear poly(ethylene/α-olefin) copolymer (het-LEAO) or commonly known as linear low-density polyethylene, homogeneous linear poly(ethylene/α-olefin) copolymer (hom-LEAO), and homogeneous branched poly(ethylene/α-olefin) copolymer (hom-BEAO), were evaluated for their melt rheological and thermodynamic properties with emphasis on their molecular structure. Short-chain branching (SCB) mainly controls the density, but it has little effect on the melt rheological properties. Long-chain branching (LCB) has little effect on the density and thermodynamic properties, but it has drastic effects on the melt rheological properties. LCB increases the pseudoplasticity and the flow activation energy for both the polyethylene homopolymer and copolymer. Compared at a same melt index and a similar density, hom-LEAO has the highest viscosity in processing among all polymers due to its linear molecular structure and very narrow molecular weight distribution. Small amounts of LCB in hom-BEAO very effectively reduce the average viscosity and also improve the flow stability. Both hom-LEAO and hom-BEAO, unlike het-LEAO, have thermodynamic properties similar to BLDPE. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Molecules of Different Types of Polyethylene Homopolymers and Copolymers

Polymer molecules with regularity in molecular structure such as polyethylene (PE) crystallize upon cooling from the molten state. A perfect PE crystal with a orthorhombic unit cell structure has a density of about 1.000 g/cc at 25°C and melts at about 141°C.[1] 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,[1] with a glass transition temperature at about −120°C, and it be-

haves 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 crystallinity is decreased, resulting in a lower density and a lower modulus.

High-density polyethylene (HDPE) used for bottles is a homopolymer of ethylene with a linear molecular structure as shown in Figure 1. HDPE crystallizes to a high degree, reaching about 70 wt %, resulting in a high density around 0.960 g/cc, as the name indicates. The conventional 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 as shown in Figure 1. BLDPE also has many SCB and crystallizes to less than 50 wt

A. **HDPE** (homopolymer)

D. **het-LEAO** (copolymer)

B. **BLDPE** (homopolymer)

E. **hom-LEAO** (copolymer)

C. **EVA** (copolymer)

F. **hom-BEAO** (copolymer)
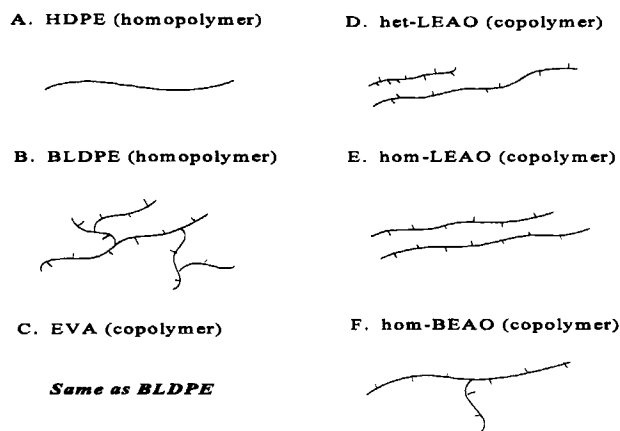
Same as BLDPE

Figure 1 Molecular structures of various PE homopolymers and copolymers.

%, mainly due to the large amount of SCB, resulting in a low density around 0.920 g/cc. Polymers with LCB are called branched polymers. Polymers with SCB, but without LCB, are usually classified as linear polymers. It is well known that BLDPE, compared at the same density and melt index [MI],[2] is much easier to process than is 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 average viscosity in processing.[3-6] A controlled amount of SCB 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.), which becomes SCB. 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 and shear sensitivities. The polymer commonly known as linear low-density polyethylene (LLDPE) is a copolymer produced by polymerizing ethylene with an α-olefin comonomer. It has a linear molecular structure without LCB like HDPE, but with much SCB. The α-olefin comonomers or the SCB are distributed nonuniformly at different intervals along a molecule and heterogeneously at different concentrations in different molecules as shown in Figure 1. LLDPE will be called a heterogeneous linear poly(ethylene/α-olefin) copolymer (het-LEAO) in this article to allow a scientific comparison with other PE copolymers based on molecular structural differences. 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. Het-LEAO does not have LCB and behaves similar to HDPE in the molten state. SCB in het-LEAO is effective in reducing the crystallinity and density, but it is not as effective as LCB in reducing the average viscosity in processing.

Homogeneous linear poly(ethylene/α-olefin) copolymer (hom-LEAO), produced by the single-site catalyst technology including metallocene and other proprietary catalysts, has been introduced in recent years.[7,8] The single-site catalyst technology produces 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 Figure 1 as well as a very narrow molecular weight distribution (MWD) of (weight average MW/number average MW) $\approx$ 2. This polymer sometimes is known as LLDPE with a very narrow MWD, but it has a different molecular structure from LLDPE with respect to the comonomer distribution as described above and shown in Figure 1. Due to the very narrow MWD, hom-LEAO has better physical properties but higher viscosities than has het-LEAO and it is even more difficult to process.

The newest PE copolymer comes from Dow produced by a proprietary constrained geometry catalyst technology, called INSITE™ Technology.[8] It is also a homogeneous poly(ethylene/α-olefin) copolymer with the same type of comonomer distribution as hom-LEAO, but it has a small amount of LCB as shown in Figure 1 and it will be called 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 INSITE catalyst technology also allows one to produce resins with higher contents of α-olefin comonomer over 20 wt %, which have very low densities below 0.880 g/cc and elastomeric properties.

In this study, PE homopolymers and copolymers, including two sets of hom-BEAO resins, are evaluated for their melt rheological and thermodynamic properties with respect to molecular composition and structure. Melt rheological and thermodynamic properties are the two most important material properties controlling the processing behavior.

Long-chain Branching Characterization

The low LCB contents in the ITP resins are difficult to measure by analytical means, but they can be conveniently represented by the Dow Rheology Index (DRI) based on melt rheological data as defined below:[8]

$$DRI \text{ (dimensionless)} = [A \cdot (\tau_0/\eta_0) - 1]/10$$

where $A = 3.65 \times 10^5$ Pa; τ_0 = characteristic relaxation time, s; and η_0 = zero shear viscosity, Pa-s. τ_0 and η_0 are determined by fitting the measured melt rheological data to a generalized Cross equation:

$$\eta/\eta_0 = 1/[1 + (\dot{\gamma} \cdot \tau_0)^n]$$

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 PE copolymers and (τ_0/η_0) increases with increasing LCB.[8] DRI = 0 indicates no LCB, and one LCB per molecule corresponds to about 30 DRI. It has been reported that the small amounts of LCB in the hom-BEAO resins are very effective in reducing the viscosity in processing, alleviating the processing difficulty associated with hom-LEAO.[8]

EXPERIMENTAL

Polymer Samples

All 13 samples used in this study are listed in Table I with the pertinent data. The [MI]s are the measured values. The densities and the MWDs (except for the samples in D series) are the nominal values reported by the producers. The MWDs of the three samples in D series were measured by gel permeation chromatography back to back to assure a meaningful comparison. Some are commercial resins and the others are experimental resins. The samples in the A (HDPE), B (BLDPE), C (EVA), and D (het-LEAO) series are extrusion film-grade resins well

known to the industry. The samples in the E (hom-LEAO) and F (hom-BEAO) series are the new homogeneous poly(ethylene/α-olefin) copolymers produced by the single-site catalyst technologies. Sample E1 from Exxon was produced by a metallocene catalyst, Sample E2 was from Mitsui by another proprietary catalyst, and the F series samples were from Dow by the INSITE technology. Samples E2, F4, and F5 are elastomeric resins with an extremely low density.

Melt Rheological Properties

The viscosity was measured using an Instron capillary rheometer. The capillary had a dimension of 1.27 mm $D \times 76.2$ mm L with a 90° entrance angle. Due to the high L/D ratio of 60 and the tapered entry of the capillary, the Bagley correction for elasticity was not necessary. The 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 covering 3.52–1174/s. The samples exhibited flow instability or melt fracture to different degrees. The onset of melt fracture was determined by visually examining the extruded strands.

Thermodynamic Properties

The specific heat (C_p) was measured using a Perkin-Elmer differential scanning calorimeter (DSC). The DSC instrument was carefully calibrated using an indium standard, confirming the accuracies of temperature scale and heat-capacity level. A specimen of less than 10 mg, taken from a pellet, was heated at 10°C/min in the first heating cycle, quenched at

Table I   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 ocetene	0.908	0.69	2.0	14
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
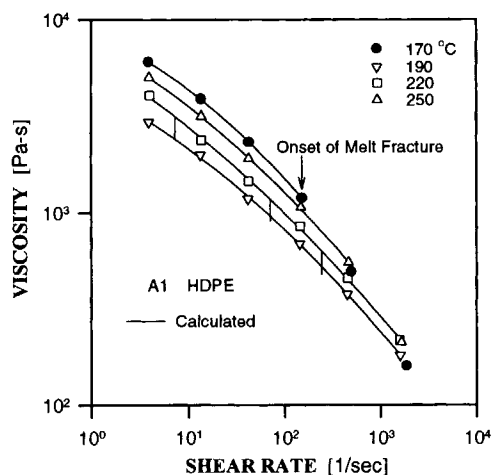
A. Viscosity as a function of Shear Rate
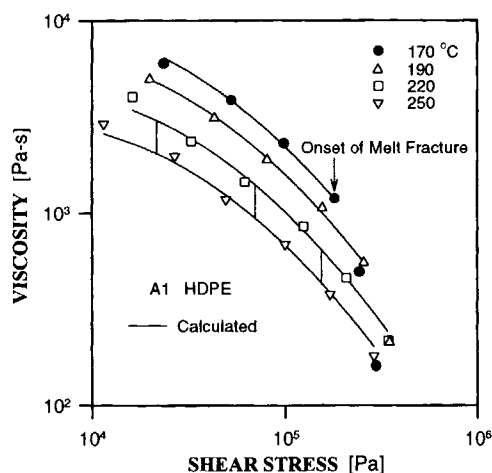
B. Viscosity as a function of Shear Stress

Figure 2   Viscosity of HDPE (Sample A1) as a function of temperature and shear.

the maximum cooling rate of about 200°C/min, and then reheated at 10°C/min in the second heating cycle. N$_2$ gas was used for purging the specimen cell. Data were taken from the second heating cycle to eliminate the different thermal histories of the pellets.

RESULTS AND DISCUSSION

Melt Rheological Properties

Viscosity as a Function of Temperature and Shear

The measured viscosity data of Sample A1 (HDPE) are presented in Figure 2 as a function of shear rate or shear stress. The temperature- and shear-depen-

dent viscosity shown in Figure 2 is typical for most polymers. The viscosity (η) is a function of both temperature (T) and the level of shearing. The level of shearing is expressed by either shear rate ($\dot{\gamma}$) as in Figure 2(A) or shear stress (τ) as in Figure 2(B). The onset of melt fracture is indicated by an arrow in Figure 2. 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 for all samples throughout this article.

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

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

$$\eta(\tau) = M \cdot \tau^{m-1} \tag{1b}$$

where N and M are constants, corresponding to the viscosity at unit shear rate or unit shear stress, respectively. The power-law exponents, n and m, represent the shear sensitivity. For polymers with pseudoplastic behavior, the power-law exponent is less than 1.0. A lower value of the exponent indicates a greater viscosity reduction with increasing shear (i.e., shear rate or shear stress). Referring to Figure 2, the viscosity decreases faster with increasing shear stress than with shear rate. Therefore, m is a smaller number than is n. The lower limit of n is zero, but m can become negative. The power-law equation with two constants is a straight line on log–log scale, and it is applicable only for a narrow range of shear. Referring to Figure 2, a straight line cannot fit the
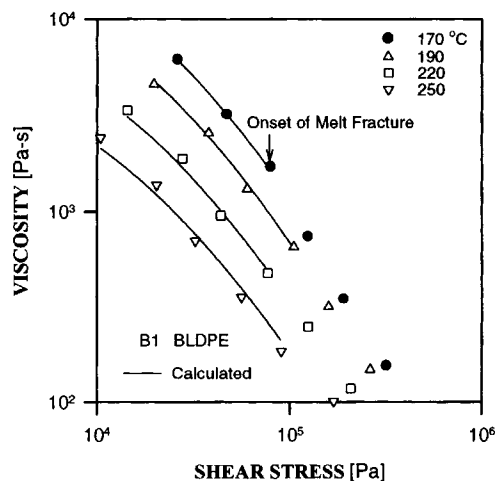

Figure 3   Viscosity of BLDPE (Sample B1) as a function of temperature and shear stress.
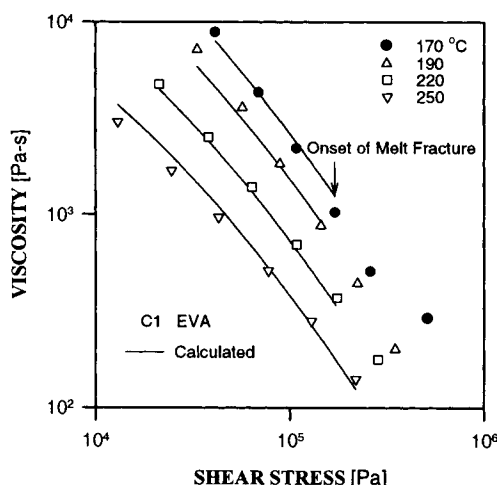
Figure 4 Viscosity of EVA (Sample C1) as a function of temperature and shear stress.

Figure 6 Viscosity of het-LEAO (Sample D2) as a function of temperature and shear stress.

data over a wide range of shear. The following quadratic equation with three fitting constants can accurately describe the viscosity at a given temperature over a wide range of shear for most polymers:

$$\log \eta(\dot{\gamma}) = A_0 + A_1 \cdot (\log \dot{\gamma}) + A_2 \cdot (\log \dot{\gamma})^2 \quad \text{(2a)}$$

$$\log \eta(\tau) = B_0 + B_1 \cdot (\log \tau) + B_2 \cdot (\log \tau)^2 \quad \text{(2b)}$$

The curves in Figure 2(A) or (B) are drawn by fitting the data to eq. (2a) or eq. (2b), respectively, at each temperature. A_0 and B_0 depend on temperature, and they are related to the viscosity at unit shear rate or unit shear stress, respectively. A_0 is meaningful, but B_0 is related to the unreasonably extrapolated viscosity value at the negligibly low of shear stress
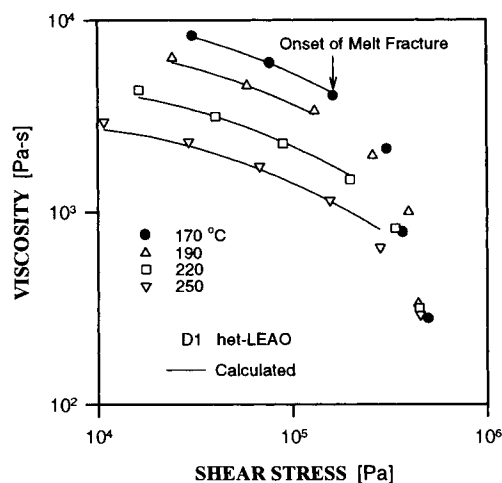
of 1 Pa with a greatly amplified fitting error. Since the curves at different temperatures in Figure 2(A) are not vertically parallel (as indicated by three markers of equal length), A_1 and A_2, depend on temperature. However, the curves in Figure 2(B) are essentially vertically parallel, making B_1 and B_2 independent of temperature. Although eq. (2a) is commonly used, eq. (2b) will be used in this article to simplify the analysis, requiring fewer fitting constants when viscosity is expressed as a function of both temperature and shear. Equation (2b) will be accurate only for the shear stress range covered in the fitting below the onset of melt fracture, which is usually about 1×10^4–5×10^5 Pa. The shear sensitivity m in eq. (1b) is obtained by differentiating $\log \eta$ in eq. (2b) with respect to $\log \tau$ as shown below:
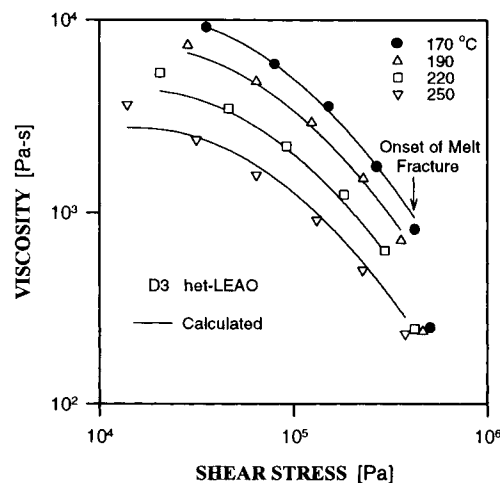

Figure 5 Viscosity of het-LEAO (Sample D1) as a function of temperature and shear stress.

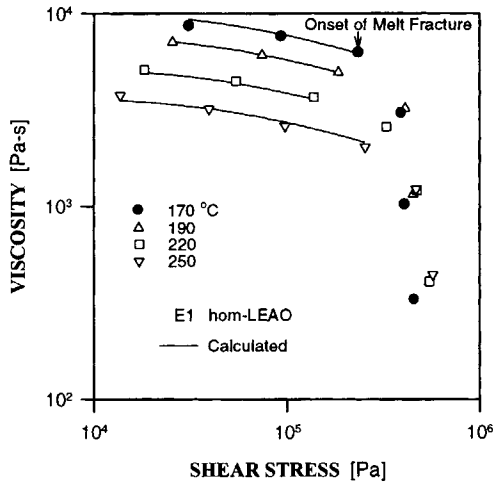**Figure 7** Viscosity of het-LEAO (Sample D3) as a function of temperature and shear stress.

Figure 8 Viscosity of hom-LEAO (Sample E1) as a function of temperature and shear stress.

$$m(\tau) = \left(\frac{d \log \eta}{d \log \tau}\right) + 1 = B_1 + 2 \cdot B_2 \cdot \log \tau + 1 \quad (3)$$

Since B_1 and B_2 are independent of T, m only depends on τ independent of T. However, n in eq. (1a) changes with both T and $\dot{\gamma}$.

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:

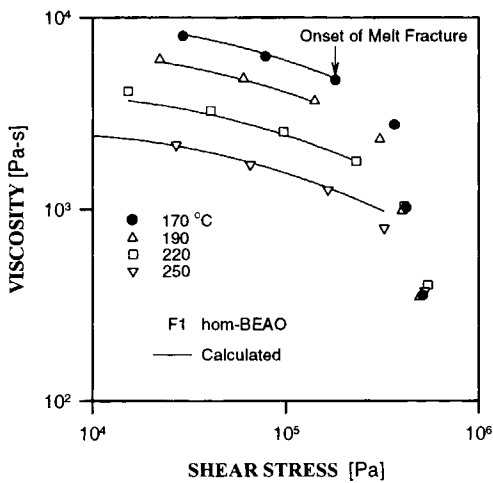$$\eta(T) = \eta(T_0) \cdot \exp\left[\frac{\Delta E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

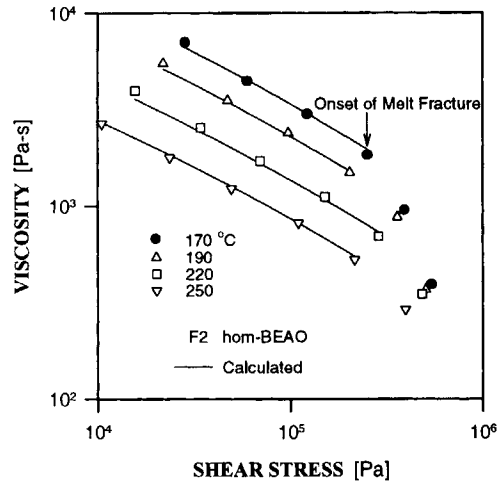**Figure 9** Viscosity of hom-BEAO (Sample F1) as a function of temperature and shear stress.

Figure 10 Viscosity of hom-BEAO (Sample F2) as a function of temperature and shear stress.

or

$$\log \eta(T) = \log \eta(T_0) + \frac{\Delta E}{(2.3)R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (4)$$

where R is the gas constant, and $\eta(T_0)$, the viscosity at the reference temperature T_0. Higher ΔE indicates greater viscosity reduction with increasing temperature. ΔE is determined from the vertical distance between the curves measured either at a constant $\dot{\gamma}$ using Figure 2(A) or at a constant τ using Figure 2(B). The vertical distance between any two curves in Figure 2(A) decreases with increasing $\dot{\gamma}$ as demonstrated by three vertical markers with a constant length. Thus, ΔE_γ determined at a constant $\dot{\gamma}$ decreases with increasing $\dot{\gamma}$. However, any two curves
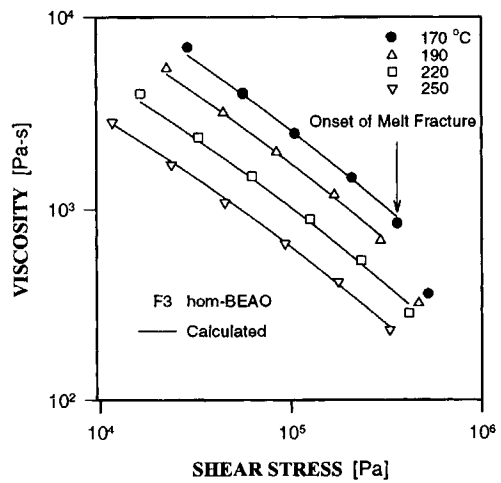

Figure 11 Viscosity of hom-BEAO (Sample F3) as a function of temperature and shear stress.
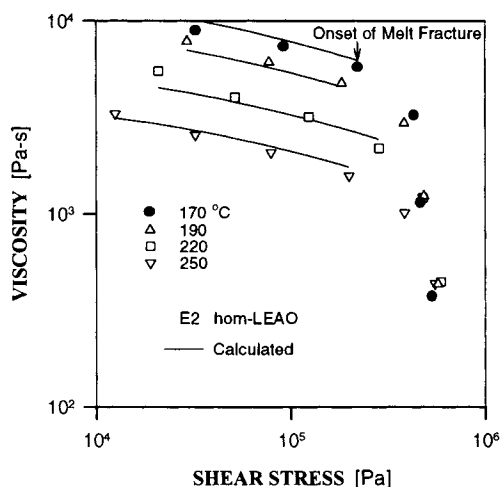
Figure 12 Viscosity of hom-LEAO (Sample E2) as a function of temperature and shear stress.

Figure 13 Viscosity of hom-BEAO (Sample F4) as a function of temperature and shear stress.

in Figure 2(B) are vertically parallel with a constant vertical distance at all levels of τ, and they can be superposed by vertical shifting. Thus, ΔE determined at a constant τ does not change with τ and it is a better characterization of a polymer. That was found to be true for all samples in this study including the branched polymer, Sample B1. It is emphasized that only the data before the onset of melt fracture should be used for fitting. Although η is usually expressed as a function of $\dot{\gamma}$, again it is desirable to express η as a function of τ in order to determine ΔE_τ.

Recognizing that ΔE_τ is constant at all shear stresses, eqs. (2b) and (4) can be combined to obtain the following equation to express η as a function of both T and τ using only four constants:

$$\log \eta(T, \tau) = [B_0 + B_1 \cdot (\log \tau)$$
$$+ B_2 \cdot (\log \tau)^2] + \frac{\Delta E_\tau}{(2.3)R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (5)$$

Viscosity data measured at several temperatures over a wide range of shear rate or shear stress can be fitted according to eq. (5) to determine the four constants: B_0, B_1, B_2, and ΔE_τ.

Recognizing that shear stress is simply the product of shear rate times viscosity, eq. (5) can be rewritten as follows to express viscosity as a function of temperature and shear rate instead of shear stress:

$$\log \eta(T, \dot{\gamma}) = [B_0 + B_1 \cdot (\log \eta + \log \dot{\gamma})$$
$$+ B_2 \cdot (\log \eta + \log \dot{\gamma})^2] + \frac{\Delta E_\tau}{(2.3)R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (6)$$
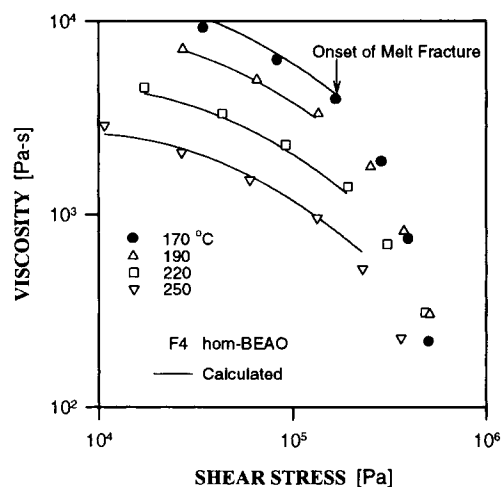
Viscosity terms are present on both sides of eq. (6), but it can be calculated at any shear rate and temperature using a numerical iterative computer program.

Figures 2–14 present the measured viscosity data as a function of shear stress and temperature for all samples. The data before the onset of melt fracture were fitted to eq. (5) for all samples to obtain the four constants listed in Table II. The apparent shear rates (before Rabinowitsch correction) at the onset of melt fracture are also listed in Table II. The curves in all figures drawn up to the shear stress at the onset of melt fracture according to eq. (5) using the four constants listed in Table II show an excellent fit to the data.
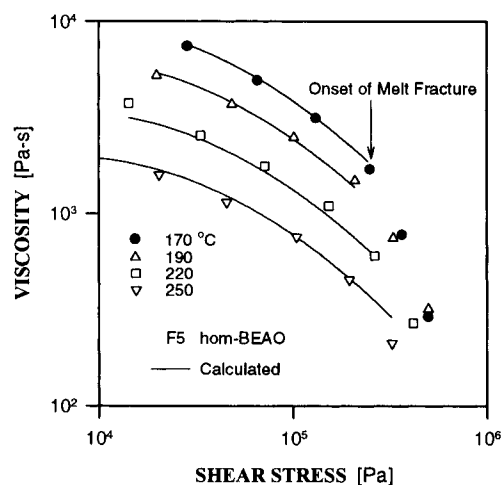

Figure 14 Viscosity of hom-BEAO (Sample F5) as a function of temperature and shear stress.

Table II   Summary of the Viscosity Measurements

ID	

	Four Fitting Constants for Viscosity in Pa-s with T_0 = 463 K				Aparent Shear Rate (/s) at the Onset of Melt Fracture at			
ID	ΔE_r	B_0	B_1	B_2	170°C	190°C	220°C	250°C
A1	28.5	−1.121	2.694	−0.366	352.2	1174	None	None
B1	44.8	0.706	2.309	−0.377	117.4	117.4	352.2	1174
C1	46.8	3.732	1.124	−0.247	352.2	352.2	352.2	1174
D1	31.7	1.444	1.308	−0.177	117.4	117.4	352.2	1174
D2	30.0	−2.474	2.998	−0.358	352.2	352.2	1174	1174
D3	32.8	−5.116	4.288	−0.512	1174	1174	1174	None
E1	25.0	2.436	0.745	−0.096	35.2	117.4	117.4	352.2
F1	32.6	2.052	0.949	−0.127	117.4	117.4	352.2	1174
F2	33.0	4.868	−0.038	−0.053	352.2	352.2	1174	1174
F3	33.7	5.043	0.046	−0.081	1174	1174	None	None
E2	31.5	3.306	0.425	−0.068	35.2	117.4	352.2	352.2
F4	39.5	−0.572	2.304	−0.295	117.4	117.4	352.2	1174
F5	38.8	−0.481	2.244	−0.294	352.2	352.2	1174	None

ΔE_r in kJ/mol, Rabinowitsch correction made. Measured by an Instron capillary rheometer using an L/D = 60 (1.27 mm D × 76.2 mm L) capillary with 90° entry.

Melt Index and Average Viscosity in Processing

Since a solid polymer is heated from the feed temperature to the melting point and then to the melt temperature in processing, the viscosities over the entire temperature range from the melting point to the melt temperature are important. Also, the melt is subjected to a wide range of shear stress. Therefore, the processability of a polymer is affected by the complex viscosity spectrum covering wide ranges of temperature and shear stress. [MI] expressed in g/10 min, which is widely used by the industry to specify the processing behavior of polymers, is the flow rate measured at a specific temperature of T_1 = 190°C and a low shear stress of τ_1 = 1.966 × 10^4 Pa using a very short capillary with length to diameter ratio of 3.8 and flat entry according to ASTM Method-1238, Condition E.[2] Although the [MI] value is supposed to represent

Table III   Viscous Properties at 190°C Calculated Using the Constants in Table II

ID	[MI]	DRI	Viscosity η_1 at T_1 and τ_1 (Pa-s × 10^{-3})	Viscosity η_2 at T_1 and τ_2 (Pa-s × 10^{-3})	Shear Sensitivity at T_1 = 190°C	
					m_1 at τ_1	m_2 at τ_2
A1	0.73	N/A	5.006	1.732	0.551	0.064
B1	0.85	N/A	4.758	0.786	0.075	−0.426
C1	0.40	N/A	10.203	1.727	0.005	−0.323
D1	1.09	N/A	6.298	3.807	0.789	0.554
D2	1.04	N/A	6.313	3.905	0.925	0.448
D3	0.79	N/A	7.217	3.629	0.892	0.211
E1	1.04	0.0	7.286	5.838	0.919	0.791
F1	1.04	1.1	5.971	4.197	0.855	0.685
F2	0.87	4.4	5.414	2.420	0.510	0.439
F3	0.69	12.0	5.514	1.868	0.348	0.239
E2	0.93	0.0	7.598	5.574	0.843	0.753
F4	0.80	2.2	7.751	4.059	0.774	0.382
F5	0.94	3.8	5.430	2.618	0.720	0.328

T_1 = 190°C, the [MI] condition; τ_1 = 1.966 × 10^4 Pa, a low shear stress equal to the [MI] condition, Condition E of ASTM Method-1238; τ_2 = 9.102 × 10^4 Pa, a high shear stress in the range of extrusion, Condition N of ASTM Method-1238.
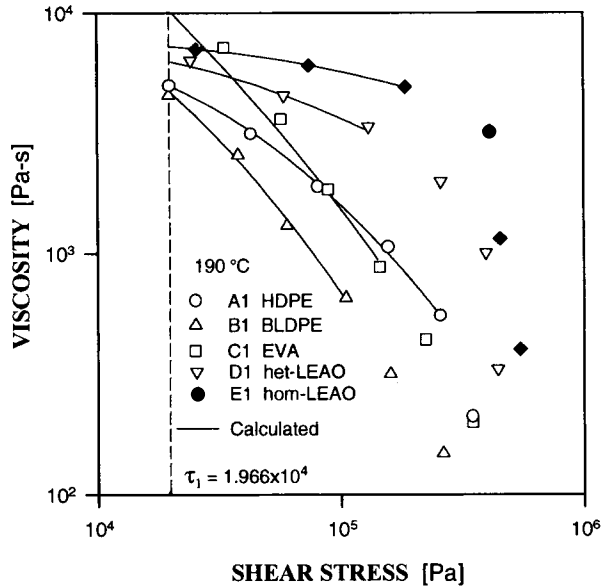
Figure 15   Viscosity of various PE homopolymers and copolymers as a function of shear stress at 190°C.

Figure 17   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.

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 viscoelastic properties. The [MI] by itself cannot properly describe the processing behavior of a polymer.
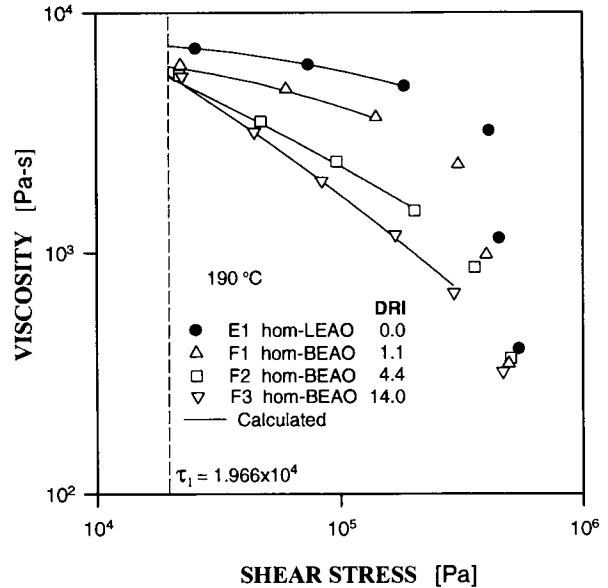
The viscosity calculated from eq. (5) at the [MI] conditions of T_1 and τ_1 will be denoted by η_1, and it will be used to indicate the viscosity level. η_1 of a given polymer will depend mainly on the weight-average MW of the polymer, increasing with in-

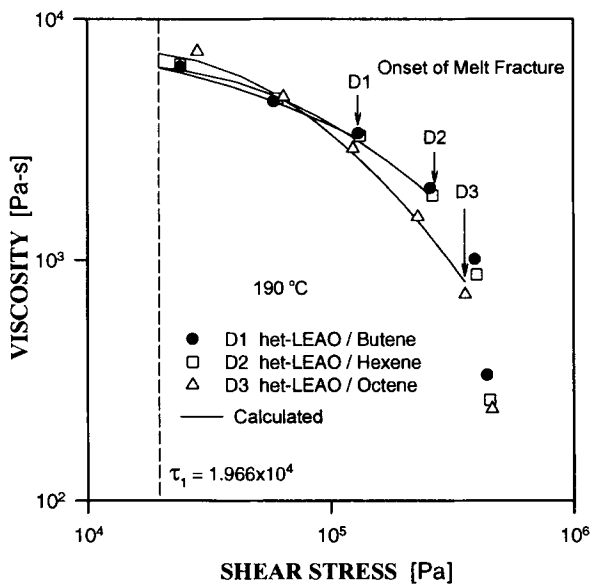**Figure 16**   Effects of the length of short-chain branching on the viscosity and flow stability of het-LEAO with about 0.917 g/cc density at 190°C.

Figure 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 250°C.
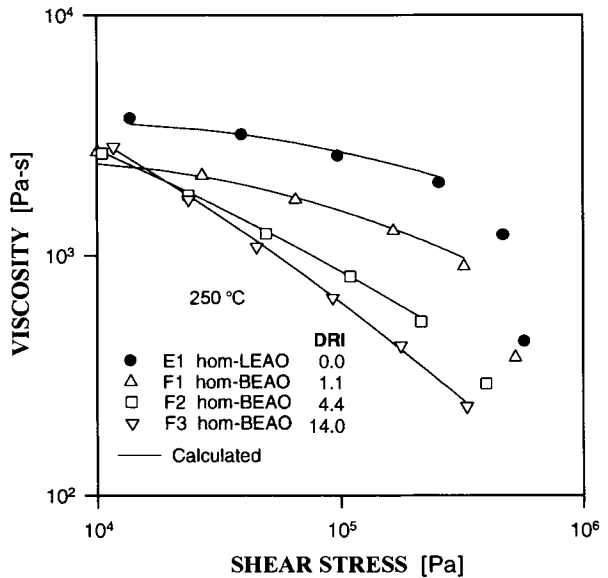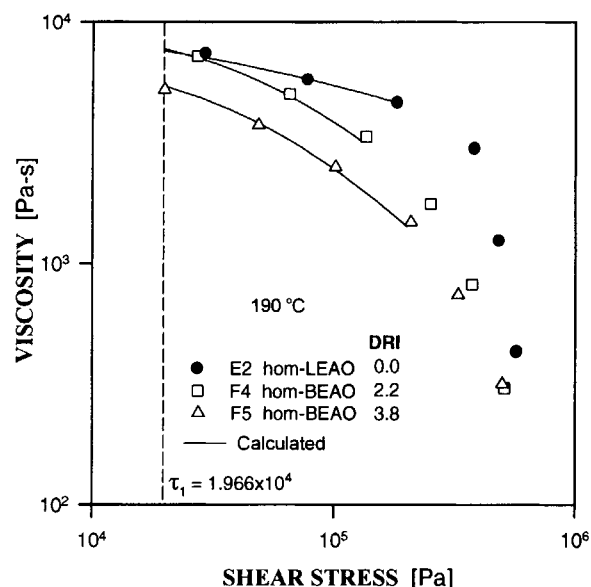
Figure 19 Effects of long-chain branching (expressed by DRI) on the viscosity and flow stability of homogeneous poly(ethylene/α-olefin) copolymer with about 0.870 g/cc density at 190°C.

creasing MW. If the elastic effect were ignored in the [MI] measurement, η_1 would be inversely proportional to [MI]. B_1 and B_2 depend on MW and MWD, making m calculated by eq. (3) to decrease with increasing MWD at a given MW or with increasing MW. ΔE_r depends on the chemical composition and structure of a polymer, but does not depend on MW or MWD. At least three constants— viscosity level (η_1), apparent flow activation energy (ΔE_r), and shear sensitivity (m)—are necessary to properly describe the viscous behavior of a polymer

in processing. The average viscosity in processing will decrease with decreasing η_1, increasing ΔE_r, and decreasing m. To compare the viscosity level and the shear sensitivity of the samples, η_1 and m listed in Table III were computed using the four constants listed in Table II. Two m values at 190°C are reported: m_1 at the low shear stress of $\tau_1 = 1.966 \times 10^4$ Pa corresponding to the [MI] measurement, Condition E (2160 g load) of ASTM Method-1238, and m_2 at a high shear stress of $\tau_2 = 9.102 \times 10^4$ Pa, corresponding to Condition N (10,000 g load) of ASTM Method-1238 (2). η_1 is found to be inversely proportional to [MI] in most cases. However, Sample F3 deviates seriously from the expected relationship. Sample F3 with a low [MI] = 0.69 was expected to have a substantially higher η_1 than that of Samples F1 and F2 with higher values of [MI]. The [MI] values and viscosities of these samples were confirmed by repeated measurements. Such deviations are believed to come from differences in elasticity. Sample F3 probably has a higher elasticity than that of Samples F1 and F2.

Dependence of Flow Activation Energy on Molecular Structure and Composition

Referring to Table II, comparison of the ΔE_r 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 that of the linear polymers (Samples A1, D1, and E1), in agreement with the previous investigators.[3-6] Thus, the viscosities of the branched polymers will decrease faster than those of the linear polymers as melt temperature increases in processing.
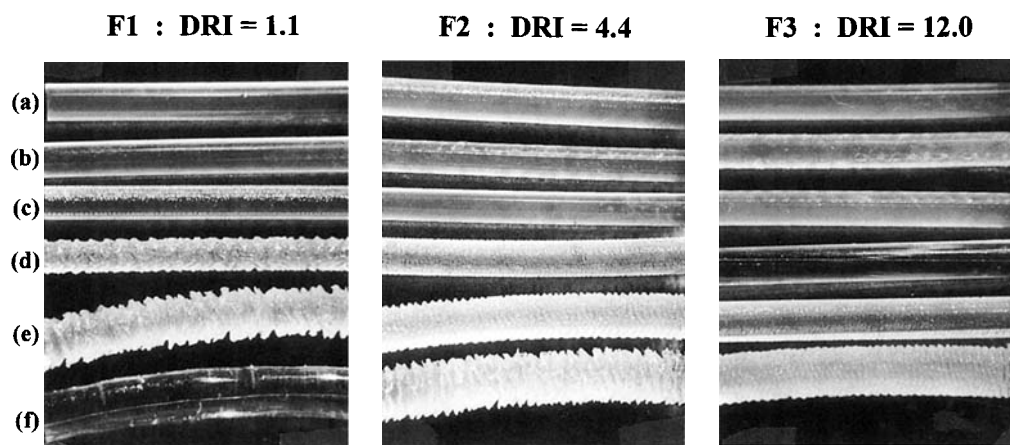

Figure 20 Photographs of the capillary strands of hom-BEAO with about 0.908 g/cc density (Samples F1, F2, and F3) at 170°C and six apparent shear rates, /s: (a) 3.52; (b) 11.74; (c) 35.2; (d) 117.4; (e) 352.2; (f) 1,174.

Comparison of the ΔE_r 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_r values of D series samples are only slightly higher than that of Sample A1, indicating that SCB has little influence on ΔE_r. A previous study[3] reported that the apparent flow activation energy of HDPE was not affected by ethyl SCB incorporated using a butene comonomer. Comparisons of the ΔE_r 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 that of hom-LEAO.

Dependence of Shear Sensitivity and Flow Stability on Molecular Structure and Composition

Figure 15 compares the viscosities of different PE homopolymers and copolymers (Samples A1, B1, C1, D1, and E1) at 190°C. The vertical dotted line indicates the shear stress τ_1 at the [MI] condition. 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 has the highest viscosity at τ_1 and the lowest [MI], but it has the highest shear sensitivity, resulting in a low average viscosity. Sample B1 has the lowest average viscosity, followed by Sample A1, Sample D1, and, finally, Sample E1. Sample E1 has the lowest shear sensitivity and, consequently, the highest average viscosity. The processing difficulty of Sample E1 in comparison to Sample B1, drawing high torque and developing high melt temperatures, is certainly understandable. The branched polymers with LCB (Samples B1 and C1) have a greatly higher shear sensitivity than that of the linear polymers. Comparison of the m values of these samples listed in Table III also leads to the same findings.

Figure 16 compares the viscosities and flow stabilities 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 to D3. Although this appears to indicate improved processability with increasing SCB length, care must be taken in the interpretation since these samples have different MWDs. Sample D3 has a broader MWD than that of Samples D1 and D2 as shown in Table I, and the observed beneficial effects for Sample D3 can be attributed to the broader MWD.

Similar comparisons are made for the hom-EAO samples E1 and F1–F3 with about 0.910 g/cc density at 190°C in Figure 17 and at 250°C in Figure 18, and also for the hom-EAO samples E2, F4, and F5

with about 0.870 g/cc density at 190°C in Figure 19, showing the effects of small amounts of LCB indicated by DRI. Figures 17–19 and also the m values in Table III clearly show that the shear sensitivity of hom-EAO very effectively increases with increasing DRI, greatly decreasing the average viscosity in processing. The viscosity curve of Sample F3 comes close to that of Sample A1. The extreme dependence of melt temperature on shear sensitivity was reported recently for het-LEAO.[9] The melt temperature of one sample with a higher shear sensitivity, extruded by a 114.3 mm (4.5 in.) D with $L/D = 24$ extruder at 75 rpm, was as much as 40°C lower than that of another sample with the same [MI].

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. Figures 17–19 seem to indicate that melt fracture occurs at a higher shear stress as DRI or LCB increases. Melt fracture definitely occurs at higher shear rates as LCB increases as can be seen in Table II and Figure 20. Figure 20 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 and then to a relatively smooth surface but with a long-range wave. As LCB (indicated by DRI) increases from Sample F1 to Sample F3, the flow stability is improved and melt fracture occurs at a higher shear rate.

Thermodynamic Properties

Examples of the DSC results are shown in Figure 21 for Samples A1, B1, C1, D1, E1, and F3, comparing different PE homopolymers and copolymers. The important values obtained from the DSC measurements are reported in Table IV 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.[10]

Referring to Table IV and Figure 21, Sample A1 (HDPE) with about 0.959 g/cc density has 70 wt % crystallinity with the melting peak at 131.5°C. Sample B1 (BLDPE) with about 0.920 g/cc density has 41 wt % crystallinity with the melting peak at 109.4°C. It is noted that the densities are the reported nominal values. Sample D1 (het-LEAO or LLDPE) has about the same density and crystallinity as has Sample B1, but its melting peak at 123.2°C
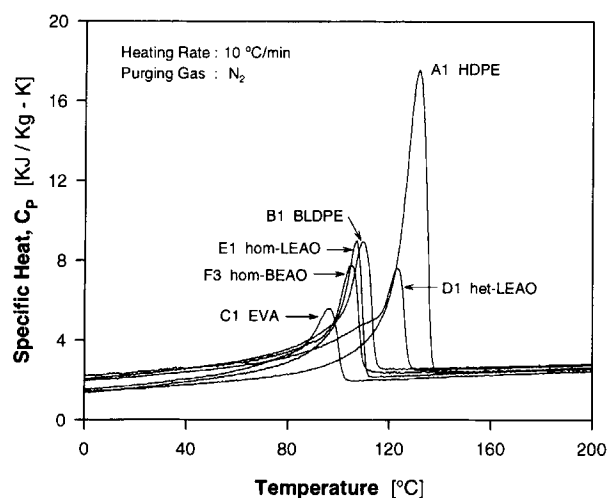
Figure 21 Differential scanning calorimeter thermo-grams of various PE homopolymers and copolymers.

is much higher than that of Sample B1. 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, close to the melt 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 ther-modynamic 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, cor-responding to only 16 wt % crystallinity. They start

to melt below room temperature at about −24°C with a melting peak around 55°C.

CONCLUSION

The melt rheological and thermodynamic properties of PE homopolymers and copolymers are found to depend on molecular structure such as SCB and LCB and the distribution of SCB as well as molec-ular composition, MW, and MWD. The MWD and molecular structure of a polymer depend on the par-ticular 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 I obtained from differ-ent producers. Thus, care should be taken in com-paring the experimental results of the samples.

The densities of PE homopolymers and copoly-mers are affected mainly by the amount of SCB, and they are not affected by small amounts of LCB. Compared at a similar density, hom-EAO has a melting peak close to that of BLDPE at a substan-tially lower temperature than that of het-LEAO. 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 pseudoplastic-ity, significantly increase the flow activation energy,

Table IV Summary of the Thermodynamic Properties

ID	Density (g/cc)	Melting Peak (°C)			Heat of Fusion (kJ/kg)	Crystallinity[a] (Wt %)
		Start	Peak	End		
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

[a] Weight % crystallinity was calculated by dividing the measured heat of fusion by the reference value of 293 kJ/kg for perfect PE crystal.

and greatly improve the flow stability. The average viscosity of hom-EAO in processing can be very effectively decreased by small amounts of LCB. The length of SCB in het-LEAO has no influence on the thermodynamic properties. As expected, the MWD influences the rheological properties, improving flow stability and increasing shear sensitivity with increasing MWD.

REFERENCES

1. J. Brandrup and E. H. Immergut, Ed., *Polymer Handbook*, Interscience, New York, 1966, pp. VI 41–52.
2. ASTM Standards, Part 27, Method D-1238.
3. L. H. Tung, *J. Polym. Sci.*, **46**, 409 (1960).
4. L. Boghetich and R. F. Kratz, *Trans. Soc. Rheol.*, **9**, 255 (1965).
5. R. A. Mendelson, W. A. Bowles, and F. L. Finger, *J. Polym. Sci. A.*, **2**(8), 105 (1970).
6. C. I. Chung, J. C. Clark, and L. Westerman, in *Advances in Polymer Science and Engineering*, K. D. Pae et al., Ed., Plenum, New York, 1972, pp. 249–273.
7. C. S. Speed, B. C. Trudell, A. K. Mehta, and F. C. Stehling, *SPE-RETEC Technical Papers of Polyolefins International Conference*, SPE, Brookfield, CT, 1991, p. 45.
8. S. Y. Lai, T. A. Plumley, T. I. Butler, G. W. Knight, and C. I. Kao, *1994 SPE-ANTEC Technical Papers*, SPE, Brookfield, CT, 1994, p. 814.
9. R. E. Christensen and C. Y. Cheng, *Plast. Eng.*, **47**(6), 31 (1991).
10. J. I. Kroschwitz, Ed.-in-chief, *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 4, p. 487.