

Shear and Elongational Rheology of Polyethylenes with Different Molecular Characteristics. I. Shear Rheology

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ABSTRACT: Four metallocene polyethylenes (PE), one conventional low density polyethylene (LDPE), and one conventional linear low density polyethylene (LLDPE) were characterized in terms of their complex viscosity, storage and loss moduli, and phase angle at different temperatures. The effects of molecular weight, breadth of molecular weight distribution, and long-chain branching (LCB) on the shear rheological properties of PEs are studied. For the sparsely long-chain branched metallocene PEs, LCB in-

creases the zero-shear viscosity. The onsets of shear thinning are shifted to lower shear rates. There is also a plateau in the phase angle, δ , for these materials. Master curves for the complex viscosity and dynamic moduli were generated for all PE samples. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 309–316, 2007

Key words: polyethylene; molecular characteristics; shear rheology; long-chain branching; master curve

INTRODUCTION

Polyethylenes (PE) are largely crystalline with their chains in a zig-zag conformation. They are produced by different polymerization processes. PEs may be divided into three categories, high-density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE), where density represents the level of crystallinity. HDPE possesses largely linear chains with little branching or comonomer, while LDPE is long-chain branched. LLDPE is LDPE with linear chains.

The uniqueness of a polymer is most frequently measured and expressed in terms of molecular weight, molecular weight distribution (MWD), degree of branching, and degree of crystallinity. Besides the knowledge of the dependence of the shearing behavior on external parameters such as shear rate and temperature, it is necessary to get some insight into the relationship between shearing properties and molecular characteristics mentioned earlier if possible. The systematic study of the relationships between molecular characteristics and the rheological behavior of PEs has been very limited in the past because of the lack of controlled MWDs and degrees of long-chain branching (LCB). The occurrence of the constrained geometry catalysts has made it possible to produce branched metallocene PE resins with controlled MWDs and degrees of LCB. In

this work, four metallocene PEs along with two conventional PEs with different molecular characteristics are studied in terms of their shear rheological behavior.

Temperature shifting of the viscosity curves

The method of reduced variables predicts that a single master curve for the shear viscosity (η) curves taken at different temperatures of a sample can be obtained by plotting reduced complex viscosity η_r^* versus reduced angular velocity ω_r by using a shift factor.¹ In the following, equations for the temperature shifting of shear viscosity are presented.

In this work, two temperature shift factors are defined by

$$(a_T)_1 = \frac{\eta_0(T)}{\eta_0(T_0)} \quad (1)$$

and

$$(a_T)_2 = \frac{\eta_0(T)T_0}{\eta_0(T_0)T} \quad (2)$$

where $\eta_0(T)$ and $\eta_0(T_0)$ are zero-shear viscosities of the melts at temperature T and reference temperature T_0 , respectively. Thus, the method of reduced variables predicts that a single master curve can be obtained by plotting reduced complex viscosity η_r^* versus reduced angular velocity ω_r , where they are defined by

$$\eta_r^* = \eta^*(\omega, T) \frac{\eta_0(T_0)}{\eta_0(T)} \quad (3)$$

$$\omega_r = \omega a_T \quad (4)$$

Assuming that the Cox-Merz rule² applies to PE samples, viscosity models are used to predict the zero-

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TABLE I
Molecular Characteristics of PE Samples

Sample ID	Sample source	MI (g/10 min)	Density (g/cm ³)	M_w	PI	M_z	LCB (1/10 ⁴ C)
PE-1	Dow Affinity PL 1840	1.0	0.909	87,400	2.43	160,200	0.57
PE-2	Exxon Exact 0201	1.1	0.902	88,700	2.14	158,900	0.79
PE-3	Exxon Exact 3132	1.2	0.900	111,000	2.04	180,400	N/A
PE-4	Dow Affinity PL 1880	1.0	0.902	115,800	2.12	183,700	0.18
PE-5	Equistar NA 952	2.0	0.919	116,000	9.1	*	*
PE-6	Mobil NTX 101	0.9	0.917	122,700	3.44	319,700	N/A

LCB, long chain branches; N/A, not applicable (PE-3 and PE-6 are linear PE resins with no long chain branches).
*, not available.

shear viscosity of polymer melts from the complex viscosity data. Two such models are considered in this work: the three-parameter Cross model and the three-parameter Carreau model.^{1,3} The three-parameter Cross viscosity model is given by

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^{1-n}} \quad (5)$$

and the three-parameter Carreau viscosity model given by

$$\eta = \eta_0 \left[1 + (\lambda\dot{\gamma})^2 \right]^{(n-1)/2} \quad (6)$$

where λ is a time constant and n is the power-law exponent. In general, the three-parameter Cross model tends to overpredict the zero-shear viscosity, whereas the three-parameter Carreau model tends to slightly underpredict the zero-shear viscosity.⁴ A scouting study reveals that eq. (1) is appropriate to generate a master curve for the complex viscosity when the three-parameter Cross model is used to predict the zero-shear viscosity, whereas eq. (2) is appropriate when the three-parameter Carreau model is used. The temperature dependence of a_T is often found to be an "Arrhenius dependence" of the following form:¹

$$a_T = \exp \left[\frac{\Delta E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (7)$$

where ΔE_a is the activation energy of flow and R is the universal gas law constant.

EXPERIMENTAL

Materials

Four metallocene polyethylenes (PE), one conventional low density polyethylene (LDPE), and one conventional linear low density polyethylene (LLDPE) are studied. The sample source, melt index (MI), density, weight-average molecular weight, polydispersity index (PI), and long-chain branches (LCB) of the PE samples are given in Table I. PE samples PE-1, PE-2,

PE-3, and PE-4 are metallocene-catalyzed resins and have narrow MWDs (PI \approx 2). PE-5 is a conventional LDPE resin, whereas PE-6 is a conventional LLDPE. PE-1, PE-2, PE-3, PE-4, and PE-6 have similar melt flow indexes. PE-1, PE-2, and PE-4 are branched copolymers of ethylene and octene-1 with controlled sparse long-chain branches. PE-3 and PE-6 are copolymers of ethylene and hexene with no LCB. All these six PE samples are blown film grades. All polymer samples used and the molecular characteristics data in Table I were provided by Dr. Donald Baird of Virginia Polytechnic Institute and State University.

Instruments and technique

Measurements of shear rheological data were done using the Advanced Rheometric Expansion System (ARES) rheometer (TA Instruments). Circular disks of PE specimens were prepared by compression molding at 180°C. The geometry used was parallel plates with diameter 25 mm. The gap was set at 1 mm. All experiments were conducted at four temperatures of 135, 150, 165, and 180°C. The linear viscoelastic region was tested by performing a dynamic strain sweep test and a 1% strain was used. Zero-shear viscosity was determined by using the ARES TA Orchestrator software to fit complex viscosity data to Carreau or Cross models.

RESULTS AND DISCUSSIONS

Effect of molecular characteristics on the shear rheology of PE melts

Complex viscosity

To illustrate the effects of molecular weight on the complex viscosity, the data are shifted on both axes by use of the zero-shear viscosity and eqs. (1)–(4). The results are presented in Figure 1. The complex viscosity data and shear viscosity data (although not shown here) have shown that the Cox-Melz rule is valid for all samples. Therefore, the complex viscosity data could be regarded as the shear viscosity data here for analyses. Figure 1 shows a very interesting feature,

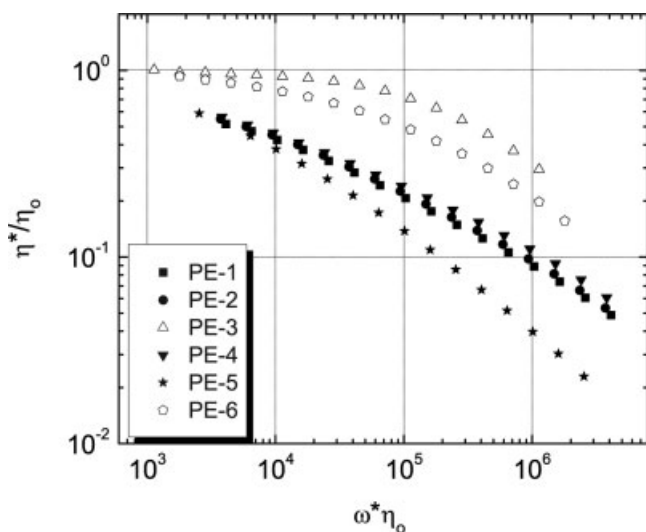


Figure 1 Shifted complex viscosity data for PEs at 165°C.

namely that the shifted viscosity curves arrange into three groups, which include linear (PE-3 and PE-6), sparsely long-chain branched (PE-1, PE-2, and PE-4), and densely long-chain branched (PE-5) PEs, respectively. It is worth mentioning here that in all figures, the solid symbols refer to branched samples and open ones to linear polymers. Apparently, the onset of shear thinning is affected by the presence of LCB on the main polymeric chains. The onsets of shear thinning for branched samples occur at lower shear rates than those for linear samples of PE-3 and PE-6. When PE-6 and PE-3 are compared, the onset of shear thinning for PE-6 occurs at lower shear rate and the transition zone between the Newtonian plateau and the high angular velocity power law zone is broadened, because of the broader MWD of PE-6. There are small differences between the three curves for the sparsely

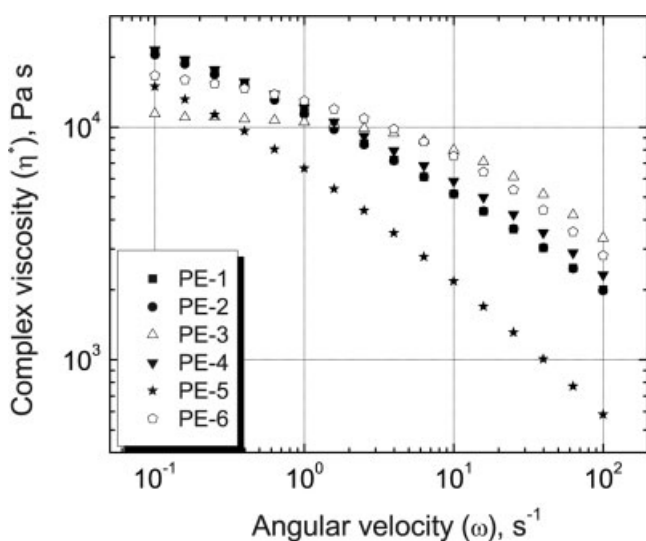


Figure 2 Complex viscosity data for PEs at 165°C.

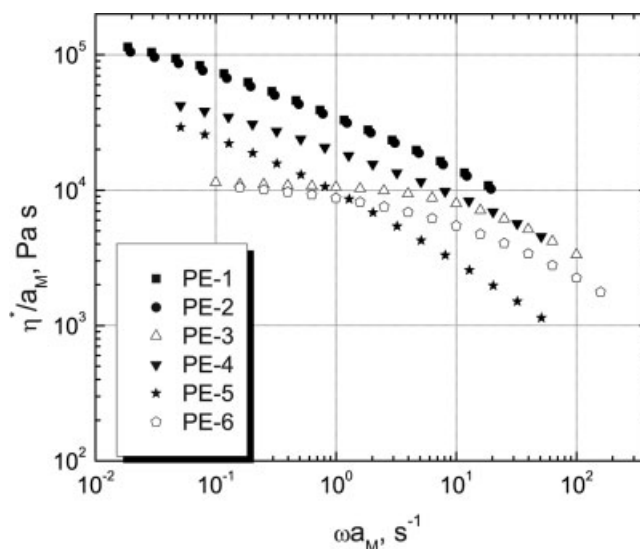


Figure 3 Shifted complex viscosity curves with respect to molecular weight at 165°C.

long-chain branched samples of PE-1, PE-2, and PE-4. These differences may result from the small differences in MWD and LCB.

The effect of molecular characteristics on the complex viscosity is also shown in Figure 2. Comparison of PE-3 and PE-6 shows that weight-average molecular weight increases the zero-shear viscosity. The sparse LCB also increases the zero-shear viscosity as illustrated by comparing PE-3 with PE-1 or PE-2, which have similar polydispersities.

To separate the effects of sparse LCB on shear viscosity from those due to molecular weight, shifted complex viscosity curves with respect to molecular weight were calculated and plotted in Figure 3, using a technique developed by Doeringhaus and Baird,⁵ who studied almost the same polymer samples at

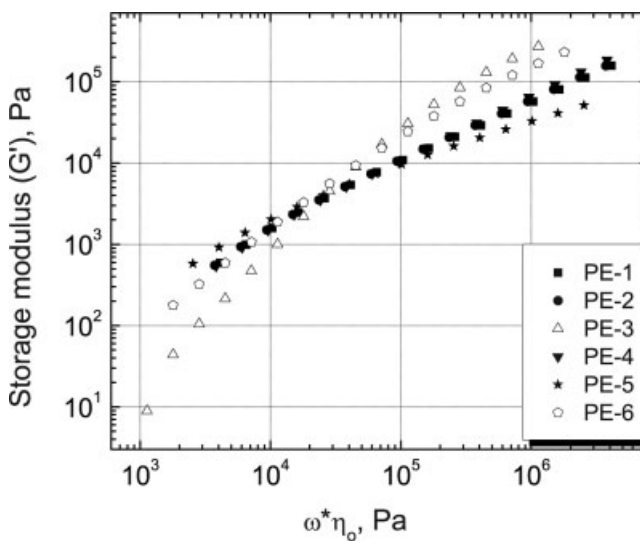


Figure 4 Shifted storage modulus data for PEs at 165°C.

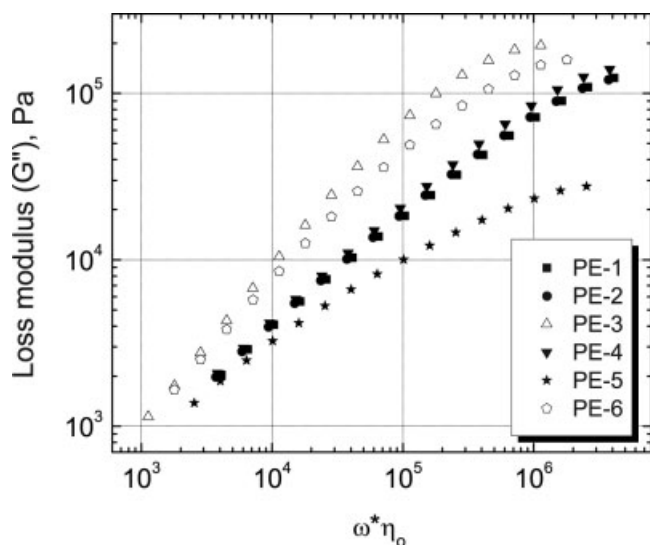


Figure 5 Shifted loss modulus data for PEs at 165°C.

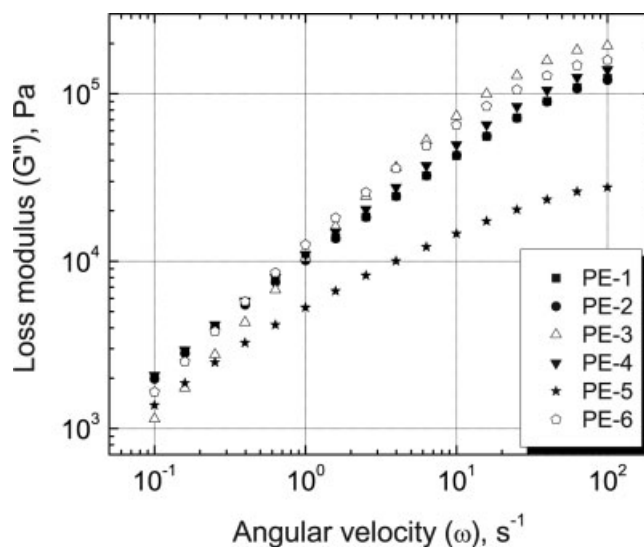


Figure 7 Loss modulus data for PEs at 165°C.

150°C. First, we calculated the zero-shear viscosity for the equivalent linear polymer having the same average molecular weight as the branched polymer with eq. (8)

$$\eta_0 = KM_w^\alpha, \quad (8)$$

set-up by Berry and Fox,⁶ with K and α values of 3.4×10^{-15} and 3.6 respectively, determined by Raju et al. for PEs at 190°C.⁷ For PE-3 and PE-6, which are linear polymers with no LCB, the zero-shear viscosities from Cross model fittings were taken into calculations. Then, shift factors with respect to molecular weight were calculated with eq. (9)

$$a_M = \frac{\eta_0(M)}{\eta_0(M_{\text{ref}})}, \quad (9)$$

where $\eta_0(M)$ is zero-shear viscosity at a given molecular weight M_w , and $\eta_0(M_{\text{ref}})$ is zero-shear viscosity at the reference M_w . PE-3 was chosen as reference material, because it is a linear and narrow MWD polymer sample, so that $M_{\text{ref}} = 111,000$ g/mol.

The shifted viscosity curves from Figure 3 reveal very significant features, concerning the effects of both long-chain branches and molecular weight on the shear rheology of the analyzed samples. First, long-chain branches increase the zero-shear viscosity, as seen from the positions of the shifted curves of PE-1,

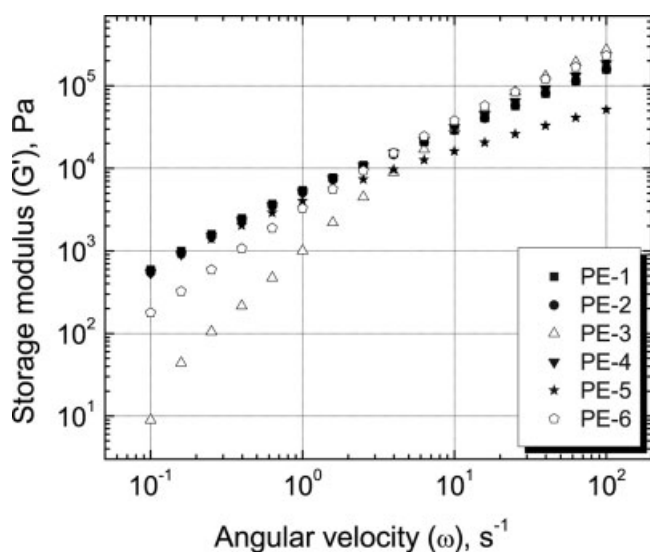


Figure 6 Storage modulus data for PEs at 165°C.

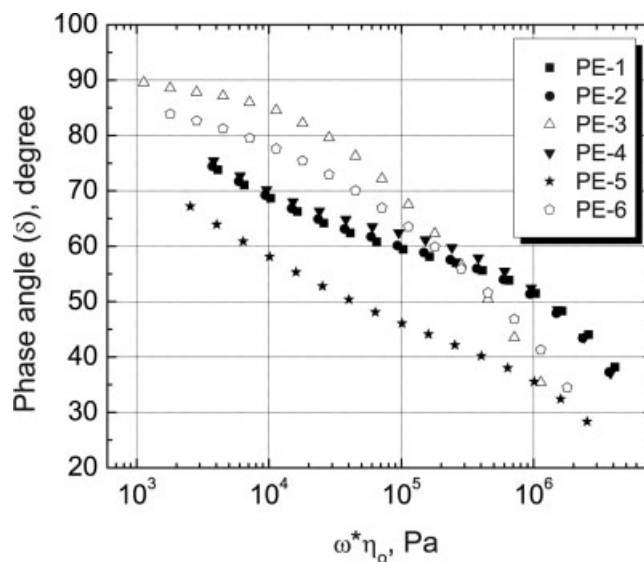


Figure 8 Shifted phase angle for PEs at 165°C.

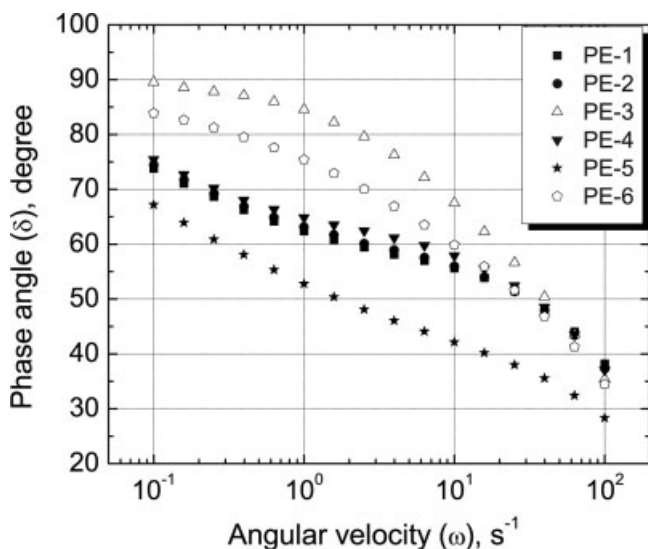


Figure 9 Phase angle for PEs at 165°C.

PE-2, PE-4, and PE-5, relative to the curves of PE-3 and PE-6. But the curve of PE-2 (LCB 0.79/10⁴C) falls a little bit under the curve of PE-1 (LCB 0.57/10⁴C) and the curve for PE-5 (that is manufactured by a free-radical, high pressure, polymerization process, and hence has 20–30 short-chain branches per 1000 carbon atoms and about 3 long-chain branches per 1000 carbon atoms⁸) falls below the curves of all sparse long-chain branched PE samples. This is in agreement with the findings of other authors,^{5,9,10} and showing that sparsely branched resins show an important increase in zero-shear viscosity up to a maximum (at about < 1 LCB/10⁴C), followed by a decrease in viscosity for densely branched polymers. Second, the curves of PE-3 and PE-6, both linear polymers with no branches, converge to the same Newtonian plateau, showing

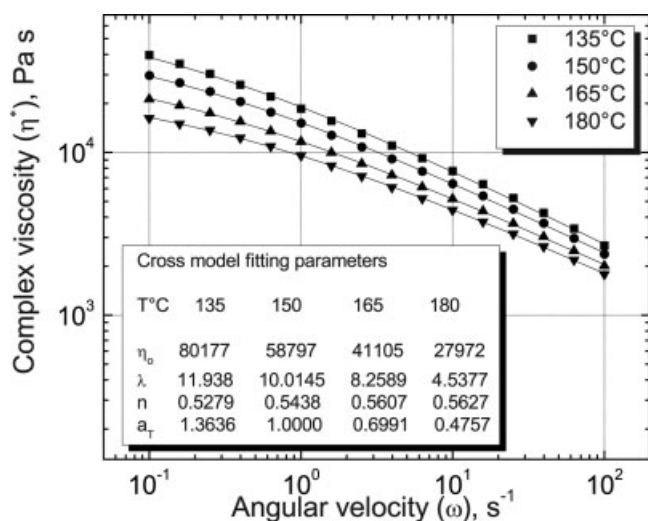


Figure 10 Complex viscosity data and Cross model fitting results of PE-1.

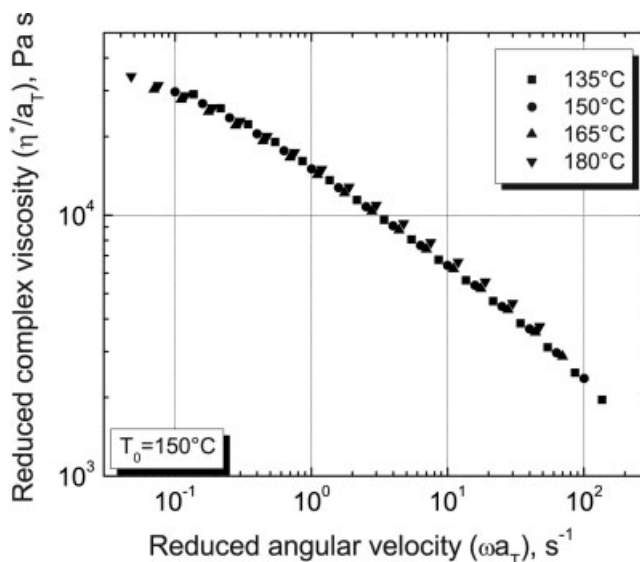


Figure 11 Master curve for the complex viscosity of PE-1 (Cross model).

only a slight difference in the onset of shear thinning behavior, which might be attributed to the small difference in the MWD (polydispersity index 2.04 vs. 3.44).

Dynamic moduli

Similarly, the dynamic moduli data were shifted and are shown in Figures 4 and 5. Again, the dynamic moduli data arrange into three groups. PE-6 has higher storage modulus at low frequencies but lower at high frequencies when compared with PE-3, due to the broader MWD of PE-6. The effect of sparse LCB can be obtained by comparing PE-3 with PE-1 (or PE-2 or PE-4), which have similar polydispersities. At low frequencies, PE-3 has lower storage modulus, but higher at high frequencies. Therefore, the effects of polydispersity and LCB on the storage modulus are similar. Both the breadth of MWD and LCB increase the storage modulus at low frequencies but decrease it at high frequencies. This result is consistent with the storage modulus curve of PE-5, which has broadest MWD and highest LCB and thus highest *G'* at low frequencies but lowest *G'* at high frequencies. The loss modulus curves are shown in Figure 5, from which it is easily seen that, on the whole range of frequencies, the effect of polydispersity or LCB is to decrease this property. And the effect is more obvious at higher frequencies.

The unshifted storage modulus data are shown in Figure 6. Compared with Figure 4, the difference of the storage modulus data between PE-3 and PE-6 is increased at low frequencies, but is diminished at high frequencies. According to the result of the effect of

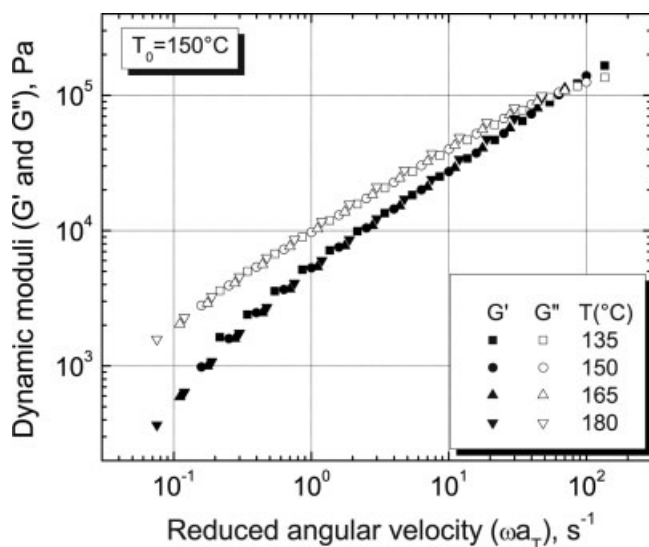


Figure 12 Master curves for the storage modulus and loss modulus of PE-1 (Cross model).

molecular weight on G' shown above, we may conclude that this increases the G' on almost the whole range of experimental frequencies. When the loss modulus data (in Fig. 7) are compared with the shifted loss modulus data (in Fig. 5), the difference between PE-3 and PE-6 data is increased at lower frequencies (PE-6 > PE-3) but decreased at higher frequencies. It may be concluded that the MW increases the loss modulus as well. This along with the effects of polydispersity and LCB explain that the loss modulus data of PE-1 and PE-2 are a little larger than the data of PE-3 at low frequencies.

Phase angle

The phase angle is another sensitive indicator of differences between materials. To illustrate the effects of molecular weight, the data for the phase angle (δ) are plotted versus the reduced zero-shear viscosity. The result is shown in Figure 8. The six curves show three different kinds of shape. There is a plateau in the phase angle for the sparsely branched materials PE-1, PE-2, and PE-4, at intermediate frequencies. The effect of broadening the MWD on the linear polymer resins behavior is again shown in this figure when PE-3 and PE-6 are compared. There are small differences between the three curves for PE-1, PE-2, and PE-4. The effect of LCB on the phase angle can be seen from the comparison of PE-3 with PE-1, PE-2, and PE-4, which have a lower phase angle at lower frequencies than PE-3 but show slightly higher phase angle at higher frequencies. The effect of LCB on phase angle at high frequencies is similar with the effect on zero-shear viscosity, if we also consider the curve for PE-5. The unshifted phase angle is shown in Figure 9. From the

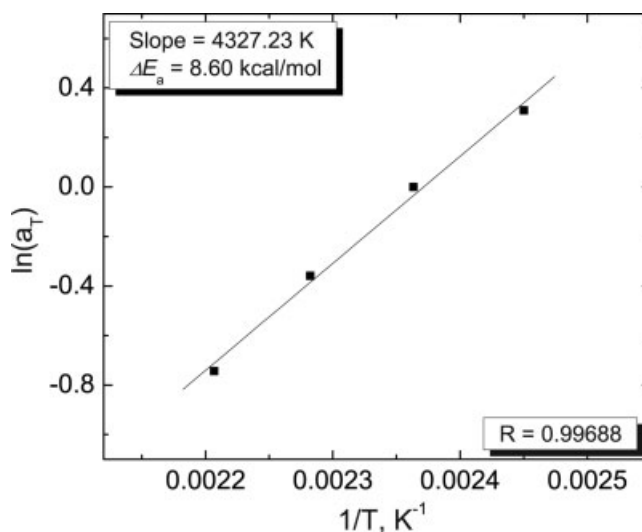


Figure 13 Arrhenius plot for the shift factors of PE-1 (Cross model).

comparison of PE-3 and PE-6 it is seen that the increase in molecular weight brings about a decrease of the phase angle on almost whole range of frequency.

Temperature shifting of complex viscosity curves of PE melts

The complex viscosity of PE-1 at four different temperatures is presented in Figure 10. Data from this figure show that changing the temperature does not have a significant effect on the functional dependence of η^* on ω ; it merely alters the zero-shear viscosity and the angular velocity at which the transition from constant complex viscosity to power-law behavior occurs.

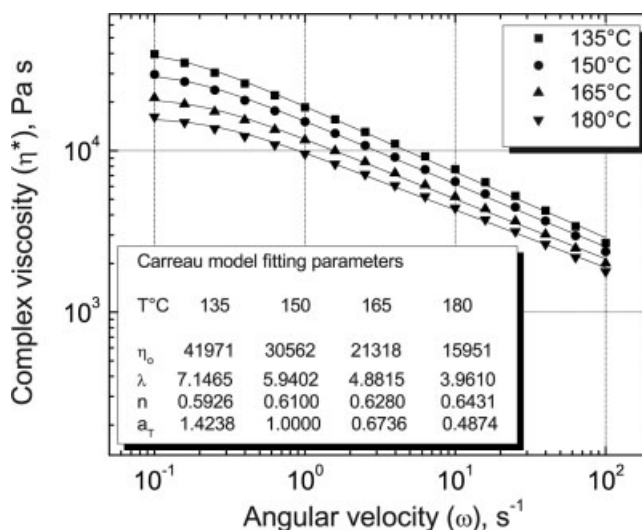


Figure 14 Complex viscosity data and Carreau model fitting results of PE-1.

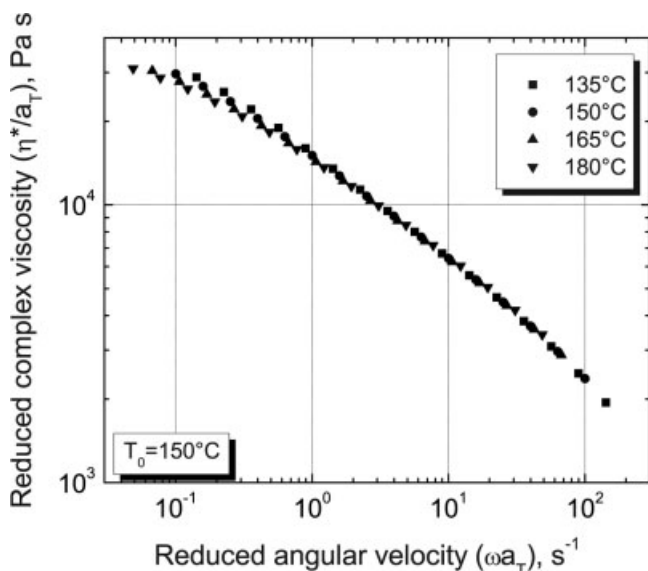


Figure 15 Master curve for the complex viscosity of PE-1 (Carreau model).

This similarity provides the basis for the method of reduced variables.

The three-parameter Cross model mentioned above was used to fit the complex viscosity data of PE-1 at each temperature. The fitted complex viscosity curves are plotted as solid lines in Figure 10. The obtained parameters (zero-shear viscosity, time constant, and power-law index) in the Cross model are also shown in the legend of Figure 10, together with the shift factors calculated using eq. (1) by choosing 150°C as the reference temperature. A master curve of the complex viscosity of PE-1 was developed and is shown in Figure 11. Similarly, master curves of dynamic moduli of PE-1 were also created using the same shift factors

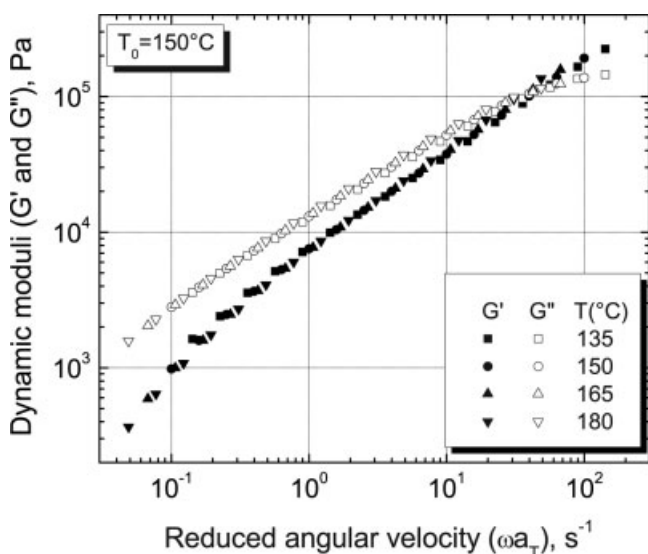


Figure 16 Master curves for the storage modulus and loss modulus of PE-1 (Carreau model).

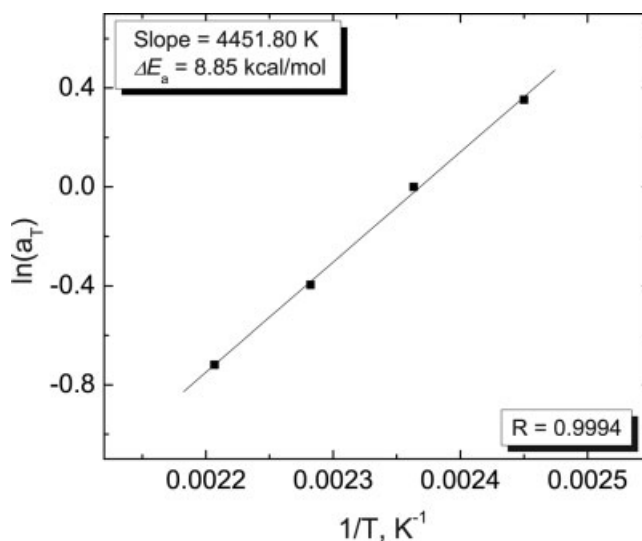


Figure 17 Arrhenius plot for the shift factors of PE-1 (Carreau model).

and shown in Figure 12. The Arrhenius plot of $\ln(a_T)$ versus $1/T$ is shown in Figure 13. From the slope of the linear fit, the activation energy of PE-1 was calculated as 8.6 kcal/mol.

The three-parameter Carreau model mentioned above was also used to fit the complex viscosity data of PE-1 at each temperature. The shift factors were calculated using eq. (2). The fitted results are presented in Figures 14–17 in the same way as the results from the Cross model.

It can be seen that complex viscosity decreases with increasing temperature. From Figures 11, 12, 15, and 16, it can be observed that both Cross and Carreau models yield good master curves for the complex viscosity and dynamic moduli. This can also be shown by the high coefficient of determination (R^2) values (higher than 0.988) for the polynomial fits of complex viscosity master curves of all PE samples, given in Table II. The shift factors show good Arrhenius dependence. From the slope of the Arrhenius plots, the activation energy for shear flow was calculated for each PE sample. The results are summarized in Table III. Both Cross and Carreau models show that there are no significant differences between activation energies of PE-1 and PE-4, which is in good agreement with the results shown in the literature.^{1,11} In addition, both models

TABLE II
Coefficient of Determination (R^2) Values for the Polynomial Fits of Complex Viscosity Master Curves of PE Samples

Model	PE-1	PE-2	PE-3	PE-4	PE-5	PE-6
Cross	0.9975	0.9968	0.9883	0.9976	0.9994	0.9985
Carreau	0.9983	0.9978	0.9897	0.9969	0.9952	0.9970

TABLE III
Molecular Data and Activation Energies for Flow for PE Samples

Sample	M_w	PI	LCB ($1/10^4$ C)	ΔE_a (kCal/mol)	
				Cross	Carreau
PE-1	87,400	2.43	0.57	8.598 ± 0.481	8.844 ± 0.216
PE-2	88,700	2.14	0.79	9.212 ± 0.138	9.098 ± 0.182
PE-3	111,000	2.04	N/A	7.461 ± 0.084	8.057 ± 0.060
PE-4	115,800	2.12	0.18	8.618 ± 0.569	8.740 ± 0.199
PE-5	116,000	9.1	*	10.501 ± 0.288	9.804 ± 0.243
PE-6	122,700	3.44	N/A	6.481 ± 0.634	7.057 ± 0.650

LCB, long chain branches; N/A, not applicable (PE-3 and PE-6 are linear PE resins with no long chain branches).

*, not available.

give the same order of activation energies which is PE-6 < PE-3 < PE-1 ~ PE-4 < PE-2 < PE-5. Conventional LDPE (PE-5) has larger activation energy, whereas linear PEs (PE-3 and PE-6) have smaller activation energies. Hence, the presence of long-chain branches increases the shear flow activation energy of PE, which is also in agreement with data from literature.¹¹⁻¹⁴

CONCLUSIONS

The shear rheology of PEs is considerably affected by molecular characteristics. Both the molecular weight and degree of LCB increases the zero-shear viscosity. The onset of shear thinning is affected by the degree of LCB. The onsets of shear thinning for branched samples occur at lower shear rates than those for linear samples. Broader MWDs result in the broadening of the transition zone between the Newtonian plateau and the high angular velocity power law zone. The molecular weight increases the storage modulus and loss modulus. At lower frequencies, both MWD and LCB increase the storage modulus and loss modulus. But at higher frequencies, both MWD and LCB decrease the storage modulus and loss modulus. Additionally, there is a plateau in the phase angle for the sparsely branched materials while for linear materials there is no plateau. MW decreases the phase angle. The MWD broadens the phase angle. Good master curves were generated for the complex viscos-

ity and dynamic moduli. Also, activation energy for shear flow was calculated from the shift factors at different temperatures.

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