Hencky Strain Shifting of Convergent Flow Measured Effective Elongational Viscosity

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ABSTRACT: The effective elongational viscosity data on a series of polyolefins as a function of the Hencky strain are shifted to a reference Hencky strain using an approach similar to that used for temperature shifting, shearing viscosity data. The basis of this shifting is the order that develops (i.e., the decrease in entropy that occurs) during forced flow through semihyperbolically convergent dies. The entropy decrease is proportional to the orientational contribution to the effective elongational viscosity. The Hencky strain shift factors are obtained from the convergent flow effective elongational rheology and the complex and capillary shear rheology. The commercial grades of polyolefins studied include polypropylene, high density polyethylene, and metallocene and conventionally catalyzed low density polyethylene. The combination of the temperature shift factors given in our companion article and the Hencky strain shift factors in this article enable the creation of master curves for the effective elongational rheology. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1397–1404, 2003

Key words: elongational viscosity; semihyperbolic die; shift factor; master curve; Hencky strain shifting; temperature and Hencky strain shifting; low density polyethylene; high density polyethylene; polypropylene

INTRODUCTION

As discussed in our previous article[1] and by authors elsewhere,[2–5] the effective elongational viscosity of polymer melts and concentrated solutions can be determined using flow through semihyperbolic convergent dies. In these semihyperbolic dies the value of R^2z is constant, where R is the radius of the die at a centerline distance z from the entrance.

Using this fact and performing momentum, mass, and energy balances, the theoretical development for the calculation of the effective elongational viscosity (η_{eff}) leads to the equations

$$\eta_{\text{eff}} = -\frac{\Delta P}{\dot{\varepsilon}\varepsilon_{\text{H}}} \qquad (1)$$

$$\dot{\varepsilon} = \frac{\partial v_z}{\partial z} \qquad (2)$$

where ΔP is the pressure drop along the die; $\dot{\varepsilon}$ is the elongational strain rate; and ε_{H} is the Hencky strain, which is defined by the equation

$$\varepsilon_{\text{H}} = \ln\frac{D_0^2}{D_e^2} \qquad (3)$$

Details on the experimental technique for the measurement of the elongational viscosity by using hyperbolic convergent dies are given elsewhere.[2] An independent comparison of this semihyperbolic convergent flow effective elongational viscosity data and similar data from a Rheometric Scientific extensional melt rheometer using the same low density polyethylene (LDPE) indicated agreement of the two techniques at the same ε_{H} and $\dot{\varepsilon}$ values.[6]

As described in detail in another study,[2] the dependence of the η_{eff} upon the ε_{H} is a result of the orientation developing in the polymeric fluid as it is being attenuated. The enthalpy change associated with the flow induced transformation to what can be considered a metastable liquid crystalline form can be estimated as follows. The effective Trouton ratio (TR) is η_{eff}/η_s (where η_s is the shear viscosity measured at the same temperature and at an equivalent magnitude shear rate). If the assumption is made that the non-Newtonian character of the fluid in excess of that reflected in η_s is due to the resistance to orientation, then the actual TR would be $\eta_e/\eta_s = 3$, where η_e is the expected and isotropic to isotropic state elongational viscosity. By measuring η_s then $\eta_e = 3\eta_s$ and substituting $3\eta_s$ into the enthalpy equation,[2] the enthalpy per unit volume (ΔH) can be calculated from the resultant equation:

$$\Delta H = -\dot{\varepsilon}\varepsilon_{\text{H}}[\eta_{\text{eff}} - 3\eta_s] \qquad (4)$$

This implies that the term $[\eta_{\text{eff}} - 3\eta_s]$ is a viscosity related measure of the orientation development due to

this flow geometry and that the fluid does not remain in an isotropic state during flow; therefore, the term $[\eta_{eff} - 3\eta_s]$ is the "orientational contribution" to the effective elongational viscosity (i.e., the "orientational viscosity"). For a Newtonian fluid $\eta_{eff} = 3\eta_s$ (i.e., TR = 3), and no orientational contribution to the effective elongational viscosity occurs. For the polymer melts in this study the TR is generally greater than 100, and thus the $\eta_{eff} - 3\eta_s$ term is essentially equal to η_{eff}.

The entropy change (ΔS) indicating the degree of orientation that develops can be determined from $\Delta G = \Delta H - T\Delta S$, where ΔG is the Gibbs free energy and T is the absolute temperature. The assumption is made that the Gibbs free energy change approaches zero for this steady-state, quasiequilibrium flow, resulting in eq. (5):[2]

$$\Delta S = \frac{\Delta H}{T} \tag{5}$$

Therefore, if TR $= \eta_{eff}/\eta_s$,

$$T\Delta S = -\dot{\varepsilon}\varepsilon_H[\eta_{eff} - 3\eta_s] = -\dot{\varepsilon}\varepsilon_H[TR - 3]\eta_s \tag{6}$$

BACKGROUND

Hencky strain related shifting of effective elongational viscosity

The $\eta_{eff} - 3\eta_s$ orientational viscosity term is somewhat analogous to the $\eta_0 - \eta_s$ term used for a polymer solution, where η_0 is the zero shear rate solution viscosity, η_s is the solvent contribution to the solution viscosity, and assuming linear behavior, $\eta_0 - \eta_s$ is the polymer contribution. If the solution viscosity is significantly higher than the solvent viscosity in concentrated solutions, then η_0 is essentially equal to $\eta_0 - \eta_s$ as η_{eff} is essentially equal to $\eta_{eff} - 3\eta_s$ for large TR values.

Multiple sets of assumptions and resulting equations were considered for shifting the effective elongational viscosity. However, only the two presented in the following discussion fit the data, and both fit it equally well as discussed later. Both involve the relaxation times for the polymer melts and solutions but involve different assumptions.

Hencky strain shift factors based upon relaxation time ratio (method 1)

A definition of a Hencky strain shift factor $[(a_H)_1]$, based upon an orientation ratio being equal to the relaxation ratio, could be approached by assuming normalized strain rate states and an appropriately corrected equivalent shear viscosity state as now follows. The $\dot{\varepsilon}\varepsilon_H$ term occurs in the derivation of the η_{eff}

as represented in eq. (1) and reoccurs in the enthalpy and entropy derivations in eqs. (4) and (6). This $\dot{\varepsilon}\varepsilon_H$ term is assumed in this derivation to be a normalized elongational strain rate (i.e., a strain rate corrected for the effects of orientation development in the polymer melt or solution). Therefore, to be at equivalent normalized elongational strain rates

$$\dot{\varepsilon}\varepsilon_H = \dot{\varepsilon}_0\varepsilon_{H_0} \tag{7}$$

and the shear viscosity at an equivalent shear strain rate (to the normalized elongational strain rate) is assumed to also be adjusted so that

$$\eta_s\varepsilon_H = \eta_{s_0}\varepsilon_{H_0} \tag{8}$$

Defining $(a_H)_1$ as

$$(a_H)_1 \equiv \frac{[T\Delta S]}{[T\Delta S]_0} = \frac{\lambda_j}{\lambda_{j_0}} = \frac{[\eta_{eff}(\dot{\varepsilon}, \varepsilon_H) - 3\eta_s]\dot{\varepsilon}\varepsilon_H}{[\eta_{eff}(\dot{\varepsilon}_0, \varepsilon_{H_0}) - 3\eta_s]\dot{\varepsilon}_0\varepsilon_{H_0}}$$

$$= \frac{[TR - 3]}{[TR - 3]_0}\left[\frac{\eta_s}{\eta_{s_0}}\right]\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right]\left[\frac{\varepsilon_H}{\varepsilon_{H_0}}\right] \tag{9}$$

and substituting eqs. (7) and (8) into eq. (9) gives

$$(a_H)_1 = \frac{[TR - 3]}{[TR - 3]_0}\left[\frac{\eta_{s_0}}{\eta_{s_0}}\left[\frac{\varepsilon_{H_0}}{\varepsilon_H}\right]\right]\left[\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}_0}\left[\frac{\varepsilon_{H_0}}{\varepsilon_H}\right]\right]\left[\frac{\varepsilon_H}{\varepsilon_{H_0}}\right] \tag{10}$$

Canceling the terms in eq. (10) gives

$$(a_H)_1 = \frac{[TR - 3]\varepsilon_{H_0}}{[TR - 3]_0\varepsilon_H} \tag{11}$$

In elongational flow measurements using convergent dies, both the stress and the elongational strain rate are affected by the Hencky strain because a zero strain rate region in which a constant viscosity independent strain rate occurs is not reached. In addition, contrary to temperature shift factors, in this derivation the stress terms are assumed to be sensitive to the flow conditions (i.e., to the Hencky strain imposed). Therefore, the stress terms in this derivation should be divided by a_H because a higher Hencky strain increases the stress, which is

$$(\tau_{ij})_r = \frac{\tau_{ij}}{(a_H)_1} \tag{12}$$

and

$$(\dot{\varepsilon}_r)_1 = (a_H)_1\dot{\varepsilon} \tag{13}$$

where $(\tau_{ij})_r$ and $\dot{\varepsilon}_r$ are the reduced stress terms and reduced elongational strain rate, respectively. The lat-

ter is defined in a similar manner to shift factors for temperature. The elongational viscosity is the difference between the axial and transverse stress terms divided by the strain rate; therefore, the reduced effective elongational viscosity should be

$$[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}_0})]_{r1} = \frac{[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})]}{(a_{\text{H}})_1^2} \quad (14)$$

and this should be plotted versus the $\dot{\varepsilon}_r$ as given in eq. (13).

Hencky strain shift factors based upon orientational viscosity ratio (method 2)

A derivation of a Hencky strain shift factor $[(a_{\text{H}})_2]$, based upon an orientational viscosity ratio, is given in the following. The equation for the temperature shifting was derived from the Rouse theory using the ratio of the relaxation times (λ_j) for the measured state and the reference.[1] The Rouse theory shows that λ_j increases with the viscosity and decreases with the temperature. For Hencky strain effects an analogous treatment would be to assume that the λ_j still increases with the viscosity but also increases with the ε_{H}. Using this assumption the $(a_{\text{H}})_2$ is defined as the ratio of the orientational viscosity at the measured Hencky strain, at the reference strain rate, divided by the orientational viscosity at the reference Hencky strain and at the reference strain rate as shown in eq. (15). The subscript zero indicates the value of the variable at the reference state (e.g., the Hencky strain to which the data is being shifted) and the reference strain rate (usually the lowest for the data set, e.g., 1 or 2.5 s^{-1}):

$$(a_{\text{H}})_2 \equiv \frac{[\eta_{\text{eff}}(\dot{\varepsilon}_0, \varepsilon_{\text{H}}) - 3\eta_s]}{[\eta_{\text{eff}}(\dot{\varepsilon}_0, \varepsilon_{\text{H}_0}) - 3\eta_s]} \quad (15)$$

Furthermore, the ratio of the effective elongational viscosity at the measured elongational strain rate and the measured Hencky strain to the effective elongational viscosity at the measured strain rate and the reference Hencky strain are assumed in this development to be equal to the ratio of the relaxation time at the measured Hencky strain to the relaxation time at the reference Hencky strain. Although the relaxation times may be a function of the strain rate, it is assumed that the ratio of relaxation times is not. The reduced effective elongational viscosity can be similarly defined with the reduced shear viscosity with respect to temperature as follows:

$$[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})]_{r2} = \eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}}) \frac{[T\Delta S]_0}{[T\Delta S]}$$

$$= \frac{[\eta_{\text{eff}}(\dot{\varepsilon}_0, \varepsilon_{\text{H}_0}) - 3\eta_s][\dot{\varepsilon}_0\varepsilon_{\text{H}_0}]}{[\eta_{\text{eff}}(\dot{\varepsilon}_0, \varepsilon_{\text{H}}) - 3\eta_s][\dot{\varepsilon}_0\varepsilon_{\text{H}}]} \quad (16)$$
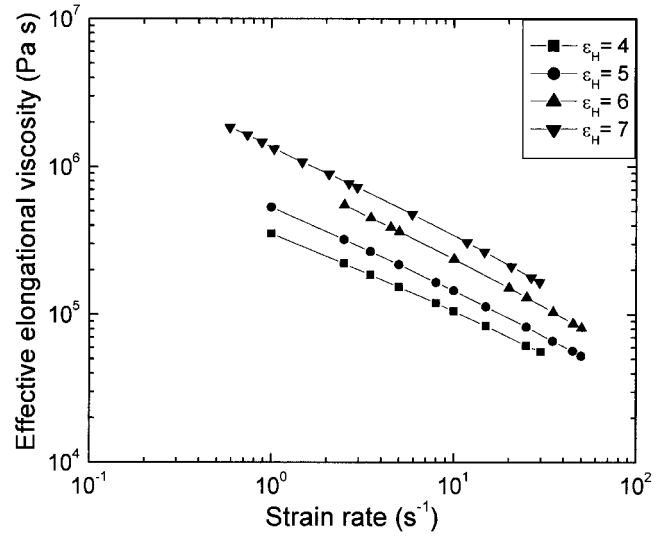

Figure 1 The effective elongational viscosity for LDPE-E at different Hencky strains and 175°C.

Canceling the $\dot{\varepsilon}_0$ in the numerator and denominator of eq. (16), substituting eq. (15) into eq. (16), and solving for the shifted value of the effective elongational viscosity at the reference Hencky strain gives eq. (17):

$$[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})]_{r2} = [\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})]\left[\frac{\varepsilon_{\text{H}_0}}{(a_{\text{H}})_2\varepsilon_{\text{H}}}\right] \quad (17)$$

This is plotted versus the reduced strain rate similar to eq. (13), that is,

$$(\dot{\varepsilon}_r)_2 = (a_{\text{H}})_2\dot{\varepsilon} \quad (18)$$

EXPERIMENTAL

Details on the materials used and experimental technique are given in our companion work in this issue.[1]

RESULTS AND DISCUSSION

Hencky strain master curves

The effective elongational viscosity curves for LDPE sample E (LDPE-E, molecular weight = 80,350 g/mol, polydispersity index = 5.15) at four temperatures and four Hencky strains are given in Figures 1–4. A "strain hardening" effect is shown by the increase of the effective elongational viscosity brought about by the increase in the Hencky strain from 4 to 7. This effect is almost independent of the strain rate and melt temperature. A "strain rate thinning" is also noticed at all temperatures and Hencky strains tested. An interesting feature of this sample is that the effect of the Hencky strain is almost the same on the entire range of strain rates and at all the temperatures. This is re-
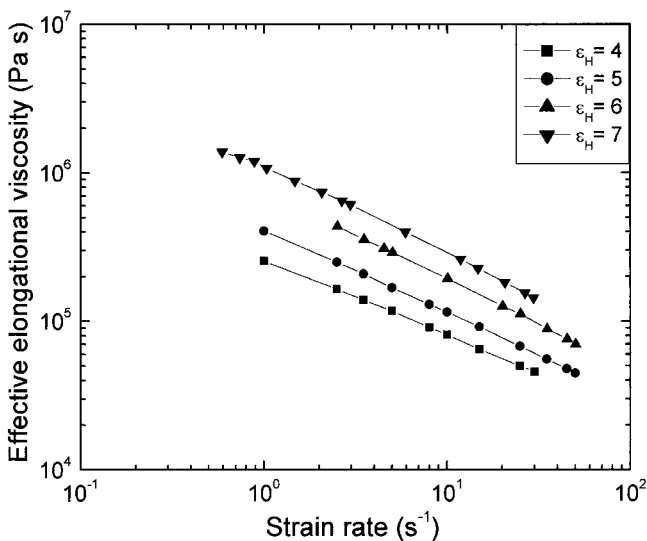
Figure 2 The effective elongational viscosity for LDPE-E at different Hencky strains and 200°C.
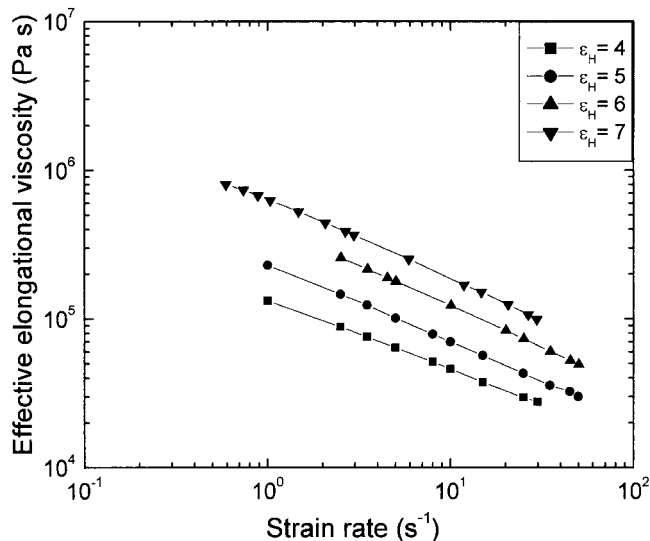

Figure 4 The effective elongational viscosity for LDPE-E at different Hencky strains and 250°C.

vealed by the parallel pattern of the effective elongational viscosity curves. This pattern was noticed for all PE samples except for the metallocene LDPEs, where a trend to a kind of Newtonian range is shown at low strain rates and a slightly lower effect of the Hencky strain is shown at higher strain rates.

The master curves with respect to the Hencky strain for the LDPE-E sample are given in Figures 5 and 6 for methods 1 and 2 of shifting, respectively. Both methods show very good agreement, according to the values of the coefficient of determination (R^2) with more compact master curves for the first method and a corresponding extended range of the reduced strain rate for the second method. Figures 7 and 8 present

master curves for the high density PE sample B (HDPE-B), showing almost the same pattern of temperature influence but a different temperature sensitivity of the effective elongational viscosity as compared with the LDPE-E sample. This is also revealed by the activation energies of 13,880 and 7,541 cal/mol for LDPE-E and HDPE-B, respectively.[1] Again, the accuracy of both shifting procedures is very good for both methods. In the case of an extrusion grade polypropylene (HGX PP), the master curves, presented in Figures 9 and 10 show a tendency toward a Newtonian range at low strain rate, mainly at high temperatures. The temperature effect on the effective elongational viscosity is comparable with that of
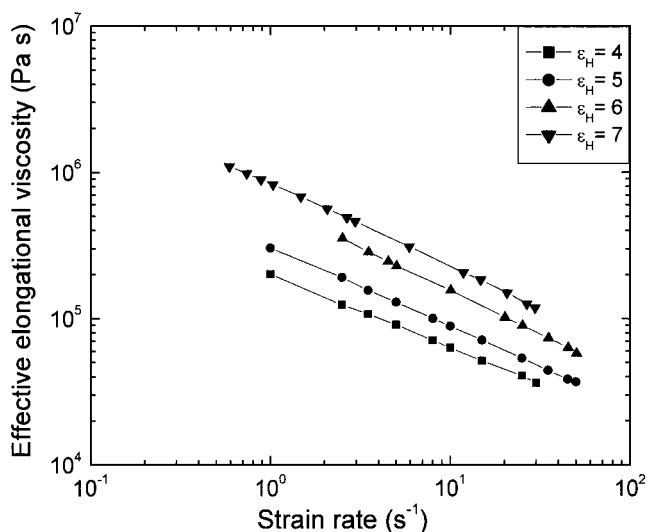

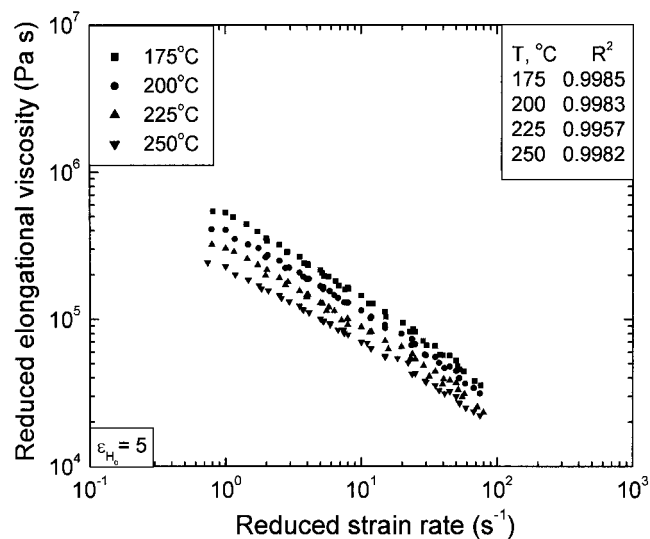**Figure 3** The effective elongational viscosity for LDPE-E at different Hencky strains and 225°C.

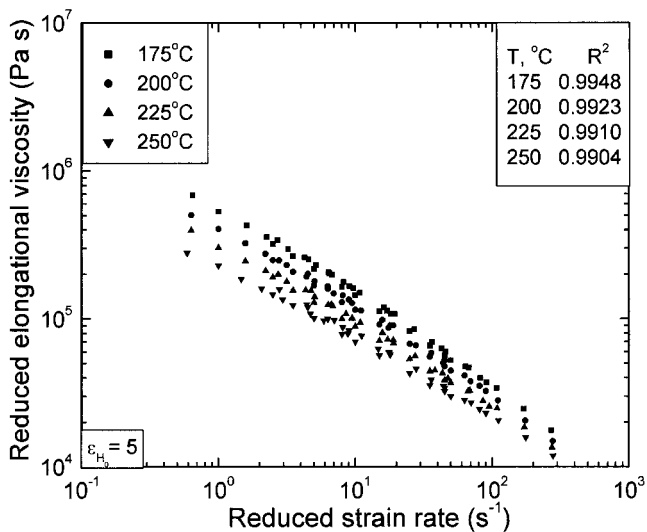**Figure 5** Master curves for the elongational viscosity of LDPE-E (method 1).

Figure 6 Master curves for the elongational viscosity of LDPE-E (method 2).

Figure 8 Master curves for the elongational viscosity of HDPE-B (method 2).

LDPE-E, as shown by the elongational flow activation energy value of 13,327 cal/mol.[1]

Comparison of Hencky strain shifting approaches

Both Hencky strain shifting approaches developed in this work and shown in Figures 5–10 for three samples give similar R^2 values, and all sets of R^2 are quite similar to that of the temperature shifting. For comparison with the temperature shifting of LDPE-E (weight-average molecular weight = 80,350 g/mol, molecular weight distribution = 5.15), the shearing viscosity shifting gave an R^2 value of 0.9988, the temperature shifting of the elongational viscosity using
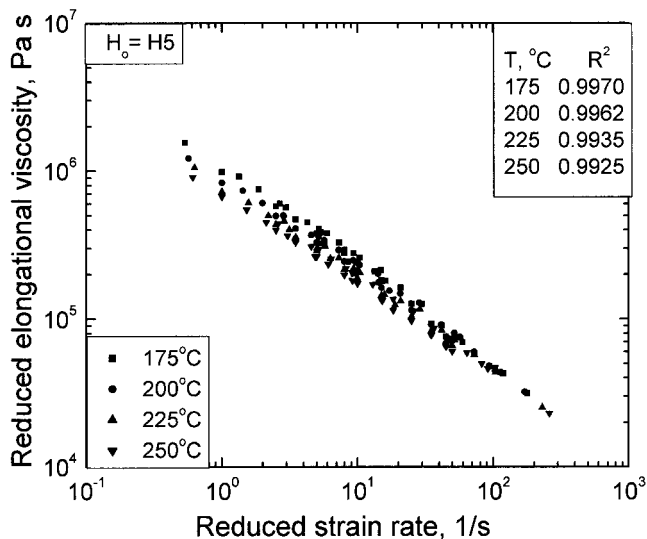
the same a_T shift factors gave R^2 values between 0.9963 and 0.99797 for Hencky strains 4 to 7,[1] the Hencky strain shifting for the first method mentioned [using $(a_H)_1$] gave R^2 values between 0.9957 and 0.9985, and the alternate method [using $(a_H)_2$] gave R^2 values in the range of 0.9904–0.9948. The agreement noted in this comparison is typical of the other samples tested as seen in Table I, where the coefficients of determination are given for all tested PE and PP samples. Other Hencky strain shifting equations were attempted, but none gave good fits to the experimental data; therefore, only the two approaches mentioned here are described in detail. If the two Hencky strain shift factors given in eqs. (11) and (15) are compared,
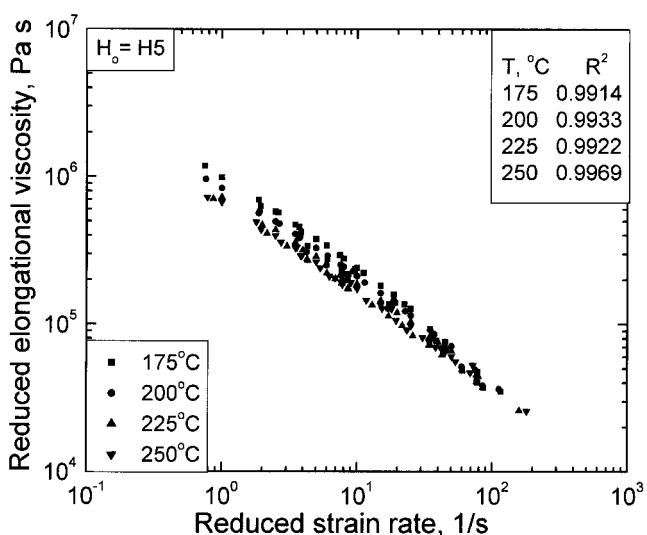

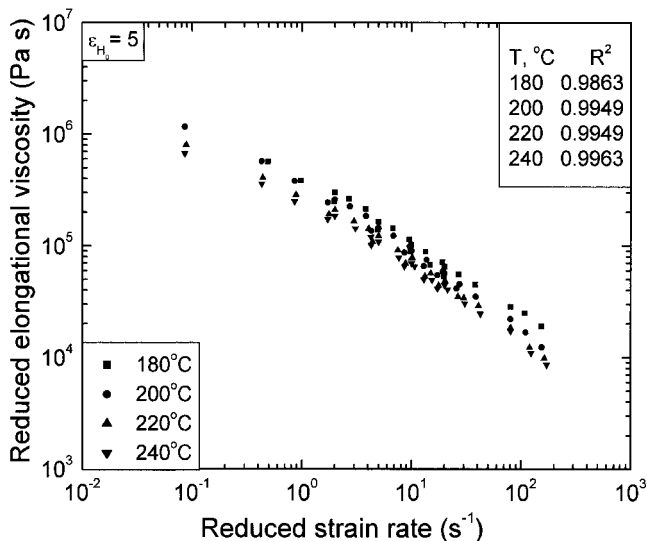**Figure 7** Master curves for the elongational viscosity of HDPE-B (method 1).

Figure 9 Master curves for the elongational viscosity of HGX PP (method 1).
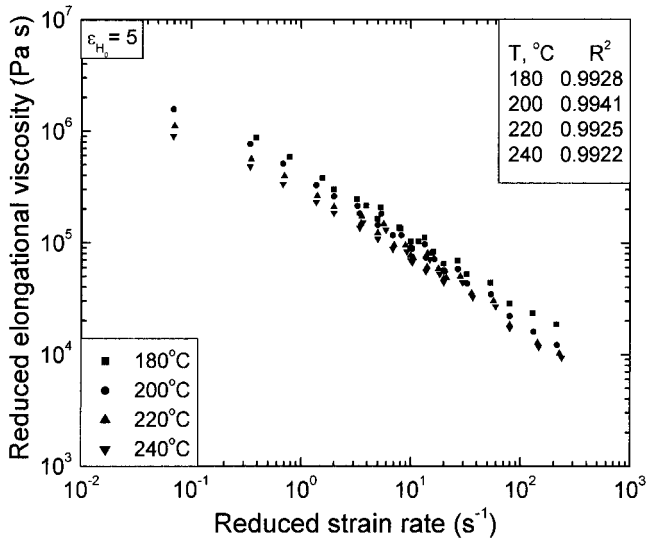
Figure 10 Master curves for the elongational viscosity of HGX PP (method 2).

it should be noted that the ratios of the orientational viscosity at the measured condition to that at the reference conditions and the shift factors are all closely related to the corresponding Hencky strain ratio. This can be shown by equating the reduced effective elongational viscosity by the first and second methods as given in eqs. (14) and (17),

$$\left[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}_0})\right]_r = \frac{\left[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})\right]}{(a_{\text{H}})_1^2} = \frac{\left[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})\right]}{(a_{\text{H}})_2}\left[\frac{\varepsilon_{\text{H}_0}}{\varepsilon_{\text{H}}}\right] \quad (19)$$

and by canceling the effective elongational viscosity at ε_{H} term on the latter two sides of eq. (19) and rearranging to

$$(a_{\text{H}})_2 = (a_{\text{H}})_1^2\left[\frac{\varepsilon_{\text{H}_0}}{\varepsilon_{\text{H}}}\right] \quad (20)$$

Substituting eq. (20) into eq. (19) shows that the shifted or reduced effective elongational viscosity in both methods is equivalent. Therefore, the only difference between the two approaches is the reduced elongational strain rate [i.e., the product of the appropriate shift factor and the measured elongational strain rate as given in eqs. (13) and (18)]. It is further noted that in most of the data the ratio of the measured effective elongational viscosity to the reference effective elongational viscosity is very close to the cube of the ratio of the measured Hencky strain to the reference state Hencky strain. Therefore, assuming TR ≫ 3 and using the following equations,

$$(a_{\text{H}})_2 \doteq \left[\frac{\varepsilon_{\text{H}}}{\varepsilon_{\text{H}_0}}\right]^3, \quad (a_{\text{H}})_1 \doteq \left[\frac{\varepsilon_{\text{H}}}{\varepsilon_{\text{H}_0}}\right]^2$$

$$(a_{\text{H}})_2 \doteq (a_{\text{H}})_1\left[\frac{\varepsilon_{\text{H}}}{\varepsilon_{\text{H}_0}}\right], \quad (\dot{\varepsilon}_r)_2 = (\dot{\varepsilon}_r)_1\left[\frac{\varepsilon_{\text{H}}}{\varepsilon_{\text{H}_0}}\right] \quad (21)$$

it is seen that the only difference between the two shifting approaches is approximately the ratio of the Hencky strains as it appears in the reduced strain rate term. The $(a_{\text{H}})_2$ shifting approach apparently fits slightly better over the lower strain rate region, and the $(a_{\text{H}})_1$ shift factor fits better over a higher strain rate region. Because the effect of the strain rate on the relaxation time has not been considered in these developments, it is quite possible that at low strain rates (i.e., low $\lambda\dot{\varepsilon}$ or $\lambda\dot{\varepsilon}\varepsilon_{\text{H}}$) the first approach is a better approximation and at high values the alternate is better. This could result from the fact that the relaxation times in eqs. (9) and (16) are assumed to be independent of elongational strain rate; and if a dependence is assumed to be related to a term such as $[1 + [\lambda\dot{\varepsilon}]^2]$ as occurs in the time dependent phenomena, then $\{[1]/[1 \pm (\lambda\dot{\varepsilon})^2]\}(a_{\text{H}})_2$ would approach $(a_{\text{H}})_1$ in value when the strain rate is near 100. The relaxation time used in

TABLE I
Coefficients of Determination (R^2) for Master Curves

| | R^2 at temperature (°C) | | | | | | | |
| | 175 (180) | | 200 (200) | | 225 (220) | | 250 (240) | |
Sample	M1	M2	M1	M2	M1	M2	M1	M2
LDPE-A	0.9936	0.9840	0.9945	0.9855	0.9848	0.9672	0.9947	0.9831
LDPE-B	0.9816	0.9805	0.9694	0.9896	0.9444	0.9890	0.9308	0.9935
LDPE-C	0.9978	0.9875	0.9962	0.9805	0.9917	0.9786	0.9846	0.9820
LDPE-D	0.9981	0.9971	0.9943	0.9961	0.9950	0.9956	0.9904	0.9966
LDPE-E	0.9985	0.9948	0.9983	0.9923	0.9957	0.9910	0.9982	0.9904
HDPE-A	0.9910	0.9894	0.9961	0.9895	0.9980	0.9877	0.9977	0.9922
HDPE-B	0.9914	0.9970	0.9933	0.9962	0.9922	0.9935	0.9969	0.9925
HDPE-C	0.9921	0.9962	0.9950	0.9966	0.9949	0.9969	0.9928	0.9934
HDPE-D	0.9846	0.9931	0.9878	0.9950	0.9902	0.9959	0.9964	0.9958
HDPE-E	0.9913	0.9951	0.9948	0.9967	0.9965	0.9964	0.9991	0.9962
HGX	0.9863	0.9928	0.9949	0.9941	0.9949	0.9925	0.9963	0.9922
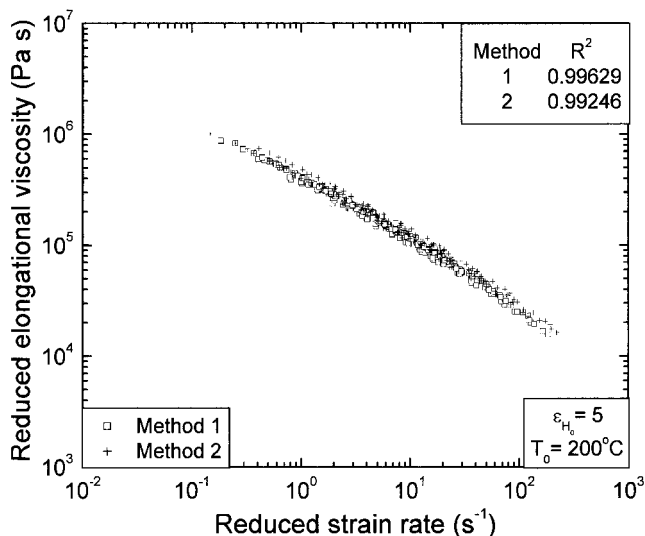
Figure 11 General master curves for the elongational viscosity of LDPE-E.

these expressions is typically the relaxation time given by the crossover point of the storage and dissipative moduli in dynamic shear measurements; for the polymer melts described herein, it is typically in the range of 0.001–0.01. The positive sign would correspond to Hencky strain ratios > 1 and the negative sign to Hencky strain ratios < 1.

Based on the approximate relationships in eq. (20), the effect of the elongational strain rate can be tested by assuming that the ratio of the measured orientational viscosity to the shifted orientational viscosity is a linear function of the Hencky strain ratio to a power c; that is,

$$\frac{[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}})]}{[\eta_{\text{eff}}(\dot{\varepsilon}, \varepsilon_{\text{H}_0})]} = b\left[\frac{\varepsilon_{\text{H}}}{\varepsilon_{\text{H}_0}}\right]^c \qquad (22)$$

where b is close to a value of one. For the LDPE-E sample in this example, the value of the exponent c decreases logarithmically from 2.4 to 1.9 as the elongational strain rate increases from 2 to 40 s^{-1} when all three shifts (i.e., Hencky 7 to 4, 6 to 4, and 5 to 4) are considered. Most of the decrease is noted in the exponent for the Hencky 5 to 4 shift that decreases from about 1.8 to 1.0 whereas the combined Hencky 7 to 4 and 6 to 4 decrease only from about 2.7 to 2.5. It has been suggested that a Hencky strain of at least 5 should be achieved to cause the entrance effects to be negligible.[7] Similar results for the value of c result when a reference state of Hencky 5 is used.

This approximate dependence of the ratio of the measured orientational viscosity to the shifted value of the orientational viscosity at the base Hencky strain and the low elongational strain rate to the cubed power of the Hencky strain ratio could be related to the molecular aspects of the orientational viscosity.

The zero shear rate viscosity of polymer melts and the intrinsic viscosity of polymer solutions is dependent upon the approximate 3.4 power of the average molecular weight (weight average for melts, viscosity average for solutions) if the average molecular weight is greater than the critical molecular weight.[8] The critical molecular weight is that weight corresponding to polymer chains being long enough for entanglements to affect the viscosity of the melt or solution. At molecular weights lower than the critical molecular weight the dependence of the appropriate shear viscosity on the average molecular weight decreases smoothly down to a linear dependence. In a similar fashion, it is quite possible that at low elongational strain rates the entanglements in the polymer chains are dominant in the effective elongational viscosity and that at higher elongational strain rates the entanglements have been effectively lessened in influence by either alignment or being "combed out." This would cause a lowering of the dependence of the orientational viscosity upon the Hencky strain ratio, and it would probably occur at a lower elongational strain rate for higher values of the Hencky strain. The suggested term $[1 \pm (\lambda\dot{\varepsilon})^2]$ as a modifier of the reduced elongational strain rate could arise from this consideration and account for it in the Hencky strain shifting.

Simultaneous shifting for both temperature and Hencky strain

General master curves for the effective elongational viscosity can be obtained by simultaneously shifting the individual viscosity curves at each temperature and the Hencky strain on the reference curve (which is
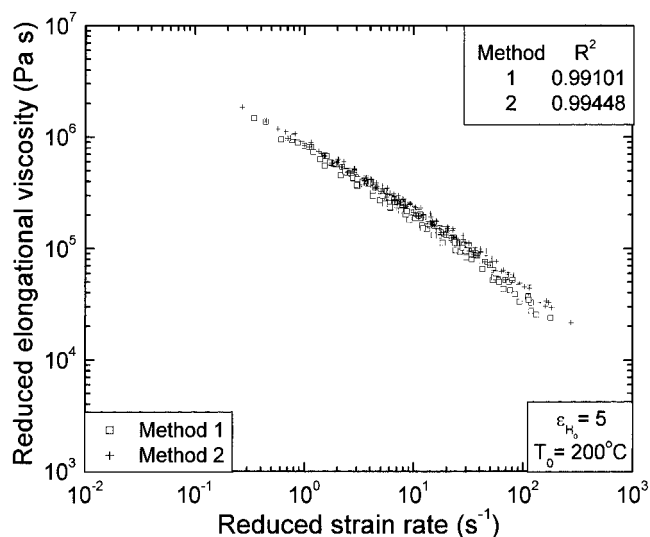

Figure 12 General master curves for the elongational viscosity of HDPE-B.
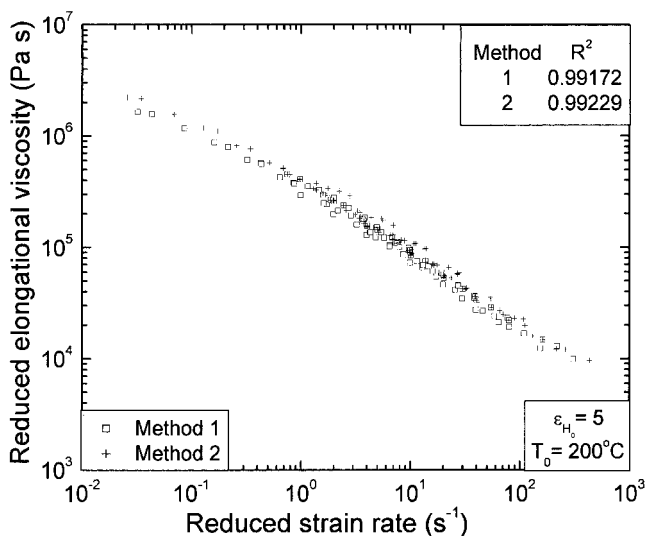
Figure 13 General master curves for the elongational viscosity of HGX PP.

the curve at 200°C and Hencky strain 5). The reduced variables are defined as

$$
\left[(\eta_{\mathrm{eff}})_{r_{\mathrm{TH}}}\right]_1 = \frac{\eta_{\mathrm{eff}} T_0}{a_T T} \frac{1}{(a_{\mathrm{H}})_1^2} \quad \text{and} \quad (\dot{\varepsilon}_r)_1 = a_T (a_{\mathrm{H}})_1 \dot{\varepsilon} \quad (23)
$$

for method 1 of shifting and

$$
\left[(\eta_{\mathrm{eff}})_{r_{\mathrm{TH}}}\right]_2 = \frac{\eta_{\mathrm{eff}} T_0}{a_T T} \frac{\varepsilon_{\mathrm{H}_0}}{(a_{\mathrm{H}})_2 \varepsilon_{\mathrm{H}}} \quad \text{and} \quad (\dot{\varepsilon}_r)_2 = a_T (a_{\mathrm{H}})_2 \dot{\varepsilon} \quad (24)
$$

for method 2.

The resulting master curves are presented in Figures 11–13. The values of the coefficient of determination show good accuracy of the general shifting, which is almost the same for all three samples.

The second method gives general master curves on a slightly extended range of strain rates. Each curve in Figures 11–13 represents the results by shifting the 15 individual viscosity curves on the reference one, which is the viscosity curve at 200°C and Hencky strain 5.

CONCLUSIONS

Two methods for the shifting of elongational viscosity curves with respect to the Hencky strain were developed. The first method is based on the relaxation time ratio and the second one is based on the ratio of orientational viscosity, which is defined as the difference between the effective elongational viscosity and 3 times the shear viscosity. Both methods were tested on five samples of LDPE and HDPE and on an extrusion grade sample of PP, showing a fairly high accuracy of the shifting techniques. Based on the temperature shift factors, a general technique for simultaneous shifting with respect to both temperature and Hencky strain was developed for building general master curves for the effective elongational viscosity.

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