

Evaluate the Nonlinear Viscoelasticity of Polyolefin Melts Using the Larson Model

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Nonlinear rheological properties of polyolefins have long been studied and predicted by using the Larson model with the damping function generally obtained from the stress relaxation measurements. In this study, we investigate the nonlinear rheological properties of high density polyethylene (HDPE) and polypropylene (PP) using the Larson model with damping functions obtained from either the dynamic frequency sweep or the stress relaxation test. Experimental measurements and their corresponding model predictions for the rheological parameters were then compared to evaluate the applicability of the Larson model to the nonlinear rheology, and the following conclusions could be achieved. The steady shear viscosity could be satisfactorily described by the Larson model with the damping functions obtained from the two different methods, except at shear rates higher than 10^3 s^{-1} . The predicted first normal stresses also account for the measured data, except for those using the stress relaxation data showing a little deviation for the PP sample. In addition, the predictions for elongation viscosity are also in good agreement with the experimental results within the short range of elongation rate achieved in this work. POLYM. ENG. SCI., 00:000–000, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Rheology is a science describing the material's deformation behaviors, permanently or temporarily deformed, under external force. We can find out the rheological behaviors in our daily life, for example, painting and squeezing the paste from tube. In addition, polymer processing methods, such as injection molding, extrusion, and

encapsulation of IC chips etc., are utilized and improved by using the rheological knowledge.

Indeed, the polymer materials have excellent properties including good processability, thus being able to substitute many other materials in the industrial applications. But, polymeric materials have the so-called viscoelastic properties, particularly important in the molding processes, which could deeply affect the quality of the molded products. For example, in the general plastic processing, the residual stress could cause the undesirable part warpage. Also, for the optical molded product, there are probably flow-induced birefringence in case of the bad part (or mold) design or under poor processing conditions. Among these, the rheological property of the polymer melt does play an important role during the processing. Therefore, the derivations and/or the further applications of the effective and reliable rheological models to describe and estimate the various viscoelastic properties of the polymer materials become very important whether from the academic or the practical point of view.

Many rheological models have been proposed for describing flow behaviors of polymers in a broad deformation range at various deformation rates and types. The Wagner, White–Metzner, KBKZ, and Larson models have been widely used to describe the viscoelastic properties of polymer melts [1–6]. For polyolefins such as low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), the Wagner model could describe the first normal stress difference (N_1) and shear viscosity (η_s) very well. On the other hand, White–Metzner model is typically used to predict the elongation viscosities (η_E) by using the rheological data from shear measurements. The KBKZ model, developed by Kaye, Bernstein, Kearsley, and Zapas, could predict the influences of viscous dissipation and heating on the flow properties. Finally, the Larson model is commonly used to describe the viscoelastic behaviors of linear polymer melts.

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Contract grant sponsor: National Science Council in Taiwan.

DOI 10.1002/pen.23788

Published online in Wiley Online Library (wileyonlinelibrary.com).

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The nonlinear viscoelastic behaviors can be studied by stress relaxation measurements [1], optical-elastic [7] and dynamic tests [8, 9]. The nonlinear viscoelasticities of LDPE and high-density polyethylene (HDPE) can also be measured by using frequency sweep tests under large deformation [9]. In general, shear storage modulus (G') in the nonlinear region is lower than that in the linear region, which is assigned to molecular disentanglement in the nonlinear region [8].

The damping function, $h(\gamma)$, has been a concept introduced in rheology since more than 30 years ago, and its implementation in the modeling of polymer melts was an essential step forward in the classification and understanding of nonlinear viscoelasticity [10]. Most of nonlinear viscoelastic behaviors can be described by utilizing $h(\gamma)$ determined from stress relaxation measurements [1].

$$h(\gamma) = \frac{G(t, \gamma)}{\dot{G}(t)} \quad (1)$$

based on the time-deformation separability principle. Here $G(t, \gamma)$ and $\dot{G}(t)$ are the relaxation modulus at time t and the linear relaxation modulus, respectively. In this study, $h(\gamma)$ was obtained from either the dynamic tests or the stress relaxation measurements, and the results from both methods were compared and discussed. In the dynamic measurement, the linear region of the shear strain was first determined with the amplitude sweep testing. Then, $h(\gamma)$ is evaluated according to

$$h(\gamma) = G'_{\text{nonlinear}} / G'_{\text{linear}} \quad (2)$$

or

$$h(\gamma) = G''_{\text{nonlinear}} / G''_{\text{linear}} \quad (3)$$

where G' and G'' are storage and loss moduli at strain amplitude γ , and the subscripts “linear” and “nonlinear” denote data collected in the linear and nonlinear regions, respectively. Equation 2 of the nonlinear storage moduli (G') was used for the calculations in this work, and the nonlinear loss moduli (G'') could be used, too. Both can get reasonably reproducible results. In addition, N_1 and elongation viscosity η_E of the samples were also measured. Finally, the experimental data were also compared with the predicted results from the Larson model to verify the accuracy of this method.

LARSON MODEL

Larson proposed that $h(\gamma)$ of polymer melts usually deviate from the Doi-Edwards theory because the retraction process proposed by Doi and Edwards may not come to completion before the reptation of the macromolecular chains begins [6, 11]. For example, side branches which are long enough to entangle with the surrounding chains might limit the retraction of the backbone chain segment lying between two side branches. Thus, on the average,

polymer chains are only partially retracted under various deformations. Larson proposed the following simple empirical expression for the instantaneous response to a sudden deformation of a partially retracting strand of the polymer chain:

$$\frac{\nabla}{\approx} \tau + \frac{2\xi'}{3G} \left(D : \tau \right) \left(\tau + G \delta \right) + \frac{1}{\lambda} \tau = 2G D \quad (4)$$

where ξ' is called the strain-softening parameter ranging from zero to unity, which is a measure of the extent of retraction during the flow. Many works use $h(\gamma)$ corresponding to the independent alignment (IA) approximation [12] ($\xi' = 0.8$). For $\xi' = 0.6$, the retraction is complete as in the case of the Doi-Edwards model, whereas for $\xi' = 0$, the response of the polymer chain segment is affine upon the deformation during flow, as in the case of the upper convected Maxwell model [6]. Larson reported that ξ' can be dependent upon either the polydispersity or the extent of branching of the polymeric materials [13]. Doi-Edwards limit has been found to be reasonably successful in describing samples of linear molecules with a narrow molecular weight distribution and exhibiting extremely strain softening. The upper convected Maxwell limit has no strain softening in shear, and extreme strain hardening in steady elongation. Thus, the range of ξ' between 0.6 and 0 describes materials of different strain softening or hardening characteristics [14]. Low-density (branched) polyethylenes can be fitted by values of $\xi' = 0.13$ –0.20 and other polymers with broad molecular weight distribution seem to be fit by values of $\xi' = 0.13$ –0.60 [13].

In shear, $h(\gamma)$, regarding the nonlinear viscoelasticity of the polymer melts physically signifying the extent of stress loss due to reduction of the entanglement density and segment orientation following deformation of a given magnitude γ , can be correlated with γ as following [13]

$$h(\gamma) = \left(1 + \frac{\xi'}{3} \gamma^2 \right)^{-1} \quad (5)$$

which arises from a semi-empirical molecular model that attempts to account for the effects of multiple long side branches.

By constructing a “superposition” of the Larson model with a series of infinite modes, we can generalize this model by writing Eq. 4 for the i th partial stress with the corresponding G_i and λ_i then we get the total stress by summing all the partial stresses. As a result, we can obtain the generalized Larson model:

$$\tau = \sum_{i=1}^{\infty} \tau_{\approx i} \quad (6)$$

$$\frac{\nabla}{\approx i} \tau + \frac{2\xi'}{3G_i} \left(D : \tau \right) \left(\tau + G_i \delta \right) + \frac{1}{\lambda_{\approx i}} \tau = 2G_i D \quad (7)$$

TABLE 1. Molecular weight, molecular weight distribution, and melt index of the high density polyethylene and polypropylene.

	M_w (g/mole)	M_n (g/mole)	MWD	MI ^a (g/10 min)
HDPE-405	119,000	18,700	6.36	5.91
PP-1080	152,000	30,400	4.94	11.0

^aTesting condition (ASTM D-1238): HDPE: 190°C 2.16 Kg, PP: 230°C/2.16 Kg.

For the shear flow, the equations for the stress can be expressed in component form for the i th mode as:

$$\frac{d\tau_{11i}}{dt} - 2\dot{\gamma}\tau_{12i} + \frac{2\xi'}{3G_i}(\dot{\gamma}\tau_{12i})(\tau_{11i} + G_i) + \frac{1}{\lambda_i}\tau_{11i} = 0 \quad (8)$$

$$\frac{d\tau_{22i}}{dt} + \frac{2\xi'}{3G_i}(\dot{\gamma}\tau_{12i})(\tau_{22i} + G_i) + \frac{1}{\lambda_i}\tau_{22i} = 0 \quad (9)$$

$$\frac{d\tau_{12i}}{dt} - \dot{\gamma}\tau_{22i} + \frac{2\xi'}{3G_i}(\dot{\gamma}\tau_{12i})\tau_{12i} + \frac{1}{\lambda_i}\tau_{12i} = G_i\dot{\gamma} \quad (10)$$

To solve the equations, the following initial conditions are set:

$$\tau_{11i}(0) = \tau_{22i}(0) = \tau_{12i}(0) = 0 \quad (11)$$

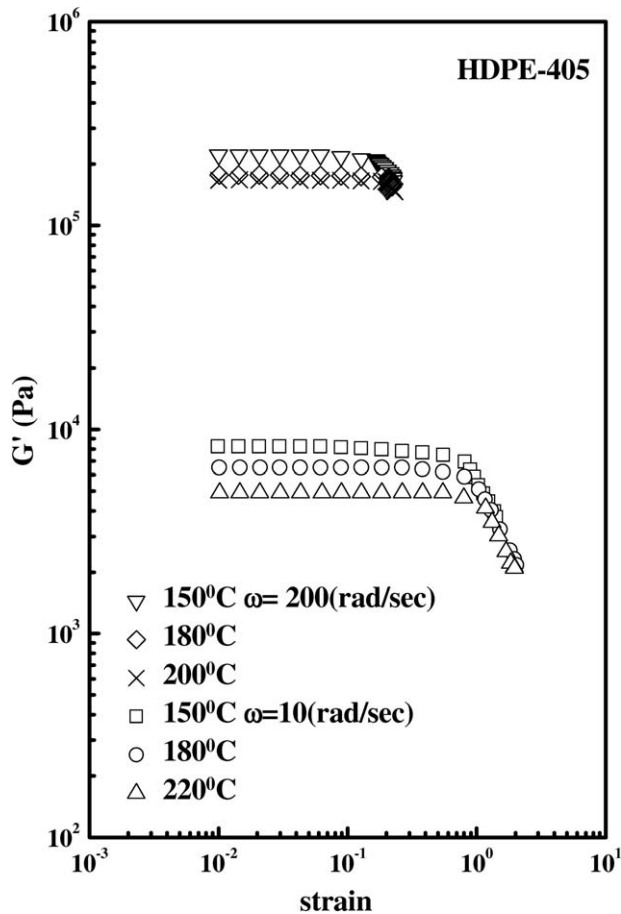


FIG. 1. Storage moduli of HDPE measured under various testing strain.

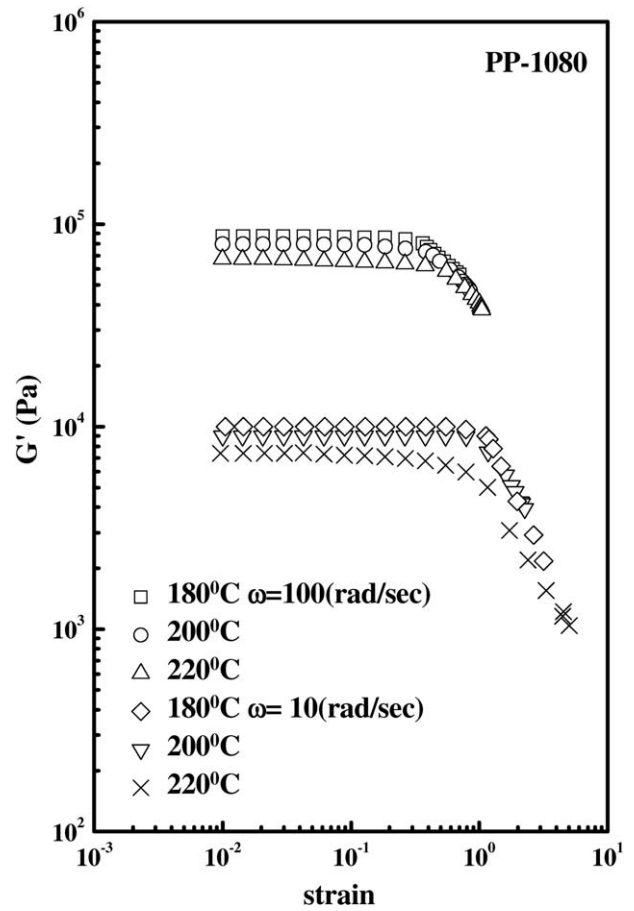


FIG. 2. Storage moduli of PP measured under various testing strain.

Then, η_s at a certain shear rate $\dot{\gamma}$ can be calculated by the following equation, if the number of modes is limited to a finite value n for convenience

$$\eta_s = \sum_{i=1}^n \left(\frac{\tau_{12i}}{\dot{\gamma}} \right) n: \text{number of modes} \quad (12)$$

Similarly, N_1 can be computed:

$$N_1 = \sum_{i=1}^n (\tau_{11i} - \tau_{22i}) \quad (13)$$

In addition, for the uniaxially extensional flow, the stress equations for the Larson model can be written as:

$$\frac{d\tau_{11i}}{dt} - 2\dot{\epsilon}\tau_{11i} + \frac{2\xi'}{3G_i}\dot{\epsilon}(\tau_{11i} - \tau_{22i})(\tau_{11i} + G_i) + \frac{1}{\lambda_i}\tau_{11i} = 2G_i\dot{\epsilon} \quad (14)$$

$$\frac{d\tau_{22i}}{dt} + \dot{\epsilon}\tau_{22i} + \frac{2\xi'}{3G_i}\dot{\epsilon}(\tau_{11i} - \tau_{22i})(\tau_{22i} + G_i) + \frac{1}{\lambda_i}\tau_{22i} = -G_i\dot{\epsilon} \quad (15)$$

subjected to the preset initial conditions:

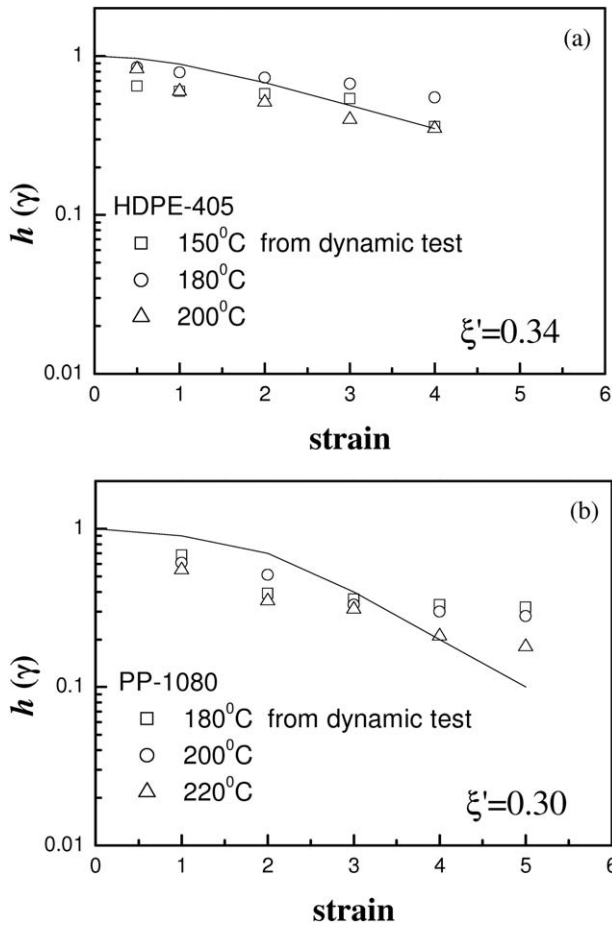


FIG. 3. Damping functions and strain-softening parameters of (a) HDPE and (b) PP obtained from the dynamic tests.

$$\tau_{11i}(0) = \tau_{22i}(0) = 0 \quad (16)$$

Thus, η_E can be found in the same way as η_s

$$\eta_E(\dot{\epsilon}) = \sum_{i=1}^n \frac{(\tau_{11i} - \tau_{22i})}{\epsilon^*} \quad (17)$$

CALCULATIONS

The linear viscoelastic parameters, G_i and λ_i , required in the Larson model were obtained by using curve-fitting of the dynamical data with an eight-mode generalized Maxwell model as:

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \quad (18)$$

$$G''(\omega) = \sum_i G_i \frac{\omega \lambda_i}{1 + \omega^2 \lambda_i^2} \quad (19)$$

The strain-softening parameter ξ' was obtained by fitting Eq. 5 to the damping function evaluated from either the dynamic testing data or the stress relaxation modulus. After such required material parameters were obtained, η_s

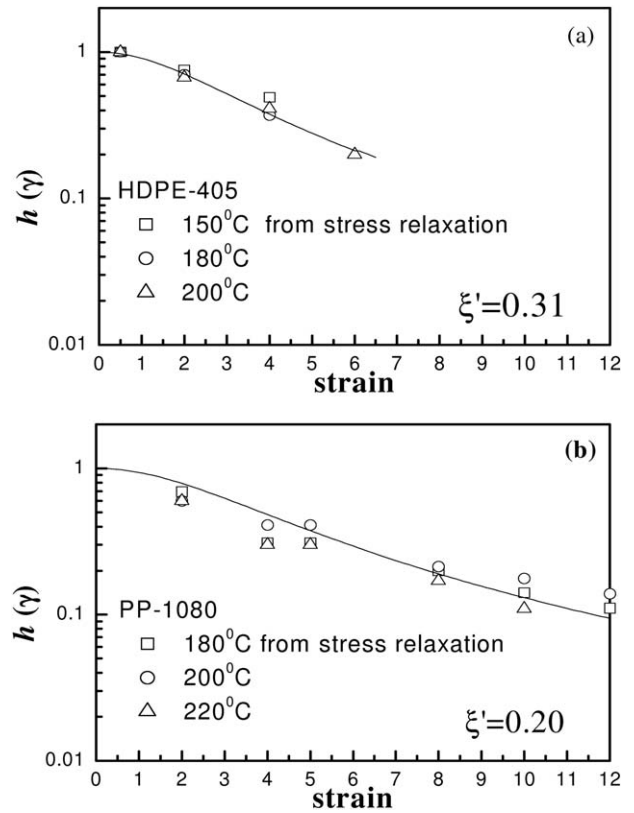


FIG. 4. Damping functions and strain-softening parameters of (a) HDPE and (b) PP obtained from the stress relaxations.

and N_1 at a shear rate $\dot{\gamma}$ could be computed by using Eqs. 8–13 and η_E at strain rate $\dot{\epsilon}$ could be estimated by using Eq. 17.

EXPERIMENTAL

Two polyolefins, high-density polyethylene (HDPE-405, USI Co., Taiwan) and polypropylene (Yungsox PP-1080, Injection Grade, Yung Chia Chem. Ind. Co., Taiwan), were used in this study. Their material characteristics including molecular weight, molecular weight distribution, and the melt index are listed in Table 1. A parallel-plate rheometer (Model MC-100, Paar Physica Co., Austria) was used to measure the viscoelastic properties of the polymers at various testing conditions. The disk-shaped sample of about 1 mm in thickness and 25 mm in diameter was placed in the chamber, and the steady and dynamic rheological tests were conducted at various temperatures, frequencies, and strains. The storage and the loss moduli, and the low-shear-rate viscosity were measured and recorded. Then, $h(\gamma)$ was evaluated from the dynamic data using Eq. 2 or 3. The high-shear-rate viscosity was measured using a capillary rheometer (Rosand Rheometer RH-720, Rosand Precision Ltd., USA).

In order to acquire the stress relaxation moduli and the first normal stress differences of the polyolefins at various conditions, another type of rheometer (Rheometrics Dynamic Analyzer, Model RDA-II, Rheometrics Inc.,

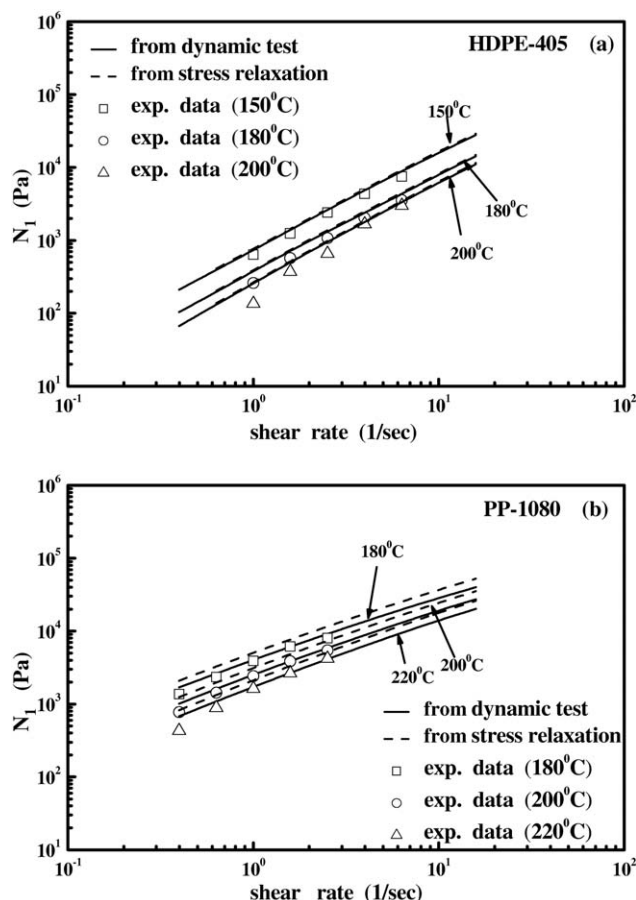


FIG. 5. First normal stress difference determined from steady shear flow for (a) HDPE and (b) PP.

USA) was used to conduct the essential viscometric tests. Then, the values of $h(\gamma)$ were calculated as the ratios of the stress relaxation moduli at various strains to that obtained in the linear region according to Eq 1.

η_E was determined by the fiber spinning method [15]. Polyolefin pellets were melted in a single extruder with a 20-mm screw having a length-to-diameter ratio of 24. The melt was extruded through an orifice die to form a molten thread. Being clamped with a pair of rollers located around 19 cm downward from the die exit, the melt was then uniaxially extended. The tensile force required to pull the melt and its diameter distribution were recorded and η_E was calculated according to the method proposed by Revenu et al. [16].

RESULTS AND DISCUSSION

Nonlinear Rheology

Figures 1 and 2 show G' as a function of γ for HDPE and PP, respectively, measured at different temperatures and frequencies. It is obvious that G' remain constant with respect to γ up to a limited value and then decrease rapidly. The plateau region of G' narrows at higher test-

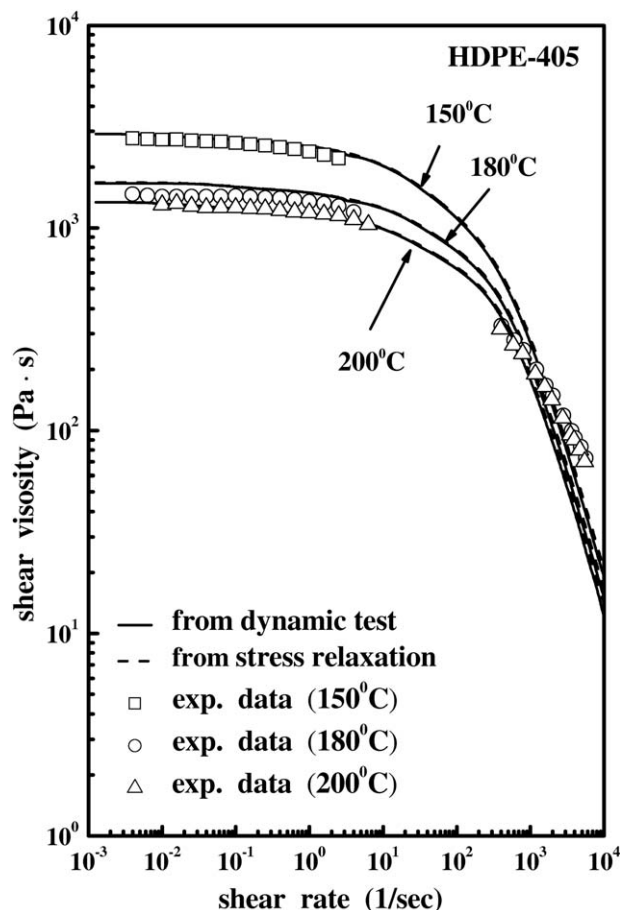


FIG. 6. Steady shear viscosity versus shear rate of HDPE.

ing frequency while the testing temperature seems to have little influence on the scope of the plateau region.

Damping Functions

Figures 3 and 4 illustrate $h(\gamma)$ obtained from the dynamic and the stress relaxation tests, respectively, for HDPE and PP at various temperatures. The damping values decrease with increasing γ in a reasonable manner showing the similar trends irrespective of the test methods. Moreover, $h(\gamma)$ is independent of temperature [17, 18], within the acceptable percentage error. The results suggest that either the dynamic test or the stress relaxation probably can be used to measure $h(\gamma)$ for HDPE and PP in this work.

Strain Softening Parameter for the Larson Model

The strain softening parameters ξ' in the Larson model of PP and HDPE were determined from $h(\gamma)$ [13] by using the quasi-Newtonian nonlinear fitting methods, as plotted in Figs. 3 and 4. The ξ' values of PP are smaller than those of HDPE probably due to the methyl pendent group in the main chain of PP restricting the retraction of

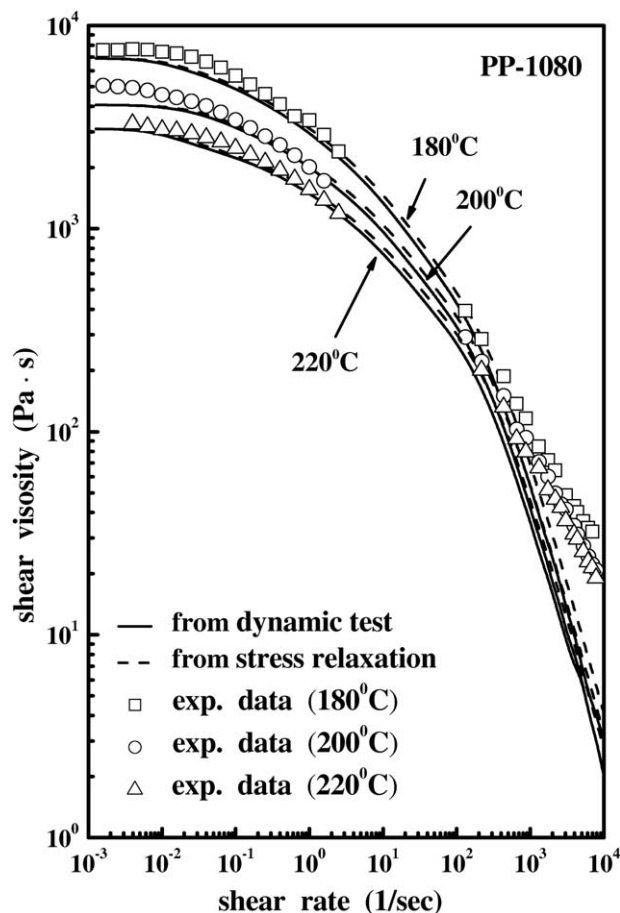


FIG. 7. Steady shear viscosity versus shear rate of PP.

the molecular strands after the molecular chains are shear deformed. The obtained ζ' values for HDPE from the dynamic and the stress relaxation test are very similar, which is consistent with the data from Larson [6]. On the other hand, the ζ' values for the PP obtained from these two kinds of tests show a noticeable deviation. This suggests that the hindrance of the methyl pendent groups to the retraction of the molecular strands may be different for the entangled PP melt subjected to nonlinear stress relaxation and dynamic oscillation deformations. The smaller ζ' value of PP in the stress relaxation, relative to that obtained from the dynamic test, implies a greater impediment of the strands to retract into the idealized tube due to regular methyl branching [13] in the process of the stress relaxation.

Comparison of Experimental Data with Predictions of Larson Model

The experimental data of N_1 vs. $\dot{\gamma}$ tested at various temperatures for HDPE and PP are demonstrated in Fig. 5, in which the predictions using the Larson model with the ζ' parameters calculated from both the dynamic and the stress relaxation tests are also plotted. The predicted

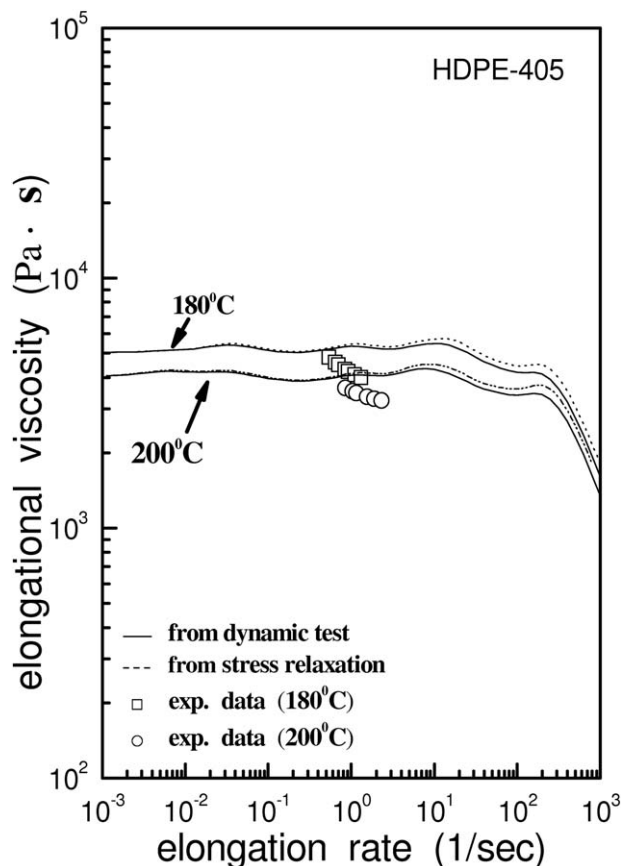


FIG. 8. Elongation viscosity versus elongation rate of HDPE.

N_1 satisfactorily accounts for the measured data except for those using the stress relaxation data showing a little deviation from the experimental data for the PP sample as shown in Fig. 5b. The predicted η_s values using the Larson model also agree with the experimental data very well, except at shear rates higher than 10^3 s^{-1} , as presented in Figs. 6 and 7 for HDPE and PP, respectively. This failure of Larson model at high shear rates could be attributed to the probability that the polymer strands could not contact to the extent, equivalent to what is described by the single strain-softening parameter(ξ) in the Larson model, because the shear rates are too fast. It is like the situation that the damping function predicted by the Doi-Edwards theory are stronger than the experimental data, because the retraction of the polymer strands is complete inside the virtual tube proposed by Doi and Edwards [10]. The experimental and the predicted η_E data are illustrated in Figs. 8 and 9 for the HDPE and PP, respectively. As a matter of fact, it is very hard to measure the extensional viscosity, but with the limited experimental data obtained, its comparison with the theoretical results using the Larson model was fairly satisfactory as shown in Fig. 8 for HDPE. It is worthy of noting that for the PP shown in Fig. 9, the predictions using ζ' determined from the stress relaxation test agree very well with the experimental data.

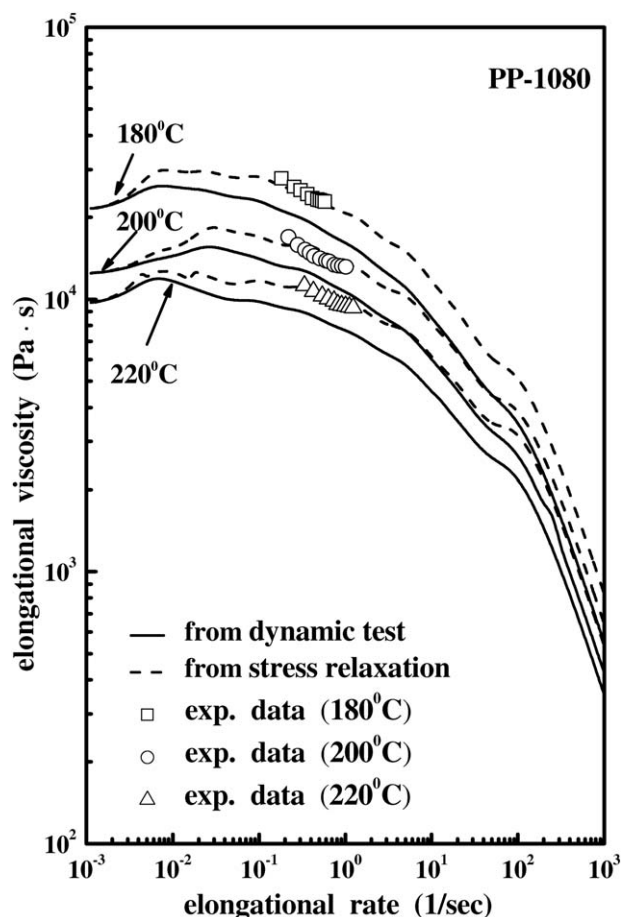


FIG. 9. Elongation viscosity versus elongation rate of PP.

The Trouton ratio defined as the ratio of η_E to η_s at the same strain rate is plotted in Fig. 10 for HDPE and PP at 180°C, together with the predicted viscosities by the Larson model. It can be found that at very low strain rates, the Trouton ratios of both HDPE and PP approach to the same value of 3. For HDPE, the Trouton ratio remains at 3 until strain rate exceeds about 1 s^{-1} , but it increases monotonically with increasing strain rate for PP, suggesting a typical nonlinear response for both polymers and a higher degree of nonlinearity for PP.

SUMMARY

The nonlinear rheological properties of the polyolefin melts in this study, such as the first normal stress difference, the elongation and steady shear viscosities, could be predicted well by using the Larson model. The required strain-softening parameter for the Larson model, usually measured from stress relaxation tests, can also be determined from the dynamic test. The results demonstrate that the predictions of the viscosities and the first normal stress difference using strain-softening parameter evaluated from either the dynamic or the stress relaxation tests could give agreeable comparison with the experimental data of the HDPE and PP, suggesting that the

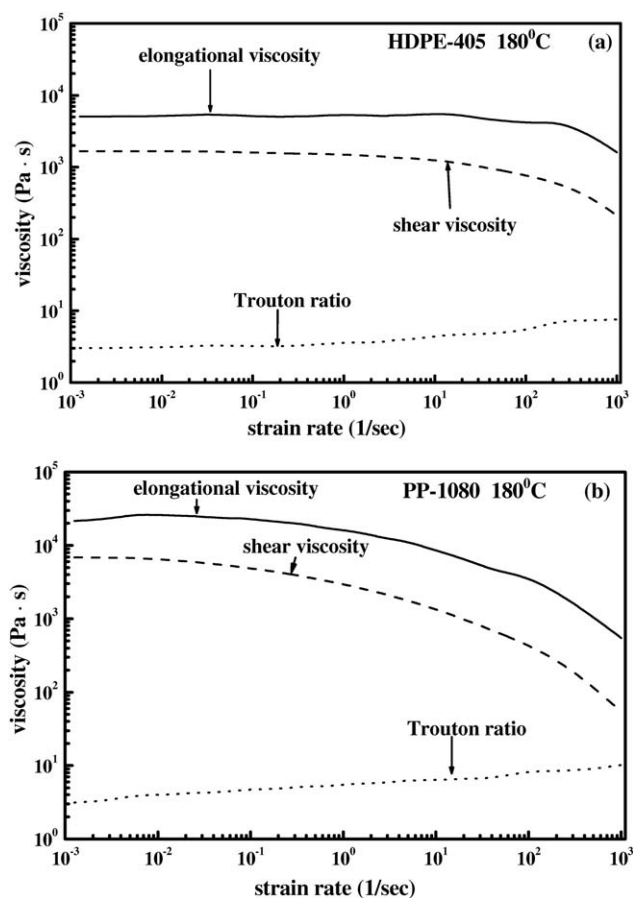


FIG. 10. Calculated viscosities and Trouton ratios of (a) HDPE and (b) PP.

dynamic test probably can also be used to predict the nonlinear rheology. Certainly, further studies extended to more kinds of polymers, such as with distinct extents of branching, will be conducted to support these findings.

NOMENCLATURE

G'	storage modulus
G''	loss modulus
n	number of modes used in the Larson model
MI	flow melt index
M_n	number average molecular weight
M_w	weight average molecular weight
MWD	molecular weight distribution
G_i	relaxation modulus of the i th mode
$h(\gamma)$	shear damping function
$G(t, \gamma)$	shear relaxation modulus
$\dot{G}(t)$	linear shear relaxation modulus
N_1	first normal stress difference
\dot{D}	rate of deformation tensor

Greek Symbols

τ	stress
$\dot{\gamma}$	shear rate

η_s	shear viscosity
$\dot{\epsilon}$	elongation strain rate
η_E	elongation viscosity
ω	frequency
ζ'	strain softening parameter
λ_i	relaxation time of the i th mode
η_0	zero-shear-rate viscosity
γ	shear strain
τ_{\approx}	extra stress tensor
δ_{\approx}	unit tensor

Superscripts

\circ	linear viscoelastic region
∇	upper-convected time derivative
cal	calculated value
exp	experimental value

Subscripts

s	shear flow
E	elongation flow
i	the i th mode
\sim	vector
\approx	tensor

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