Empirical Viscosity Model for Polymers with Power-Law Flow Behavior

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ABSTRACT: The aim of this study is the creation of an empirical model that can be used to predict the viscosity of a semicrystalline polymer melt for polymer process control. We have developed an empirical viscosity equation from both analysis and experimentation that takes into consideration the effect of temperature on both the flow behavior and the consistency index in the power law. The analysis is based on previously published literature, whereas the experimental data have been obtained from both the literature and laboratory investigations. The coefficients of the empirical model for low-density polyethylene and polypropylene have been obtained from the experimental data derived from capillary rheometer measurements in the laboratory. This empirical model is able to produce results matching the experimental data with remarkable accuracy. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3045–3057, 2003

Key words: viscosity; modeling; processing; polyethylene (PE); poly(propylene) (PP)

INTRODUCTION

In engineering practice today, the shear viscosity of a polymer melt in most calculations is a function of the shear rate, temperature, and pressure.[1] The effect of pressure on viscosity is relatively insignificant in most polymer processing operations in cases in which pressures do not exceed 35 MPa (5000 psi).[2] For most polymer processing operations, the viscosity can, therefore, be approximately expressed in terms of the melt temperature and shear rate.

The flow curves of the viscosity plotted against the shear rate in logarithmic scales of polymers at various temperatures are approximately equivalent to parallel straight lines. A relationship of straight lines on a logarithmic scale indicates that the viscosity and shear rate can be described by a power-law equation.[3] Equation (1) shows this equation:

$$\eta = m\dot{\gamma}^{n-1} \tag{1}$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, m is the consistency index, and n is the power-law index. The power-law equation, including the temperature effect,[2] can be written as follows:

$$\eta = m_r a_T \dot{\gamma}^{n-1} \tag{2}$$

where m_r is the consistency index at the reference temperature (T_r) and a_T is a shift factor, which is a function of the temperature.

In the literature, a number of attempts have been reported concerning the relationship between the viscosity, shear rate, and temperature of polymer melts. For example, Williams et al.[4] found that for a wide variety of polymer melts, the viscosity can be empirically described by the Williams–Landel–Ferry (WLF) equation. The WLF equation is frequently cited in the published literature.[2,5–9] For a constant shear rate, the WLF equation can be written as follows:

$$\log a_T = \frac{-C_1^r(T - T_r)}{C_2^r + (T - T_r)} \quad \text{or}$$

$$\log \eta = \log \eta_r - \frac{C_1^r(T - T_r)}{C_2^r + T - T_r} \tag{3}$$

where η_r is the viscosity at T_r, C_1^r and C_2^r are constants, and T is the temperature. To solve coefficients C_1^r and C_2^r, we require the viscosity values η_r, η_1, and η_2 at the three different temperatures T_r, T_1, and T_2, and they are written as follows:

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TABLE I
η of LDPE at Various Values of T and $\dot{\gamma}$

$\dot{\gamma}$ (s^{-1})	η (Pa s)			
	$T = 443$ K	$T = 463$ K	$T = 483$ K	$T = 503$ K
20	3248.24	2821.85	2211.42	1640.12
40	2215.25	1819.95	1538.61	1267.07
100	1280.01	1122.31	936.592	737.910
200	813.357	717.771	637.464	496.787
400	517.728	436.762	411.669	326.47

TABLE III
ln η of LDPE at Various Values of T and ln $\dot{\gamma}$

ln $\dot{\gamma}$	ln η			
	$T = 443$ K	$T = 463$ K	$T = 483$ K	$T = 503$ K
2.996	8.0859	7.9451	7.7014	7.4025
3.689	7.7031	7.5066	7.3386	7.1445
4.605	7.1546	7.0231	6.8422	6.6038
5.298	6.7012	6.5762	6.4575	6.2082
5.991	6.2495	6.0794	6.0202	5.7883

$$\log \eta_1 = \log \eta_r - \frac{C_1^r(T_1 - T_r)}{C_2^r + T_1 - T_r} \quad (3a)$$

$$\log \eta_2 = \log \eta_r - \frac{C_1^r(T_2 - T_r)}{C_2^r + T_2 - T_r} \quad (3b)$$

The WLF equation is applied only for fixed shear rate conditions. The limitations on its use make it inconvenient to apply the WLF equation when varied ranges of temperatures and shear rates are involved. There are two other frequently used models that include the effects of the temperature and shear rate on the viscosity. One of these is the Arrhenius equation or Andrade's equation.[10] It is applicable to semicrystalline and amorphous polymers above $T_g + 100°C$ (where T_g is the glass-transition temperature). The applications of Andrade's equation can be found in many recently published articles.[11–17]

Andrade's equation has the form

$$\eta = m_r e^{(E/R)(1/T - 1/T_r)} \dot{\gamma}^{n-1} \quad (4)$$

or

$$\ln \eta = \ln m_r + \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) + (n-1)\ln \dot{\gamma} \quad (4a)$$

where $R = 8.31432$ J/(mol K) is the universal gas constant and E is the activation energy. For some commercial polymers such as low-density polyethylene (LDPE) and polypropylene (PP), E is 30 and 40 kJ/mol,[19] respectively.

A second often used equation is an empirical equation[2,18] similar to Andrade's equation. This traditional empirical equation can be described as

$$\eta = m_r e^{\alpha_T(T_r - T)} \dot{\gamma}^{n-1} \quad (5)$$

or

$$\ln \eta = \ln m_r + \alpha_T(T_r - T) + (n-1)\ln \dot{\gamma} \quad (5a)$$

where α_T is a temperature coefficient that can be considered constant as long as the temperature range considered is relatively small.

Andrade's and traditional empirical equations assume that the relationship between the viscosity and shear rate in logarithmic scales for a constant temperature can approximately correspond to a straight line and that the curves for different temperatures are approximately parallel to each other for the same material. In other words, if one of them is plotted as a master curve, the other curves can be approximately produced by the vertical shifting of this master curve in the direction of the constant shear rate (abscissa). Therefore, the viscosities of other curves can be obtained by the viscosity of the master curve times a shift factor when the shear rate is kept constant. The shift factors in these equations are supposed to be proportional to the temperature difference between the current and master curve at a fixed shear rate. n in these conditions is considered constant. If the fact that n varies with the temperature is taken into consideration, it should fit the measured data more accurately.

TABLE II
η of PP at Various Values of T and $\dot{\gamma}$

$\dot{\gamma}$ (s^{-1})	η (Pa s)				
	$T = 463$ K	$T = 483$ K	$T = 503$ K	$T = 523$ K	$T = 543$ K
20	1444.67	1171.50	718.291	719.127	437.332
40	983.773	828.158	609.091	570.326	308.786
100	562.233	483.051	392.026	360.950	292.061
200	351.335	310.049	269.384	339.162	199.940
400	216.819	193.690	166.027	152.268	130.817

TABLE IV
ln η of PP at Various Values of T and ln $\dot{\gamma}$

ln $\dot{\gamma}$	ln η				
	T = 463 K	T = 483 K	T = 503 K	T = 523 K	T = 543 K
2.996	7.2756	7.0660	6.5769	6.5780	6.0807
3.689	6.8914	6.7192	6.4120	6.3462	5.7326
4.605	6.3319	6.1801	5.9713	5.8887	5.6770
5.298	5.8617	5.7367	5.5961	5.8265	5.2980
5.991	5.3791	5.2663	5.1122	5.0256	4.8738

This article proposes a practical empirical model that can be used to predict the viscosity of a semi-crystalline polymer melt. For polymer extrusion, the most important process in the polymer manufacturing industry, it is important to predict the viscosity of the melt as accurately as possible for control in the processing range of temperatures and shear rates.

DEVELOPMENT OF THE PROPOSED EMPIRICAL VISCOSITY MODEL

In this study, we have developed a model that is intended to accurately predict the viscosity of a polymer melt in polymer processing. The fact that n varies with the temperature is taken into account in the proposed model. To prove the accuracy of the model, we have performed experimental tests of rheological measurements for LDPE and PP and compared previous and proposed models by using the experimental data as samples.

In the development of eqs. (4) and (5), we have assumed that n in eq. (1) is constant. Actually, it can be seen from the published literature[20,21] that the tangents of flow curves (i.e., n) change from one curve to another. In this study, m and n are no longer assumed to be constant. Instead, they are supposed to have a linear relationship with temperature.

Take the natural log of both sides of the power law (equation (1)), and let $p = n - 1$ and $q = \ln m$. Then,

$$\ln \eta = p \ln \dot{\gamma} + q \qquad (6)$$

If ln η is plotted against ln $\dot{\gamma}$, eq. (6) is a straight line for a constant temperature, where p and q are the tangent and intercept of the plotted straight line, respectively. For several different temperatures, the plotted straight lines are traditionally assumed to be parallel to one another. In this study, we assume that p and q have linear relation with T of the form

$$p = c \cdot T + d \qquad (7)$$

$$q = b \cdot T + f \qquad (8)$$

Substituting eqs. (7) and (8) into eq. (6), we obtain

$$\ln \eta = (bT + f) + (cT + d)\ln \dot{\gamma}$$

or

$$\eta = ae^{bT}\dot{\gamma}^{cT+d} \qquad (9)$$

where a is equal to e^f; η is the viscosity (usually Pa s or N s/m^2); T is the melt temperature (K); $\dot{\gamma}$ is the shear rate (s^{-1}); and a, b, c, and d are constants depending on the material used. T appears in the powers of both the exponential function and shear rate.

Equation (9) is applicable to semicrystalline polymers because it is derived from eqs. (7) and (8) and the power law. Although eqs. (7) and (8) have been obtained from experimental data both in the published literature[20,21] and in this study, they are correct for semicrystalline polymers.

Comparing eq. (9) with eq. (5), we find that they have quite similar forms. The coefficients m_r and α_T in eq. (5) are the same as a and b in eq. (9). $T_r - T$ in eq. (5) can be replaced by T to get eq. (9). That is, by applying eq. (9), one does not need to know T_r as that in eq. (5). The power $n - 1$ of the shear rate in eq. (5) is similar to $cT + d$ in eq. (9), and it is the main difference between the two equations. Equation (9) can be viewed as a modified form of eq. (5). For some

TABLE V
Coefficients p and q in Eq. (6) for LDPE

T (K)	p	q
443	−0.6146	9.9541
463	−0.6118	9.7889
483	−0.5577	9.3907
503	−0.5480	9.1042

TABLE VI
Coefficients p and q in Eq. (6) for PP

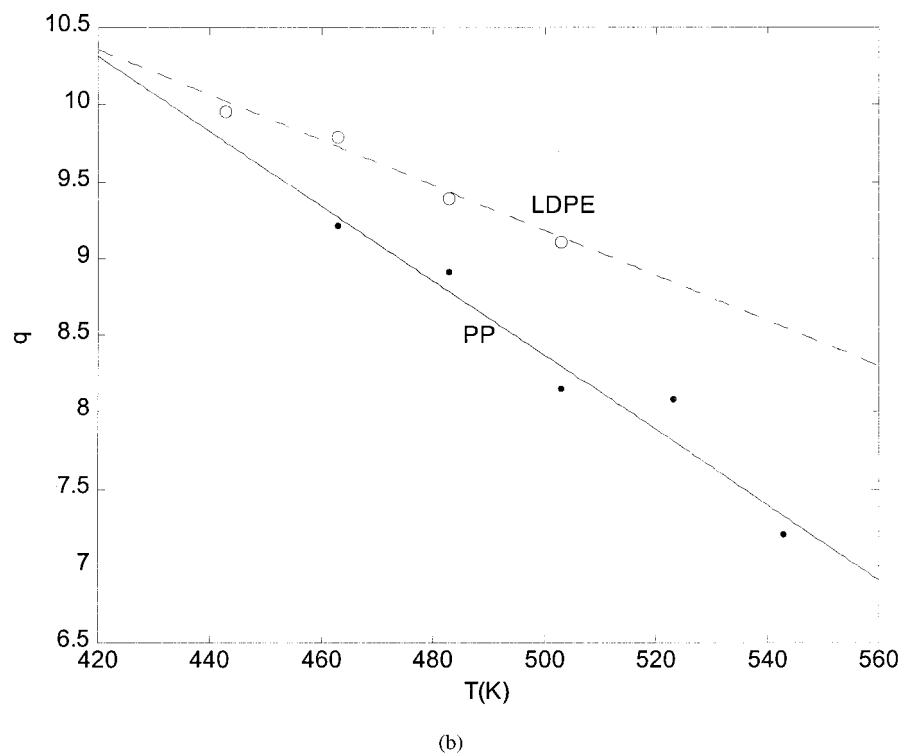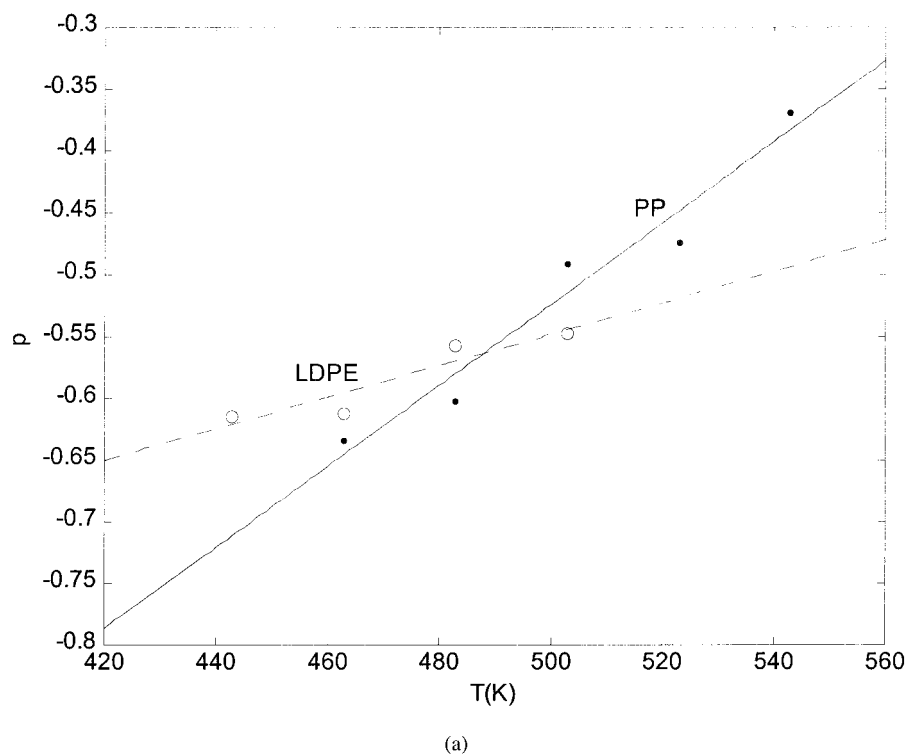| T (K)	p	q
463	−0.6338	9.2102
483	−0.6022	8.9130
503	−0.4914	8.1528
523	−0.4745	8.0758
543	−0.3697	7.2019

Figure 1 (a) p versus T for (○) LDPE and (●) PP and (b) q versus T for (○) LDPE and (●) PP.

polymers, such as LDPE, for which the n values do not exhibit significant variation over a range of temperatures, the difference between eqs. (9) and (5) is minor.

For polymers that have a drastic change of n or for which the range of application temperatures is wide, the differences can be large.

TABLE VII
Coefficients in Eq. (9) for LDPE and PP

	T (K)	a	b	c	d
LDPE	443–503	15,124,259.59	−0.0147	0.00127	−1.1831
PP	463–543	814,090,865.35	−0.0243	0.00328	−2.1639

The coefficients in eqs. (3)–(5) and (9) can be obtained from the experimental data. The differences are as follows:

1. Equation (3) requires three sets of viscosity data at three different temperatures for several different shear rates to solve the coefficients C_1^r and C_2^r.
2. Equation (4) needs at least one set of data, with viscosities over various shear rates at a fixed value of T_r, to find coefficients m_r and n.
3. Equation (5) requires two sets of data to find coefficients m_r, n, and α_T.
4. Equation (9) needs three sets of data to find coefficients a, b, c, and d.

The procedure for data analysis with the proposed model can be described as follows:

Step 1. Measure the viscosities of the polymer at the selected temperature and shear rate ranges. The selected ranges are chosen according to the practical application in the industrial manufacturing process.

Step 2. Take the natural log for the collected data.
Step 3. Find the relationship between ln η and ln $\dot{\gamma}$

Because the relationship between ln η and ln $\dot{\gamma}$ at a fixed temperature is supposed to be linear, it can be written in the form of eq. (6). Coefficients p and q are constants at a fixed temperature and can be found with linear regression.

Step 4. Find the relationship between coefficients p, q, and T. The fitting equations between variables p (or q) and T can be found with the linear regression method as eqs. (7) and (8).
Step 5. Combine the relationship between ln η, ln $\dot{\gamma}$, p, and q.

From eqs. (6)–(8), we can get the proposed empirical eq. (9). Two simple programs were written in macro commands of Matlab to help to find the coefficients of eq. (9). The inputs are viscosity matrices. The outputs are coefficients a, b, c, and d.

EXPERIMENTAL

The materials used in this study were PP and LDPE. PP (grade name HT031) was manufactured by Quarain (Quarain, Kuwait) with a melt-flow index (MFI) of 2.1 g/10 min and a density of 0.908 g/cc. LDPE (grade name LE660) was obtained from Borealis
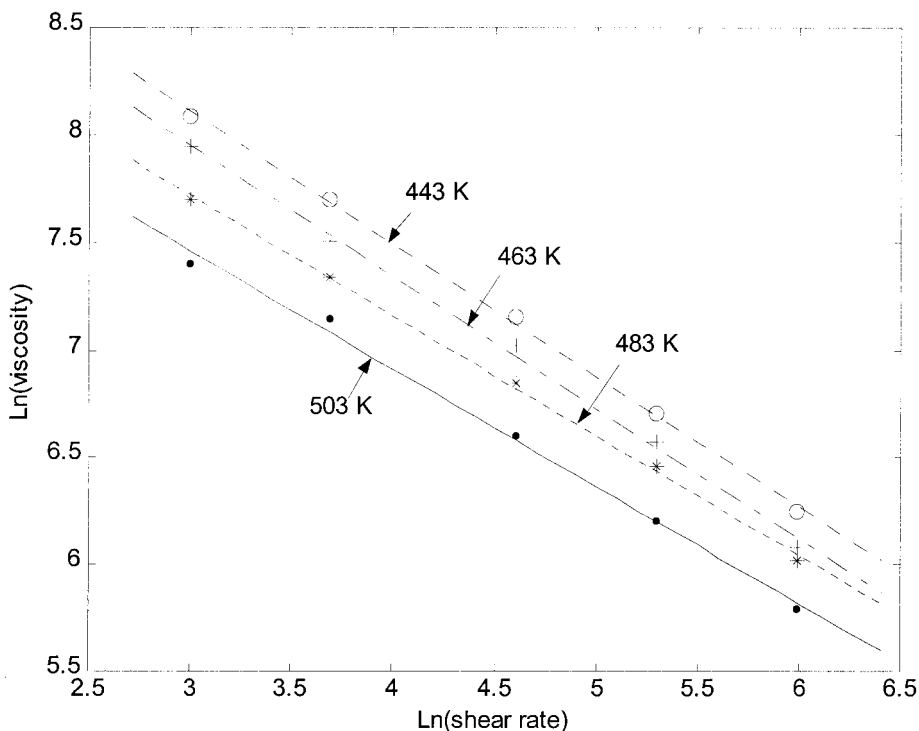

Figure 2 Plots of ln η against ln $\dot{\gamma}$ for LDPE at the following temperatures: (○) 443, (+) 463, (*) 483, and (●) 503 K.
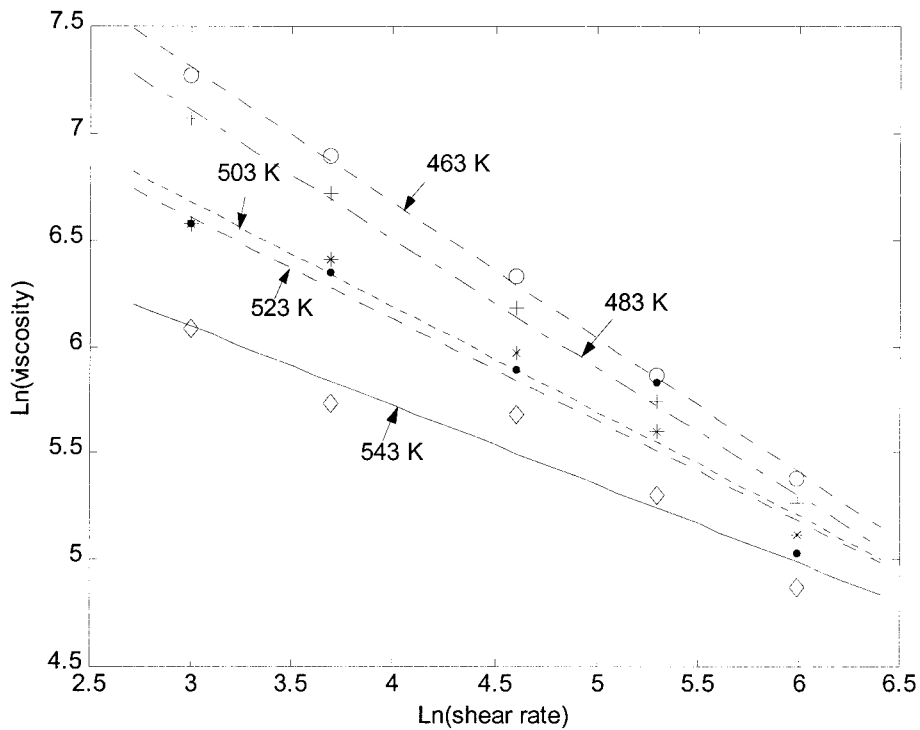
Figure 3 Plots of ln η against ln $\dot{\gamma}$ for LDPE at the following temperatures: (○) 463, (+) 483, (*) 503, (●) 523, and (◇) 543 K.

(Kongens Lyngby, Denmark) with an MFI value of 4.0 g/10 min and a density of 0.921 g/cc.

Rheological measurements for LDPE and PP were carried out with a Rosand dual-capillary rheometer

(Gloucestershire, UK). The Rosand control software was capable of measuring the rheological data at up to 16 shear rates during one test. One barrel housed a zero-length die, and the other was fitted with a 16-mm
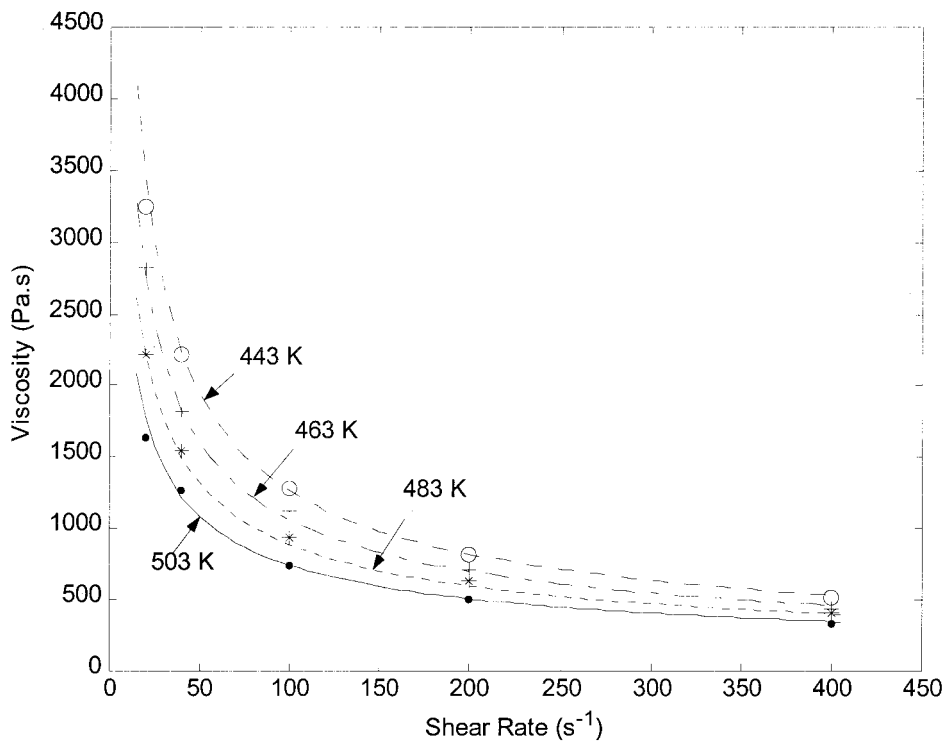

Figure 4 Comparison of the experimental data and the proposed model for LDPE at the following temperatures: (○) 443, (+) 463, (*) 483, and (●) 503 K.
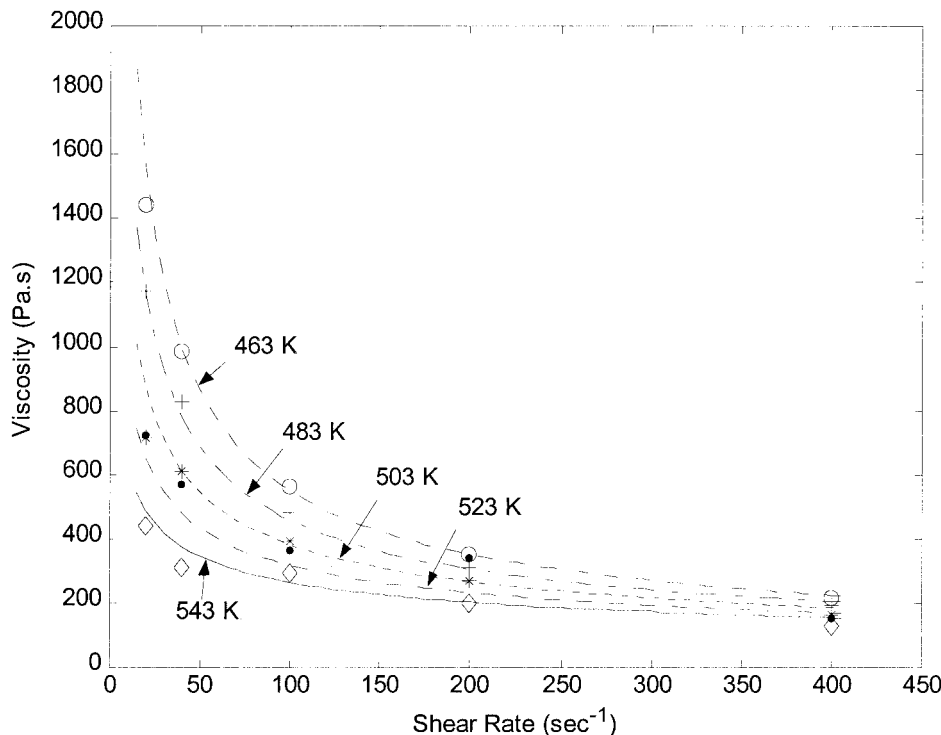
Figure 5 Comparison of the experimental data and the proposed model for PP at the following temperatures: (○) 463, (+) 483, (*) 503, (●) 523, and (◇) 543 K.

die 1 mm in diameter; the calculated rheological data were Bagley-corrected. The test temperatures of LDPE were between 443 and 503 K, and those of PP were between 463 and 543 K. The shear rates were chosen between 20 and 400 s^{-1}, for the measured ranges were encountered in most of the polymer extrusion processing. The ranges of the temperatures and shear rates to be measured were selected according to the empirical data derived from published materials[22] concerning polymer extrusion.

Tables I and II show the measured viscosities of LDPE and PP at various temperatures and shear rates in the selected ranges.

RESULTS AND DISCUSSION

To prove the effectiveness of the proposed model at producing results matching those of the experimental

data and to compare the differences between eqs. (3)–(5) and (9), we chose the measured data in Tables I and II as samples. The standard deviations (σ) between the measured and calculated values of eqs. (3)–(5) and (9) for all the experimental conditions were used as the accuracy evaluation method. The interpolation and extrapolation situations of the presented models were assumed to show the stability of these models.

Model verification for the proposed equation

Following the steps described previously, we obtained the data in Tables III and IV, which we acquired by taking the natural log for the data in Table I and II. Tables V and VI list the values of p and q. If p and q in Tables V and VI are plotted against T, it is found that p is proportional to T and that q is inversely proportional to T, as shown in Figure 1(a,b).

TABLE VIII
η Calculation Equations for LDPE

Equation	Name	Equation
(4)	Andrade's equation[10]	$\eta = 21{,}038.9e^{3608.233(1/T-1/443)}\,\dot{\gamma}^{-0.6146}$
(5)	Traditional empirical equation[2,18]	$\eta = 21{,}038.9e^{0.008397(443-T)}\,\dot{\gamma}^{-0.6146}$
(3)	WLF equation[4]	$\eta = 10^{3.5116+0.2280(T-443)/T-537.63}$ at $\dot{\gamma} = 20$ (s^{-1})
		$\eta = 10^{3.3454-1.0869(T-443)/T-208.352}$ at $\dot{\gamma} = 40$ (s^{-1})
		$\eta = 10^{3.1072+0.3609(T-443)/T-589.42}$ at $\dot{\gamma} = 100$ (s^{-1})
		$\eta = 10^{2.9103-2.078(T-443)/T+302.45}$ at $\dot{\gamma} = 200$ (s^{-1})
		$\eta = 10^{2.7141-0.1527(T-443)/T-421.66}$ at $\dot{\gamma} = 400$ (s^{-1})
(9)	Proposed empirical equation	$\eta = 15{,}124{,}259.59e^{-0.0147T}\,\dot{\gamma}^{0.00127T-1.1831}$

TABLE IX
Comparisons of Calculated ηs for LDPE

T (K)	$\dot{\gamma}$ (s^{-1})	Measured data (Pa s)	Calculated data (Pa s)				Error			
			Eq. (4)[18]	Eq. (5)[4]	Eq. (3)[10]	Eq. (9)	Eq. (4)	Eq. (5)	Eq. (3)	Eq. (9)
443	20	3248.24	3337.86	3337.86	N/A	3432.65	2.8%	2.8%	N/A	5.7%
	40	2215.25	2180.06	2180.06	N/A	2231.85	−1.6%	−1.6%	N/A	0.7%
	100	1280.01	1241.40	1241.40	N/A	1263.32	−3.0%	−3.0%	N/A	−1.3%
	200	813.36	810.80	810.80	N/A	821.39	−0.3%	−0.3%	N/A	1.0%
	400	517.73	529.56	529.56	N/A	534.05	2.3%	2.3%	N/A	3.2%
463	20	2821.85	2347.83	2821.85	N/A	2758.08	−16.8%	0.0%	N/A	−2.3%
	40	1819.95	1533.44	1843.04	N/A	1825.08	−15.7%	1.3%	N/A	0.3%
	100	1122.31	873.19	1049.49	N/A	1057.37	−22.2%	−6.5%	N/A	−5.8%
	200	717.77	570.31	685.45	N/A	699.68	−20.5%	−4.5%	N/A	−2.5%
	400	436.76	372.49	447.69	N/A	462.99	−14.7%	2.5%	N/A	6.0%
483	20	2211.42	1700.28	2385.61	N/A	2216.07	−23.1%	7.9%	N/A	0.2%
	40	1538.61	1110.51	1558.12	N/A	1492.44	−27.8%	1.3%	N/A	−3.0%
	100	936.59	632.36	887.25	N/A	884.99	−32.5%	−5.3%	N/A	−5.5%
	200	637.46	413.01	579.49	N/A	596.01	−35.2%	−9.1%	N/A	−6.5%
	400	411.67	269.75	378.48	N/A	401.39	−34.5%	−8.1%	N/A	−2.5%
503	20	1640.12	1263.34	2016.82	1307.76	1780.58	−23.0%	23.0%	−20.3%	8.6%
	40	1267.07	825.13	1317.25	1330.76	1220.43	−34.9%	4.0%	5.0%	−3.7%
	100	737.91	469.85	750.08	718.83	740.72	−36.3%	1.6%	−2.6%	0.4%
	200	496.79	306.88	489.90	569.49	507.70	−38.2%	−1.4%	14.6%	2.2%
	400	326.47	200.43	319.97	399.47	347.98	−38.6%	−2.0%	22.4%	6.6%
						SSE	1,474,311	200,184.4	125,501.1	73,352.29
						σ	271.51	100.05	158.43	60.56

N/A = not applicable.

Table VII lists the coefficients a, b, c, and d of eq. (9) for both LDPE and PP. These coefficients were calculated with the data in Tables I and II as the input matrices for the program.

Figures 2 and 3 plot the measured the natural log of the viscosity against the natural log of the shear rate for LDPE and PP, respectively, at different temperatures. Once again, it can be seen from Figures 2 and 3 that the tangents of the plotted lines are not constants. Instead, they vary with the temperature.

Figures 4 and 5 show the measured and calculated viscosities (solid and dashed lines) for LDPE and PP, respectively. It can be seen from the comparisons in Figures 4 and 5 that eq. (9) shows favorable agreement with the measured data, although there is a slight inaccuracy in Figure 5 for 523 and 543 K. The deviation between the measured and calculated values for PP at T = 503, 523, and 543 K when the

shear rates are less than 50 s^{-1} may be caused by (1) degradation of the melt or (2) errors due to the measurements.

Model comparison

To compare the accuracy of eqs. (3)–(5) and (9), we first have to find the coefficients in these equations. Then, we substitute the experimental conditions into these equations to calculate the errors between the measured and calculated data. The details of the calculation procedures are shown in the appendix.

Table VIII lists the viscosity equations for LDPE after all the calculated coefficients are substituted into eqs. (3)–(5) and (9). The comparisons of the calculated data of eqs. (3)–(5) and (9) and measured data for LDPE are shown in Table IX.

TABLE X
η Calculation Equations for PP

Equation	Name	Equation
(4)	Andrade's equation[10]	$\eta = 9998.1 e^{4810.98(1/T-1/463)} \dot{\gamma}^{-0.6338}$
(5)	Traditional empirical equation[2,18]	$\eta = 9998.1 e^{0.0123(463-T)} \dot{\gamma}^{-0.6338}$
(3)	WLF equation[4]	$\eta = 10^{3.1598+0.2275(T-463)/T-532.99}$ at $\dot{\gamma} = 20$ (s^{-1})
		$\eta = 10^{2.9929+0.2655(T-463)/T-554.00}$ at $\dot{\gamma} = 40$ (s^{-1})
		$\eta = 10^{2.7499+0.41704(T-463)/T-609.522}$ at $\dot{\gamma} = 100$ (s^{-1})
		$\eta = 10^{2.5457+0.9254(T-463)/T-823.90}$ at $\dot{\gamma} = 200$ (s^{-1})
		$\eta = 10^{2.3361+0.31658(T-463)/T-612.24}$ at $\dot{\gamma} = 400$ (s^{-1})
(9)	Proposed empirical equation	$\eta = 814{,}090{,}865.35 e^{-0.0243T} \dot{\gamma}^{0.00328T-2.1639}$

TABLE XI
Comparisons of Calculated ηs for PP

T (K)	$\dot{\gamma}$ (1/s)	Measured data	Calculated data				Error			
			Eq. (4)[18]	Eq. (5)[4]	Eq. (3)[10]	Eq. (9)	Eq. (4)	Eq. (5)	Eq. (3)	Eq. (9)
463	20	1444.67	1497.34	1497.34	N/A	1552.70	3.6%	3.6%	N/A	7.5%
	40	983.77	965.00	965.00	N/A	992.60	−1.9%	−1.9%	N/A	0.9%
	100	562.23	539.90	539.90	N/A	549.43	−4.0%	−4.0%	N/A	−2.3%
	200	351.34	347.95	347.95	N/A	351.24	−1.0%	−1.0%	N/A	0.0%
	400	216.82	224.25	224.25	N/A	224.54	3.4%	3.4%	N/A	3.6%
483	20	1171.50	973.78	1171.50	N/A	1163.14	−16.9%	0.0%	N/A	−0.7%
	40	828.16	627.58	755.00	N/A	778.15	−24.2%	−8.8%	N/A	−6.0%
	100	483.05	351.12	422.41	N/A	457.40	−27.3%	−12.6%	N/A	−5.3%
	200	310.05	226.29	272.23	N/A	306.01	−27.0%	−12.2%	N/A	−1.3%
	400	193.69	145.84	175.45	N/A	204.72	−24.7%	−9.4%	N/A	5.7%
503	20	718.29	655.33	916.57	N/A	871.31	−8.8%	27.6%	N/A	21.3%
	40	609.09	422.34	590.70	N/A	610.03	−30.7%	−3.0%	N/A	0.2%
	100	392.03	236.29	330.49	N/A	380.79	−39.7%	−15.7%	N/A	−2.9%
	200	269.38	152.28	212.99	N/A	266.60	−43.5%	−20.9%	N/A	−1.0%
	400	166.03	98.14	137.27	N/A	186.65	−40.9%	−17.3%	N/A	12.4%
523	20	719.13	454.58	717.11	62.10	652.70	−36.8%	−0.3%	−91.4%	−9.2%
	40	570.33	292.97	462.16	301.37	478.23	−48.6%	−19.0%	−47.2%	−16.1%
	100	360.95	163.91	258.57	288.88	317.01	−54.6%	−28.4%	−20.0%	−12.2%
	200	339.16	105.64	166.64	229.72	232.27	−68.9%	−50.9%	−32.3%	−31.5%
	400	152.27	68.08	107.40	132.82	170.18	−55.3%	−29.5%	−12.8%	11.8%
543	20	437.33	323.94	561.06	95,008.06	488.94	−25.9%	28.3%	21,624.5%	11.8%
	40	308.79	208.77	361.59	11.55	374.91	−32.4%	17.1%	−96.3%	21.4%
	100	292.06	116.80	202.30	177.17	263.91	−60.0%	−30.7%	−39.3%	−9.6%
	200	199.94	75.28	130.38	191.50	202.36	−62.4%	−34.8%	−4.2%	1.2%
	400	130.82	48.51	84.03	93.40	155.16	−62.9%	−35.8%	−28.6%	18.6%
						SSE	438,507.9	115,892.7	521,571.5	65,886.09
						σ	148.07	76.12	322.98	57.40

N/A = not applicable.

The errors in Table IX are defined as follows: (calculated value − measured value)/measured value × 100%. The sum square due to error (SSE) is equal to $\Sigma e_i^2 = \Sigma(x_i - s_i)^2$, where x_i is the calculated value, s_i is the measured value, and i is the test item number. The mean square due to error (MSE) is equal to SSE/n, where n is the total number of tests; the standard deviation σ is equal to $\sqrt{MSE}$. σ can be regarded as an indicator evaluating the total average error between the calculated and measured data, and a smaller value of σ indicates greater accuracy of the model.

To solve C_1^r and C_2^r of eq. (3) (the WLF equation), we need three sets of given data. The measured data at 443, 463, and 483 K have been used as the given data to solve the coefficients in this study; that is, the calculated data are exactly the same as the given data. Therefore, these data cannot be used in comparisons, and they are shown as N/A (not applicable) in Table IX.

From the comparison of σ in Table IX, we find that the compared models in order of accuracy are eqs. (9), (5), (3), and (4); that is, the proposed empirical model is the most accurate one. Table X lists the equations after all the calculated coefficients have been substituted into eqs. (3)–(5) and (9).

The comparisons of the calculated data of eqs. (3)–(5) and (9) and the measured data for PP are shown in Table XI. It can be seen from Tables IX and XI that the σ values of the proposed empirical equation are smaller than those of the other equations. This result confirms that the proposed empirical equation is an accurate model for predicting the viscosity of LDPE and PP.

Furthermore, to prove that the proposed model is also accurate in interpolation, we have taken the data sets in Table I at $T = 483$ K and in Table II at $T = 503$ K away from the model building procedure of eq. (9).

TABLE XII
Coefficients in Eq. (9) for Interpolation

	T (K)	a	b	c	d
LDPE	443–503	14,177,784.03	−0.0146	0.0012	−1.1451
PP	463–543	1,863,747,130.97	−0.0261	0.0035	−2.2491

TABLE XIII
Comparisons of σ for Data Interpolation

	T (K)	σ			
		Eq. (4)[10]	Eq. (5)[2]	Eq. (3)[4]	Eq. (9)
LDPE	483	348.60	86.74	43.71	47.82
PP	523	222.42	103.89	322.98	95.60

TABLE XIV
Coefficients in Eq. (9) for Data Extrapolation

	T (K)	a	b	c	d
LDPE	443–503	14,177,784.0257	−0.0146	0.0012	−1.1451
PP	463–543	1,863,747,130.97	−0.0261	0.0035	−2.2491

These data sets are used for model comparisons. The coefficients of eq. (9) are recalculated as shown in Table XII.

The coefficients C_1^r and C_2^r are solved by the substitution of $T_r = 443$ K, $T_1 = 463$ K, and $T_2 = 503$ K together with related η_r, η_1, and η_2 at $\dot{\gamma} = 20\ \mathrm{s}^{-1}$ (Table I) into eqs. (3a) and (3b). The coefficients for eqs. (4) and (5) are kept the same as previously calculated values. The calculation results are shown in Table XIII, from which detailed data have been omitted for the purpose of simplification.

It can be seen from Table XIII that both the WLF equation and the proposed empirical equation are accurate in interpolation for LDPE, but the WLF equation is not accurate for matching the viscosity of PP. Both the traditional and proposed empirical equations are accurate in interpolation for PP; however, the latter is more accurate than the former.

In the same way, for extrapolation, the data sets in Table I at $T = 503$ K and in Table II at $T = 543$ K are removed from the model building procedure of eq. (9), and the coefficients of eq. (9) are recalculated as shown in Table XIV. The coefficients for eqs. (3)–(5) are kept the same as the previously calculated values. The calculation results are shown in Table XV. Both the proposed and traditional empirical equations are accurate in extrapolation for LDPE and PP, and the former is more accurate than the latter.

Figures 6–8 show comparisons of the experimental data and the calculated values with different models for LDPE and PP at several temperatures. Again, the proposed empirical equation can predict the viscosity of LDPE and PP more accurately than the other models.

By comparing the differences between eq. (4) (Andrade's equation) and eq. (5) (the traditional empirical equation), we find that the power terms of the exponents are $(E/RTT)(T_r - T)$ and $\alpha_T(T_r - T)$, respectively; that is, E/RTT and α_T are similar, but their calculated values are not the same. The coefficients m_r

and n in eq. (4) are found from one set of experimental data at $T_r = 443$ K for LDPE and at $T_r = 463$ K for PP. The coefficients m_r, n, and α_T in eq. (5) are found from two sets of experimental data at $T_r = 443$ K and $T = 463$ K for LDPE and at $T_r = 463$ K and $T = 483$ K for PP. Therefore, the calculated coefficients for eqs. (4) and (5) should be different. Because the same data are given for both equations at T_r, the calculated results are expected to be the same at 443 K for LDPE and at 463 K for PP, but the results for the other temperatures can be different (see Tables IX and XI). Similarly, the obvious deviations between the measured and calculated values for LDPE and PP can also be found in Figures 6–8.

It can be seen from a comparison of the proposed empirical model with other models that the proposed model is on average more accurate with respect to the measured data than the others.

The advantage of this equation is that it is relatively simple and accurate at matching the experimental data over the application range of temperatures and shear rates. The drawback of the proposed model is that it heavily depends on the viscosity measurements as a function of the shear rate and temperature for each material under investigation; that is, three sets of experimental data are required to find the coefficients in eq. (9).

The equation is proposed for use in practical industrial applications. The suitable range of temperatures and shear rates is based on manufacturing experience.[22] The fact that n and m vary with the temperature is considered in the proposed empirical equation, and that is why this model can make a more accurate prediction of the measured data.

CONCLUSIONS

A proposed empirical viscosity equation has been developed in this study. The model has taken into account the fact that n and m vary with the temperature. The coefficients have been calculated with the experimental data taken from capillary rheometer measurement of viscosities of LDPE and PP in the laboratory. From comparisons of σ for various calculation methods, we have proven that this proposed empirical model is capable of predicting the viscosities of both LDPE and PP with remarkable accuracy. Although only the viscosities of LDPE and PP are analyzed in

TABLE XV
Comparisons of σ for Data Extrapolation

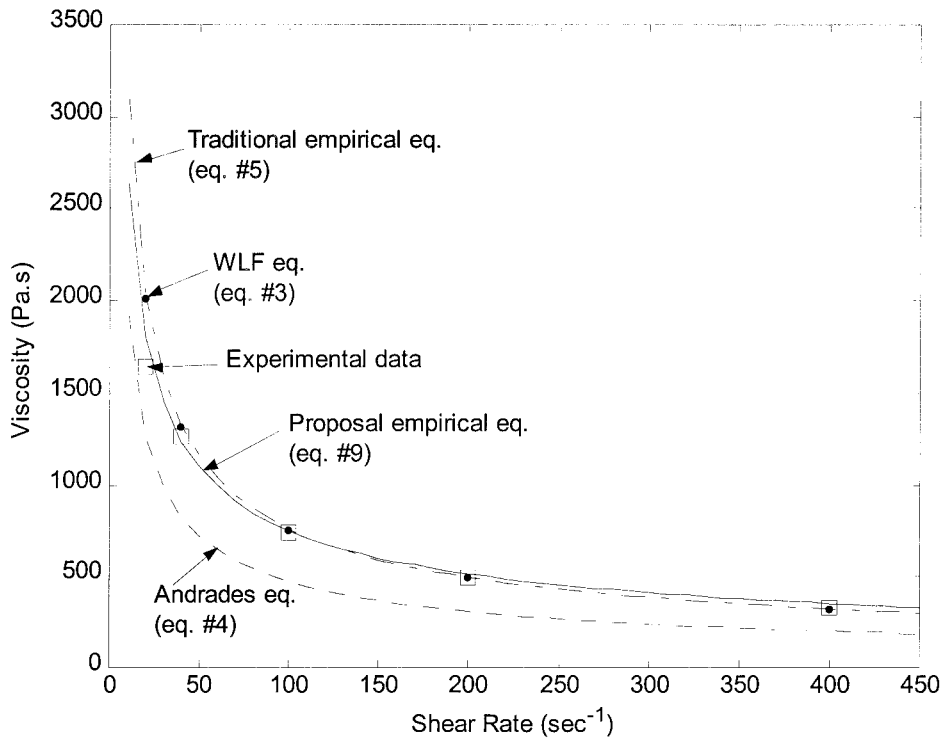|		σ			
	T (K)	Eq. (4)[10]	Eq. (5)[2]	Eq. (3)[4]	Eq. (9)
LDPE	503	303.67	170.09	158.43	112.19
PP	543	123.20	81.46	42,293.6	81.12

Figure 6 Comparison of the experimental data and the calculated values of the models for LDPE at $T = 503$ K.

this study, it is believed that the proposed empirical model is also suitable for all semicrystalline polymers. Although the coefficients in the equation may be different, the form should be the same.

This proposed empirical model can be applied to the polymer extrusion process for the purpose of quality control and with the viscosity as one of the main controlled parameters.
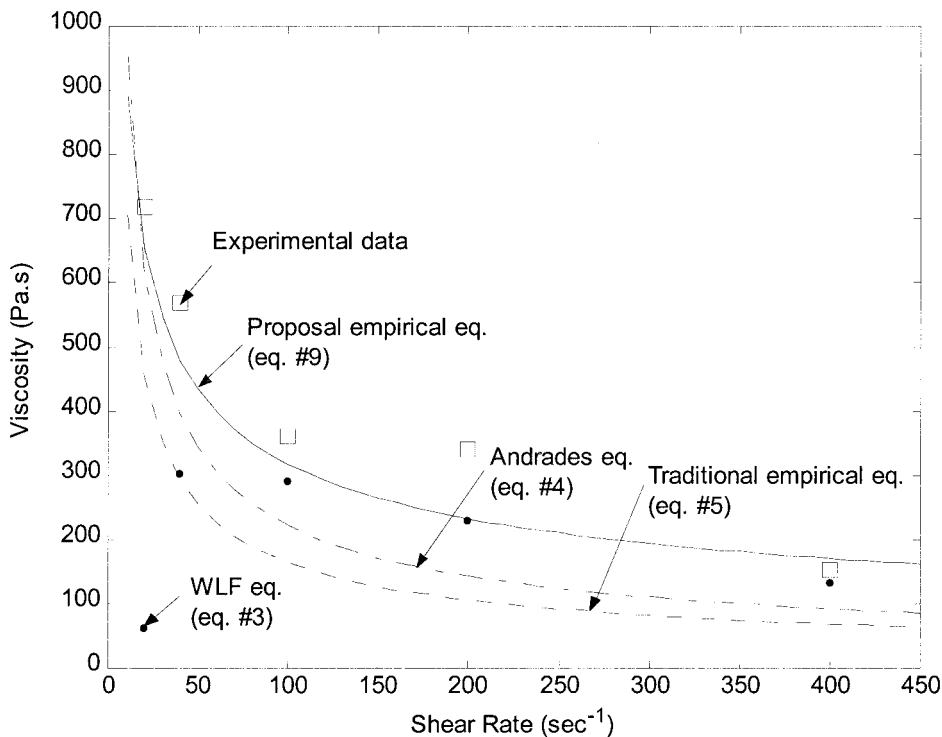

Figure 7 Comparison of the experimental data and the calculated values of the models for PP at $T = 523$ K.
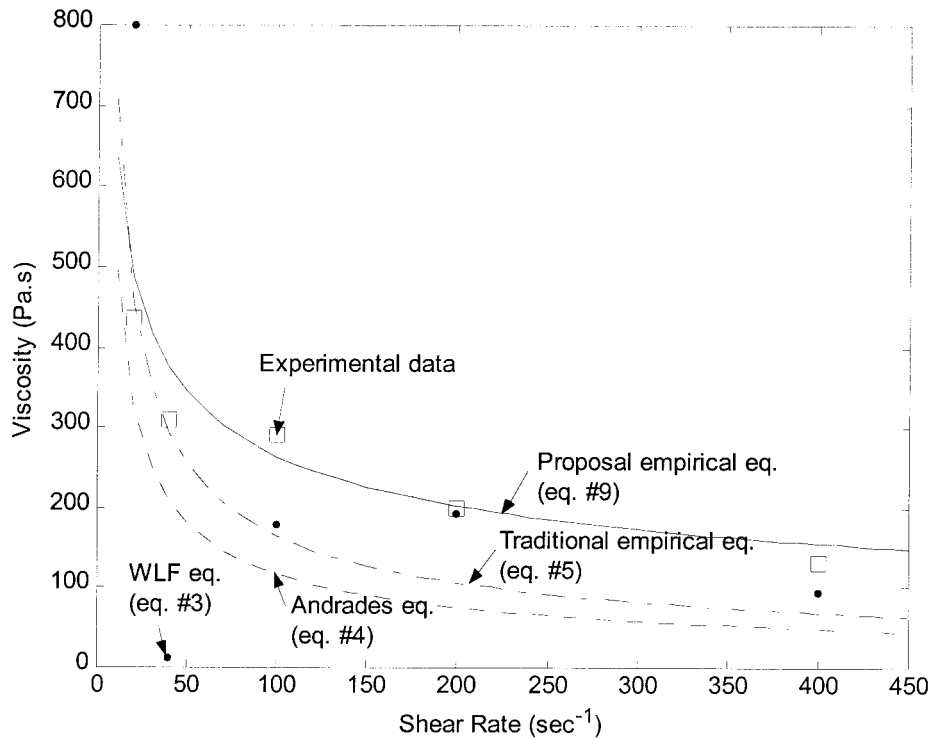
Figure 8 Comparison of the experimental data and the calculated values of the models for PP at $T = 543$ K.

APPENDIX: CALCULATION PROCEDURES FOR FINDING THE COEFFICIENTS OF EQS. (3)–(5) AND (9)

Because the coefficients for eqs. (3)–(5) and (9) are material-dependent, the solution and comparison procedures can be described as follows.

LDPE

Let T_r be 443 K. Substituting $E = 30,000$ J/mol [19] and $R = 8.31432$ J/(mol K) and inserting $T = 443$ K (i.e., T_r) and $n - 1 = -0.6146$ (i.e., p; see Table V) into eqs. (4a) and (5a), we get the following:

$$\ln \eta = -0.6146 \ln \dot{\gamma} + \ln m_r \qquad (A.1)$$

Equation (6) at 443 K is $\ln \eta = -0.6146 \ln \dot{\gamma} + 9.9541$. Let this be equal to eq. (A.1); therefore, m_r is 21038.9. Equation (4) becomes $\eta = 21038.9e^{3608.233(1/T-1/443)} \dot{\gamma}^{-0.6146}$.

To obtain the coefficient α_T in eq. (5a), use $T_r = 443$ K, $T = 463$ K, $n - 1 = -0.6146$, and $\ln m_r = 9.9541$:

$$\ln \eta = 9.9541 - 20\alpha_T - 0.6146 \ln(\dot{\gamma}) \qquad (A.2)$$

Let the linear equation for $\ln \eta$ and $\ln \dot{\gamma}$ at $T = 463$ K be

$$\ln \eta = -0.6146 \ln \dot{\gamma} + k \qquad (A.3)$$

where k is a constant. Substituting $\dot{\gamma} = 20$ s^{-1} and $\eta = 2821.85$ (Table I) into eq. (A.3), we get $k = 9.7862$. Let eq. (A.2) equal eq. (A.3): $\alpha_T = (9.9542 - 9.7862)/20 = 0.008397$. Equation (5) becomes $\eta = 21,038.9e^{0.008397(443-T)} \dot{\gamma}^{-0.6146}$.

To solve the coefficients in eq. (3), we substitute $T_r = 443$ K, $T_1 = 463$ K, and $T_2 = 483$ K together with related η values at $\dot{\gamma} = 20$ s^{-1} (Table I; i.e., $\eta_r = 3248.24$, $\eta_1 = 2821.85$, and $\eta_2 = 2211.42$), into eqs. (3a) and (3b), and we get $C_1^r = -0.2280$ and $C_2^r = -94.629$. Therefore, eq. (3) becomes $\eta = 10^{3.5116+0.2280(T-443)/T-537.63}$.

The other equations at $\dot{\gamma} = 40, 100, 200,$ and 400 s^{-1} can be found in a similar way. Table VIII lists the equations after the substitution of all the coefficients into eqs. (3)–(5) and (9).

PP

Similarly, using $T_r = 463$ K, $T = 483$ K, $n - 1 = p = -0.6338$ (Table VI), $E = 40000$ J/mol,[19] and $R = 8.31432$ J/(mol K), we obtain $m_r = 9998.1$. Therefore, eq. (4) becomes $\eta = 9998.1e^{4810.98(1/T-1/463)} \dot{\gamma}^{-0.6338}$.

To obtain the coefficient α_T, we substitute the aforementioned T_r, T, $n - 1$, and m_r values into eq. (5a):

$$\ln \eta = 9.2102 - 20\alpha_T - 0.6338 \ln \dot{\gamma} \qquad (A.4)$$

Let the linear equation of $\ln \eta$ and $\ln \dot{\gamma}$ at $T = 483$ K be

$$\ln \eta = -0.6338 \ln \dot{\gamma} + k \qquad (A.5)$$

where k is a constant. Substituting $\dot{\gamma} = 20$ s^{-1} and $\eta = 1171.50$ (Table II) into eq. (A.5), we obtain $k = 8.9648$. Let eq. (A.4) equal eq. (A.5): $\alpha_T = 0.01227$. Equation (5) becomes $\eta = 9998.1 e^{0.0123(463-T)} \dot{\gamma}^{-0.6338}$.

The coefficients C_1^r and C_2^r in eq. (3) are solved by the substitution of $T_r = 463$ K, $T_1 = 483$ K, and $T_2 = 503$ K together with related η values at $\dot{\gamma} = 20$ s^{-1} (Table II; i.e., $\eta_r = 1444.67$, $\eta_1 = 1171.5$ and $\eta_2 = 718.291$) into eqs. (3a) and (3b), and we get $C_2^r = -0.2275$ and $C_1^r = -69.99$. Therefore, eq. (3) becomes $\eta = 10^{3.1598+0.2275(T-463)/T-532.99}$.

The other equations at $\dot{\gamma} = 40, 100, 200,$ and 400 s^{-1} can be obtained in the same way. Table X lists the equations after the substitution of all the coefficients into eqs. (3)–(5) and (9).

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