On the Computation of Viscosity-Shear Rate Temperature Master Curves for Polymeric Liquids

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Abstract: Two numerical algorithms for constructing viscosity-shear rate temperature master curves for polymeric liquids from two sets of viscosity-shear rate measurements at two different temperature values, based upon the temperature-time superposition principle, are developed. It is shown that simultaneous fitting of the data produces more accurate results than fitting the data independently. Numerical examples based upon both artificial and laboratory data are given.

1   Introduction

Viscosity is a fluid property that represents a material's internal resistance to deform. Mathematically, viscosity is defined as the ratio of shear stress, τ, and shear rate, $\dot{\gamma}$, i.e.,

$$\eta \equiv \frac{\tau}{\dot{\gamma}} \tag{1}$$

Fluids are classified as Newtonian if the relation (1) is linear, i.e., if η is a constant independent of $\dot{\gamma}$ and non-Newtonian otherwise. Most polymeric liquids are non-Newtonian fluids. Viscosity is an easily measured property of polymeric liquids. Among the instruments used for experimental measurements of viscosity are extrusion viscometers and capillary and parallel plate rhometers.

For polymeric liquids, viscosity dependence on shear rate can, in general, be described by the following "viscosity" curves, having the following important properties:

1. $\lim_{\dot{\gamma} \to 0^+} \eta = \eta_0$, where η_0 is called the zero shear viscosity.

2. As shown in Figure 1(a), shear rate values below which viscosity levels out are too small. In order to show the approach of viscosity to its limiting value, while also showing high shear rate behavior, it is usually the case that a plot of $\log(\eta)$ versus $\log(\dot{\gamma})$ is used, as in Figure 1(b).
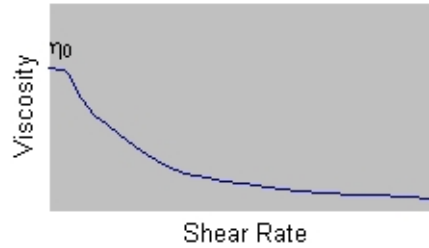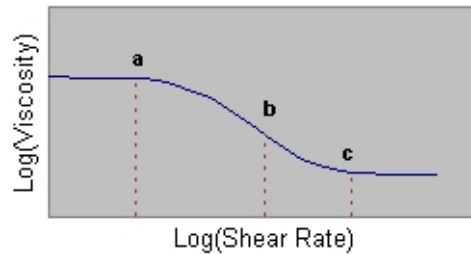
Figure 1(a)

Figure 1(b)

3. Experimental measurement of zero shear viscosity using available tools is not possible for most polymeric liquids.

4. $\eta(\dot\gamma)$ is a decreasing function of $\dot\gamma$. This behavior is known as "pseudoplastic" behavior.

5. As shown in Figure 1(b), for sufficiently low shear rate values $(\log(\dot\gamma) \leq a)$, viscosity becomes independent of shear rate, i.e., the material exhibits Newtonian behavior. For $a \leq \log(\dot\gamma) \leq b$, the dependence of $\log(\eta)$ on $\log(\dot\gamma)$ is non-linear. Finally, for $b \leq \log(\dot\gamma) \leq c$, η has a power law dependence on $\dot\gamma$. As $\dot\gamma$ increases beyond c, the viscosity curve levels out, and the material tends toward Newtonian behavior again.

6. $\eta(\dot\gamma)$ possesses a horizontal asymptote, which, for most polymeric liquids, is impossible to determine experimentally due to polymer degradation at high shear rates.

Experimental data provided by a viscosity measuring instrument for a given polymeric liquid at a given temperature consists of several points on the viscosity curve. Determination of the viscosity curve over a wide range of shear rate values is essential for solving the flow equations. This is usually done by fitting the data points to one of the viscosity models. In this paper we will consider the

following models:

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0}{\tau^*}\dot{\gamma}\right)^{1-n}} \tag{2}$$

$$\eta = \frac{\eta_0}{\left(1 + \frac{\eta_0}{\tau^*}\dot{\gamma}\right)^{1-n}} \tag{3}$$

known as the Modified Cross and Carreau models, respectively, where η_0 represents the zero shear rate viscosity, τ^* represents the critical shear stress roughly characterizing transition shear stress from the Newtonian range to the pseudoplastic region, and n represents the shear rate sensitivity, $0 < n < 1$, where $1 - n$ roughly characterizes the slope of the line over the pseudoplastic region in the logarithmic plot.

The mathematical problem of fitting a given set of data points on the viscosity curve by either the Modified Cross or Carreau models consists of determining the three parameters η_0, τ^*, and n which minimize the distance between the model used and the given data. This is represented mathematically as the solution of a non-linear algebraic system of equations for the three model parameters.

Viscosity is a decreasing function of temperature. The temperature-time superposition principle of viscoelasticity describes the dependence of viscosity on temperature as follows. It states that a change in the temperature from T_1 to T_2 does not affect the functional dependence of η on $\dot{\gamma}$, but merely alters the zero shear viscosity and the shear rate at which transition from Newtonian to pseudoplastic behavior occurs. As temperature increases, the viscosity curve at T_1, in the $\log(\eta)$ versus $\log(\dot{\gamma})$ plot, is shifted by a "shift factor" $\log(a_T)$ given by

$$a_T = \frac{\eta_0(T_1) \cdot T_2 \cdot \rho_2}{\eta_0(T_1) \cdot T_2 \cdot \rho_1} \tag{4}$$

where ρ_1, ρ_2 denote the densities at the temperature values T_1 and T_2, respectively. Accordingly, it is possible to construct a temperature master curve $\eta(\dot{\gamma}, T)$ from which viscosity curves for various temperature values may be obtained. The main purpose of this paper is to present two numerical algorithms for constructing this temperature master curve and compare their ease of use and effectiveness.

The rest of the paper is organized in four sections. In section 2 the effect of temperature on the viscosity, based upon the Arrhenius law, is described. In section 3 two methods for constructing a temperature master curve from two sets of data points at two different temperature values are described. In section 4 numerical results are presented and comparisons between the two methods of section 3 are given. In section 5 some concluding remarks are outlined.

2 Effect of Temperature on Viscosity

The temperature effect on the viscosity function $\eta(\dot{\gamma})$ is described in many references ([1], [2], [4]) by the Arrhenius law. This law states that for thermorheologically simple fluids the shift factor a_T is given by

$$\log a_T = \frac{E_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5}$$

where E_0 is the fluid activation energy in J/mol and $R = 8.314$ J/molK is the universal gas constant. It follows that if E_0 is known, the temperature master curve $\eta(\dot{\gamma}, T)$ (see Figure 2) can be constructed.
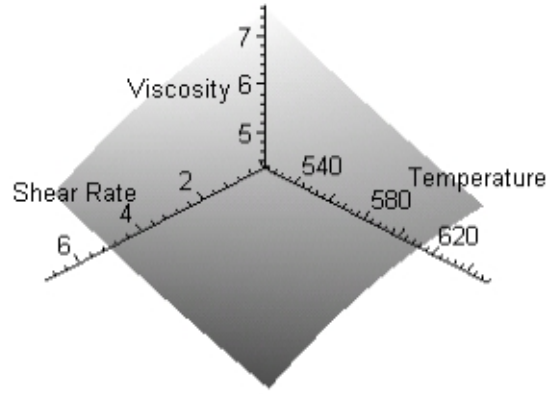

Figure 2

Temperature master curves corresponding to Modified Cross and Carreau models can be obtained by combining (2), (3), (4), and (5) as

$$\eta = \left(\frac{\eta_0}{1 + \left(\frac{\eta_0}{\tau^*}\frac{\dot{\gamma}}{a_T}\right)^{1-n}}\right)\left(\frac{1}{a_T}\right) \tag{6}$$

$$\eta = \left(\frac{\eta_0}{\left(1 + \frac{\eta_0}{\tau^*}\frac{\dot{\gamma}}{a_T}\right)^{1-n}}\right)\left(\frac{1}{a_T}\right) \tag{7}$$

where the ratio $\frac{T_2 \cdot \rho_2}{T_1 \cdot \rho_1}$ is taken to be unity. This assumption has been shown to be valid over ordinary temperature ranges for most polymeric liquids.

Remark: Equation (5) describes temperature dependence well for thermorheologically simple (partially crystalline) material. This is because glass transition

regions for such materials lie well below their fluid states. For amorphous thermoplastic materials, however, the glass transition regions are close to their fluid states. Free volume effects predominate and the Arrhenius-WLF equation

$$\log a_T = \frac{E_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) - b_1\left(\frac{T_1 - T_2}{b_2 + T_2 - T_1}\right) \tag{8}$$

should be used instead of (5), where b_1 and b_2 are parameters to be determined. It follows that for amorphous thermoplastic materials, construction of the temperature master curves (6) and (7) requires knowledge of three parameters, namely E_0, b_1, and b_2, rather than just E_0 as for the case for partially crystalline materials. In this paper, we restrict our attention to partially crystalline materials and therefore assume equation (5).

3   Construction of Temperature Master Curves

While many references ([1], [3], [4], and the references therein) describe the concept of a master curve, none present any numerical methods for its construction. In this section we present two numerical algorithms for the construction of the temperature master curves (6) and (7) for partially crystalline materials with a shift factor described by (5). Each of our two methods assumes knowledge of two sets of capillary rheometer measurements $\left(\dot\gamma_j^{(1)}, \eta_j^{(1)}\right)$, $\left(\dot\gamma_j^{(2)}, \eta_j^{(2)}\right)$, $j = 1, \ldots, M$ at two different temperature values T_1 and T_2, respectively, for some polymer. Both methods are based upon minimization techniques and applications of Newton's method [2].

(i) Method of Independent Fit

In this method, we first fit one of the models (2) or (3) to the data set for temperature T_1. This yields an estimate of the zero shear viscosity $\eta_0(T_1)$. Then, independent of the first computation, we fit the model to the data for temperature T_2 from which we obtain an estimate of $\eta_0(T_2)$. Estimates of the shift factor a_T and the material's activation energy E_0 are then be obtained from (4) and (5) and used to construct (6) or (7). Below we describe an iterative technique for fitting one set of data by models (2) and (3).

It turns out that the algebraic system of equations for determining the parameters η_0, τ^*, and n, which minimize the distance between a given set of data points and the model under consideration, is singular. Using the normalization below in conjunction with an outer iteration for evaluating the zero shear viscosity we are able to remove the singularity and carry out the minimization problem. Using the normalization

$$\xi = \frac{\eta}{\eta_0} \qquad \delta = \eta_0 \cdot \dot\gamma \tag{9}$$

the models (2) and (3) become

$$\xi(\alpha, \beta, \delta) = \frac{1}{(1 + \beta \cdot \delta)^\alpha} \tag{10}$$

$$\xi(\alpha, \beta, \delta) = \frac{1}{1 + (\beta \cdot \delta)^\alpha} \tag{11}$$

where $\beta = \frac{1}{\tau^*}$ and $\alpha = 1 - n$.

Our method involves an "inner" iteration for α and β and an "outer" iteration for η_0. For a given value of η_0, we construct the normalized data (δ_i, ξ_i), $i = 1, \cdots, M$, set

$$F(\alpha, \beta) \equiv \sum_{i=1}^{M} \left(1 - \frac{\xi(\alpha, \beta, \delta_i)}{\xi_i} \right)^2 \tag{12}$$

and determine α, β which minimize $F(\alpha, \beta)$. We do this by applying Newton's method [2] to the non-linear algebraic system

$$\frac{\partial F}{\partial \alpha} = \sum_{i=1}^{M} \left(\frac{1}{\xi_i^2} \right) (\xi_i - \xi(\alpha, \beta, \delta_i)) \left(\frac{\partial \xi(\alpha, \beta, \delta_i)}{\partial \alpha} \right) = 0$$

$$\frac{\partial F}{\partial \beta} = \sum_{i=1}^{M} \left(\frac{1}{\xi_i^2} \right) (\xi_i - \xi(\alpha, \beta, \delta_i)) \left(\frac{\partial \xi(\alpha, \beta, \delta_i)}{\partial \beta} \right) = 0 \tag{13}$$

with initial guesses $\eta_0^{(0)} = \eta_1$, $\alpha^{(0)} = 1 - s$, and $\beta^{(0)} = \frac{1}{\dot{\gamma} \cdot \eta_0^{(0)}}$ where s is an approximation of the power law index obtained using a linear best fit. Then, a new value of η_0 is computed using fixed-point iteration of

$$\eta_0^{(k+1)} = \eta_1 \left[1 + \left(\eta_0^{(k)} \cdot \beta^{(k+1)} \cdot \dot{\gamma}_1 \right)^{\alpha^{(k+1)}} \right], \quad k \geq 1 \tag{14}$$

for the Modified Cross model, and

$$\eta_0^{(k+1)} = \eta_1 \left[1 + \left(\eta_0^{(k)} \cdot \beta^{(k+1)} \cdot \dot{\gamma}_1 \right) \right]^{\alpha^{(k+1)}}, \quad k \geq 1 \tag{15}$$

for the Carreau model. Then the whole process of normalization of data, computation of α and β, and computation of η_0 is repeated.

Note that the above iterative method for η_0 depends heavily on the first data point $(\dot{\gamma}_1, \eta_1)$. In practice, a modification that places equal emphasis on all data points should be used. This would require the solution of a second minimization problem. Notice further that, in this method of independent fit, the two resulting viscosity curves at the temperature values T_1 and T_2 will usually (due to data inaccuracy) have different values for

the parameters τ^* and n and will therefore not be in agreement with the temperature-time superposition principle. Accordingly, the resulting temperature master curves will be less accurate than those obtained in the following method.

(ii) Method of Simultaneous Fit

In this method the two sets of data at the temperature values T_1 and T_2 are fit by two curves of one of the models (2) or (3) simultaneously such that the resulting viscosity curves are consistent with the properties of the temperature-time superposition principle. The numerical results of Section 4 show that this method enables the construction of a more accurate temperature master curve than the one obtained by the method of independent fit.

For given $\eta_0^{(1)}$ and $\eta_0^{(2)}$, corresponding to T_1 and T_2, respectively, the function to be minimized here is

$$F(\alpha, \beta) \equiv \sum_{i=1}^{M} \left[\left(1 - \frac{\xi(\alpha, \beta, \delta_i^{(1)})}{\xi_i^{(1)}} \right)^2 + \left(1 - \frac{\xi(\alpha, \beta, \delta_i^{(2)})}{\xi_i^{(2)}} \right)^2 \right] \qquad (16)$$

where $(\delta_i^{(j)}, \xi_i^{(j)})$ are the jth normalized data, $j = 1, 2$. Then $\eta_0^{(1)}$ and $\eta_0^{(2)}$ are calculated by an outer iteration using two equations (with the same values of α and β) similar to (14) for the Modified Cross model and (15) for the Carreau model. Since both curves are fitted simultaneously, with the same α and β (hence τ^* and n), the method ensures that the fitted curves obey the temperature-time superposition principle, allowing for more precise calculation of the temperature master curve.

4   Numerical Results and a Comparison of Methods

Computer programs, in QuickBasic 4.5 with double-precision calculations, were written to implement the algorithms developed in section 3.

We will now compare the effectiveness of the simultaneous fit and the independent fit with two means of analysis. The first and second examples, using the Modified Cross and Carreau models, respectively, study the accuracy of the activation energy, E_0, calculated by the two fits. The third and fourth examples, using the Modified Cross and Carreau models, respectively, examine the error in calculating a given viscosity curve using the temperature master curve constructed by each of the two methods.

For the first example comparing the accuracy of the simultaneous fit to that of the independent fit, we choose parameters to create an arbitrary temperature master curve based on the Modified Cross model. We use $\eta_0 = 1500$ Pa-sec at $T = 548$K, $E_0 = 40000$ J/molK, $n = 0.5$, and $\tau^* = 100000$ Pa. From this master

curve, we generate exact viscosities for two different temperatures. To simulate experimental error, we perturb each viscosity value slightly by adding a random number between -12 and 12 and rounding to the nearest integer. (See the data in Table 1). Then, we fit the data both simultaneously and independently and compare the resulting activation energy in each case with the "exact" value of E_0.

Shear Rate (1/sec)	Perturbed Viscosity (Pa-sec) at $T = 548$K	Perturbed Viscosity (Pa-sec) at $T = 573$K
1	1330	940
2	1290	890
5	1185	830
10	1075	785
20	975	714
50	800	580
100	670	500
200	535	425
500	405	310
1000	310	247

Table 1

Fitting the data simultaneously produces $E_0 = 39978$ J/molK, an error of 0.055% compared to the actual value $E_0 = 40000$ J/molK, while fitting the data independently gives $E_0 = 39439$ J/molK, an error of 1.4%. The simultaneous fit, in conjunction with the Modified Cross model, exhibits a more precise calculation of E_0.

Following the same procedure as above, but basing the master curve on the Carreau model, we generate exact data and perturb it (Table 2). Again, we fit the data simultaneously and independently, and calculate activation energies.

Shear Rate (1/sec)	Perturbed Viscosity (Pa-sec) at $T = 548$K	Perturbed Viscosity (Pa-sec) at $T = 573$K
1	1480	1020
2	1472	1010
5	1450	1000
10	1390	970
20	1320	925
50	1140	825
100	940	725
200	760	580
500	510	418
1000	370	310

Table 2

Simultaneous fitting gives $E_0 = 39978$ J/molK, an error of 0.055% compared to the actual value $E_0 = 40000$ J/molK, while fitting the data independently produces $E_0 = 39650$ J/molK, an error of 0.875%. Once again, the simultaneous fit demonstrates a more precise calculation of E_0, this time using the Carreau model.

As a second example for comparing the accuracy of the simultaneous and independent fits, we use experimental data, from a capillary rheometer, obtained for a single material at three different temperatures. We select the data sets for two of the temperatures ($T = 463$K, $T = 543$K) (see Table 3), and use both the simultaneous and independent fits to create two temperature master curves (using the Modified Cross model).

Shear Rate (1/sec)	Viscosity (Pa-sec) at $T = 463$K	Viscosity (Pa-sec) at $T = 543$K
50	1933	1128.4
100	1231.6	723.5
200	771.5	452
500	400.4	244.8
1000	245.2	151.6
2000	145.2	90.7
3500	108.9	58.2

Table 3

At the third temperature, $T = 503$K, the simultaneously fit master curve produces the parameters $\eta_0 = 31785$ Pa-sec, $E_0 = 44604$ J/molK, $n = .29545$, and $\tau^* = 21901$ Pa, while the independently fit master curve gives $\eta_0 = 14212$ Pa-sec, $E_0 = 55157$ J/molK, $n = .29843$ and $\tau^* = 27485$ Pa. Using each of these sets of parameters, we calculate expected data for $T = 503$K, and compare with the experimental data at that temperature (see Table 4).

Shear Rate (1/sec)	Experimental Viscosity (Pa-sec) at $T = 503$K	Calculated Viscosities (Pa-sec) from Simultaneously Fit Master Curve	Calculated Viscosities (Pa-sec) from Independently Fit Master Curve
50	1433.4	1480.9	1316.58
100	924.8	925.39	839.52
200	615.3	574.31	528.24
500	337.5	303.76	282.73
1000	200	187.09	175.19
2000	115.3	115.06	108.24
3500	70.7	77.66	73.28

Table 4

The average relative error for the simultaneously fit master curve is 5.38%,

while the average relative error for the independently fit data is 8.84%. The simultaneous fit with the Modified Cross model demonstrates a more accurate estimation of viscosity at a given temperature and shear rate.

Finally, we follow the above procedure to estimate viscosity with the two fits and examine their accuracy, but this time we use the Carreau model. We use the same data as before (Table 3). At the third temperature, $T = 503K$, the simultaneously fit master curve produces the parameters $\eta_0 = 8249$ Pa-sec, $E_0 = 46128$ J/molK, $n = .27377$, and $\tau^* = 44631$ Pa, while the independently fit master curve gives $\eta_0 = 6791$ Pa-sec, $E_0 = 37972$ J/molK, $n = .27$, and $\tau^* = 46545$ Pa. Using each of these sets of parameters, we generate expected data for $T = 503K$, and compare with the experimental data at that temperature (see Table 5).

Shear Rate (1/sec)	Experimental Viscosity (Pa-sec) at $T = 503K$	Calculated Viscosities (Pa-sec) from Simultaneously Fit Master Curve	Calculated Viscosities (Pa-sec) from Independently Fit Master Curve
50	1433.4	1522.83	1449.42
100	924.8	954.6	914.43
200	615.3	588.03	564.59
500	337.5	305.8	293.5
1000	200	185.57	177.83
2000	115.3	112.39	107.48
3500	70.7	74.92	71.51

Table 5

The average relative error for the simultaneously fit master curve is 5.57%, while the average relative error for the independently fit master curve is 6.08%. The simultaneous fit again demonstrates a more accurate estimation of viscosity at a given temperature and shear rate, this time while employing the Carreau model.

5   Conclusions

In this paper we have developed two methods for approximating a viscosity-shear rate temperature master curve for a polymeric liquid using two sets of viscosity-shear rate data points at two different temperature values. In our constructions we used the Arrhenius law, i.e., we assumed that the polymer under consideration was thermorheologically simple. The Arrhenius law is not suitable to use for polymers that are not thermorheologically simple. For example, for amorphous thermoplastic polymers, one should use the Arrhenius-WLF equation (8) instead. In order to produce a reasonably accurate temperature master curve based on the Arrhenius-WLF equation, accurate estimations of the three parameters E_0, b_1, and b_2 are needed. It follows that more than two

experimental viscosity curves should be used. Considerations of the numerical computations of the parameters for the Arrhenius-WLF equation along with other expressions for the shift factor will be the subject of a forthcoming paper.

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