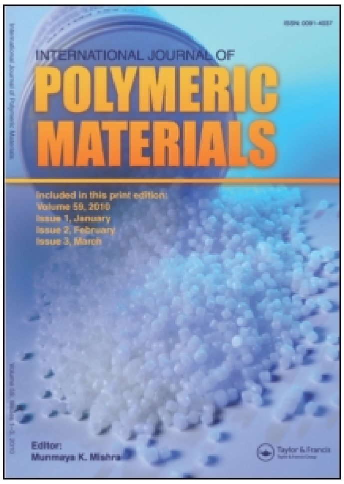

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Mathematical Models of Polymer Melt Viscosity in Shearing Flow. Polystyrene and Polypropylene Melts—2

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The dependence of Polypropylene and Polystyrene melt viscosity on temperature, shear rate and shear stress has been examined. The thermo-activation theory of non-Newtonian viscous-elastic polymeric fluids has been further developed to describe the experimental data and to derive the general equation having clear physical significance.

Computer calculations have been carried out to obtain the best set of constants in the equations and the correlation coefficients between the experimental and computed data for each resin and each equation. The correlation coefficients obtained are very high (0.989 to 0.997). The values obtained for $E_0\dot{\gamma}$ and E_τ are in good agreement with the literature data.

Joint solution of the equations $\eta = f(T, \dot{\gamma})$ and $\eta = F(T, \tau)$ gives an equation for the dependence of shear rate on temperature and shear stress.

KEY WORDS: Polymer, Melt, Shear, Temperature, Model, Viscosity

Polymer melt viscosity is the most important property for plastics processing. Almost 90% of all processing operations employ polymers in viscous-elastic state. Therefore the physical and mechanical properties of final products depend on melt viscosity in most cases. Variation of polymer melt viscosity as a function of temperature and shear rate influences the choice of the production equipment and processing conditions. Consequently, measurements of melt viscosity under a wide range of temperatures and shear rates became a standard test. "However, any predictions of melt viscosity outside the experimental region should be made with caution because an equation having clear physical significance and being in good quantitative agreement with experiment, has not yet been found."[1]

Several theories of non-Newtonian viscosity in polymeric fluids have been developed because of the great practical and theoretical importance of the problem. Frenkel–Eyring theory is based on the consideration of viscous-elastic flow as a process of consecutive jumps of molecular-kinetic units from one equilibrium position to another over a potential energy barrier.[2,3] Hydrodynamic theories describe variation of molecular configurations under stress and the influence of such variations on melt flow.[4] Structural theories of non-Newtonian flow consider reversible breakdown-recovery of the polymer structure.[5,6] Comprehensive reviews of various theories have been given in several books on Polymer Melt Rheology.[1,7,8]

Development of an equation being in good quantitative agreement with experiment and having clear physical significance, requires minimum two steps. The first step is to derive the semi-empirical mathematical model for the dependence of non-Newtonian fluid viscosity on temperature and deformation conditions. Such a model has been developed for Polyethylene melt viscosity in shearing flow.[9] The equations obtained have been based on the theory of absolute reaction rates and on the experimental data.

It has been found that PE melt viscosity can be described as a function of temperature and shear rate or temperature and shear stress under a wide range of experimental conditions and with very high correlation between the experimental and calculated data. It has also been demonstrated that different types of PE melts (LDPE, LLDPE, HDPE) obey the same equations and the only difference is in the values of constants in these equations. The following equations have been successfully applied to more than twenty PE materials:

$$\eta = A * \exp[(E_0\dot{\gamma} - a[\dot{\gamma}])^{1/m}/RT]; \tag{1}$$

$$\eta = B * \exp\{(E_t/RT) - b(\tau)^s\}; \tag{2}$$

where:

η is PE melt viscosity in shearing flow,
$E_0\dot{\gamma}$ is the activation energy of viscous-elastic flow under condition of $\dot{\gamma} = \text{const.}$,
E_τ is the activation energy of viscous-elastic flow under condition of $\tau = \text{const.}$,
T is the temperature of experiment, K,
R is the gas constant,
$A; a; m; B; s; b$ are constants of the material.

Activation energies of viscous-elastic flow for various PE resins ($E_0\dot{\gamma}$ and E_τ) have been in good quantitative agreement with the values published by several other authors.[10,11,12]

The goal of this study has been to confirm that equations of types (1) and (2) are valid for Polypropylene and Polystyrene viscous-elastic fluids in shearing flow.

THEORETICAL AND PRACTICAL APPROACHES

Applicability of Eqs. (1) and (2) to polymer melt viscosity allows us further develop the thermo-activation theory of non-Newtonian viscous-elastic liquids in shearing flow. The concept permits us to consider viscous-elastic flow as a process of consecutive jumps of a molecular-kinetic segment under the influence of thermal fluctuations. The role of shear conditions is seen in reducing the potential barrier (increasing the probability of the jump) and in directing the flow alone the stress vector. Therefore the process of viscous-elastic flow is very similar to creep and relaxation of the polymeric materials tested under the temperatures below Tg or below the melting point. Thermal fluctuation patterns of failure and deformation of plastics have been widely studied and discussed elsewhere.[12–15] The mechanical properties of plastics could be predicted, if the behaviour of polymers under stress, the physical constants characterising this behaviour and the relationship between constants and the composition and structure of the material would be known. According to the theory, deformation and fracture develop in a stressed body not as instantaneous acts, but each takes place in time as a result of thermal fluctuations. Fracture, i.e. the splitting of the body into parts involves the scission of the chemical bonds in the main chain, whereas deformation and stress relaxation can occur by means of scissions and subsequent regeneration of the intermolecular bonds only. These processes could be considered from two viewpoints—kinetic and energetic. Below are given the kinetic laws of deformation and failure, because the kinetic equations of failure and deformation are very similar to Eqs. (1) and (2). The similarity could be found not only by the appearance of the equations, but also by the physical significance of the constants and by the similarity of deformation and viscous-elastic flow mechanisms. The processes of fracture and deformation are described by very similar formulas. The mechanical durability of solids has been determined from the following equation:

$$\tau = \tau_0 * \exp\{[U_0 - \gamma\sigma)/RT] * (1 - T/T_p)\}; \qquad (3)$$

The time to appearance of critical deformation (creep or softening) is described by the formula:

$$Q = Q_0 * \exp\{[U'_0 - \gamma\sigma)/RT] * (1 - T/T'_p)\}; \qquad (4)$$

where:

σ	is the acting stress;
T	is the absolute temperature, K;
U_0	is the activation energy of the chemical bonds failure;
U'_0	is the energy required for the displacement of a segment consisting of "n" units;
γ and γ'	are coefficients characterising the effectiveness of the acting stress (i.e. to what extent the mechanical field reduces the energy of the bonds);
τ_0 and Q_0	are constants characterising period of vibrations of the effective molecular-kinetic units;
T_p and T'_p	are the critical temperatures of failure or softening (deformation), at which the process takes place under any stress during the minimum time—τ_0 or Q_0, respectively.

It is well known that $U_0 < U'_0$, although U_0 involves scission of chemical, and U'_0 is related to intermolecular (weaker) bonds. When a body is stressed, processes of deformation (softening) and failure develop at different rates. We find the process whose completion requires the least time. Since temperature and stress vary in their effect on τ and Q, they determine whether failure will take place ($\tau < Q$), i.e. the material is glass-like and brittle, or whether considerable deformation will occur ($Q > \tau$), i.e. the material is in a leathery—elastic state. Formulas (3) and (4) give expressions for the limiting stresses and temperatures which the material is capable of bearing under static loading for a given period of time "t".

Equations (3) and (4) are valid not only for simple types of loading (under static tension), but also for more complex stressed states.[14–18] The appearance of equations varies, but the basic physicochemical constants are retained. For instance, in simple compression and even in penetration (the Vicat "needle" test) formula (4) holds good and the value of U_0' coincides with U_0' in tension.

Several more complicated equations have been developed for quasi-brittle failure of welded joints,[19–20] for abrasion wear of plastics[18] the rate of wear is given by the expression:

$$I = I_0 * \exp\{[-(U_0 - \eta\gamma P^{1/3})/RT] * (1 - T/T_p)\}; \qquad (5)$$

where:

P is the normal load;
η is the coefficient of friction.

All of the equations presented are valid on the condition that the constants included in each of them do not depend on stress or temperature. However, if the structure of the material is changed as a result of orientation, crystallization, etc., the experimental data usually do not obey Eqs. (3–5). The results obtained for the materials with variable structure have been described by several similar semi-empirical equations of the type:

$$\tau = A * \exp[(U/RT) - a\sigma]; \qquad (6)$$

$$\tau = B * \sigma^{-6} * \exp(U/RT); \qquad (7)$$

$$I = C * P^{\nu} * \exp(-U/RT); \qquad (8)$$

where:

τ is the critical time of failure or deformation; $b > 1$, and $\nu > 1$.

EXPERIMENTAL

Experimental data on melt viscosity of six industrial Polypropylenes and Polystyrene resin have been obtained by means of Instron capillary rheometer or from the literature. Variation of melt viscosity has been determined over a wide range of shear rates (from 2.25 sec^{-1} to 3000 sec^{-1}) and over a temperature interval spans approximately 120°C. Results of measuring the apparent melt viscosity using a die with $L/R = 80$, and also corrected data have been examined for the validity of the equations similar to Eqs. (1) and (2).

The first problem is to find a coordinate system, on which the dependence of η on $\dot{\gamma}$ and on T are linear for different resins tested. It has been found that the experimental points fall on straight lines with the coordinates: $\log \eta$ vs. $(\dot{\gamma})^{1/6}$ for Polypropylene melts tested (Figure 1) and $\log \eta$ vs. $(\dot{\gamma})^{1/7}$ for Polystyrene melt (see Figure 2). Each straight line is related to a constant test temperature. The

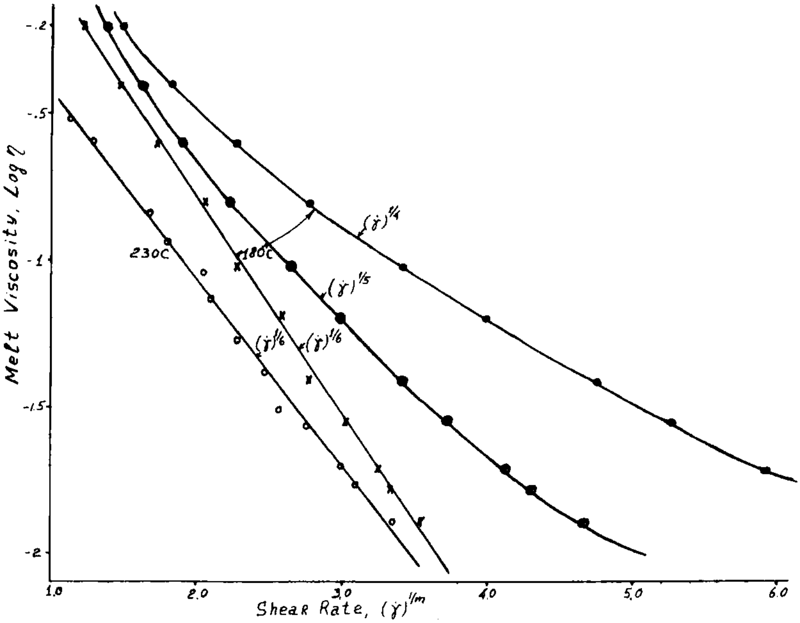

FIGURE 1 Dependence of Polypropylene melt viscosity on shear rate for Novamont 243.4, at different temperatures.

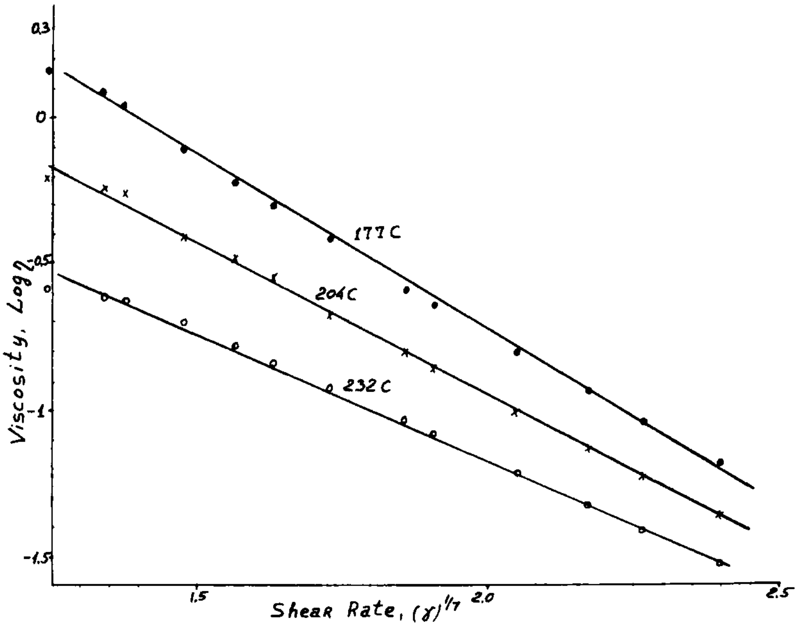

FIGURE 2 Dependence of Polystyrene (685 D) melt viscosity on shear rate at different temperatures.

isotherms are convergent and the point of their intersection makes the shear rate limit on applicability of the proposed equation (see Figure 3).

The final form of the equation for the dependence of melt viscosity on temperature and shear rate could be determined after replotting the experimental data on coordinater $\log \eta$ vs. $1/T$, (see Figure 4). Since the points, related to a constant shear rate, fall on convergent straight lines with these coordinates too, it is possible to calculate the values of E from the slopes of the straight lines (see Figure 5 and 6). The point of convergence for the straight lines on $\log \eta$ vs. $1/T$, is not equal to $1/T = 0$, for all Polypropylene and Polystyrene resins tested. It means that Eq. (1) can not be used in the original form. The point of straight lines intersection forms the temperature limit on applicability of the proposed equation and makes it necessary to introduce a new constant into the equation for

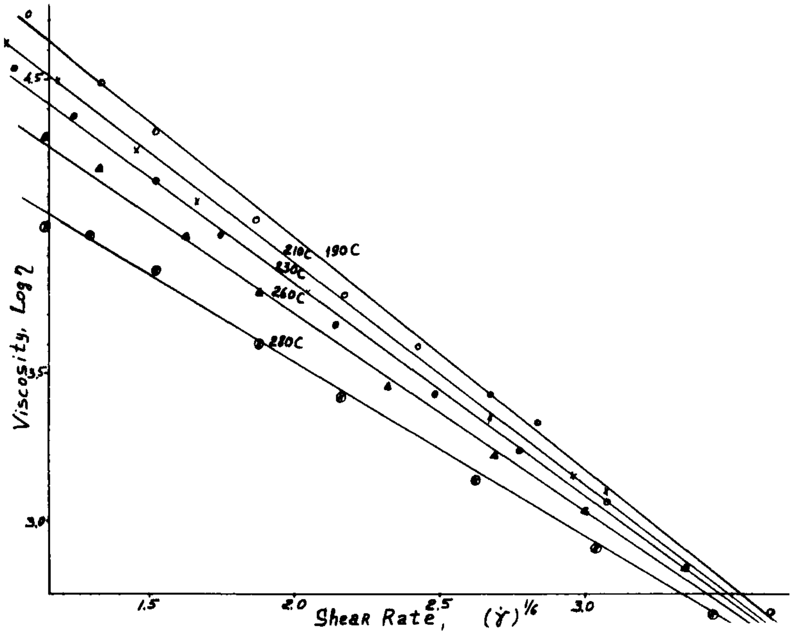

FIGURE 3 Dependence of Polypropylene (Shell LF 6100) melt viscosity on shear rate at different temperatures.

the dependence of polymer melt viscosity on temperature and shear rate.

Therefore, the equation for Polypropylene and Polystyrene melts should be written in the final form as follows:

$$\eta = A * \exp\{[(E_0\dot{\gamma} - a(\dot{\gamma})^{1/m})/RT] * (1 - T/T_p)\}; \tag{9}$$

where:

T_p is the temperature limit of applicability of Eq. (9).

The validity of Eq. (2) for Polypropylene and Polystyrene melts has also been examined. The dependence of melt viscosity on shear stress is linear with the coordinates $\log \eta$ vs. $(\tau)^{1/2}$ for all the resins tested so far including Polyethylene resins. It means that Eq. (2) could be used for all the polymer melts without any changes. (See Figures 7 and 8).

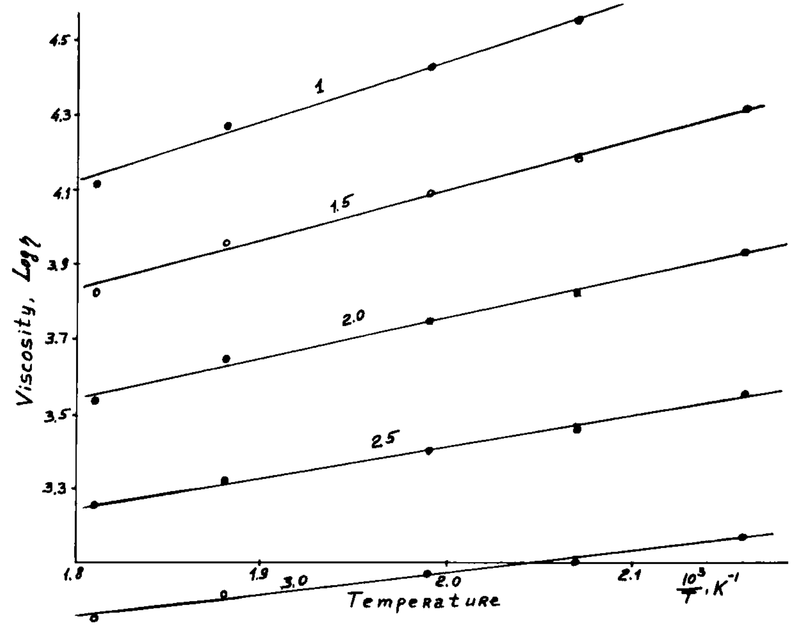

FIGURE 4 Dependence of Polypropylene (Arco 8670) melt viscosity on temperature at different shear rates.

After obtaining the basic idea concerning the type of equation could be expected for the dependence of melt viscosity on temperature and shear rate and on temperature and shear stress, the experimental data have been introduced into the computer. The best set of constants for each equation and for each resin have been determined. Statistical analysis for each equation and for each constant have been performed.

RESULTS AND DISCUSSION

The constants of Eqs. (2) and (9) calculated by the computer are presented in Tables I; II. The results confirm that Eq. (2) is valid with very good precision for all the polymer melts tested so far (coefficient of determination R^2 is between 0.95 and 0.99). The

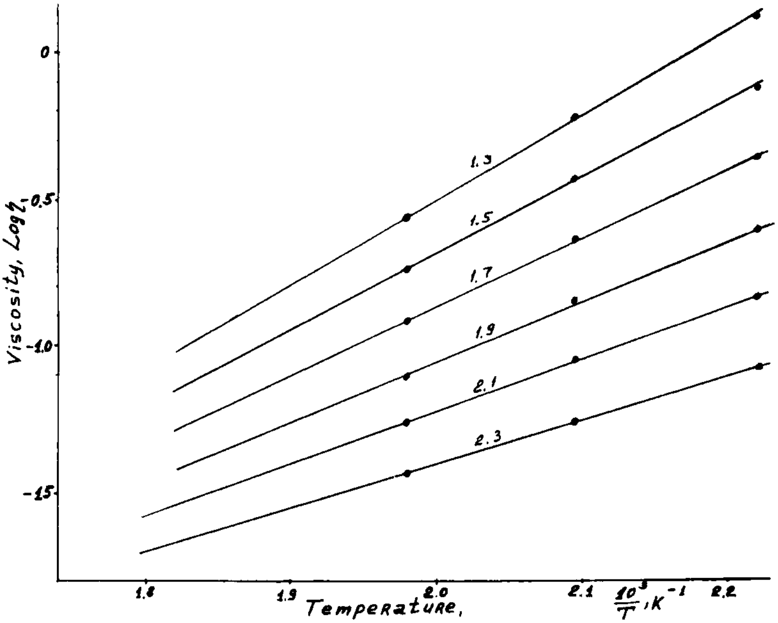

FIGURE 5 Dependence of Polystyrene (685 D) melt viscosity on temperature at different shear rates.

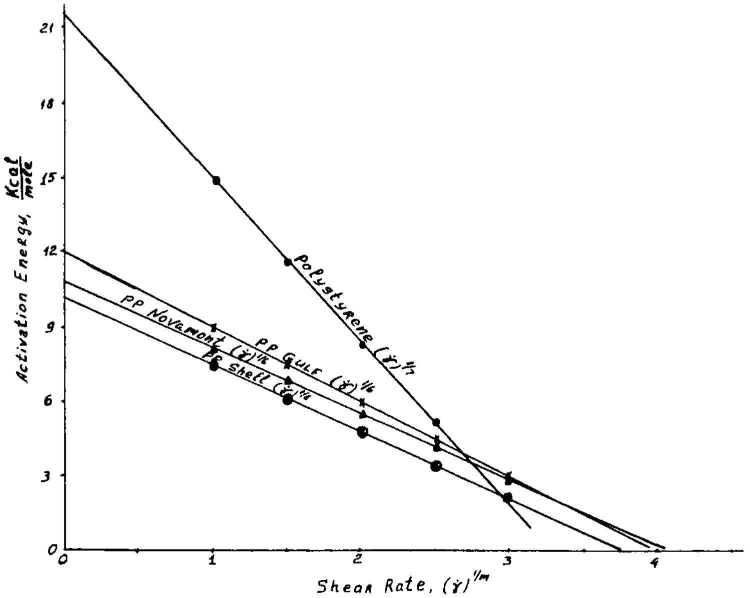

FIGURE 6 Dependence of the Activation Energy for different Polypropylene and Polystryene melts on shear rate.

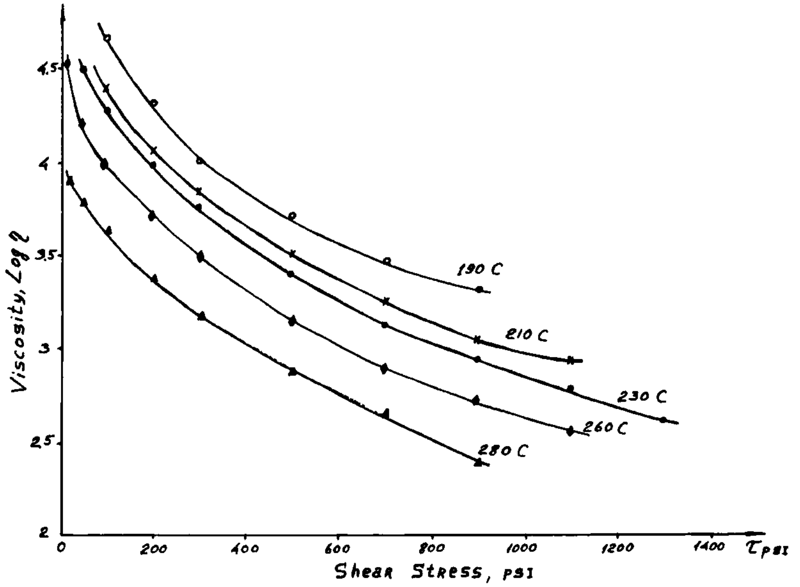

FIGURE 7 Dependence of Polypropylene (Eastman 612F) melt viscosity on shear stress at different temperatures.

form of the equation is exactly the same for different polymer melts (see Figure 9):

$$\eta = B * \exp[(E/RT) - b * (\tau)^{1/2}]; \qquad (2)$$

It means that Eq. (2) can be used to calculate the polymer melt viscosity at any point of interest for the processing purposes and also for comparison of different resins intended for processing on the same equipment. The values of constant E_τ determined from the experimental data for different PE, PP, and PS resins (see Table II) coincide with the activation energy of viscous-elastic flow for corresponding polymer melts published in literature (see Table II).

According to the statistical analysis Eq. (9) which contains an additional constant *Tp*, compare to Eq. (1), is valid for all Polypropylene resins and Polystyrene melts tested. Therefore equation (1) could be considered as a special case of Eq. (9).

According to the data of Tables (I) and (II), the activation energy

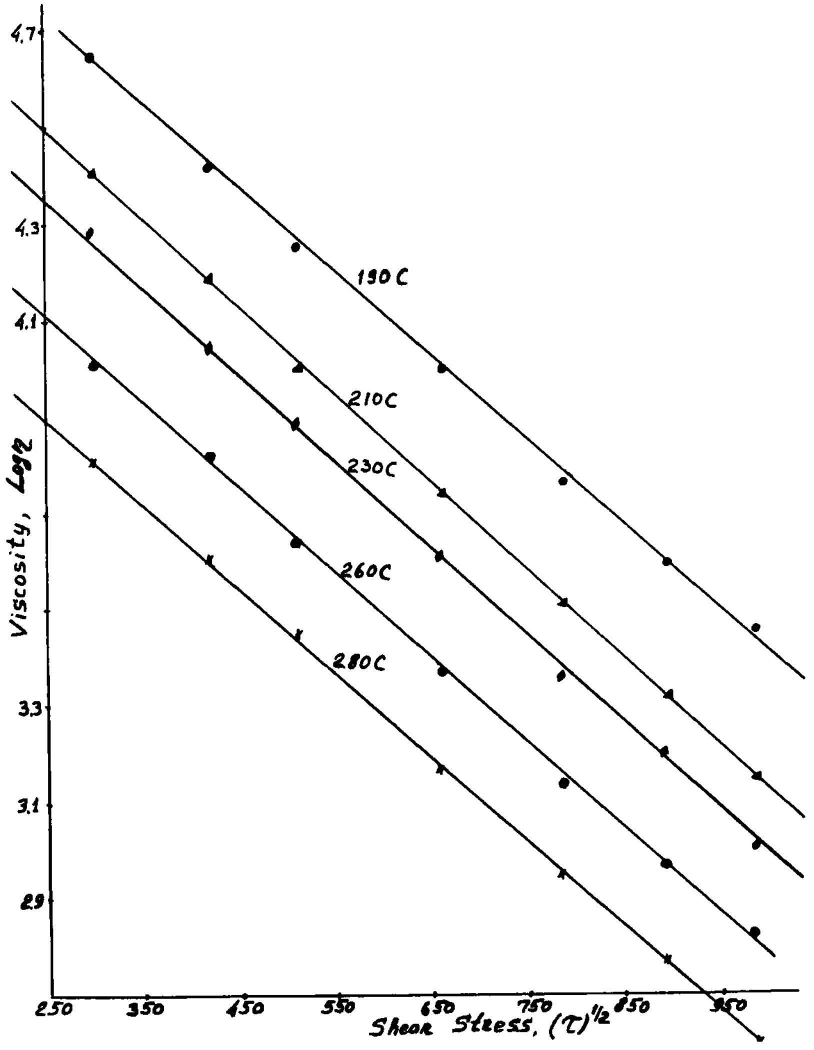

FIGURE 8 Dependence of Polypropylene (Arco 8670) melt viscosity on shear stress at different temperatures.

TABLE I

Constants of Eq. (9).

Polymer	Log B	$E_0\dot{\gamma}$, Kcal/ mole.	α	1000/Tp, K^{-1}	R-sq	E_0/α
PP Shell	2.444	10.34	2.662	0.7638	0.992	3.9
PP Nova	2.336	10.83	2.606	0.8186	0.993	4.15
PP ARCO	2.425	10.225	2.48	0.84	0.985	4.12
PP Gulf	2.372	12.15	3.0	0.96	0.991	4.05
PS 685 D	−2.303	21.6	6.512	1.373	0.997	3.32

of viscous-elastic flow in Eqs. (2) and (9) are of the same magnitude. The validity of Eqs. (2) and (9) for the same set of experimental data opens up the opportunity to establish the physical significance of each equation and the constants in each of them. It also means that more reliable equation could be found for the dependence of shear rate on the temperature and shear stress.

Similarity of the equations established for Polymer Melt Viscosity in shearing flow and the equations describing the deformation durability of polymers in leathery-elastic state indicates that the mechanisms of both processes could also be similar. It suggests that viscous-elastic flow occurs as a result of breaking down of all intermolecular bonds of the effective molecular segment with its

TABLE II

Constants of Eq. (2).

Polymer	Log A	E_τ, Kcal/ mole	d	R-sq
PP Shell LF 6100	0.176	10.88	0.0043	0.984
PP Nova. 243.4		11.725		
PP Arco 8670	0.289	10.37	0.0081	0.986
PP East. 612F	−0.0312	11.2	0.147	0.976
PP Gulf	0.356	12	0.179	0.964
PP BASF Nov. 1320H	0.30	9.83	0.0034	
POLYSTYRENE 685D	−10.8	25.3	1.0736	0.983

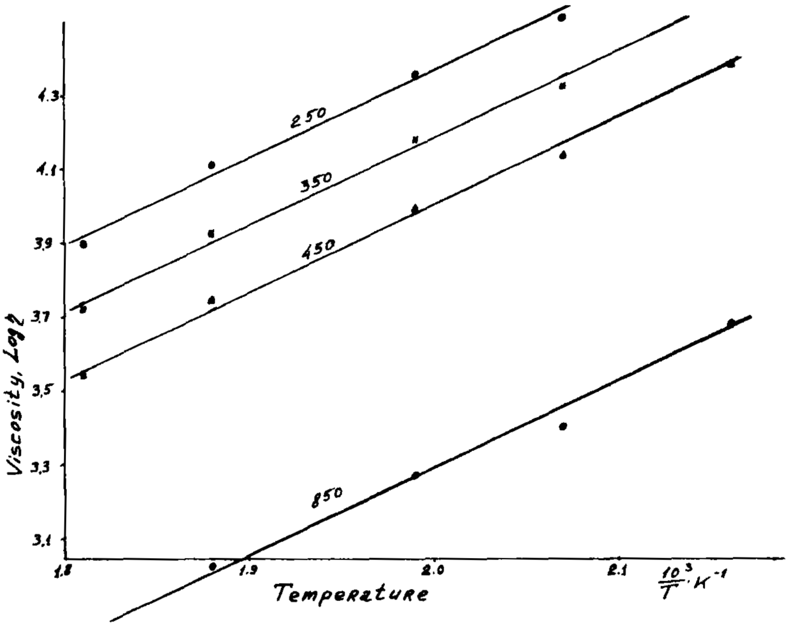

FIGURE 9 Dependence of Polypropylene (Arco 8670) melt viscosity on temperature at different shear stresses.

neighbours, and subsequent reistablishment of the bonds in a new location. Shear stress is considered as an additional factor accelerating and directing the flow but the thermal fluctuations (not the average molecular configuration established in the polymeric fluid. It means that Eqs. (2) and (9) should have the same activation energy (see Tables I, II). The mechanism of viscous-elastic flow

TABLE III

Values of constants $E_0\dot{\gamma}$ and E_τ for various polymers.

Polymer	$E_0\dot{\gamma}$, Kcal/ mole,	E_τ, Kcal/ mole	Literature, E_τ
Polypropylene	10.7	11	11
Polystyrene	21.6	25.3	23
LDPE	7–8.5	10–12	12
LLDPE	5–6	6–8	7
HDPE	4–5	4.5–6	6

described above is exactly the same as the mechanism of stress relaxation or leathery–elastic deformation in amorphous polymers under the temperatures below Tg but above the point of brittleness. Very high activation energies of viscous elastic flow indicate that polymer melt flow is a cooperative process. The activation energy is a function of the number of units in the effective molecular segment and the energy of unit intermolecular bonds:

$$E_0 = E_{0i} * n; \tag{10}$$

where:

E_{0i} is the unit activation energy of breaking the intermolecular bonds;

n is the number of molecular units in the effective molecular-kinetic segment.

Eq. (10) relates the average values of activation energy for non-Newtonian viscous-elastic flow to the molecular characteristics of the polymeric fluid in question. Parameter E_{0i} is the cohesion energy of the polymer, and n is the number of monomer units in the effective molecular segment participated in the elementary jump.

Both components on the right side of Eq. (10) are basically known or could be determined from independent experiments. Therefore the activation energy of viscous-elastic flow could be estimated even before the experimental results have been obtained. According to Eq. (9) the effective activation energy of viscous-elastic flow can be expressed as follows:

$$E = E_0\dot{\gamma} - a(\dot{\gamma})^{1/m}; \quad \text{or} \quad E_0 - a(\dot{\gamma}_{cr})^{1/m} = 0; \qquad E_0\dot{\gamma} = a(\dot{\gamma}_{cr})^{1/m}; \tag{11}$$

where:

$\dot{\gamma}_{cr}$ is the convergence point for straight lines on coordinates $\log \eta$ vs. $(\dot{\gamma})^{1/m}$, where melt viscosity does not depend on temperature.

Consequently two separate equations have been found to describe the dependence of melt viscosity on temperature and shear rate or on temperature and shear stress. Equating the right sides of these two equations gives a correlation between τ, $\dot{\gamma}$, and T:

$$(\dot{\gamma})^{1/m} \cdot \left(\frac{1}{T} - \frac{1}{T_p}\right) = C + \beta'(\tau)^{1/2}; \tag{12}$$

where:

C and β' are constants

Eq. (12) contains temperature dependence of shear rate and the values of constants do not vary under a wide range of temperatures and shear conditions. The dependence of shear rate on shear stress is presented on Figure 10 for Polypropylene resin (Arco 8670). According to the results shown on Figure 10, the experimental data fall on convergent straight lines related to constant temperatures of experiment. Therefore even with more complicated dependence of polymer melt viscosity on shear rate and temperature, the dependence of shear rate on shear stress and temperature remains valid (see Figure 11).

The results obtained for the dependence of non-Newtonian melt viscosity of different polymers on shear conditions and temperature indicate that reliable semi-empirical equations for polymer melt

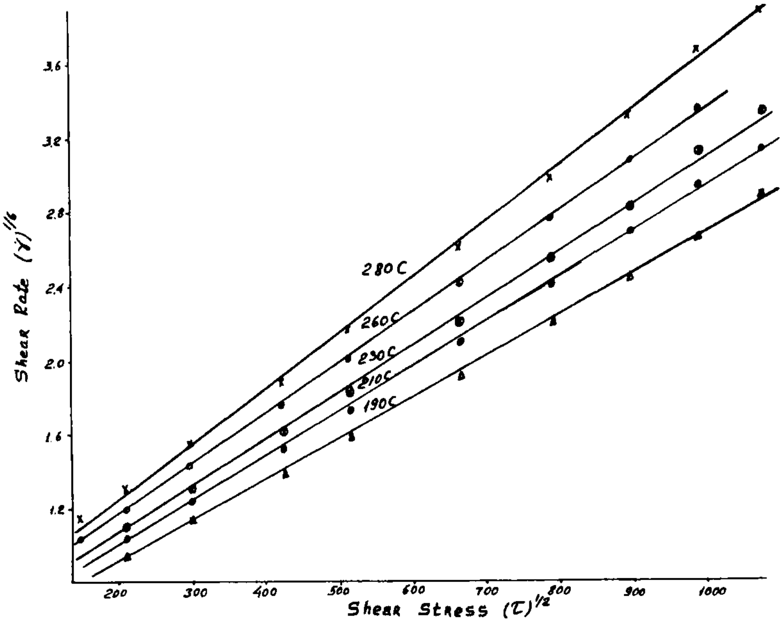

FIGURE 10 Dependence of Polypropylene (Arco 8670) shear rate on shear stress at different temperatures.

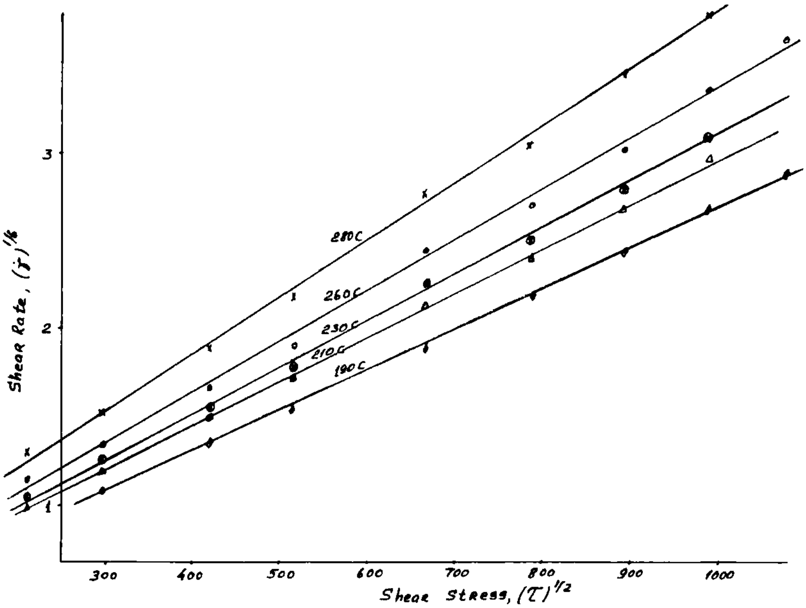

FIGURE 11 Dependence of Polypropylene (Shell LF 1600) shear rate on shear stress at different temperatures

viscosity have been derived. The correlation between the experimental and calculated data is extremely high and the equations are valid in a wide range of shear and temperature conditions (see Figure 12). Basic similarity of the mechanisms of leathery-elastic deformation and viscous-elastic melt flow has also been established. Such similarity will allow us to determine the physical significance of the constants in proposed equations for polymer melt viscosity in shearing flow. This is the second part of the problem in developing the equations having clear physical significance and being in good quantitative agreement with experiment.

CONCLUSIONS

1. The validity of thermoactivation equations previously derived for Polyethylene melt viscosity in shearing flow has been confirmed for Polypropylene, and Polystyrene melts.

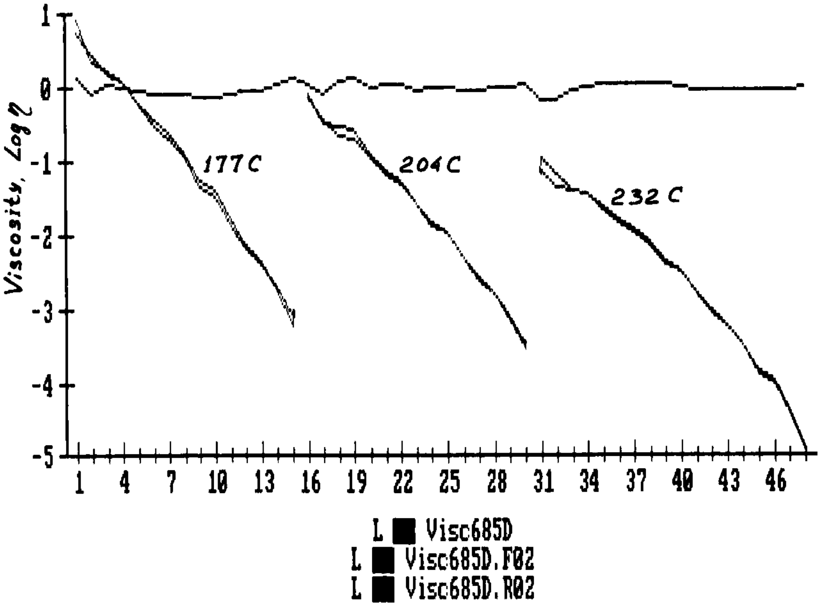

FIGURE 12 Correlation of the experimental and calculated data for Polystyrene (685 D) melt viscosity at different constant temperatures and the residual values between the experimental and calculated data for each point.

2. Eq. (2) is valid for all the materials tested and the dependence of log η on (τ) is linear for all melts under a wide range of test temperatures and shear stresses. It means that General Equation has been developed for the dependence of melt viscosity on temperature and shear stress.

3. Eq. (9) which contains the additional constant T_p, compare to Eq. (1), is valid for Polypropylene and Polystyrene melts tested. Therefore Eq. (1) could be considered as a special case of Eq. (9) which describes the experimental data for the dependence of polymer melt viscosity on temperature and shear rate.

4. Joint solution of the equations $\eta = f(T, \dot{\gamma})$ and $\eta = F(T, \tau)$ gives an equation for the dependence of $\dot{\gamma}$ on τ and T. Correlation between shear stress, temperature and shear rate could be obtained from the experimental data or by joint solution of Eq. (9) and (2). The constants of Eq. (12) do not change the values in a wide range of temperatures and shear conditions.

5. Similarity of Eqs. (2) and (9) with the equations describing the deformation durability of polymers in leathery–elastic state indicates that the mechanisms of both processes are similar.

6. The results suggest that viscous-elastic flow occurs as a result of breaking down all the intermolecular bonds of the effective molecular segment with its neighbours, and subsequent reistablishment of the bonds in a new location.

7. The activation energy of viscous-elastic flow of polymer melts could be presented as a function of the number of units in effective molecular segment and the energy of unit interaction (Eq. 10). Both components on right side of Eq. (10) could be determined from independent experiments.

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