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Mathematical Models of Polymer Melt Viscosity in Shearing Flow 1. Polyethylene Melts

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The dependence of polymer melt viscosity on temperature, shear rate and shear stress has been examined. The theory of absolute reaction rates and the influence of a potential gradient on the kinetics of heat-activated processes have served as the basis for this study. Experimental data on LDPE, LLDPE, HDPE and Blends have been used to derive semi-empirical equations correlating PE melt viscosity with temperature and shear rate, or temperature and shear stress.

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. Correlation coefficients obtained are very high.

Joint solution of the equations to $\eta = f(T; \dot{\gamma})$ and $\eta = F(T; \tau)$ gives an equation $\dot{\gamma} = \phi(\tau; T)$ similar to power law equation incorporating the dependence of shear rate not only on shear stress but also on temperature. The activation energy of melt flow for various PE resins has been determined from the equations proposed for the conditions of $\dot{\gamma} = \text{const}$, and $\tau = \text{const}$. The values obtained for $E_{0\dot{\gamma}}$ and E_{τ} are in good agreement with the literature data.

Polymer melt viscosity in shearing flow is one of the most important properties for processing of plastics. Therefore, the dependence of melt viscosity on such parameters as temperature, shear rate and shear stress has been subjected to intensive experimental study.

Because of the great practical and theoretical importance of the problem, several theories of non-Newtonian viscosity in polymeric systems have been developed. 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.^{1,2} Structural theories of non-Newtonian flow consider reversible breakdown-recovery of the polymer structure.^{3,4} Hydrodynamic theories describe variation of molecular configurations under stress and the influence of such variation on melt flow.⁵ However, an equation for polymer melt viscosity in shearing flow having clear physical significance and being in good quantitative agreement with experiment, has not yet been found.⁶

Temperature dependence of polymer melt viscosity is usually considered separately from stress and rate dependence. The study of this dependence is important to the understanding of the mechanism of melt flow and to the development of optimum polymer processing conditions. Two basic concepts have been created.

One of them is related to the theory of absolute reaction rates; the other is based on consideration of free-volume.^{7,8} Comprehensive reviews of various theories have been given in several books on polymer melt rheology.^{6,9,10}

The goal of this study was to develop semi-empirical equations for the dependence of polymer melt viscosity on temperature and shear rate and on temperature and shear stress. The approach was based on the theory of absolute reaction rates, on the theoretical consideration of heat activated processes and on the experimental data.

THEORETICAL AND PRACTICAL APPROACHES

According to Eyring theory of absolute reaction rates, the dependence of liquid viscosity on temperature can be described by the following equation:

$$\eta = \left[\frac{hN}{V} \exp\left(-\frac{\Delta S^*}{R}\right) \right] \exp \frac{\Delta H^*}{RT}; \quad (1)$$

where h is Planck's constant,

R is the gas constant,

N is the Avogadro number,

V is the molar volume,

ΔS^* and ΔH^* are respectively the entropy and heat of activation of viscous flow

T is the absolute temperature, K.

Entropy does not depend on temperature, and molar volume varies only slightly with temperature, therefore Eq. (1) can be approximated as follows:

$$\eta = A \exp\left(\frac{E}{RT}\right); \quad (2)$$

where E is the activation energy of flow,

A is constant.

Eq. (2) was obtained by DeGusman (1913) and Arrhenius (1916) from experimental data and was derived theoretically by Frenkel (1925) and by Andrade (1930). Experimental data on melt flow of a wide variety of polymers could be described by Eq. (2). However, the activation energy (E) of the flow process depends on shear rate and this dependence is unknown. Viscosity measurements are carried out under the gradient of the mechanical potential. Therefore, some uncertainty always exists in applying Eq. (2). A theoretical approach to the problem of the influence of a potential gradient on the kinetics of heat activated processes is given in the article published by A. Tobolsky, R. Powell and H. Eyring.¹¹ According to the theory, visco-elastic flow is a process of consecutive jumps of the molecular-kinetic units from one equilibrium position to another. Deformation of the energy barrier under influence of a potential gradient (see Figure 1) is also considered in deriving the dependence of melt viscosity on shear rate.

Frenkel-Eyring theory has been applied to obtain an equation which correlates non-Newtonian viscosity with temperature and shear rate. The theory assumes that a molecular-kinetic unit will jump when it obtains the energy high enough to overcome the potential barrier E . The time between jumps can be calculated by the equation derived from the theory of absolute reaction rates.

$$t = t_0 \exp\left(\frac{E}{RT}\right); \quad (3)$$

where t is the time between jumps,

t_0 is the period of vibrations of atoms in the molecule and is equal to 10^{-13} sec.

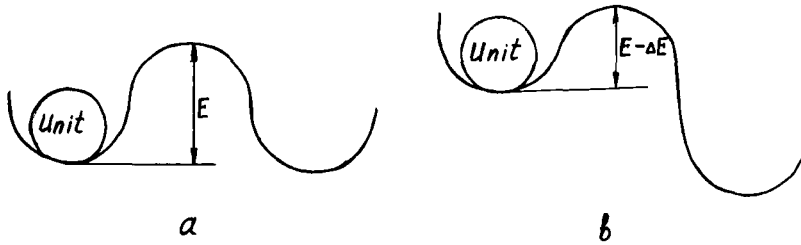


FIGURE 1 Potential energy barrier: a. without a potential gradient (E). b. with a potential gradient ($E - \Delta E$).

E is the activation (energy) barrier,
 RT is the energy of thermal motion.

A similar equation has been written to calculate the number of units which will overcome the barrier and jump.

$$U = U_0 \exp\left(-\frac{E}{RT}\right); \quad (4)$$

where U is the number of units which can overcome the potential energy barrier, E
 U_0 is the total number of units in the system.

The barrier is uniform in all directions without the potential gradient (Figure 1a) and the U units which have enough energy will jump in all directions with the same probability. This means that no net mass transfer will occur.

If the potential gradient is applied (Figure 1b) the energy barrier is deformed in such a manner that barrier is lower in the direction of the potential gradient and higher in the opposite direction. Thus, more jumps, will be performed over a lower barrier ($E - \Delta E$) than in the opposite direction (according to Eqs. (3) and (4)). In this case mass transfer will appear. The degree of the energy barrier deformation depends on the magnitude of the potential gradient.

Since measurements of liquid viscosity are carried out under the influence of a mechanical gradient, the energy barrier is deformed and reduced in the direction of this gradient:

$$E = \{E_0 - f(\sigma, T)\} \geq 0; \quad (5)$$

where E is the effective activation of energy of flow,

E_0 -is energy barrier without the influence of a potential gradient,
 $f(\sigma, T)$ is an unknown function of the mechanical stress and temperature.

Consequently, Eq. (2) can be rewritten in the form:

$$\eta = A \exp\left[\frac{E_0 - f(\sigma, T)}{RT}\right]; \tag{6}$$

According to Eq. (6), the melt viscosity does not depend on temperature and shear conditions, if the effective activation energy (E) has been reduced to 0 by the mechanical stress applied. Several unsuccessful attempts to determine $f(\sigma, T)$ in Eq. (6) have been undertaken. Eyring has derived the following equation based on the theory:¹¹

$$\eta = A \exp\left(\frac{E_0}{kT}\right)(Z/shZ); \tag{7}$$

where A is a constant depending on the polymer structure,

$$Z = \frac{w\tau}{kT}$$

τ is the shear stress

w is the effective volume of the kinetic unit.

The term (z/shZ) has been revealed by G. Bartenev for normal experimental conditions and an equation similar to Eq. (6) has been derived.¹²

$$\eta = A \exp\left(\frac{E_0 - \kappa\omega\tau}{kT}\right); \tag{8}$$

where κ is a parameter depending on shear stress (τ), ($\tau \rightarrow 0, \kappa = 0$;
 $\tau \rightarrow \infty, \kappa = 1$)

Eq. (8) does not describe the polymer melt viscosity as a function of shear stress because it is well known that the activation energy of viscous flow does not depend on shear stress. Based on this experimental fact and Frenkel–Eyring theory, Bartenev has obtained the

following equation:¹³

$$\eta = c(M/M_{cr})^n \exp\left(\frac{E}{kT} - \alpha\tau\right); \quad (9)$$

where M is the molecular mass of the polymer,
 M_{cr} is the minimum molecular mass of the polymer causing
 non-Newtonian melt viscosity,
 k is the Boltzmann constant,
 C , n and α are constants.

Eq. (9) to be valid requires a linear dependence of $\log \eta$ on shear stress, however the experimental data show that the linear relation between $\log \eta$ and τ may be assumed only in a narrow range of shear stresses (see Figure 2). Consequently, Eq. (9) could not find a broad application.

Analysis of the theoretical and semi-empirical equations developed so far indicates that primary emphasis has been given to the

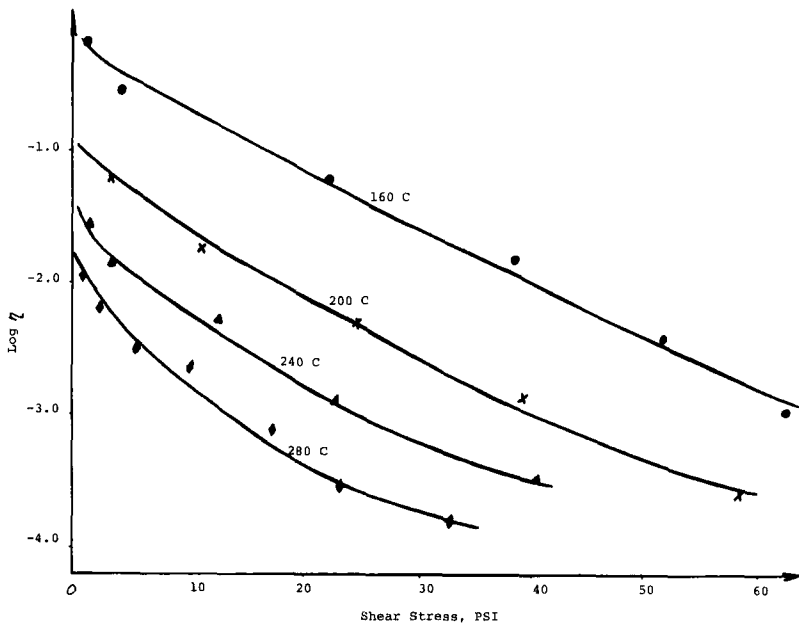


FIGURE 2 Dependence of melt viscosity on shear stress for LLDPE Dow 2047 at different temperatures. ($\log \eta$ vs. τ)

theoretical aspects of the problem. Experimental data for melt viscosity of different polymers obtained under a wide range of shearing conditions have not been examined to derive a general equation containing constants which have different values depending on the molecular structure of the specific polymer. The idea of the present study has been to examine the experimental data and to find a semi-empirical equation (in the form similar to Eq. (6)) for the dependence of polymer melt viscosity on temperature and shear rate, and also on temperature and shear stress. Joint solution of the equations $\eta = f(T, \dot{\gamma})$ and $\eta = F(T, \tau)$ gives an equation for $\dot{\gamma} = \phi(T, \tau)$.

The first problem was to find a coordinate system, on which the dependence of η on $\dot{\gamma}$ and on τ are linear. Examination of the curves η vs $\dot{\gamma}$ and η vs τ shows that curves are concave; however, $\log \eta$ vs. $\log \dot{\gamma}$ are convex (See Figure 3). This fact indicates that the coordinate system exists on which the dependence will be relatively

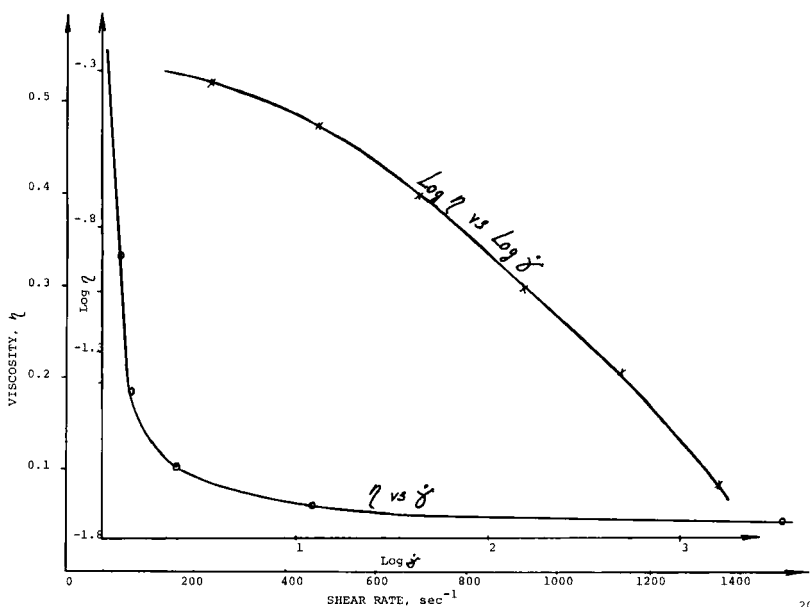


FIGURE 3 Dependence of melt viscosity on shear rate for Dow 592 LDPE at 190°C

linear. Finally, Eq. (6) was written in the following form:

$$\eta = A \exp\left(\frac{E_{0\dot{\gamma}} - \alpha(\dot{\gamma})^{1/m}}{RT}\right); \quad (10)$$

where $m = 4; 5; 6$ or 7 (for $m < 4$ the dependence of $\log \eta$ vs $(\dot{\gamma})^{1/m}$ is not linear (see Figure 4)).

Eq. (10) is very similar to Eq. (6) because of the power law equation:¹⁴

$$\tau = K\dot{\gamma}^n; \quad (11)$$

where $n < 1$ for pseudo plastic fluids.

Dependence of η on T and τ was based on Eq. (2) and on the fact that the influence of τ on the activation energy of viscous flow depends on temperature. Therefore the dependence of η on τ and T has been proposed as follows:

$$\eta = c \exp\left(\frac{E_{\tau} - d \cdot T \cdot (\tau)^S}{RT}\right) = C \exp\left(\frac{E_{\tau}}{RT} - d'(\tau)^S\right); \quad (12)$$

where c, d, d' and S are constants.

Eq. (12) is very similar to Eq. (9) but contains coefficient "S" and

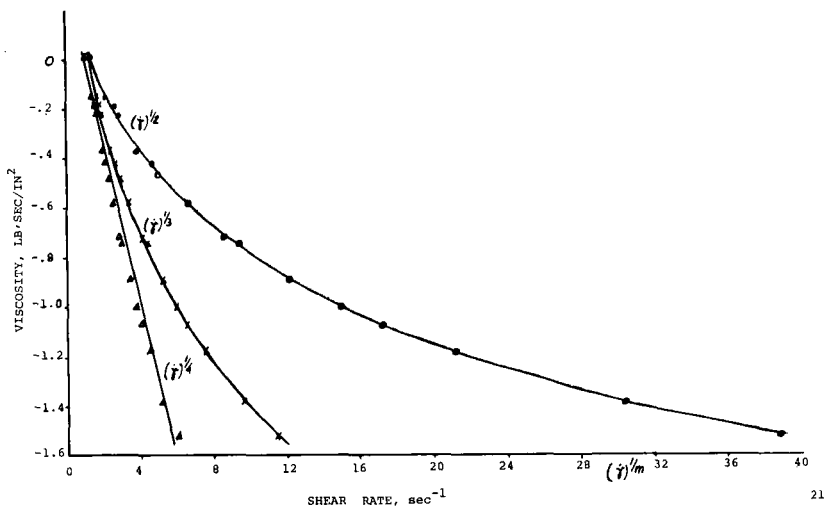


FIGURE 4 Dependence of viscosity on shear rate for low density polyethylene Dow 682 at 190°C

therefore has more flexibility in describing the experimental data for various systems.

Experimental data on melt viscosity of 12 different Polyethylene (PE) resins (LD, LLD and HD) have been obtained by means of Instron capillary rheometer. Variation of the 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 of approximately 120 C. Results of measuring the apparent viscosity using a die with $L/R = 80$ and also corrected data have been introduced into the computer to examine the validity of Eqs (10) and (12).

The computer has determined the best set of constants for each m and has calculated the correlation coefficient between the experimental and calculated data for each PE resin and m in Eq. (10). The applicability of Eq. (12) has been examined for $S = 1/2$ only.

RESULTS AND DISCUSSION

Results obtained from the computer for Eq. (10) are presented in Table I. Analysis of the data shows that correlation coefficient (R)

TABLE I
 Constants of Eq. (10) and correlation for different PE resins and various $m(4, 5, 6,$
 and 7)

Material	m	Log A	$E_{0v} \frac{\text{Kcal}}{\text{mole}}$	$\alpha \frac{\text{Kcal}}{\text{mole} \cdot \text{Sec}^{-1/m}}$	R_m
Dow 682	(4)	-3.14363	7.157	0.62293	0.92001
	(5)	-3.16768	7.7149	1.0024	0.9061
	(6)	-3.1849	8.2547	1.4155	0.8953
	(7)	-3.1977	8.783	1.8498	0.88687
Plexar 2109 Chemplex	(4)	-3.0049	6.71346	0.659	0.91392
	(5)	-2.98419	7.17575	1.02065	0.89978
	(6)	-2.96719	7.64366	1.43884	0.8892
75.7% 682 18.8% 61500184	(7)	-2.95356	8.11757	1.8781	0.88047
	(4)	-2.71018	6.3752	0.6442	0.99025
	(5)	-2.73746	6.9318	1.0243	0.99459
Dow 0.97	(6)	-2.75636	7.46826	1.43614	0.99659
	(7)	-2.77017	7.9924	1.8681	0.99756
	(4)	-1.75156	4.823	0.6609	0.99535
	(5)	-1.81625	5.415	1.0219	0.99789
	(6)	-1.86129	5.962	1.407	0.9988
	(7)	-1.89427	6.481	1.8077	0.999

TABLE I (contd)

Material	<i>m</i>	Log <i>A</i>	$E_{0\dot{\gamma}}$ $\frac{\text{Kcal}}{\text{mole}}$	$\alpha \frac{\text{Kcal}}{\text{mole} \cdot \text{Sec}^{-1/m}}$	R_m
Dow 748	(4)	-4.44266	8.45284	0.4581	0.9958
	(5)	-4.44266	8.8265	0.739	0.9974
	(6)	-4.44266	9.201	1.046	0.99768
	(7)	-4.44266	9.575	1.37	0.99748
Dow 2045	(4)	-2.44056	5.9896	0.6814	0.96366
	(5)	-2.44841	6.390	1.0106	0.95797
	(6)	-2.45416	6.796	1.3564	0.95378
	(7)	-2.45851	7.1934	1.713	0.95095
92% TR-130 8% MB	(4)	-1.99256	5.364	0.71866	0.95215
	(5)	-2.00963	5.9159	1.124	0.9403
	(6)	-2.02113	6.454	1.55964	0.93116
	(7)	-2.02937	6.984	2.01422	0.92404
Reclaim	(4)	-2.96738	6.8945	0.6856	0.91953
	(5)	-2.9934	7.51	1.1043	0.90489
	(6)	-3.01097	8.1046	1.561	0.8935
	(7)	-3.02357	8.68695	2.041	0.88458
Dow 0.32	(4)	-2.83	6.0	0.4687	
Dow 592	(4)	-3.6465	7.87	0.588	0.9372
	(5)	-3.6465	9.36	0.951	0.9273
	(6)	-3.6465	8.847	1.3486	0.9196
	(7)	-3.6365	9.33	1.768	0.9136
GPX-1	(4)	-2.4159	5.777	0.552	0.9542
	(5)	-2.4292	6.074	0.793	0.9489
	(6)	-2.2385	6.36	1.042	0.945
	(7)	-2.445	6.64	1.295	0.9422
Surlyn 16523B	(4)	-4.46	8.72	0.461	0.91961
	(5)	-4.448	9.079	0.7456	0.9099
	(6)	-4.44	9.443	1.056	0.9024
	(7)	-4.34	9.81	1.384	0.8964
Dow 529	(4)	-3.509	7.289	0.576	0.951
	(5)	-3.509	7.7864	0.9416	0.9381
	(6)	-3.509	8.282	1.343	0.9276
	(7)	-3.509	8.778	1.767	0.91924
Dow 2047	(4)	-2.944	6.041	0.4294	0.91604
	(5)	-2.957	6.448	0.7037	0.91267
	(6)	-2.967	6.846	1.005	0.90884
	(7)	-2.9745	7.236	1.322	0.90533

between the experimental and calculated melt viscosity is high for all PE resins tested (the lowest $R = 0.914$ and the highest is 0.996). Values of $R \geq 0.90$ demonstrate that Eq. (10) is applicable for modelling the polyethylene melt viscosity in shearing flow. Comparison of the correlation coefficients obtained for various m (4, 5, 6 and 7) indicates that for most PE resins tested R_4 is higher than any

others. Therefore, for uniformity of the conclusions, Eq. (10) has been used for all PE resins and blends tested in the following form:

$$\eta = A \exp\left(\frac{E_{0\dot{\gamma}} - \alpha(\dot{\gamma})^{1/4}}{RT}\right); \tag{10a}$$

According to the data of Table I the activation energy of viscous flow of linear low density polyethylene (LLDPE) is lower than E_0 for low density polyethylene (LDPE); this is a well known fact. One of the highest values of E_0 was obtained for Dow 748 (7 MI; LD resin). The lowest E_0 was obtained for Dow 0.97 (0.5 MI; LLD resin). Comparison of values of E_0 for different LD and LLDPE resins with literature data¹⁵ indicates that E_0 in Eq. (10) is lower than activation energies of viscous flow which were published by different authors. However, the activation energy of viscous flow can be calculated under two different conditions $\dot{\gamma} = \text{const}$ and $\tau = \text{constant}$. It was shown elsewhere¹⁶ that $E_\tau > E_0\dot{\gamma}$.

Experimental data of E_τ published for various PE resins¹⁷ recently show good correlation with $E_{0\dot{\gamma}}$ obtained in this work (see Table II). The rest of the published data were most probably obtained under conditions of $\tau = \text{constant}$ because this method is considered more reliable.

From the data of Table I it can be seen that $\log A$ correlates with value of $E_{0\dot{\gamma}}$ (see Figure 5). This effect is known in chemical kinetics as the "compensation effect." Dependence of $E_{0\dot{\gamma}}$ on $(\dot{\gamma}_i)^{1/4}$ is presented in Figure (6); $(\dot{\gamma}_i)^{1/4}$ is found from the following equation: $E_{0\dot{\gamma}} - \alpha(\dot{\gamma}_i)^{1/4} = 0$. These correlations can be used to calculate the constants of Eq. (10) if the activation energy of viscous flow is known. It seems that $E_{0\dot{\gamma}}$ is a constant of the material.

The next part of the study was to show that Eq. (12) is valid for

TABLE II

Constant $E_{0\dot{\gamma}}$ $\frac{\text{Kcal}}{\text{mole}}$, obtained from different sources

Material	$E_{0\dot{\gamma}}$ from Table I	Literature data
LDPE	7-8.5	7.5-9
LLDPE	4.9-6	4.5-6.5
HDPE	4-4.8	4-5

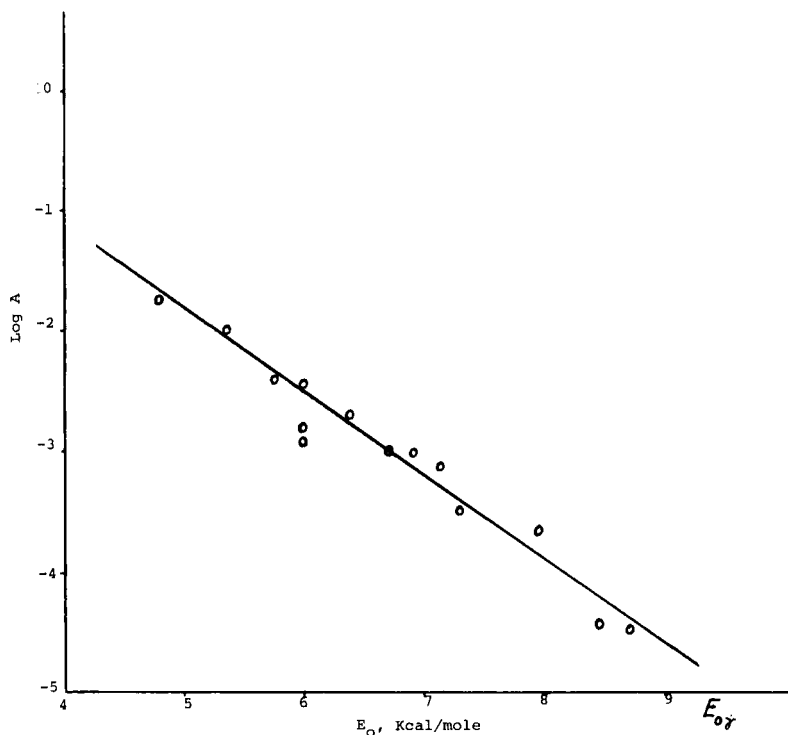


FIGURE 5 Dependence of coefficient A in Eq. (10a) on activation energy of melt flow ($E_{0\dot{\gamma}}$) from data of Table I.

the dependence of melt viscosity on temperature and shear stress. The first problem was to find the coordinate system in which η depends linearly on τ . It has been found that experimental data falls on straight lines in coordinates $\log \eta$ vs $(\tau)^{1/2}$, (see Figures 7 through 10); the isotherms are parallel to each other. This is a significant difference from the straight lines for $\log \eta$ vs $(\dot{\gamma})^{1/m}$ which are convergent. The next step was to replot the experimental data on the coordinates $\log \eta$ vs $1/T$ for various constant shear stresses (see Figures 11 to 12). Points fall satisfactorily on straight lines in this coordinate system, too, and lines for different shear stresses are parallel. The slope of these lines determines the activation energy of viscous flow E_{τ} . Because the lines are parallel, E_{τ} does not depend

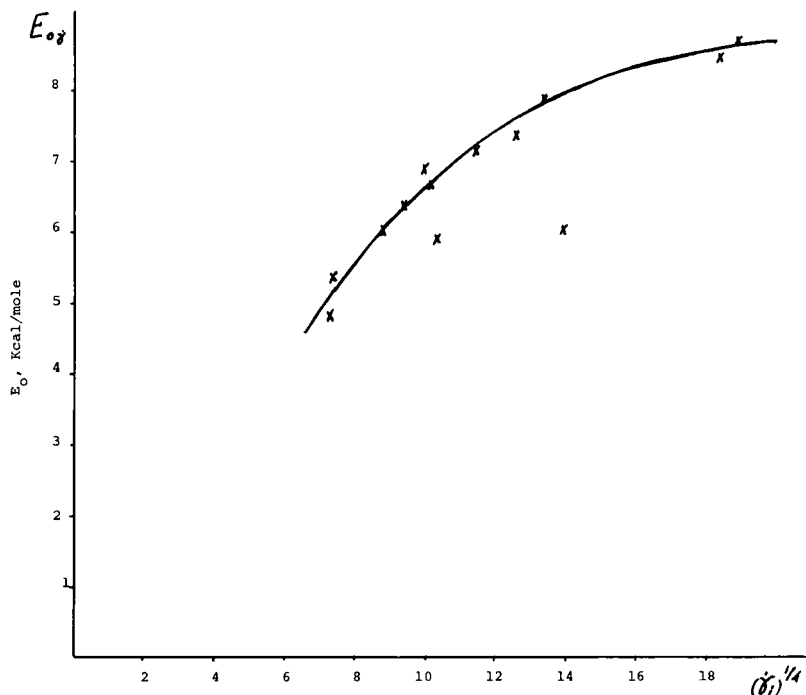


FIGURE 6 Dependence of $E_{0\dot{\gamma}}$ on $(\dot{\gamma}_i)^{1/4}$ from data of Table I.

on τ . The last step was to plot the dependence of $\log \eta$ (extrapolated to $1/T = 0$) on $(\tau)^{1/2}$ (see Figure 13). If this dependence is linear on the suggested coordinate system, it is possible to determine the remaining constants, and finally to confirm that Eq. (12) is valid in the proposed form.

Constants E_τ were determined for several PE resins and for comparison with $E_{0\dot{\gamma}}$ are presented in Table III. According to data obtained, the values of E_τ are higher than corresponding values of $E_{0\dot{\gamma}}$ and also much closer to the published data. It seems, from data on E_τ , that the order of resins established by values of $E_{0\dot{\gamma}}$ would be the same as that found if E_τ were considered.

Consequently two separate equations were 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

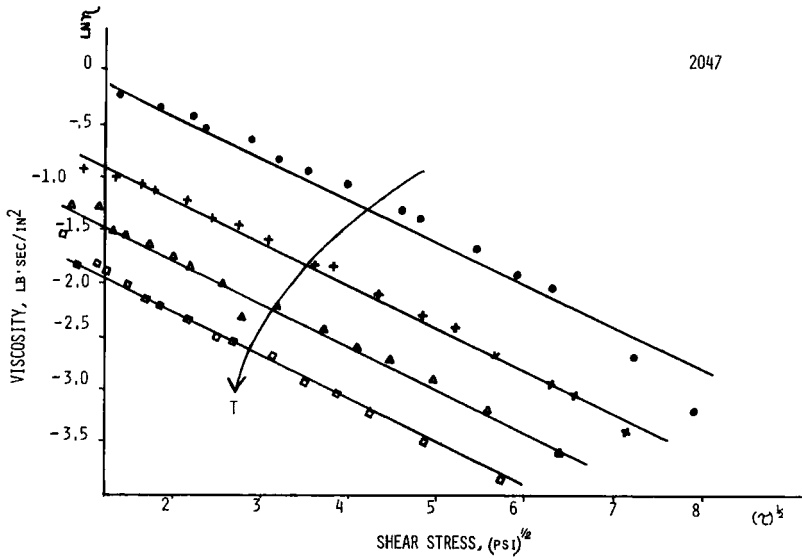


FIGURE 7 Dependence of melt viscosity on shear stress at different temperatures for LLDPE Dow 2047. • 160°C, X 200°C, Δ 240°C, ◇ 280°C.

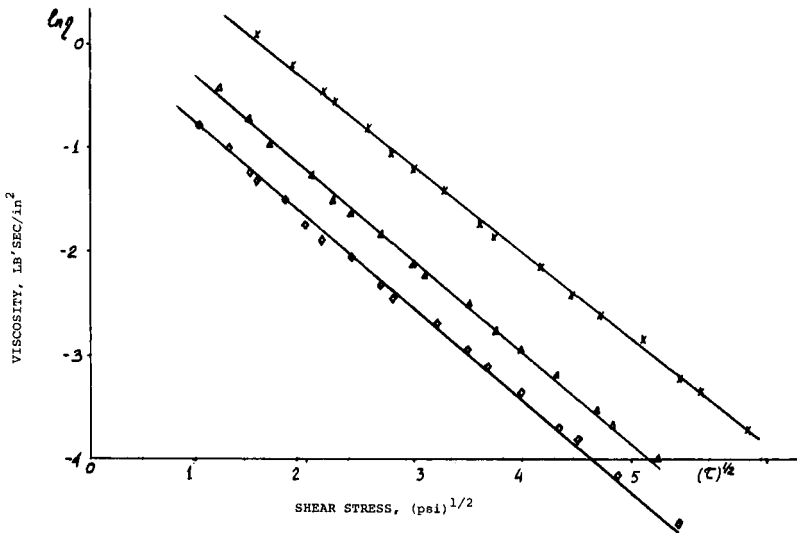


FIGURE 8 Dependence of melt viscosity on shear stress at different temperatures for reclaim. X 190°C, Δ 230°C ◇ 250°C

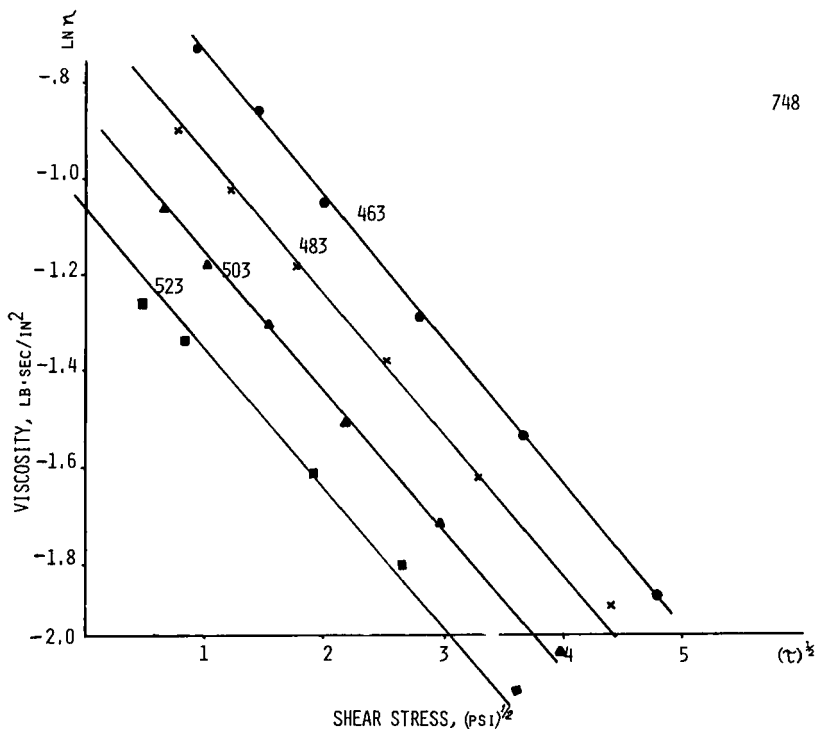


FIGURE 9 Dependence of melt viscosity on shear stress at different temperatures for LDPE DOW 748. ○ 190°C, X 210°C, △ 230°C, ● 250°C.

equations gives a correlation between τ , $\dot{\gamma}$ and T :

$$(\dot{\gamma})^{1/m} = DT - \Delta E + NT(\tau)^{1/S}; \tag{13}$$

where D and N are constants,

$$\Delta E = E_\tau - E_{0\dot{\gamma}}$$

Eq. (13) is basically similar to the power law equation. Dependence of shear rate on shear stress for Dow 748 LDPE is plotted on coordinates $(\dot{\gamma})^{1/4}$ vs. $(\tau)^{1/2}$ for different temperatures (see Figure 14). Experimental data for each temperature fall on straight lines and the equation which describes the data can be written in the following form:

$$(\dot{\gamma})^{1/4} = a + bT + \lambda(T)(\tau)^{1/2}; \tag{14}$$

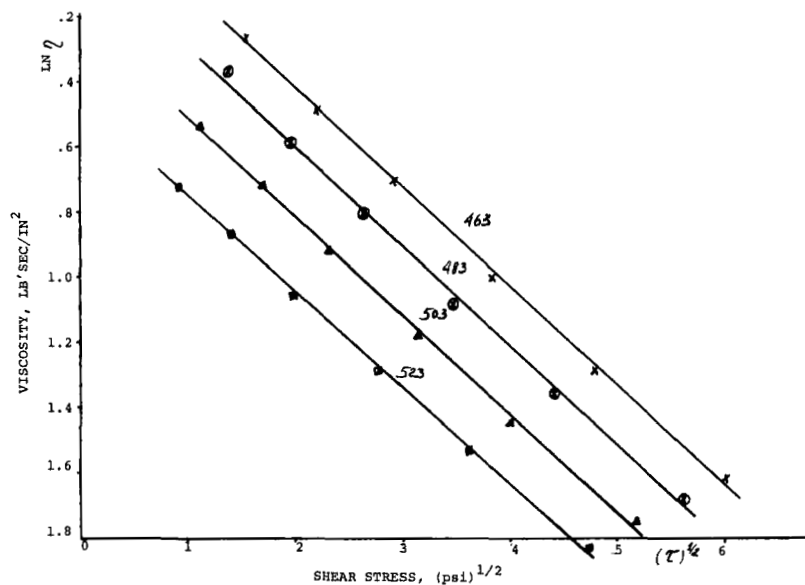


FIGURE 10 Dependence of melt viscosity on shear stress at different temperatures for LDPE DOW 592. X 190°C, ⊗ 210°C, ▲ 230°C, ◆ 250°C.

where a and b are constants; and $\lambda(T)$ is a function of temperature. Formula (14) is exactly the same as eq. (13) obtained from Eqs. (10) and (12). Existence of the coefficient $(a + bT)$ is related to a difference in values of E_τ and $E_{0\dot{\gamma}}$ and indicates that values of $\eta_0(\tau = 0$ and $\dot{\gamma} = 0)$ calculated from Eqs (10) and (12) are different and that this difference increases with test temperature. Linearity of $(\dot{\gamma})^{1/m}$ vs $(\tau)^{1/S}$ where M and S are the same as in Eqs. (10) and (12) can be used as a verification of the values of constants m and S . Constant "a", which should be equal to ΔE , was determined from the data of Figure 14 and proved to be negative and very close in magnitude to the value of ΔE obtained from Table 3.

Equations of type (10) are usually valid under conditions of constant material structure which determines the property under question. If variation of temperature or shear rate results in change of the melt structure one may expect that the values of constants in the equations will change, but the form of the equations will remain the same.

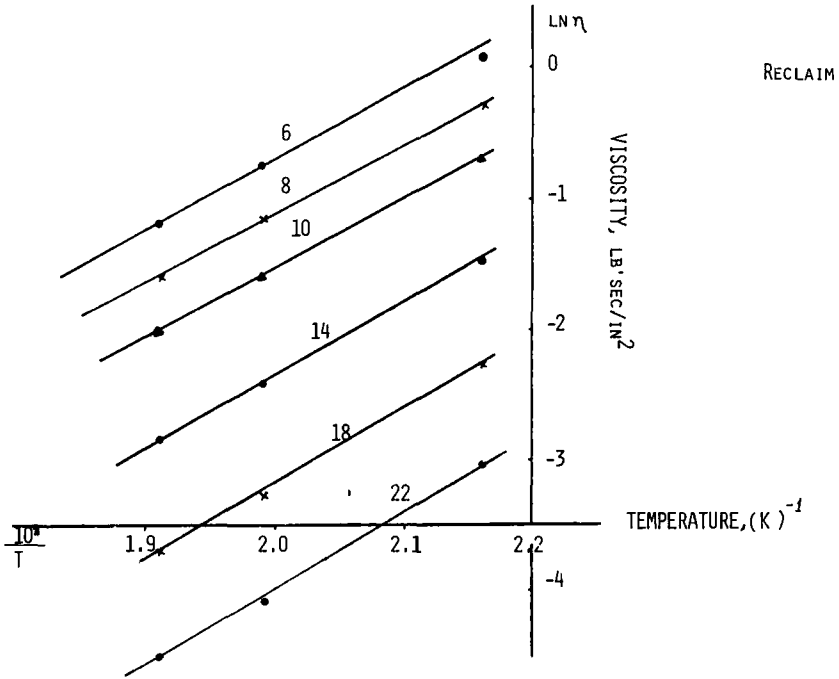


FIGURE 11 Dependence of reclaim melt viscosity on temperature for different shear stresses. Numbers near straight lines are shear stresses, in lbs.

CONCLUSIONS

1. Semi-empirical equations to describe the dependence of polymer melt viscosity in shearing flow on temperature and shear rate and on temperature and shear stress have been derived. The equations are based on the thermo-activation theory of melt flow and on existing experimental data.

2. 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 which is similar to the power law equation.

3. Experimental data on melt viscosity of various polyethylene resins were described by the proposed equations.

Constants of the equations and correlation coefficients between

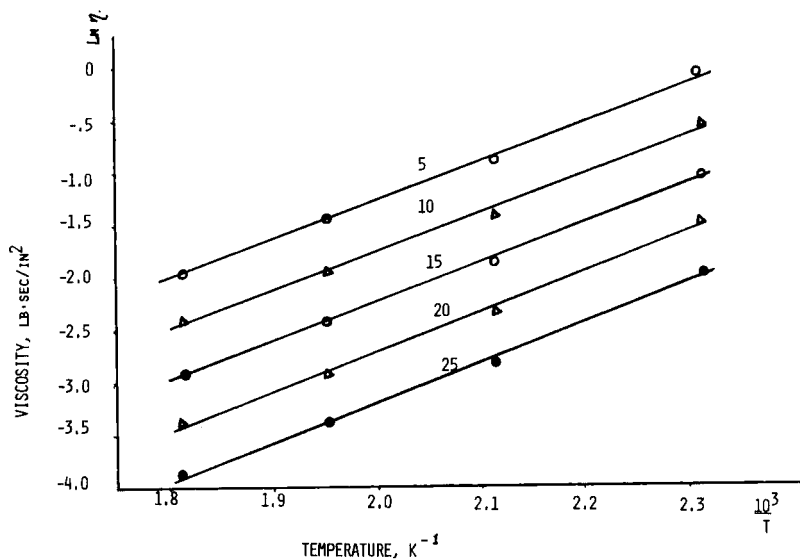


FIGURE 12 Dependence of melt viscosity on temperature for different constant shear stresses. Numbers near straight lines are shear stresses.

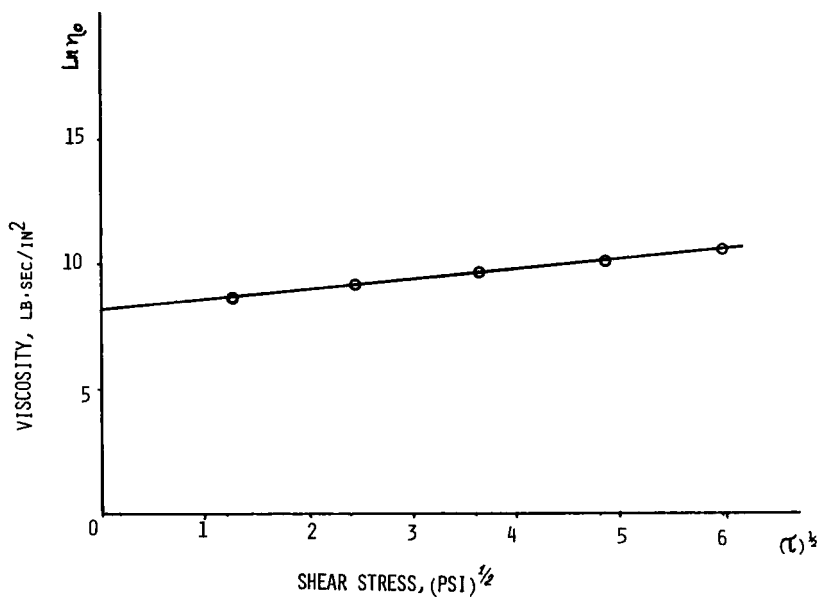


FIGURE 13 Dependence of viscosity (extrapolated to $1/T = 0$) on shear stress for LLDPE Dow 2047.

TABLE III
 Values of $E_{0\gamma}$ and E_t for various PE resins

Activation energy of viscous flow, $E, \frac{\text{kcal}}{\text{mole}}$	PE Resin										
	HMWHDPE 9255F	MMWHDPE TR-130	LLDPE Dow 0.97	LLDPE Dow 2045	LLDPE Dow 2047	Reclaim	LDPE Dow 682	LDPE Dow 592	LDPE Dow 748		
$E_{0\gamma}$	4.0	4.8	4.9	6	6.1	6.9	7.2	7.9	8.45		
E_t	4.2	5.8	5.9	7.4	7.6	10.4	10.6	10.9	11.2		

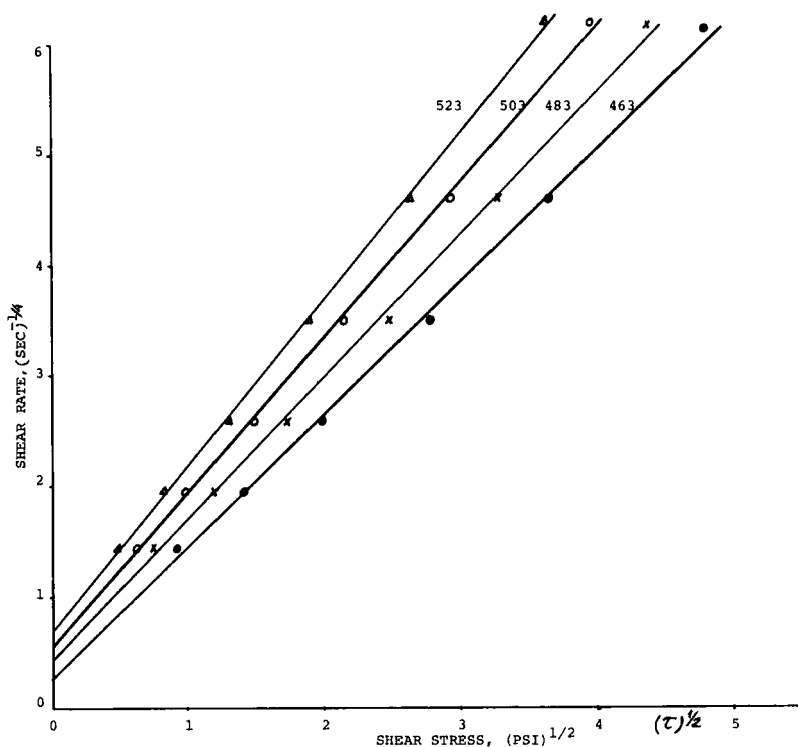


FIGURE 14 Dependence of shear rate on shear stress for different temperatures. LDPE Dow 748. ● 190°C, X 210°C, ○ 230°C, Δ 250°C.

experimental and calculated data were determined by the computer. Correlation-coefficients are relatively high for both equations (between 0.194 and 0.996).

4. Correlation between the constants of equation (10) has been demonstrated.

5. The activation energy of melt flow of various polyethylene resins was determined for conditions of $\dot{\gamma} = \text{constant}$ and $\tau = \text{constant}$. The values obtained for $E_{0\dot{\gamma}}$ and E_{τ} are in good agreement with literature data.

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