

The Dynamic Viscosity of Polypropylene Melt

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Synopsis

The dynamic viscosity of polypropylene melt was determined as a function of frequency and temperature. The temperature-shift Arrhenius energy was calculated in several ways. The influence of temperature on the elastic and viscous components was quantitatively discussed.

INTRODUCTION

The temperature dependence of the melt viscosity of polypropylene has been studied by several investigators.¹⁻⁵ These studies have been made under various conditions. Mendelson¹ carried out his experiments using capillary flow techniques; van der Vegt³ subjected the polymer to rotational shear as well as capillary flow; and Adamese and co-workers⁴ sheared the polypropylene melt in an oscillatory manner. The values for the Arrhenius energy of flow ($E\eta$) as determined by the first two techniques are not in agreement with the third; the present authors considered that this discrepancy, for a linear polymer such as polypropylene, was worthy of further work. In this investigation, the temperature dependence under oscillatory shear was studied. A number of different methods of interpretation of data were considered, and the Arrhenius energy values were compared with literature.

EXPERIMENTAL

The instrument used was a Weissenberg rheogoniometer Model R.18, incorporating an air-bearing head.⁶ A 2-degree cone of 5.0 cm diameter and a flat platen of the same diameter were used in oscillation. The temperature range was 195°-260°C. Nitrogen gas was passed through the furnace system during each run. The frequency range and amplitude range were 0.006 to 6 sec⁻¹ and 50 to 500 microns, respectively; thus these experiments were considered to be small-amplitude sinusoidal deformations. The viscosities plotted in Figure 1 were measured from stress-strain amplitudes taken as an average over several wavelengths. These amplitudes were reproducible to $\pm 1\%$. Viscosity was found to be independent of the amplitude of the applied strain.

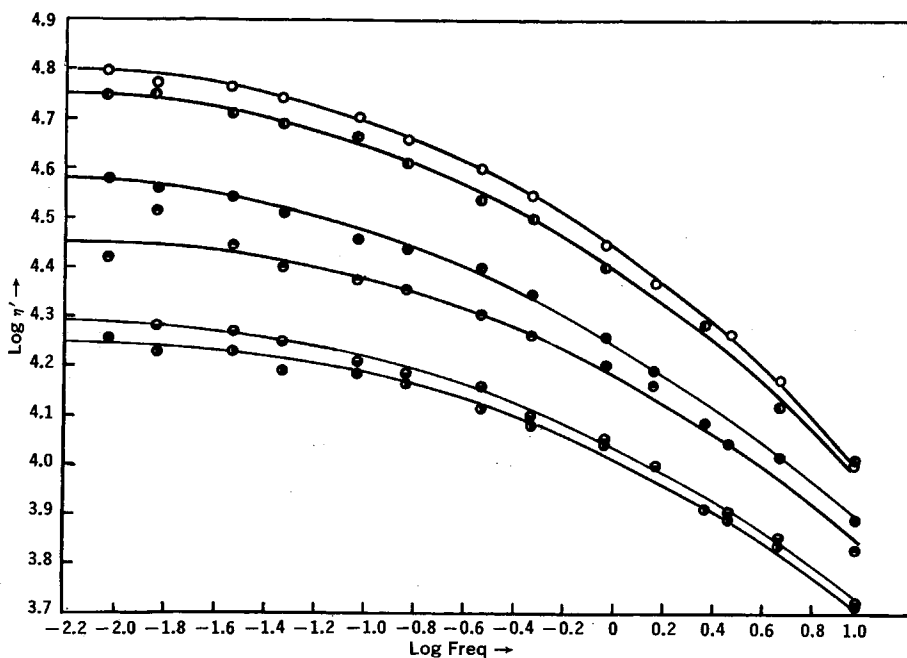


Fig. 1. Dynamic viscosity: (O) 195°C; (●) 210°C; (●) 222°C; (●) 231°C; (●) 246°C; (●) 260°C.

Testing of polypropylene under oscillatory shear can be evaluated in the following manner (see Fig. 2). The oscillation of the cone can be described⁷ by

$$\gamma(t) = \gamma_0 e^{i\omega t} \quad (1)$$

where γ_0 is the amplitude of the applied strain, ω is the frequency, and t is the time. Then the rate strain is

$$\dot{\gamma}(t) = i\omega\gamma(t). \quad (2)$$

The stress can also be described by a sinusoidal function with the same frequency as the rate of strain⁸:

$$P_{12}^* = P_0 e^{i\omega t + i\phi} \quad (3)$$

where P_0 is the amplitude of the tangential stress and ϕ is the phase difference between the stress and strain. The viscosity is the real part η' of the complex viscosity⁷:

$$\eta^* = \eta' - i\eta'' \equiv \frac{P_{12}^*}{\dot{\gamma}(t)}. \quad (4)$$

Thus the dynamic viscosity is

$$\eta' = \frac{P_0 \sin \phi}{\gamma_0 \omega}. \quad (5)$$

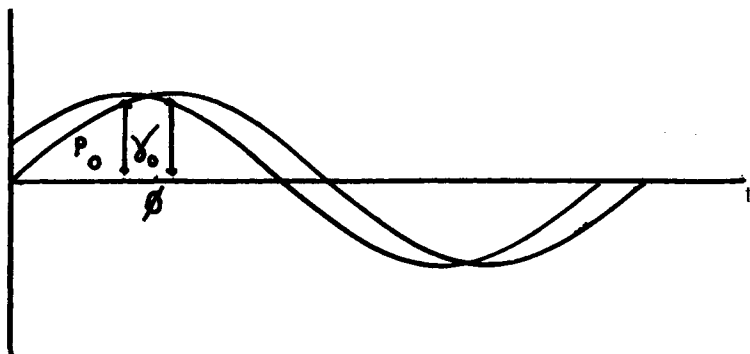


Fig. 2. Typical strain and stress curves for a viscoelastic material.

Bogie and Harris⁹ have pointed out that the amplitude is subject to attenuation, and the phase difference, to a shift at higher frequencies due to the filter system of the rheogoniometer. The present authors have found, as did van Rijn,¹⁰ that this can be compensated for in most cases. Where there was attenuation, corrections were made.

The material studied was Enjay polypropylene grade 115 supplied by Esso Chemical Canada. This material is FDA stabilized and has a melt flow index of 5.0.

RESULTS AND DISCUSSION

Oscillatory measurements were carried out at different temperatures. Plots of log viscosity versus log shear are shown in Figure 1. As can be seen from the curves, molten polypropylene has a pseudoplastic rheological behavior, the viscosity decreasing with increasing shear rate. The effect of temperature is apparent.

Effect of the Method of Determining η'_0

The viscosity of zero shear rate, η'_0 , for polypropylene was determined in three ways: (1) from extrapolation of the log η' versus log f plot (Fig. 1); (2) from a method developed by Cross¹¹; and (3) from a method employing the theory developed by Walters and Kemp.¹²

The η'_0 as obtained from extrapolation gave rise to an Arrhenius energy of flow (E_η) of 10.3 kcal/mole (Fig. 3). It has been pointed out by Mendelson¹ that, for constant shear stress,

$$a_T = \dot{\gamma}_w(\text{ref})/\dot{\gamma}_w(T) = \eta_{\text{app}}(T)/\eta_{\text{app}}(\text{ref}) \quad (6)$$

where a_T is a temperature shift factor. A capillary flow shear rate, $\dot{\gamma}_w$, is considered at an arbitrarily chosen reference temperature, $\dot{\gamma}_w(\text{ref})$, and the temperature in question, $\dot{\gamma}_w(T)$. Similarly, η_{app} is a viscosity, taken from steady shear studies. Using a_T in an Arrhenius-type plot, one obtains a shift factor energy, E_a . Applying this concept to the oscil-

latory data at zero shear, the E_a in the present case is 10.3 kcal/mole. Mendelson's work yielded an $E_a = 10.0$ kcal/mole for polypropylene. Another earlier capillary flow study² resulted in an E_η value of 9.3 kcal/mole. An Arrhenius energy of 11 kcal/mole was obtained by van der

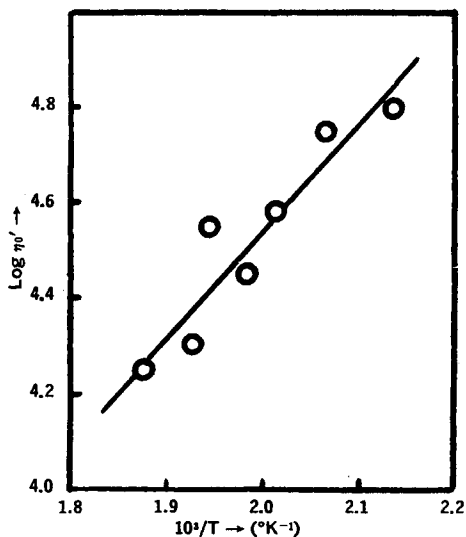


Fig. 3. Arrhenius plot for extrapolated η_0 .

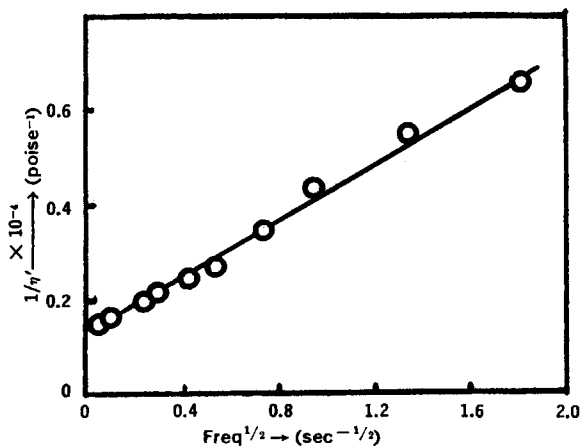


Fig. 4. Test of Cross theory, polypropylene at 195°C.

Vegt.³ The above measurements were likely carried out on polymers of comparable properties; thus it seems probable that the dependence of a_T on temperature is the same for oscillatory as for steady shear, at zero shear.

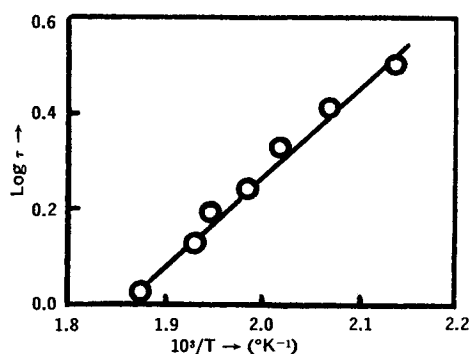


Fig. 5. Arrhenius plot of relaxation time from Cross calculation.

Another method for handling the data is to use the following equation correlated by Cross for non-Newtonian bulk flow:

$$\eta = \eta_{\infty} + \frac{\eta_0 + \eta_{\infty}}{1 + \tau f^b} \quad (7)$$

where b is chosen empirically in order to get the data to fit the equation, η_0 and η_{∞} are the limiting viscosity values at frequency $f = 0$ and $f = \infty$, respectively, and τ can be related to relaxation time. The present data fit $b = \frac{1}{2}$ (Fig. 4) using the least-squares method, and the correlation coefficients in all cases were greater than 0.99, the standard error in $1/\eta'$ was less than $\pm 4\%$. This value of b compares favorably with other polymer melts under oscillatory shear.¹¹ If one recalls Ferry's definition of a_T , i.e., the ratio of relaxation times at two different temperatures, then

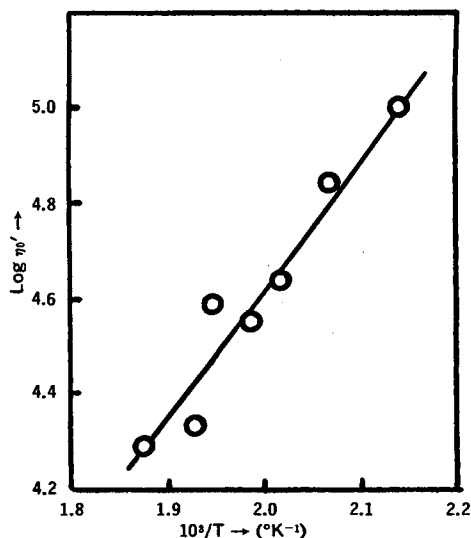


Fig. 6. Arrhenius plot of η_0 from Cross calculation.

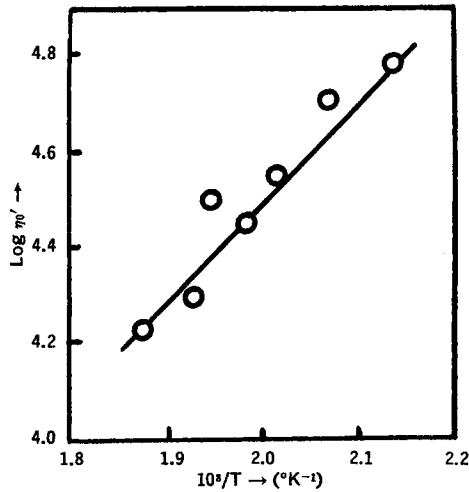


Fig. 7. Arrhenius plot for η_0' from Walters theory.

one should be able to relate an Arrhenius-type plot of τ to that of a_T . From Figure 5, a value of 9.2 kcal/mole is obtained for E_T (shift energy), which is in fair agreement with the values obtained by Mendelson and van der Vegt. However, an Arrhenius-type plot of η_0' produces a value of 13.0 kcal/mole for the energy of flow (Fig. 6). Adamese and co-workers⁴ obtained a value of 16.0 kcal/mole from oscillatory shear, although this value was obtained using only two temperatures.

An attempt was also made to relate the data to the theory of Walters and Kemp.¹² However, the data only fit at the very limit as the shear approaches zero; Walters and Kemp suggest "that this interpretation of the experimental results is best suited to reasonably viscous liquids that

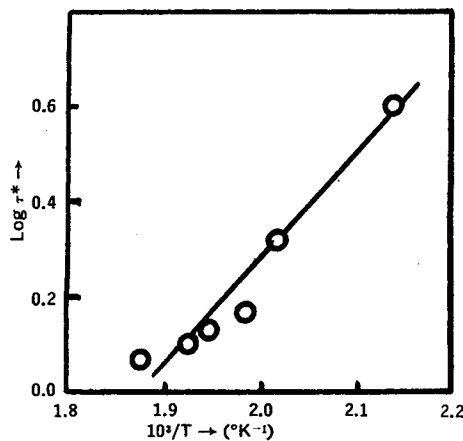


Fig. 8. Arrhenius plot relaxation time from Walters theory.

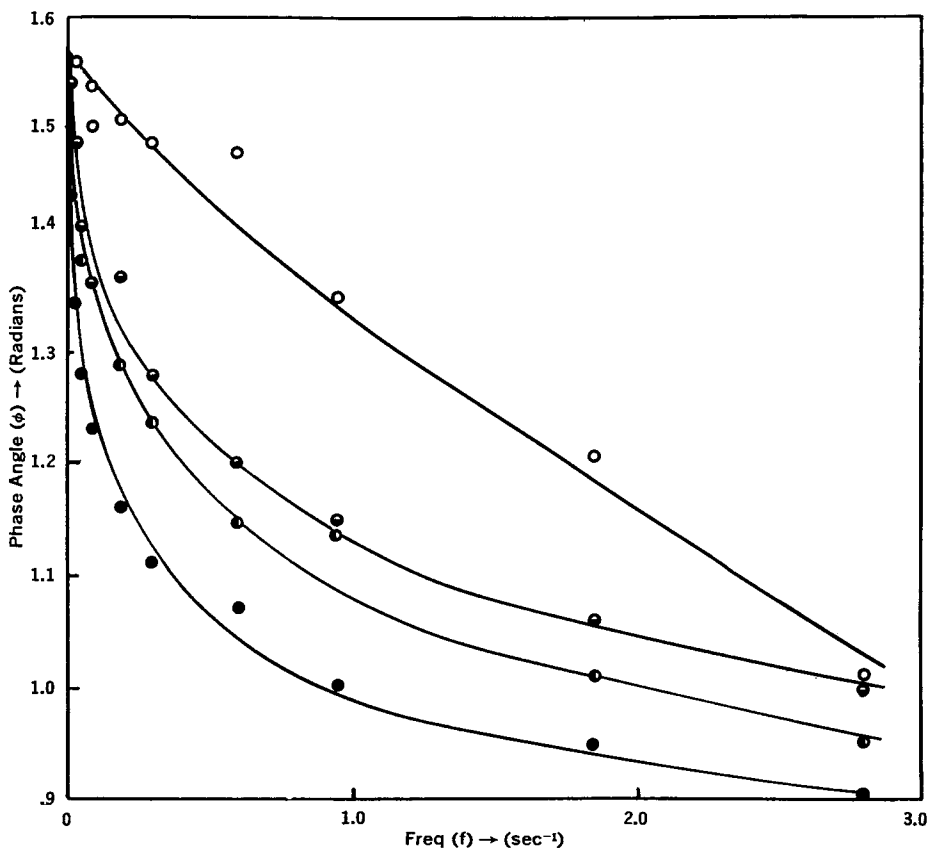


Fig. 9. Plot of phase difference vs. frequency: (○) 195°C; (◐) 231°C; (◑) 246°C; (●) 270°C.

are not highly elastic... if η' and G are known over a limited (low) frequency range." Predictions of the theory yield

$$\eta' = \int_0^\infty N(\tau)d\tau - 4\pi^2f^2 \int_0^\infty \tau^2N(\tau)d\tau \tag{8}$$

$$\frac{G}{2\pi f} = -2\pi f \int_0^\infty \tau N(\tau)d\tau + 8\pi^3f^3 \int_0^\infty \tau^3N(\tau)d\tau \tag{9}$$

where

$$\int_0^\infty N(\tau)d\tau = \eta'_0$$

$$\int_0^\infty \tau N(\tau)d\tau = \eta'_0\tau^*$$

τ^* being a "characteristic" relaxation time. This can be considered to be a "measure" of the important relaxation times. The other "moments"

τ^2 and τ^3 were not determined owing to lack of fit of the theory. G is the dynamic rigidity and $N(\tau)$ is a distribution function of relaxation time τ . Plots of η' versus f^2 and of $G/4\pi^2f^2$ versus f^2 in the very low frequency range yielded the above integrals from which Arrhenius energy of flow and shift were obtained (Figs. 7 and 8). These were found to be 10.0 and 9.9 kcal/mole, respectively. This close agreement with previous data, it should be observed, is better than the actual theoretical fit.

Relationship of the Phase Difference with Temperature

The phase difference between the stress (output) and the strain (input) gives a measure of the elastic to viscous components of the polymer (or vice versa). The effect of the temperature on a number of representative curves is seen in Figure 9, which is a plot of phase angle ϕ versus frequency f . In addition to the kinetic runs, shear experiments were carried out below T_m , that is, on rigid polypropylene, and at 270°C in order to extend the range. The tests below T_m were carried out on the same instrument as the melt work, but solid sample holders were used in place of the platens. All of the curves were found to fit the equation

$$\phi = Af^m + C \quad (10)$$

where $C = 1.57$ (phase angle in radians = 90°). The above equation was tested by means of a statistical F -test, which checked the linear, quadratic, and the higher-order regressions, i.e., the linear regression component was found to be significant, the quadratic regression components and residual (high orders) were found to be not significant. The fit was extremely good in all cases for the melt. Those experiments performed on the solid samples had poor correlation coefficients, i.e., 0.60–0.70, but they did satisfy the F -test. A and m were determined and plotted against temperature in Figures 10 and 11. In Figure 11, A would be asymptotic to $A = 0$, i.e., a viscous fluid, neglecting fluid inertia,¹² gives a stress 90°

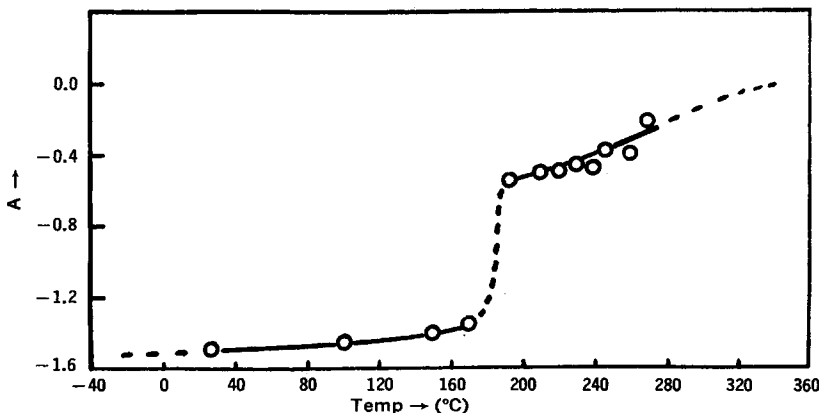


Fig. 10. Plot of coefficient A vs. temperature.

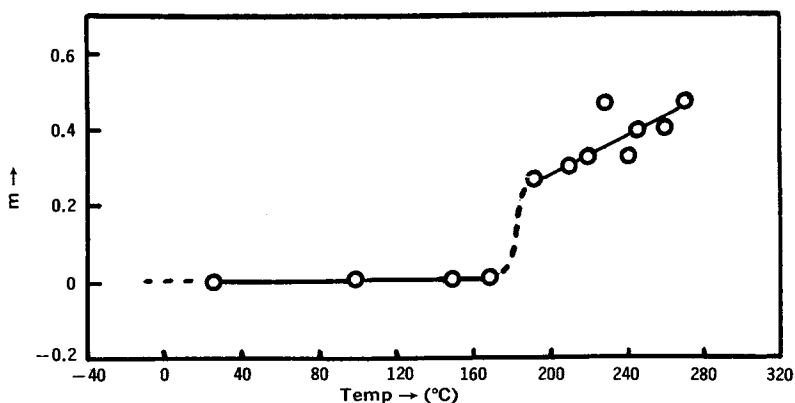


Fig. 11. Plot of exponent m vs. temperature.

out of phase with the strain (a line $\phi = 1.57$). As the compound approaches a completely elastic state, A approaches -1.57 . Considering this in conjunction with Figure 11, one can see that m approaches zero at the low temperatures, i.e., $\phi \rightarrow 0$, giving the expected result of an elastic compound having the stress and strain in phase. It can be seen that in the region of T_m there is a definite transition from a primarily viscous to an elastic response. The overall temperature effect on A and m is well described in Figures 10 and 11.

SUMMARY OF RESULTS

The shift Arrhenius energy for polypropylene melt under oscillatory shear is 10 kcal/mole. It appears that, if the Arrhenius energy is considered in terms of flow, it may be dependent on the method of calculation, whereas the Arrhenius energy measured from the shift in the curves (relaxation) at different temperatures apparently is not. It also appears that small-amplitude sinusoidal shear gives the same Arrhenius energy of flow as capillary and steady shear methods.

The effect of temperature on the elastic and viscous components of polypropylene can be quantitatively discussed using the equation $\phi = Af^m + C$.

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