On the Characterization of Non-Newtonian Flow. III

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Synopsis

A method is developed for testing extrapolation procedures of shear stress–shear rate data by using the dependence of the flow activation energy on shear. Three polyethylene types are studied, and it is concluded that the difference in flow activation energy observed between conventional low density polyethylene and high density polyethylene is due mainly to long chain branching.

Introduction

The flow activation energy of a polymer is strongly dependent on its molecular structure. For a Newtonian material, the viscosity (η_0) is independent of the shearing stress (S) or the shear rate ($\dot{\gamma}$). The change in viscosity with temperature (T) is expressed by Andrade's equation

$$\eta_0 = A \exp\{(E)_0/RT\} \tag{1}$$

where $(E)_0$ is the flow activation energy, a constant over a limited temperature range. Bestul and Belcher[1] deduce that for non-Newtonian materials "the variation of viscosity with temperature at fixed shearing stress is independent of shearing stress. However, the variation at fixed rate of shear is always less than that at very low shearing stress, and decreases with increasing rate of shear."

In this paper, simple equations describing the non-Newtonian flow of polymers are used to predict the drop in flow activation energy with shearing stress and shearing rate. Experimental results are then used to test the validity of extrapolating procedures used with shear stress–shear rate data.

Experimental

A series of commercial high (HDPE) and low (LDPE) density polyethylenes were studied. In addition, experimental ethylene–butene-1 random copolymers (EXPE) spanning the density range of commercial polyethylenes were studied. Some long chain branches may be present in these resins, but the main drop in density is due to ethyl branching. The non-Newtonian flow behavior was determined by means of an extrusion rheometer[2] at various temperatures ranging from 150 to 220°C.

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The die employed had a length-to-diameter ratio of 19.4. The uncorrected shear stress–shear rate data were curve fitted to the following equation[3]

$$\log \eta/\eta_0 = (\eta/\eta_0 - 2) \log [1 + (\dot{\gamma}\tau)^{1/3}] \qquad (2)$$

which at high shear reduces to

$$\eta/\eta_0 = (\dot{\gamma}\tau)^{-2/3} \qquad (3)$$

The parameter τ is defined by Bueche[4] as

$$\tau = KMr\eta_0/T \qquad (4)$$

Flow activation energies were obtained at zero shear by using extrapolated viscosity data and at three shear stresses and three shear rates in the non-Newtonian region available to us with the above instrument.

Results

Representative data are summarized in Table I for the three resin types. A sharp drop in flow activation energy at constant shear rate, $(E)_{\dot{\gamma}}$, is observed, compared to the zero shear value. At constant shear stress, $(E)_s$, the change is small. In agreement with Schott and Kaghan,[5] $(E)_s$ was observed to drop and then to increase, in some cases, at high shear stresses. This is unexpected as we shall show below. Schott and Kaghan have applied corrections to their data for entrance losses in reporting this. The experimental error must be greater than the drop in $(E)_s$ or eq. (1) fails over the temperature range employed. Philippoff and Gaskins,[6] covering a very broad temperature range (108–230°C.), report an increase in $(E)_s$ from 12.8 to 19.0 kcal./mole for a conventional low density polyethylene.

The non-Newtonian viscosity (η) is a function of shear as well as of temperature

$$\eta = \eta_{(S,T)} \qquad (5)$$

Differentiation yields

$$\frac{(\delta\eta/\delta T)s}{(\delta\eta/\delta T)_{\dot{\gamma}}} = 1 - \dot{\gamma}\frac{(\delta\eta)}{(\delta S)_T} \qquad (6)$$

From this last relationship Bestul and Belcher[1] deduced and confirmed experimentally that

$$(\delta\eta/\delta T)_s > (\delta\eta/\delta T)_{\dot{\gamma}} \qquad (7)$$

Substitution of the partial derivatives of

$$\eta = Ae^{(E)_s/RT} \qquad (1a)$$

and

$$\eta = Ae^{(E)_{\dot{\gamma}}/RT} \qquad (1b)$$

into eq. (6) yields[7]

$$(E)_s/(E)_{\dot{\gamma}} = 1 - \dot{\gamma} \, (\delta\eta/\delta \, S)_T \qquad (8)$$

which can be simplified to

$$(E)_s/(E)_{\dot{\gamma}} = 3 \qquad (9)$$

in the case of eq. (3). Figure 1 is a test of this relation for data of four resins from Table I. The values of $(E)_s$ is taken at a shear stress of 8.9 $\times$ 10^5 dynes/cm.^{2} and is assumed to have reached its limiting value. It may be concluded that eq. (3) is valid for conventional and high density polyethylenes. Another test for eq. (3) will be made below.

Starting from

$$\eta_0/\eta = 1 + \dot{\gamma}\tau \qquad (10)$$

and

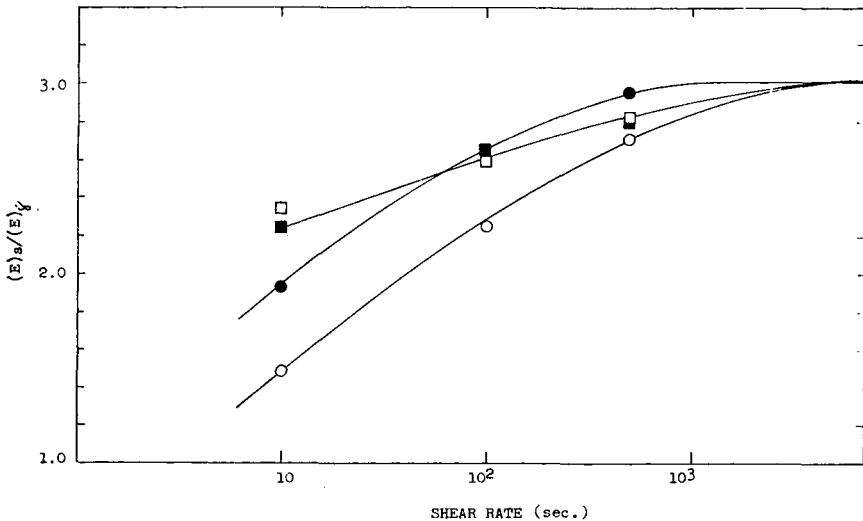$$\eta/\eta_0 = (\dot{\gamma}\tau)^b \qquad (3a)$$

Fig. 1. Test of eq. (9) for (O, ●) conventional and (□, ■) high density polyethylenes.

which describe the behavior of eq. (1) at low and high shear rates, respectively, substituting eq. (4) for τ and differentiating with respect to temperature at constant shear rate and $\overline{M}r$, one obtains

$$[(E)_0 - (E)_{\dot{\gamma}}]/[(E)_0 + RT] = 1 - (\eta/\eta_0) \qquad (11)$$

and

$$[(E)_0 \quad (E)_{\dot{\gamma}}]/[(E)_0 + RT] = -b \qquad (12)$$

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TABLE I
Flow Activation Energy Data for Various Polyethylenes at Various Shear Ranges

Type	Density, g./cm.³	$(E)_S$, kcal./mole				$(E)\dot{\gamma}$, kcal./mole		
		Zero	2.2 × 10⁵ dynes/cm.²	4.4 × 10⁵ dynes/cm.²	8.9 × 10⁵ dynes/cm.²	10 sec.⁻¹	100 sec.⁻¹	500 sec.⁻¹
LDPE	0.923	15.9	13.2	12.8	11.7	6.5	5.1	4.7
LDPE	0.924	15.3	12.6	12.5	11.0	7.5	4.9	4.1
LDPE	0.929	16.0	13.0	12.7	12.7	7.0	5.1	4.8
LDPE	0.935	16.8	12.3	12.1	11.3	5.9	4.3	3.8
EXPE	0.924	9.0	7.8	7.7	8.1	5.0	4.5	4.3
EXPE	0.929	10.6	8.0	8.5	8.1	5.0	4.5	3.9
EXPE	0.938	8.7	7.6	8.0	7.7	3.5	3.0	2.5
EXPE	0.950	7.9	7.9	7.8	8.0	5.1	4.0	3.3
HDPE	0.949	8.2	6.7	6.9	7.4	3.4	2.8	2.5
HDPE	0.950	6.4	6.0	6.6	6.3	2.7	2.4	2.2
HDPE	0.951	6.8	5.8	6.1	6.0	2.7	2.3	2.1
HDPE	0.963	8.0	7.2	7.4	7.1	3.7	3.1	2.9

where η/η_0 and b are taken at temperature T. Substitution of eq. (9) in eq. (12) yields

$$(E)_0 - (E)_s = -[b/(1 + b)]RT = 2RT \qquad (13)$$

Equation (13) indicates a temperature dependence and that the activation energy as expressed by Andrande's equation should be determined as a tangent to the curve. We have assumed a semilogarithmic linear relationship over the temperature range of 150–220°C. Equation (13) offers a test of the extrapolation to zero shear. $2RT$, at 190°C., is 1.8 kcal. On checking Table I, the low density polyethylenes have $(E)_0$ values too high by about 2.5 kcal. Extrapolation on linear paper indicates that more reasonable values for the four LPDE's are 13.3, 12.8, 14.3, and 12.5, respectively. It may be concluded that the extrapolation to zero shear by means of eq. (2) is good for EXPE and HDPE but poor for LDPE. In view of the previous deduction, it may also be concluded that the difference between LDPE and HDPE must occur at very low shear rates.

A plot of the flow activation energy ratio as expressed by eqs. (12) and (13) versus η_0/η should result in a slowly rising curve with a limiting value of 0.67 on the ordinate, as in Figure 2. As expected, LDPE resins are off. The scatter observed is negligible when considering that an extrapolated value (η_0) enters in both coordinates and that $\overline{M}r$ is not being held constant. Schott and Kaghan[5] obtained $(E)_0$ values by a different procedure, and when their data are treated by the present method a good extrapolation to a value of 0.67 can be made for LDPE and HDPE (Fig. 3).
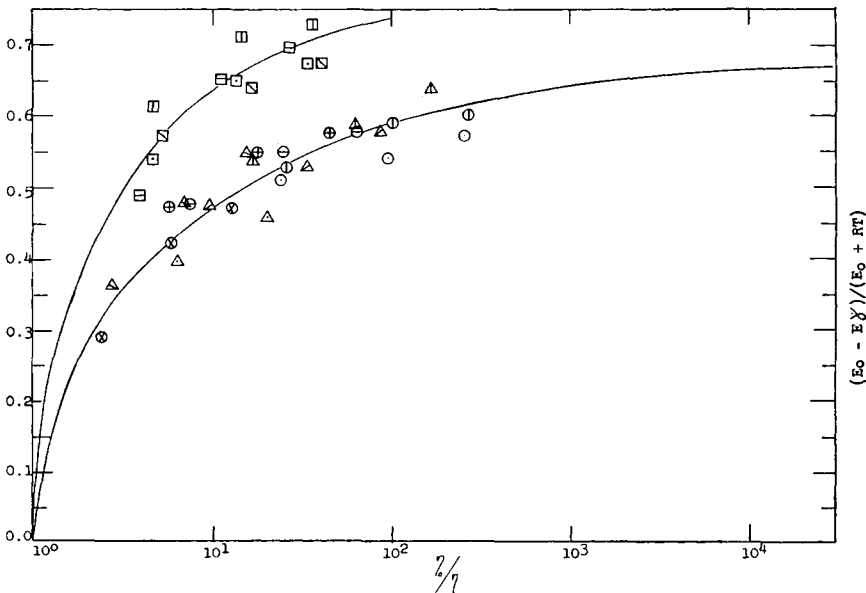

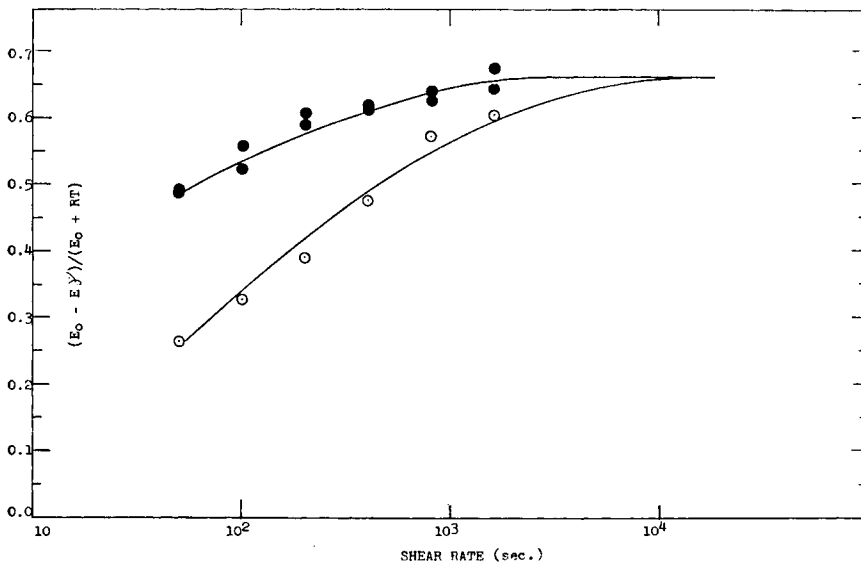Fig. 2. Reduction of flow activation energies: (O) HDPE; (□) LDPE; (△) EXPE.

Fig. 3. Extrapolation to the limiting non-Newtonian slope: (●) LDPE; (○) HDPE.

The data of Bestul and Belcher[1] on a GR-S rubber when treated by the methods illustrated in Figures 1 and 2 yield a limiting slope at high shear rates of 0.83 which is in close agreement with a value of 0.75 reported by Bueche[8] for GR-S rubber.

A series of HDPE's of approximately the same E_0 appeared to obey the following relationship in the non-Newtonian region

$$\eta = (k^{1/m}/\dot{\gamma}\eta_0)e^{E\dot{\gamma}/mRT} \tag{14}$$

where m and k are constants. This equation predicts that the critical shear stress for non-Newtonian flow is inversely proportional to molecular weight if $(E)_0$ is independent of molecular weight. Further deductions are possible by keeping other parameters and combinations thereof constant.

Conclusion

It is found that the flow activation energy as a function of shear decreases to a less extent at constant shear stress than at constant shear rate. This behavior can be predicted a priori if an equation describing the non-Newtonian flow of the resin under study is known. On the other hand, extrapolation procedures of shear stress–shear rate data can be tested by the dependence of the flow activation energy on shear.

The experimental polyethylenes are butene–ethylene copolymers ranging from 4 to 22 ethyl branches/1000 CH_2. It may be concluded that the difference in flow activation energy observed between DLPE and HDPE is due mainly to long chain branching.

References

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Résumé

On a développé une méthode pour vérifier les procédés d'extrapolation des résultats donnant la force de cisaillement en fonction de la vitesse de cisaillement. On s'est servi de la variation de l'énergie d'activation du processus d'écoulement sous cisaillement. On a étudié trois types de polyéthylène et on en a conclu que la différence d'énergie d'activation d'écoulement qui s'observe entre le polyéthylène conventionnel de basse densité et le polyéthylène de haute densité est surtout due à des ramifications de chaînes.

Zusammenfassung

Es wurde eine Methode zur Prüfung von Extrapolationsverfahren für Scherspannungs–Schergeschwindigkeitsdaten auf Grundlage der Abhängigkeit der Aktivierungsenergie des Fliessens von der Scherung entwickelt. Aus der Untersuchung von drei Polyäthylenarten geht hervor, dass der beobachtete Unterschied der Aktivierungsenergie des Fliessens von konventionellem Polyäthylen niedriger Dichte und Polyäthylen hoher Dichte durch Langkettenverzweigung hauptsächlich verursacht wird.