JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 2779-2784 (1965)

Studies of Non-Newtonian Flow I. Criterion of Flow Instability

W. S. OVERDIEP and D. W. VAN KREVELEN,
Department of Chemical Engineering, Technological University, Delft, and *Central Research Institute of Algemene Kunstzijde Unie and Affiliated Companies, Arnhem, Netherlands*

Synopsis

It is shown that the flow instability of polymer melts occurring above a certain critical shear stress is a direct result of the degree of non-Newtonian behavior of the flowing liquid. Melt fracture, elastic turbulence, and slip-stick effects are a consequence of this instability, which frequently leads to periodic phenomena. The condition for the occurrence of flow instability is derived.

INTRODUCTION

The striking phenomena occurring in the rapid extrusion of polymer melts through a capillary were first reported by Spencer and Dillon well over fifteen years ago.[1] Since then, many investigators have occupied themselves with these melt-fracture phenomena.

Beyond a certain critical shear stress the extrudate begins to show deviating shapes. The extruded thread then is, for instance, undulated or helical, or shows peculiar distortions at regular intervals.

In the literature it has frequently been mentioned that there may be a transition from one shape to another. Schott and Kaghan[2] have demonstrated that in the extrusion of high-pressure polyethylene above the critical shear stress first the helix effect occurs, which in the supercritical region changes into the distortion phenomenon which Tordella[3] has quite characteristically termed "bamboo effect."

According to Eckert[4] the two effects occur in reverse order in the extrusion of neoprene.

In the last few years three explanations have been offered for these flow instabilities and the resulting deformations of the extrudate.

1. Elastic Turbulence at the Capillary Inlet

Tordella[3] and Bagley[5] have shown that in the case of an unstable flow of branched polyethylene through a capillary, small amounts of polymer periodically flow from the dead space above the capillary inlet into the capillary. These amounts were found back in the extrudate as the junctures of the bamboo structure.

Schulken and Boy[6] pointed out, that apart from the shear rate, the shear acceleration at the capillary inlet may be responsible for the occurrence of melt fracture.

Vinogradov[7] introduced an elastic Reynolds number, which indicates the ratio between elastic and viscous forces. A sudden velocity change at the capillary inlet will give rise to elastic oscillations which are no longer damped by the viscosity of the medium when the critical value of the elastic Reynolds number is reached.

2. Elastic Response at the Capillary Outlet

Spencer[10] has explained the helix effect in the extrusion of polystyrene on the basis of the elastic response of the melt as it leaves the capillary. The extrudate may be regarded as consisting of a skin, in which, on account of the high velocity gradient at the capillary wall, a very large amount of elastic energy is stored, and a core with a relatively small amount of elastic energy. This system is unstable and on contraction of the skin a helical thread is formed.

3. Slip-Stick at the Capillary Wall

Benbow and Lamb[8] and Tordella[9] have proved by experiment that above the critical shear stress there occurs a slip-stick effect at the capillary wall. They regarded this effect as the initiator of the flow instability.

In our opinion the flow instability of polymer melts above a certain critical shear stress is a direct result of the degree of non-Newtonian behavior of the flowing liquid. The subject of this paper is to elucidate this view.

THEORETICAL CONSIDERATIONS

For liquid flow in a pipe, generally the resistance per unit length of the pipe encountered by the liquid will decrease with increasing pipe diameter.

Hence

$$(\partial F/\partial D)_Q < 0 \tag{1}$$

where F = resistance per unit pipe length, D = diameter of pipe, and Q = volume rate of flow. If this condition is not fulfilled, that is, in case

$$(\partial F/\partial D)_Q \geqslant 0 \tag{2}$$

the liquid will meet the same, or a much lower resistance, if the stationary boundary layer at the wall is not infinitesimally thin, but has an appreciable thickness, so that the effective cross-sectional area of flow is considerably smaller (cf. Fig. 1).

It is virtually impossible that such a velocity profile should be stable. Equation (2) may therefore be regarded as a condition for unstable flow.

Now

$$F = \tau_w \pi D \tag{3}$$

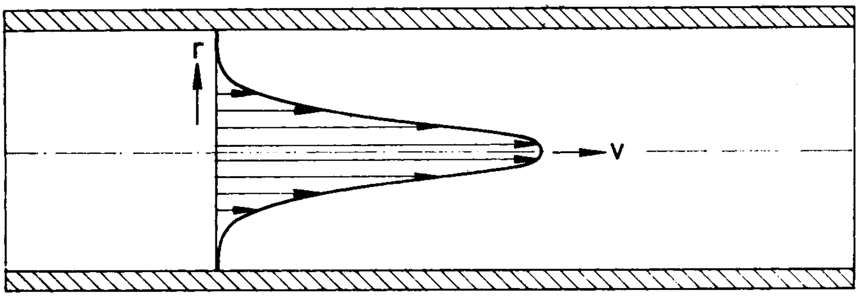

Figure 1.

where τ_w = shear stress at pipe wall, so that

$$(\partial F/\partial D)_Q = \pi D(\partial \tau_w/\partial D)_Q + \pi \tau_w \quad (4)$$

and the criterion for unstable flow therefore is

$$D(\partial \tau_w/\partial D)_Q + \tau_w \geqslant 0 \quad (5)$$

Rabinowitsch[11] has derived the relation between shear stress and velocity gradient at the wall for liquids flowing through a pipe:

$$\dot{\gamma}_w = 1/4[3\dot{\gamma}_{Nw} + \tau_w(d\dot{\gamma}_{Nw}/d\tau_w)] \quad (6)$$

where $\dot{\gamma}_w = |dv/dr|_R$ = absolute value of the velocity gradient at the wall and $\dot{\gamma}_{Nw} = 32Q/\pi D^3$. ($\gamma_{Nw}$ numerically corresponds to the velocity gradient at the wall for a Newtonian liquid flowing through the same pipe with the same volume rate of flow Q.)

With eq. (6) it is therefore possible to calculate for non-Newtonian liquids the velocity gradient at the wall from the measured values of shear stress and volume rate of flow. A condition is that the velocity at the wall should be zero.

Now

$$d\dot{\gamma}_{Nw} = (32/\pi D^3)dQ - (96Q/\pi D^4)dD$$
$$= \dot{\gamma}_{Nw}[(dQ/Q) - (3/D)dD] \quad (7)$$

Combination of eqs. (6) and (7) gives

$$\dot{\gamma}_w = 1/4\dot{\gamma}_{Nw}[3 + (\tau_w/Q)(dQ/d\tau_w) - 3(\tau_w/D)(dD/d\tau_w)] \quad (8)$$

Hence

$$D(\partial \tau_w/\partial D)_Q = 3\tau_w \cdot \dot{\gamma}_{Nw}/(3\dot{\gamma}_{Nw} - 4\dot{\gamma}_w) \quad (9)$$

Combination of eqs. (5) and (9) gives:

$$3\dot{\gamma}_{Nw}/(3\dot{\gamma}_{Nw} - 4\dot{\gamma}_w) \geqslant -1 \quad (10)$$

For a pseudoplastic liquid

$$\dot{\gamma}_w > \dot{\gamma}_{Nw}$$

always holds.

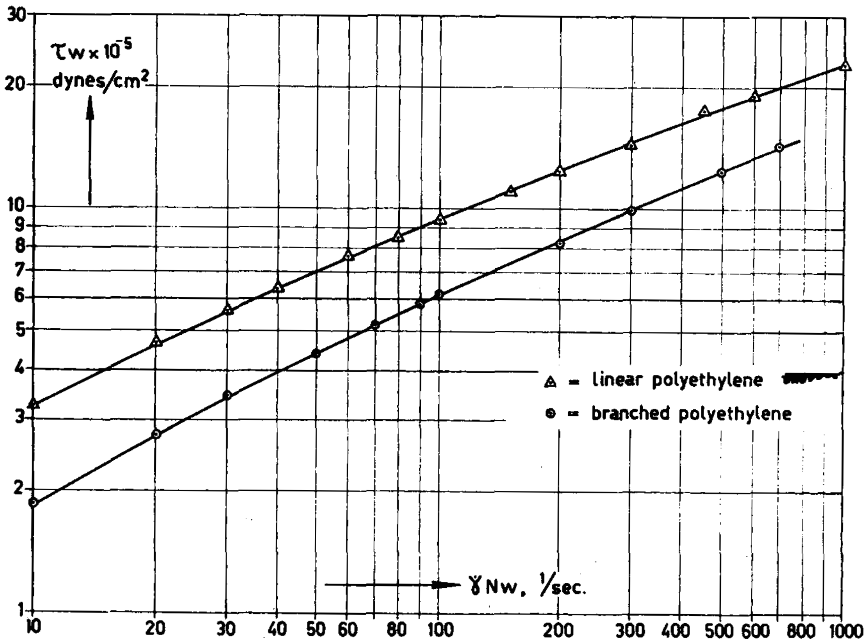

Figure 2.

It follows that for these liquids the denominator in the left-hand side of eq. (10) will always be negative.

From eq. (10) the following condition for instability may be derived:

$$3\dot{\gamma}_{Nw} \leqslant 4\dot{\gamma}_w - 3\dot{\gamma}_{Nw}$$

or

$$\dot{\gamma}_w/\dot{\gamma}_{Nw} \geqslant 1.5 \qquad (11)$$

DISCUSSION

Using a capillary viscometer, Bagley[12] has determined the relation between τ_w and $\dot{\gamma}_{Nw}$ for a linear and a branched type of polyethylene at 190°C. (Fig. 2).

From this relation Bagley has calculated $\dot{\gamma}_w$ as a function of $\dot{\gamma}_{Nw}$ by means of the Rabinowitsch formula.

In Figure 3 we show the relation between $\dot{\gamma}_w/\dot{\gamma}_{Nw}$ and τ_w/τ_{wcr}, τ_{wcr} being the critical shear stress at the capillary wall at which melt fracture occurs.

From Figure 3 it will be seen that $\dot{\gamma}_w/\dot{\gamma}_{Nw}$ increases more and more according as the shear stress at the capillary wall becomes greater. This means that the liquid will deviate increasingly from the Newtonian behavior.

With linear polyethylene melt fracture starts at $\dot{\gamma}_w/\dot{\gamma}_{Nw} = 1.5$, which is entirely in agreement with theoretical expectations. For branched poly-

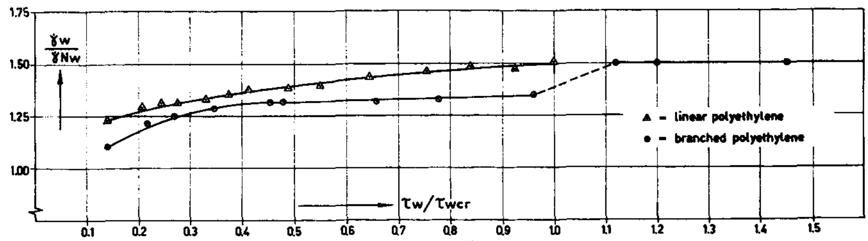

Figure 3.

ethylene the course of the curve in Figure 3 is slightly different. Besides, there are no measuring points near the critical point, but above the critical point $\dot{\gamma}_w/\dot{\gamma}_{Nw}$ has the constant value of 1.5.

From this constant value of 1.5 above the critical point in the case of branched polyethylene no special phenomena are to be expected apart from melt fracture. Accordingly, no such phenomena have been found.

For linear polyethylene, however, a special phenomenon was found to occur, viz., a sudden increase of the volume rate of flow just above the critical point. If in the supercritical region $\dot{\gamma}_w/\dot{\gamma}_{Nw}$ exceeds the value 1.5 (no measurements with linear polyethylene have been made in this region), then according to theory $(\partial F/\partial D)_Q > 0$. In that case, apart from unstable flow, a substantial decrease of the resistance also may be expected, which in turn may cause a strong increase of Q. This might explain the discontinuity in the rheological behavior of linear polyethylene.

We believe that the foregoing shows all the phenomena connected with melt fracture to be a logical consequence of the degree of non-Newtonian behavior of polymer melts.

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Résumé

On montre que l'instabilité de l'écoulement des polymères fondus observée au dessus d'une certaine force de cisaillement critique résulte directement du degré de comportement non-Newtonien du liquide s'écoulant. La rupture à l'état fondu, la turbulence élastique et les effets de glissement sont une conséquence de cette instabilité, conduisant fréquemment à des phénomènes périodiques. On déduit la condition de l'existence de l'instabilité a l'écoulement.

Zusammenfassung

Es wird gezeigt, dass die oberhalb einer gewissen kritischen Schubspannung auftretende Fliessinstabilität von Polymerschmelzen ein direktes Ergebnis des Grades an nicht-Newtonschem Verhalten der strömenden Flüssigkeit ist. Schmelzbruch, elastische Turbulenz und Gleit-Hafteffekte sind eine Folge dieser Instabilität, welche häufig zu Periodizitätsphänomenen führt. Die Bedingung für das Auftreten einer Fliessinstabilität wird abgeleitet.

Received March 25, 1965