

FORMATION OF SYNTHETIC FIBERS

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assumption that Ψ_1/τ^2 is constant.¹⁶⁵ In effect, G is taken as constant also, and this leads to

$$\frac{d}{d_0} = [1 + (\kappa\tau_w \xi)^2/2]^{1/6}, \quad (2-58)$$

where

$$\kappa = \Psi/2\tau_w^2.$$

Equation (2-58) gives a fair approximation of the experimental data, particularly when the calculated value of d/d_0 is multiplied by 1.1, which is the amount of swelling encountered for slow-flowing Newtonian fluids.¹⁶⁶

The findings of the various authors quoted above seem to indicate that the mechanism of die swelling in extrusion is much more complex than it had been assumed in any of the theories proposed thus far.

Here it must be noted that the elastic properties of polymer melts cannot be considered as a material property only. It is reasoned that molecular entanglements of some sort are responsible for creating network-like structures resembling vulcanized rubber. These entanglements are not constant; rather they appear to vary depending on the thermal and shear history of the melt. It was noticed that the recoverable shear, for instance, may be much smaller for a polymer which has been dissolved and precipitated than for the original sample. After some thermal treatment, the elastic component increases again. Despite all the changes in the recoverable shear, melt viscosity can remain unchanged during all the cycles of experiments.¹⁰⁰ Should the recoverable shear be measured several times on the same polymer specimen, then the next experiment would show a somewhat smaller elastic component while the viscous component remained the same. The higher the shear rate applied, the more pronounced the result of experiment will be.

A series of experiments conducted to ascertain the influence of shearing on subsequent properties of polymer melt show the great significance of this phenomenon. Depending on the intensity of shearing in a capillary, with no detectable changes in molecular weight, a polymer flow may change to require shear stress higher or lower by 10 to 20% at the same shear rate. It has also been shown that not only the magnitude of shearing but the pattern of perturbations, i.e. differences in the geometry of capillary entrance, or polymer dissolution and subsequent reprecipitation, as well as the type of solvent used,²⁴¹ can have an equally serious influence on the melt flow of the polymer.⁹⁴

Another feature which is usually considered as a consequence of liquid elasticity is melt fracture.^{87,101,102} When shear rate is increased during the extrusion of polymer melt through a capillary beyond a certain critical value, $\dot{\gamma}_{cr}$, the surface of the extrudate loses its smoothness. The extrudate may assume

a helical shape or may become rough with irregularly spaced thin and thick sections. It was noticed¹⁰¹ that a relationship exists between weight average molecular weight and critical shearing stress τ_{cr} beyond which the melt fracture occurs:

$$M_w \tau_{cr} = \text{Const.} \quad (2-59)$$

Using Eq. (2-22) describing shear modulus, Hooke's law in shear may be written as

$$\tau M = RT\rho S_R \quad (2-60)$$

This equation should hold also when melt fracture occurs, thus:

$$\tau_{cr} M = RT\rho S_{R,cr} \quad (2-61)$$

Closer analysis of this relationship suggests that the recoverable shear a polymer can withstand before melt fracture, appears to be constant and independent of molecular weight. Originally it was assumed^{87,190} that τ_{cr} is approximately 10^6 dyn/cm². Newer determinations¹⁸⁸ show that τ_{cr} varies within a relatively narrow range of 0.68×10^6 to 2.15×10^6 dyn/cm². Increase of molecular weight causes decrease of τ_{cr} , but molecular weight distribution is believed to have no influence on τ_{cr} . The temperature dependence of the recoverable shear at the fracturing point is relatively small. The numerical values of $S_{R,cr}$ for different polymers do not vary appreciably and are usually around 7 as long as the polymers are linear.⁸⁷

It has been established empirically that the geometry of the capillary entrance has a very significant influence on the magnitude of the critical shear rate. This effect as obtained for polypropylene with capillaries having conical entries is presented in Figure 2-22 in relation to the angle of the cone. Different polymers show somewhat different behavior for entrance angles larger than 60°, but for smaller entrance angles, the effect is practically parallel.

It is assumed that what is generally called melt fracture results from three different causes.²⁴² With increasing shear rate there first appears a surface roughness or just a dull appearance, sometimes called shark skin. This roughness originates in the exit of capillary.¹⁶⁷⁻¹⁷² At significantly higher shear rates, elastic flow turbulence which originates already at the entry to the capillary occurs.^{94,170,171,173-175} In the intermediate region of shear rates, one encounters oscillatory flow which results from the flow velocity at the wall being other than zero (wall slippage).^{170,171,189,190}

The most important, if not the only, means of increasing the shear rate at which fractured flow will occur is through the application of conical entrances with sharp angles (20° to 30° included angle). Parabolic or hyperbolic surfaces may be used also.^{173,174}