JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 747–750 (1967)

Derivation and Correction of Polyethylene Melt Strength Equation

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Synopsis

The following equation for the determination of polyethylene melt strength (MS) has been derived:

$$\text{MS(poise)} = 1.492 \times 10^7(\Delta l)^2 r_0{}^2/(\text{MF})$$

where Δl is the length (inches) of extruded polymer cord required for 50% decrease in diameter of the cord, r_0 is the radius (inches) of the molten polymer cord as it first emerges from the melt indexer die, and MF is melt flow rate in grams/10 min. The required measurements are made on the initially extruded 0.5-in. portion of the polymer cord from a conventional melt indexer using the standard 0.0825-in.-diameter die and 2160-g. load and a temperature of 230°C. This melt strength equation was derived by using the assumption that the melt strength can be expressed as melt viscosity at low shear rates. Melt strengths of polyethylenes having similar melt indices have been shown to have over a 37-fold difference.

When a molten plastic is extruded from the orifice of a melt indexer, the diameter of the extrudate changes because of the stress applied to the melt by the weight of the material which has preceded it. The extrudate takes the form of a truncated cone shown in Figure 1. By measuring the change in the diameter of the extruded cord over the first $^1/_2$ in. (230°C., load 2160 g.), we can calculate a melt viscosity at extremely low shear rates (0.1 to 0.01 sec.$^{-1}$). Depending on their melt viscosities, different polymers will have a different Δl, which is defined in Figure 1. We named the melt viscosity under these low shear rates the melt strength (MS), since this melt viscosity indicates how well the melt can support its own weight. Rate of crystallization can effect the results, but the use of a 230°C. melt temperature usually eliminates this factor.

The equation used to calculate the melt strength is derived as follows:

$$\text{MS} = \tau/\dot{\gamma} \tag{1}$$

where τ is the shear stress defined as

$$\tau = (\text{weight})(g)/(\text{area}) \tag{2}$$

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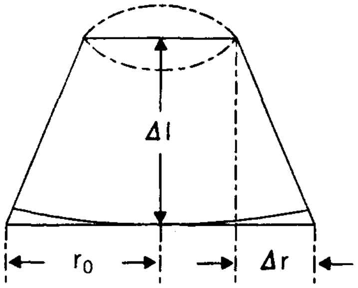

Fig. 1. Shape of extruded cord: Δl = length of the cord (inches) required for 50% decrease in diameter of the cord; r_0 = radius (inches) of the cord as it first emerges from the die; $(r_0 - \Delta r)/r_0 = \Delta r/r_0 = 0.50$ by definition.

or

$$\tau = \frac{\pi(\Delta l)\,[r_0^2 + r_0(r_0 - \Delta r) + (r_0 - \Delta r)^2]\rho g}{3\pi(r_0 - \Delta r)^2} \tag{3}$$

and $\dot{\gamma}$ is the shear rate defined as

$$\dot{\gamma} = \frac{\text{(melt flow rate)(displacement or strain)}}{\text{(weight)}} \tag{4}$$

or

$$\dot{\gamma} = \frac{3(\mathrm{MF})r_0^2}{\pi(\Delta l)\,[r_0^2 + r_0(r_0 - \Delta r) + (r_0 - \Delta r)^2]\rho(r_0 - \Delta r)^2} \tag{5}$$

In these equations the melt density ρ of polyethylene, is 0.755 g./cm.^{3} at 230°C., g is the acceleration constant, MF is the melt flow rate in grams/10 min. at 230°C., and $r_0^2/(r_0 - \Delta r)^2$ is a measure of the displacement for the shear rate. This displacement is derived in eqs. (6) and (7).

The volume V in which the shear rate occurs is constant and may be expressed as:

$$V = \pi l_1(r_0 - \Delta r)^2 = \pi l_2 r_0^2 \tag{6}$$

Thus, the displacement during the measurement is:

$$l_1/l_2 = r_0^2/(r_0 - \Delta r)^2 \tag{7}$$

The MS can then be expressed by using eqs. (1), (3), and (5) as follows:

$$\mathrm{MS} = \frac{\pi(\Delta l)^2[r_0^2 + r_0(r_0 - \Delta r) + (r_0 - \Delta r)^2]^2\rho^2 g}{3^2 r_0^2(\mathrm{MF})} \tag{8}$$

After the terms are rearranged and the values for g and ρ are substituted, eq. (8) can be written:

$$\mathrm{MS} = \frac{\pi(\Delta l)^2 r_0^2(980.7)(0.755)^2}{9(\mathrm{MF})}\left[1 + \left(\frac{r_0 - \Delta r}{r_0}\right) + \left(\frac{r_0 - \Delta r}{r_0}\right)^2\right]^2 \tag{9}$$

Then, the terms are cleared up, 0.50 is substituted for $(r_0 - \Delta r)/r_0$, and eq. (9) becomes:

$$\mathrm{MS} = \frac{5{,}973(\Delta l)^2 r_0^2}{(\mathrm{MF})} \frac{(\mathrm{g.})(\mathrm{in.})^4(\mathrm{min.})}{(\mathrm{cm.})^5(\mathrm{sec.})^2} \tag{10}$$

The units of the terms are changed so that MS can be expressed in poises as follows:

$$\mathrm{MS(poise)} = \frac{1.492 \times 10^7 (\Delta l)^2 r_0^2}{(\mathrm{MF})} \tag{11}$$

Note that the constant in eq. (11) is different from that in the equation reported by Guillet et al.[1] by a factor of 41.62 or $(2.54)^4$. This difference was due to a mistake in converting the units of the actual equation used from inches to centimeters. The actual data reported by Guillet et al. in Tables I–III[1] are correct, but eq. (1) in the same paper is in error.

Downs[2] criticized the derivation of eq. (11) on three counts.

(*1*) The extrudates do not have the form of a truncated cone. Downs found for linear polyethylenes that a more linear plot is obtained if the diameter of the extruded cord is plotted against the logarithm of the length up to 60 in. However, the first 6 in. of extruded cord did appear to approximate a truncated cone. We found this to be true for branched polyethylenes; therefore, all of our measurements were made only over the first $^1/_2$ in. of the extruded cord. Both the Δl and r_0 were calculated[1] by extrapolation of the measurements at $^1/_{16}$, $^1/_4$, and $^1/_2$ in. Although the weight of the extrudate used in eqs. (3) and (5) is not strictly correct, it gives a reasonable approximation of the true weight and gives a reasonable basis on which to compare polymers.

(*2*) It is not necessary to use eq. (4) to obtain a true measure of shear rate, although Downs admits that this equation is related to shear rate. The use of eq. (4) is allowed by basic definitions and does permit us to rank polymeric melt strength without any further measurements.

(*3*) The polymer stability and the amount of polymer in the melt indexer in some cases do not allow the achievement of a 50% reduction in diameter. Also, with some polymers only the first few inches of the extrudate are molten and the remainder is solid. The use of a 230°C. melt temperature improves the measurement of melt viscosity and helps to eliminate the effect of crystallization. Further, the use of only the initial $^1/_2$ in. of extrudate allows all of the stress to be applied in the melt and eliminates long term changes in the melt flow due to polymer degradation.

In summary, an equation for the determination of polyethylene melt strength has been derived. We have assumed that the melt strength can be expressed as melt viscosity at low shear rates. For this calculation, only the melt flow and three measurements of the diameter (at $^1/_{16}$, $^1/_4$, and $^1/_2$ in.) of a cord extruded from a melt indexer at 230°C. are required.

Equation (11) was used[1] and showed over a 37-fold difference in the melt viscosities of polyethylenes having similar melt indices.

References

1. J. E. Guillet, R. L. Combs, D. F. Slonaker, D. A. Weemes, and H. W. Coover, Jr., *J. Appl. Polymer Sci.*, **9**, 757 (1965).

2. G. Downs, British Hydrocarbon Chemicals, Ltd., Grangemouth, England, private communication, August 6, 1965.

Résumé

L'équation suivante pour la détermination de la force à la scission du polyéthylène (MS) a été dérivée. MS (poise) = $1.492 \times 10^7 (\Delta l)^2 r_0^2/(\mathrm{MF})$, où Δl est la longueur en pouces de la corde de polymère éxtrudé requise pour une diminution de 50% du diamètre de la corde, r_0 est le rayon en pouces de la corde de polymère fondu ainsi qu'il sort tout d'abord de l'extrudeur et MF est la vitesse d'écoulement de la masse fondue en g/10 min. Les mesures requises sont faites sur la partie initialement extrudée de 0.5 pouces de la corde de polymère au départ d'un extrudeur conventionnel utilisant un piston standard de 0.0825 pouces de diamètre et 2160 g. de charge et une température de 230°C Cette équation de force à la fusion a été dérivée utilisant l'hypothèse que la force à la fusion peut être exprimée par la viscosité a l'état fondu et les faibles tensions de cisaillement. Les forces à la tension du polyéthylène ayant des indices de fusion similaires ont été montrées avoir des différences au delà de 37 fois plus élevées que les autres.

Zusammenfassung

Folgende Gleichung wurde zur Bestimmung der Festigkeit einer Polyäthylenschmelze (MS) abgeleitet: MS (Poise) = $1{,}492 \times 10^7(\Delta l)^2 r_0^2/(\mathrm{MF})$, wo Δl die Länge (in Zoll) des extrudierten Polymerstranges, bei welcher eine Abnahme des Strangdurchmessers um 50% stattfindet, r_0 der Radius (in Zoll) des geschmolzenen Polymerstranges beim Austritt aus dem Schmelzindexapparat und MF die Fliessgeschwindigkeit der Schmelze in g/10 min ist. Die erforderlichen Messungen werden am zuerst aus einem konventionellen Schmelzindexapparat durch die Standarddüse mit 0,0825 in. Durchmesser unter einer Belastung von 2160 g und bei einer Temperatur von 230°C extrudierten Teil (0,5 in.) des Polymerstranges ausgeführt. Die Schmelzfestigkeitsgleichung wurde unter der Annahme abgeleitet, dass die Schmelzfestigkeit bei niedriger Schubgeschwindigkeit als Schmelzviskosität ausgedrückt werden kann. Die Schmelzfestigkeit von Polyäthylenproben mit ähnlichem Schmelzindex unterschied sich um über das 37-fache.

Received August 24, 1966
Revised September 12, 1966
Prod. No. 1502