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Time-Dependent Capillary Flow of Polyethylene Melt

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Synopsis

The variation of output rate with extrusion time is examined experimentally for capillary flow of high density polyethylene melt. The increase in output rate is divided into two parts. One of these is due to the decrease in the amount of the material in the reservoir and is well interpreted from the consideration of the so-called reservoir effect. The other part is mainly attributed to the disentanglement or orientation of polymer chain during flow in the reservoir.

INTRODUCTION

When a polymer melt is continuously extruded through a capillary orifice under ostensibly invariant conditions, the apparent viscosity of the material varies with extrusion time in a complex manner. This behavior has been investigated by several researchers.[1–9] Schreiber has summarized this subject in a recent review.[9] It is accepted that at least three major contributing factors are involved in the long-term increase in the output rate observed in the case of the dead-weight type capillary extrusion rheometer. The relative importance of those factors varies from case to case and depends as much on the material used as on the chosen conditions of extrusion. Under the condition of the measurement of the melt index, the so-called reservoir effect is considered to be the main factor.

However, no attempt has yet been made to separate experimentally the magnitude of contribution of those factors. The main objectives of this study were, first, to examine experimentally the variation of output rate with extrusion time and, secondly, to analyze the results on the basis of the reservoir effect after the separation of its contribution from the other.

EXPERIMENTAL

The material was a high-density polyethylene, Sholex 6009 (melt index = 0.9, annealed density = 0.96) which contained antioxidant (about 0.15% by weight based on the resin). Owing to the relatively high content of antioxidant the material did not undergo appreciable chemical change during the experimental run.

Experiments were in most cases carried by using a standard melt indexer[10] at 190.0 ± 0.2°C. Two orifices with flat entries were used, one was 2.094 mm. in diameter and 8.02 mm. in length (standard orifice for measuring the melt index) and the other was 1.00 mm. in diameter and 4.00 mm. in length.

The procedure of measuring the output rate was similar to that of the measurement of melt index,[10] but a 1-kg. load was applied for the first 15 min. after the sample was charged in the reservoir. The extrusion time t was taken from the moment when the specified load was applied after the preheat time. The extrudate was cut every specified interval of time and weighed as usual. The volumetric output rate Q was calculated from the weight of the extrudate by assuming that the specific volume at 190°C. is 1.298, the value under ordinary pressure.[11] The position L of the piston, which is equal to the length of the melt in the reservoir, was also noted continuously. One experimental run was carried on until the material in the reservoir was almost extruded. Under the same load, we carried ten or more runs with varying sample charges.

Additional data were obtained by using a nitrogen gas-driven capillary viscometer. In this case, a loose-fitting ball was used to prevent gas channeling. The value of L was obtained by calculation, since the direct observation of L was impossible. It will be shown (in Figure 2) that the calculated value of L is the correct one.

RESULTS

Typical results are shown in Figure 1, where the output rate Q and the length L of the material in the reservoir are plotted against extrusion time t for three runs under 3.1 kg. load. The output rate–extrusion time relations are quite similar to those reported in the literature[1,3] for high-density

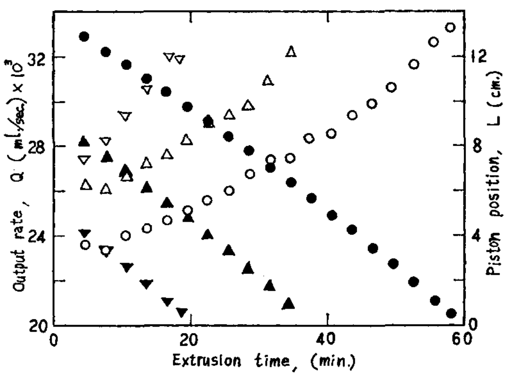

Fig. 1. Dependences of (○, △, ▽) output rate Q and of (●, ▲, ▼) piston position L on extrusion time t under 3.1 kg. load.

polyethylene. The slight decrease in Q is followed by a gradual increase in Q. The decrease in L with t is not linear but is accelerated. This is more clearly shown in Figure 2, where ΔL, the difference in two successive readings of L, is plotted against t. Calculated values of ΔL are also shown in this figure. Within the experimental error, both observed and calculated values agree over the entire range of the extrusion time.

By using relations such as those shown in Figure 1, it is possible to evaluate Q_t as a function of L and Q_L as a function of t, where Q_t is the output rate at the same t and Q_L the output rate at the same L. Data

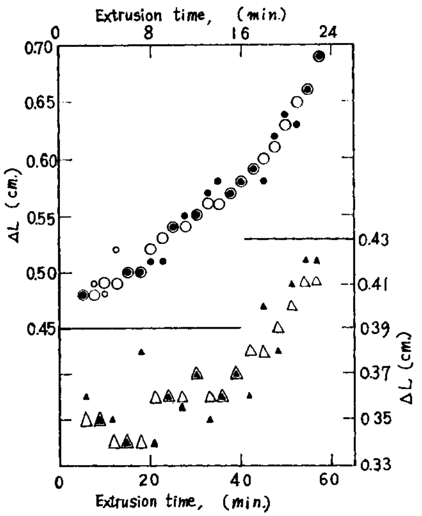

Fig. 2. Relations between ΔL and t: (Δ) calculated, 2.16 kg. load; (▲) observed, 2.16 kg. load; (O) calculated, 5.0 kg. load, (●) observed, 5.0 kg. load.

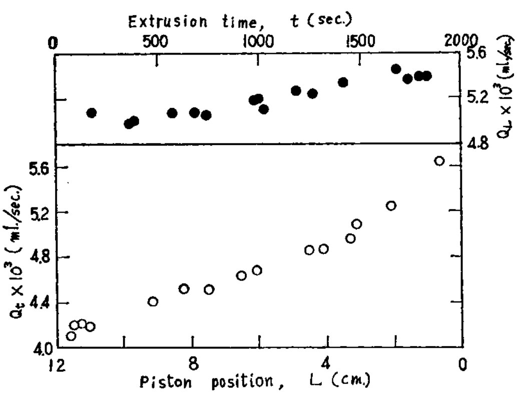

Fig. 3. Variation of output rate with L and t: (O) Q_t vs. L at t = 525 sec.; (●) Q_L vs. t at L = 3 cm.

obtained under 4.1 kg. load are taken to show typical results. In Figure 3, Q_t/L and Q_L/t relations are shown. It should be noted that each plot belongs to a different experimental run. Thus, the increase in output rate with extrusion time can be separated into two parts, one of which is the contribution of the reservoir effect.

DISCUSSION

Reservoir Effect

From the viewpoint that a capillary extrusion rheometer is a system of two capillaries in series, it follows[7–9] that

$$Q = C[1 + (L/l_c)(r/R)^{1+(3/n)}]^{-n} \tag{1}$$

where R is the radius of the reservoir, r is the radius of the capillary, l_c is the corrected capillary length[12] ($l_c = l + el$, e being the end correction coefficient $\fallingdotseq$ 2.0 under the conditions[13] covered in this study), and n is given by

$$\dot{\gamma} = K\tau^n \tag{2}$$

where $\dot{\gamma}$ is the rate of shear and τ is the shear stress.

To analyze the experimental data (Q_t/L relation) on the basis of eq. (1), it is convenient to take a reference length L_s. (We take somewhat arbitrary L_s = 7 cm. throughout this study.) The output rate at L_s is denoted as $Q_{t,s}$ and then $Q_t/Q_{t,s}$ is plotted against L. Figure 4 shows such plots for results obtained under 7.1 kg. load. In this case the value of Q_t was taken

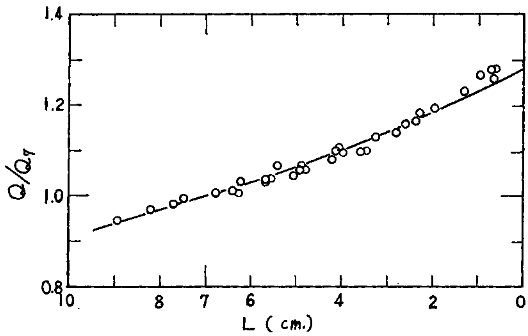

Fig. 4. Test of the applicability of eq. (1) for results of 7.1 kg. load. The curve is calculated with n = 1.9 (e = 2.0).

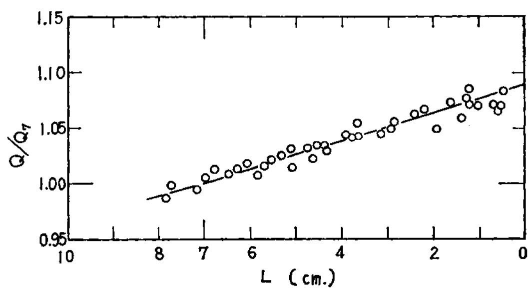

Fig. 5. Test of the applicability of eq. (1) for results obtained by a nitrogen gas-driven viscometer under a pressure of 10 kg./cm.². The curve is calculated with n = 2.0 (e = 2.0).

as follows. As shown in Figure 3, values of Q_L in a short interval of time can be practically regarded as equal. It is convenient, therefore, to make use of data obtained within a short interval of time. We take a somewhat arbitrary time interval of $t_{F/2} \pm \Delta t$, where $t_{F/2}$ is $^1/_2 \times t_F$, Δt is taken as $^1/_{20} \times t_F$, and t_F is the time necessary to extrude the material completely when as much material as possible is charged in the reservoir.

The calculated curve with $n = 1.9$ is also shown in Figure 4. The curve represents the data points fairly well except for the region of small L. Thus, it is deduced that $n = 1.9$ for flow under 7.1 kg. load. Figure 5 shows similar plots for results obtained by the gas-driven capillary rheometer. It is noteworthy that data points do not deviate appreciably from the calculated curve even in the region of small L. In a similar way, we estimated values of n under various conditions; these are tabulated in Table I.

TABLE I
Values of n

Load, kg.	n			
	Melt indexer			N_2 gas-driven viscometer, 2.09 mm. diameter × 8.02 mm. reservoir effect
	Standard die		1 mm. diameter × 4 mm., reservoir effect	
	Reservoir effect	Flow curve		
2.16	1.8	1.8	—	—
3.1	1.8	1.8	—	—
4.1	1.8	1.9	—	—
5.0	1.9	1.9	—	—
7.1	1.9	2.0	2.0	2.0[a]
10.0	2.0	2.1	2.0	—

[a] Pressure of 10 kg./cm.^{2} for the apparatus corresponds to 7.1 kg. load for melt index apparatus.

Since n is given by eq. (2), the value n is obtained from the rate of shear–shear stress relation. The rate of shear $\dot{\gamma}$ and the shear stress τ are calculated from the relations

$$\gamma = (n + 3)Q_0/\pi r^3 \qquad (3)$$

and

$$\tau = Pr/2(l + 2r) \qquad (4)$$

where Q_0 is the output rate at $L = 0$ and P is the applied pressure. As shown in Figure 3, data points in the region of small L deviate slightly from the calculated curve. When L becomes small, the flow of the material may be disturbed by some complex factors. Thus, the true output rate Q_0 at $L = 0$ may be obtained by calculation rather than the extrapolation of the experimental data at small L once the exponent n is correctly evaluated, and $Q_{t,s}$ is given in good accuracy. Figure 6 shows plots of log $\dot{\gamma}$ against log τ. This relation gives a true flow curve, since necessary corrections,[12] the capillary end correction and the Rabinowitsch correction, were applied. All data obtained by two capillaries and two apparatus constitute a single curve. This figure shows that the exponent n in eq. (2) is not a constant

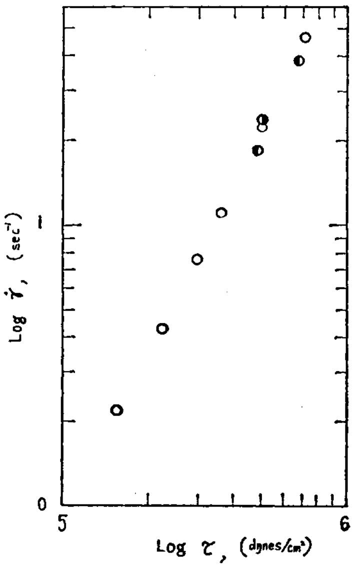

Fig. 6. Flow curve: (O) melt indexer, standard die; (◐) melt indexer, 1 mm. diameter × 4 mm. die; (◑) N_2 gas-driven viscometer, 2.09 mm. diameter × 8.02 mm. die (same dimensions as those of the standard die).

but varies with shear stress, even in a relatively narrow region of shear stress. Thus, n is given as

$$n = d \log \dot{\gamma}/d \log \tau \tag{5}$$

By using eq. (5), we evaluated the value of n at each load; the n thus obtained are tabulated in Table I. These values are nearly equal to those obtained from the consideration of the reservoir effect.

Variation of Q_L with t

As shown in Figure 3, the output rate increases with time even when the comparison is made at the same L. We found that when log Q_L is plotted against log t, a straight line relation is obtained and that the slope m ($=d \log Q_L/d \log t$) is nearly equal for the same load and different L but m differs for different load; thus the slope m can be regarded as the measure of the increase in Q_L with t. On the other hand, ΔQ_L is conveniently defined as follows:

$$\Delta Q_L = (Q_{L,F} - Q_{L,F/5})/Q_{L,F/5} \tag{6}$$

TABLE II
Increase in Q_L with t

			Measure of increase in Q_L		Shear rate at the		
Apparatus	Die	Load, kg.	$m = d \log Q_L/d \log t$	ΔQ_L, %	Capillary wall $(n+3)Q_0/\pi r^3$, sec.$^{-1}$	Clearance between reservoir wall and piston V_0/δ, sec.$^{-1}$ [a]	Reservoir wall $4Q_0/\pi R^3$, sec.$^{-1}$
Melt indexer	Standard die	2.16	0.027	4.3	2.19	0.68	0.020
		3.1	0.034	4.8	4.27	1.3	0.038
		4.1	0.045	7.3	7.51	2.3	0.067
		5.0	0.050	8.1	11.0	3.3	0.096
		7.1	0.052	9.0	22.3	6.7	0.19
		10.0	0.055	9.3	46.8	13.7	0.40
	1 mm. diam.	7.1	0.030	5.5	18.5	0.58	0.017
	× 4 mm.	10.0	0.037	6.6	38.9	1.2	0.036
N_2 gas-driven viscometer	Standard die	7.1[b]	0.040	8.1	23.8	—	0.044

[a] V_0 is the velocity of the material in the reservoir and δ the clearance between reservoir wall and piston.
[b] Pressure 10 kg./cm.^{2} for the apparatus corresponds to 7.1 kg. load for melt indexer.

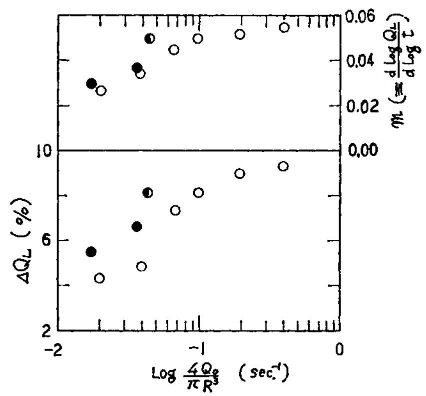

Fig. 7. Plots of ΔQ_L (increase in output rate at the same L) and m ($= d \log Q_L/d \log t$) against log $4Q_O/\pi R^3$ (apparent shear rate at the reservoir wall): (O) melt indexer, standard die; (●) melt indexer, 1 mm. diameter × 4 mm. die; (◐) N_2 gas-driven viscometer, 2.09 mm. diameter × 8.02 mm. die (same dimensions as those of standard die).

where $Q_{L,F}$ and $Q_{L,F/5}$ are the values of Q_L at t_F and at $t_{F/5}$, respectively, t_F is, as defined earlier, the time necessary to extrude the material completely when as much material as possible is charged in the reservoir, and $t_{F/5} = {}^1/_5 t_F$.

In Table II the values of m and ΔQ_L are tabulated along with the shear rates at the capillary wall, at the clearance between the reservoir wall and the piston, and at the reservoir wall. It is clearly shown that ΔQ_L or m is independent of shear rate at the capillary wall and is related to some factors dominant in the reservoir.

In the recent review of Schreiber,[1] two other contributing factors are described besides the reservoir effect: the frictional heating of melt in the clearance between the piston and the reservoir wall and the melt orientation producing a real reduction in melt viscosity. The former was first pointed out by Marker and co-workers[2] and the latter by Schreiber and Rudin.[1,5,6]

Frictional heating may certainly contribute to the increase in output rate. It is not conceivable, however, that its effect appears gradually with extrusion time in the region of large L. Owing to the low thermal conductivity of the melt, heat generated by friction in the clearance between the piston and the reservoir wall will be accumulated in the region near the piston. When such a portion of material is extruded, in other words, when L becomes small, the output rate may suddenly increase because of the decrease in viscosity due to the temperature rise. This may be one of the causes of the deviation of data points from the calculated curve in the region of small L as shown in Figure 4, the data obtained by the melt indexer apparatus. On the other hand, the appreciable deviation of data points from the calculated curve is not observed in Figure 5 the result obtained by the nitrogen gas-driven viscometer, in which frictional heating may be far less than that generated in the melt indexer apparatus.

In Figure 7, values of ΔQ_L and m are plotted against the apparent shear rate $4Q_0/\pi R^3$ at the reservoir wall. It is shown that ΔQ_L or m is closely related to the flow in the reservoir. From this fact, as pointed out by Schreiber, it may be deduced that the shearing action due to the flow of the material in the reservoir results in the disentanglement or orientation of polymer chains and reduces the viscosity of the system, thus the output rate increases gradually with t even when the reservoir effect is completely removed.

Although the contribution of the orientation effect was much smaller than that of the reservoir effect under the conditions covered in this study, the relative importance varies depending on the material used and chosen conditions of extrusion. In some case the frictional heating which had minor effect on this study may play an important role. At any rate, the magnitude of contribution of those factors can be evaluated by following the method described in this paper.

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