The Capillary Flow of Silicones

DONALD L. JOHNSON* and ERIC BAER,† *Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois*

The flow of molten polymers through capillaries recently has received considerable attention. Experimental results from capillary flow data can be used in evaluating various aspects of the non-Newtonian and viscoelastic flow behavior of polymer melts. The data can also be applied to polymer processing such as in extrusion die design.[1]

In this paper, the results of flow studies with Viscasil silicone fluids in a capillary viscometer are reported. Both entrance and exit effects were investigated, as well as the complex nature of the non-Newtonian flow in the capillary.

EXPERIMENTAL

The data were obtained with a capillary viscometer very similar to melt indexer of the American Society of Testing Materials.[2] The test liquid was maintained at a temperature ±0.1°C. in a thermostatted stainless-steel reservoir 5 in. in diameter. In the center of the base, capillary tubes 0.324 cm. in diameter having various L/D ratios were attached. In all experiments a flat entry was used. The pressure could be regulated to between 0 and 300 psi.

Swelling measurements of the issuing vertical capillary jet were made with a vernier microscope (Griffen and George, Model No. 1507). To minimize gravitational effects, the jet was extruded into a cylinder containing alcohol. The alcohol level was kept about $1/4$ in. from the tip of the capillary. The tip of the capillary was carefully machined to a sharp 30° angle and inspected under a microscope before use.

The experiments were performed with silicone fluids of various bulk viscosities (cstokes): Viscasil 5,000, Viscasil 30,000, Viscasil 60,000, and Viscasil 100,000. The physical properties of these fluids are reported by the manufacturer.[3] In all experiments the fluids were maintained at 25°C.

DISCUSSION OF RESULTS

The discussion is divided into three parts. First, the flow data are discussed with the assumption of a power law fluid. Second, the viscoelastic

* Present address: Department of Chemical Engineering, Washington University, St. Louis, Missouri.
† Present address: Case Institute of Technology, Cleveland, Ohio.

nature of entrance effects are analyzed according to the method proposed by Bagley.[4,5] Finally, the results of swelling measurements at the capillary exit are discussed.

Power Law Fluid

It is well known that the power law formula can readily be used in flow calculations involving a nonlinear liquid.   When more complex rheological models are used the solutions of the resulting mathematical expressions are usually very cumbersome.   For a fluid flowing in a capillary of length L, the power law can be written as follows:

$$\tau_r = (\Delta P/2L)r = m(-dv/dr)^n \tag{1}$$

τ_r is the shear stress, dv/dr is the velocity gradient in the radial direction r, ΔP is the pressure drop, and m and n are the consistency and flow index, respectively.   Integration of eq. (1) in the usual manner[6] gives

$$\log G_n = 1/n \log P - 1/n \log 2Lm/R - \log (3n + 1)/4n \tag{2}$$

where $G_n = 4Q/\pi R^3$, Q is the volumetric flow rate, and R the capillary radius.   According to eq. (2), if the fluid obeys the power law, a plot of log G_n versus log P will give a straight line.   From the slope, n is found, and m is obtained from the intercept.

The flow data for three silicone fluids are given in Figures 1, 2, and 3. The flow behavior was studied in capillaries with different L/R ratios.   In
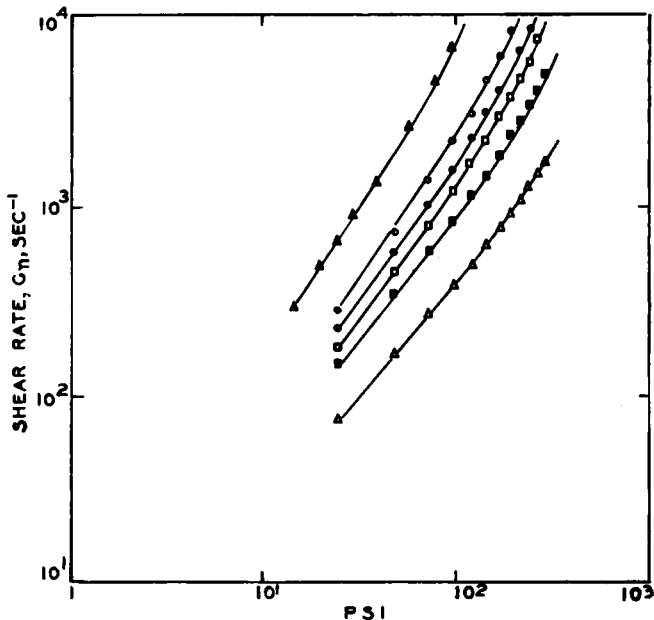

Fig. 1. Log shear rate vs. log pressure for Viscasil 30,000.   L/R values (▲) 5; (●) 13; (O) 10.2; (□) 16; (■) 22; (△) 40.

all cases, at low pressures the data fell on straight lines from which n and m could be calculated. However, at high pressures in nearly all cases appreciable deviations from linearity were observed. In Table I, the values for the flow index and consistency are given. It is interesting to note that both n and m vary with L/R. In Figure 4, n versus L/R, and
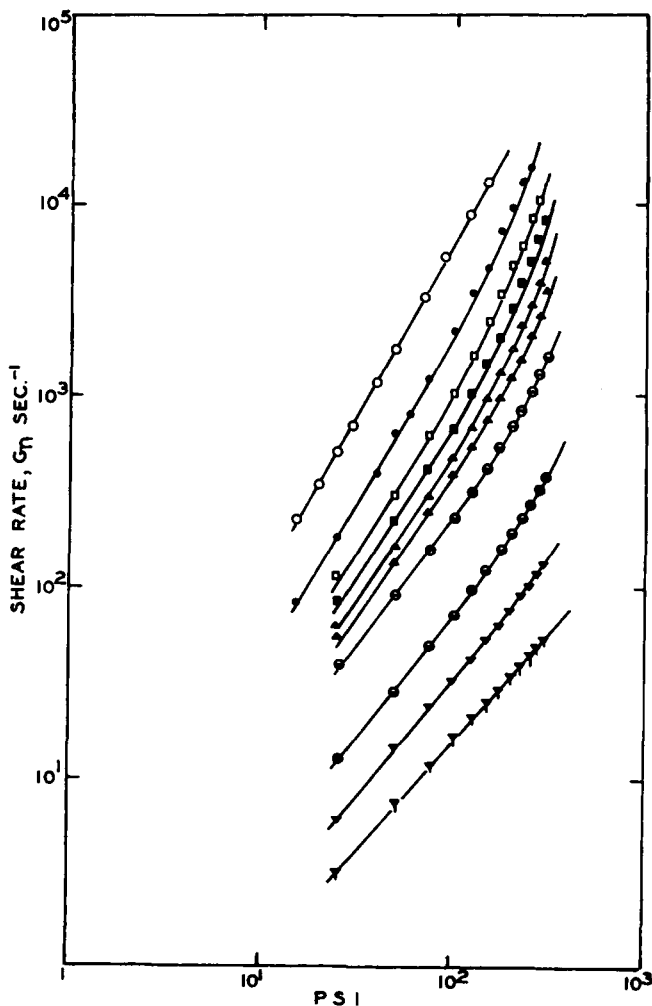

Fig. 2. Log shear rate vs. log pressure for Viscasil 60,000. L/R values (O) 2; (●) 5; (□) 8; (■) 10.2; (△) 13; (▲) 16; (⊖) 22; (◉) 40; (▽) 80; (▼) 160.

m/η_0 (the consistency divided by the Newtonian viscosity, η_0) versus L/R are shown for the three fluids. As L/R increases to large values, both n and m/η_0 approach unity. This indicates that in the limit, as L/R becomes very large, the fluid will behave as a Newtonian liquid. All the data for the three fluids fall on the same curves, indicating that the flow
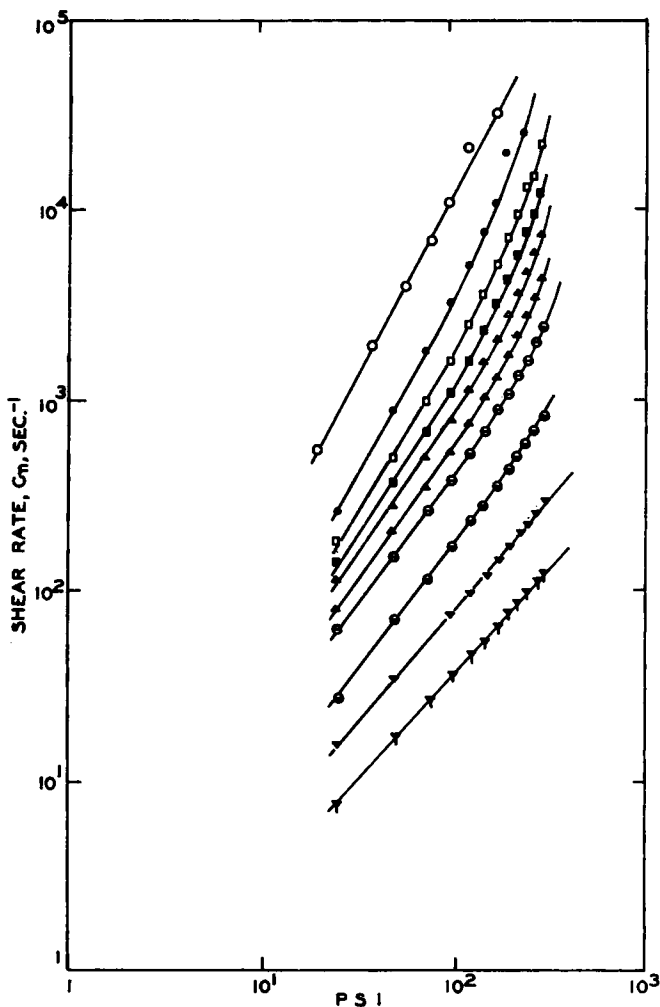
Fig. 3. Log shear rate vs. log pressure for Viscasil 100,000. L/R values the same as Fig. 2.

index and consistency are primarily dependent on L/R and are independent of the molecular weight of the fluid.

Entrance Effects

Recently Bagley[4,5] has shown, for polyethylene, that entrance effects are strongly dependent on the elastic properties of the melt. For a Newtonian fluid in fully developed flow, the relations for the maximum shear rate G_n and the shear stress at the wall of the capillary τ_R are

$$G_n = 4Q/\pi R^3 \tag{3}$$

$$\tau_R = \Delta PR/2L \tag{4}$$

TABLE I
Values of Flow Index n and Consistency m Determined from Figures 1, 2, and 3

L/R	n	m, dyne cm.$^{-2}$ sec.^{n}
	Viscasil 30,000	
5	0.65	2310
10.2	0.75	1080
13	0.78	838
16	0.80	720
22	0.81	634
40	0.84	538
	Viscasil 60,000	
2	0.55	9820
5	0.63	4800
8	0.70	2640
10.2	0.73	2230
13	0.75	1860
16	0.78	1670
22	0.81	1290
40	0.84	1180
80	0.90	862
160	0.93	741
	Viscasil 100,000	MM
2	0.55	12400
5	0.63	5900
8	0.70	3600
10.2	0.73	3100
13	0.75	2980
16	0.78	2150
22	0.81	1870
40	0.84	2110
80	0.90	1580
160	0.93	1340

In order to account for entrance effects, eq. (4) can be modified to

$$\tau_s = \Delta P/(2(L/R) + e) \tag{5}$$

where e is the total end correction. Bagley found, surprisingly, that eq. (5) could be applied to polyethylene, a non-Newtonian fluid.

The end correction is determined at constant G_n by plotting ΔP versus L/R on linear graph paper. By extrapolating to $\Delta P = 0$, e can be determined ($e = -L/R$). Figures 5, 6, and 7 are plots of ΔP versus L/P for the silicone fluids. In all cases, the data fall on straight lines. By using the end correction in eq. (5) it is possible to calculate corrected flow curves which are independent of the L/R ratio. In Figure 8 the corrected flow curves for the three silicone fluids are compared with the corrected flow curve for polyethylene.

The end correction versus the corrected shear stress is shown in Figure 9, and also a comparison is made with Bagley's data for polyethylene. At
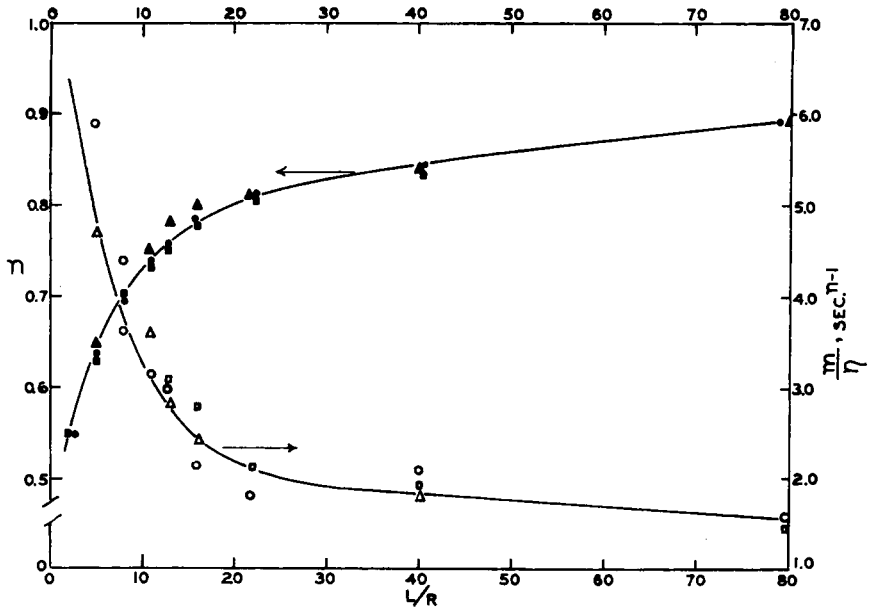
Fig. 4. Variation of the flow index and consistency with L/R. (▲,△) Viscasil 30,000; (■,□) Viscasil 60,000; (●,○) Viscasil 100,000.
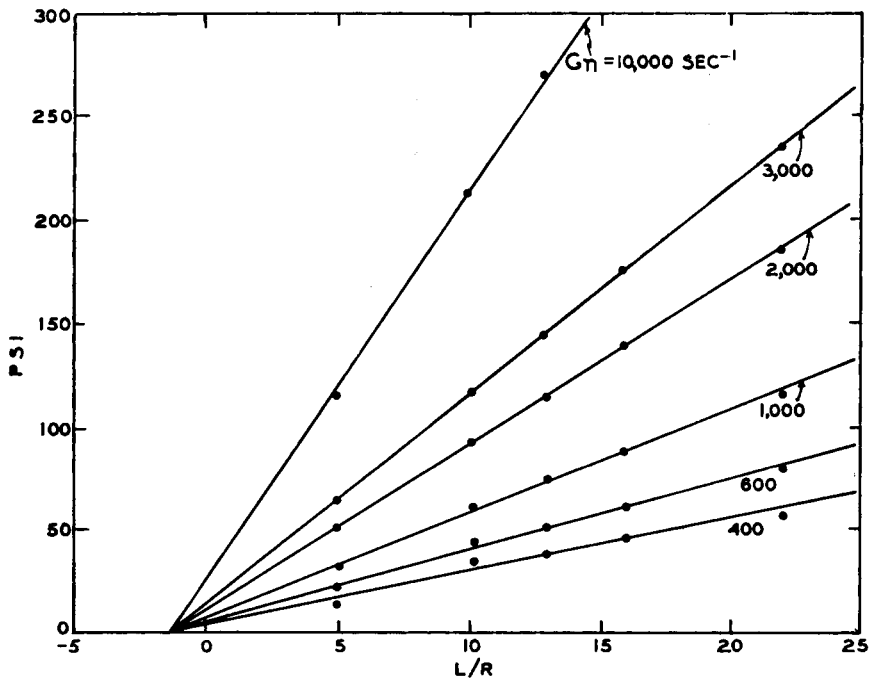
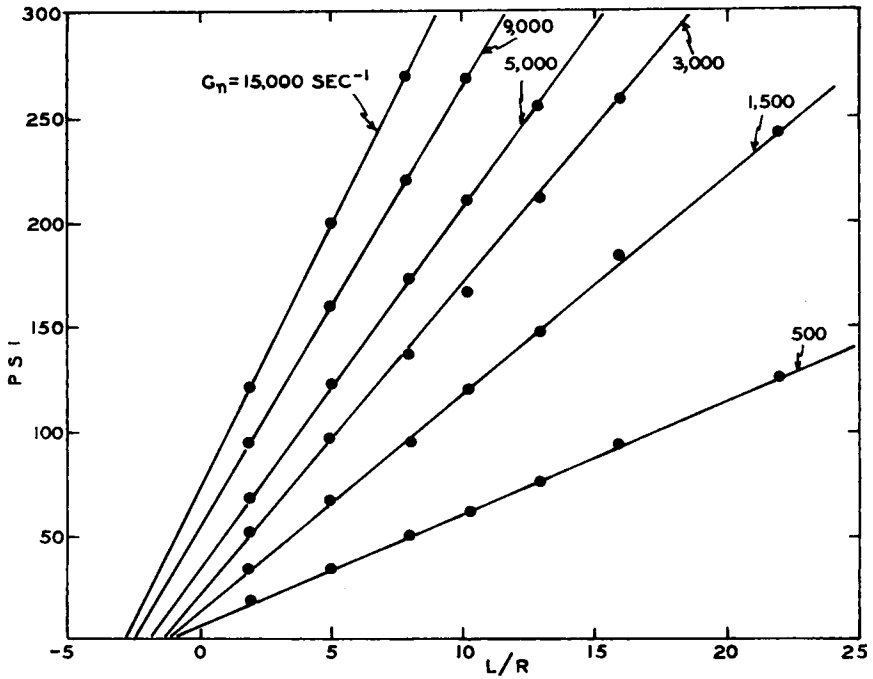Fig. 5. Pressure vs. L/R at constant shear rate for Viscasil 30,000.

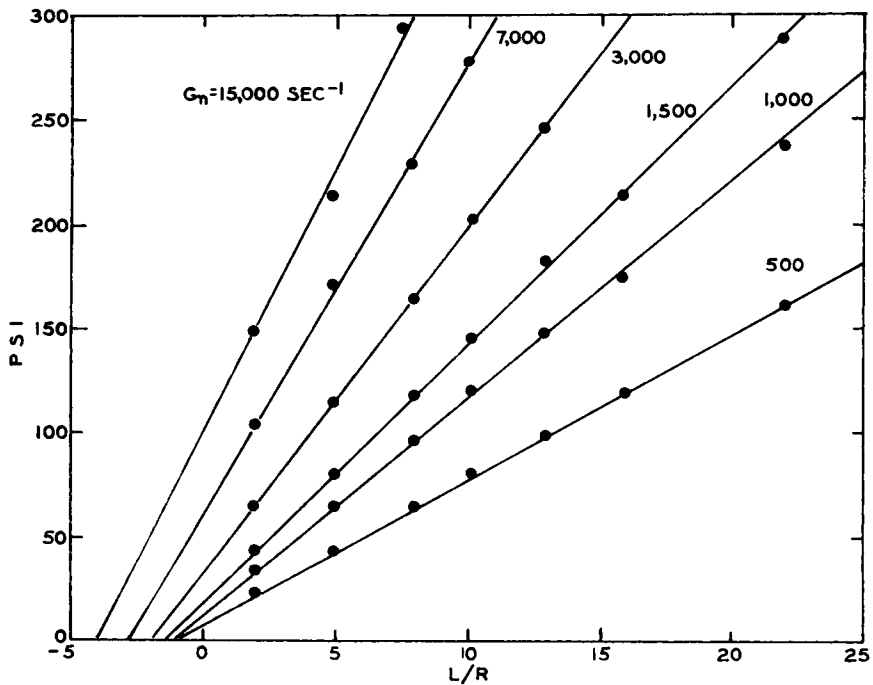Fig. 6. Pressure vs. L/R at constant shear rate for Viscasil 60,000.

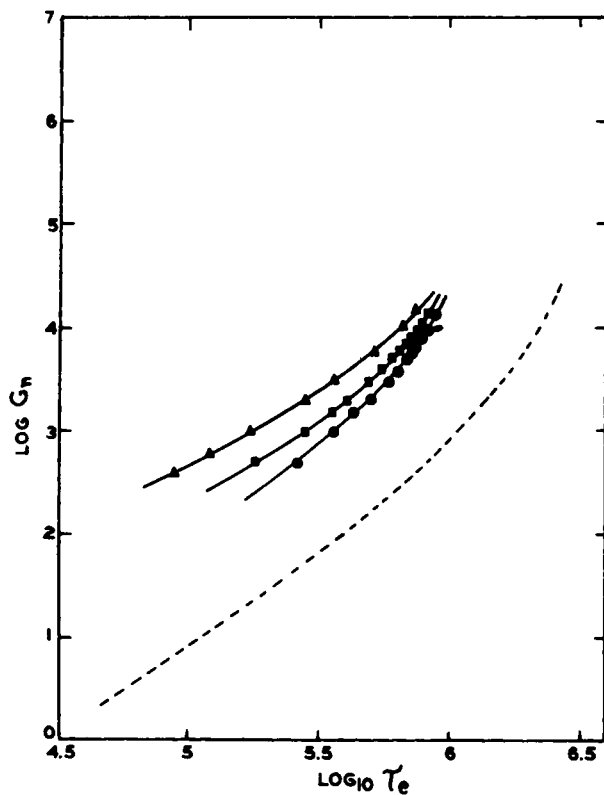Fig. 7. Pressure vs. L/R at constant shear rate for viscasil 100,000.

Fig. 8. A Comparison of corrected flow curves of Viscasil fluids and polyethylene (melt index 7.0, $T = 190°C.$; values are). (▲) Viscasil 30,000; (■) Viscasil 60,000; (●) Viscasil 100,000; (−) polyethylene.
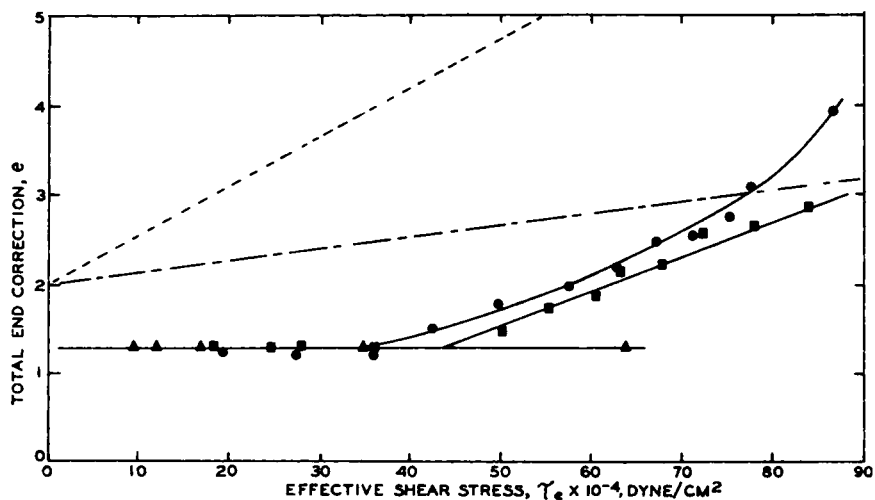

Fig. 9. Total end correction vs. corrected shear stress. Filled symbols the same as Fig. 8 and (−−) is polyethylene; (——) polyethylene.

low shear stresses, the end correction has a constant value of 1.3 for all three fluids and is independent of the shear stress. However, at high shear stresses, the end correction increases and becomes dependent on the shear stress. The end correction for polyethylene is dependent on the shear stress even at low stresses. Extrapolation to zero shear stress gives a value of 2 for the end correction.

The total capillary end correction is composed of a viscous part and an elastic part. That is,

$$e = n + g \qquad (6)$$

where n is the viscous part of the total end correction and g is the elastic part of the total end correction. The viscous part, n, sometimes referred to as the Couette term, is dependent only on the entrance geometry of the apparatus and predominates at low shear stresses. Since the entrance conditions in Bagley's apparatus and in the apparatus used in this work were different, it is not surprising that different Couette terms were obtained for both systems. In general, the elastic part of the end correction increases as the shear stress is increased. A comparison of the silicone fluids with polyethylene (Fig. 9) shows that for a shear stress of less than 3×10^5 dynes/cm.^{2} the total end correction for the silicone fluids is composed mainly of a viscous part and the elastic contribution is negligible. However, for polyethylene at these low shear stresses, the elastic part of the end correction is already relatively large and cannot be neglected.

Swelling of Capillary Jets

When a viscoelastic fluid extrudes from a capillary tube, the issuing liquid stream expands. Recently McIntosh and McKelvey[7] and Middle-
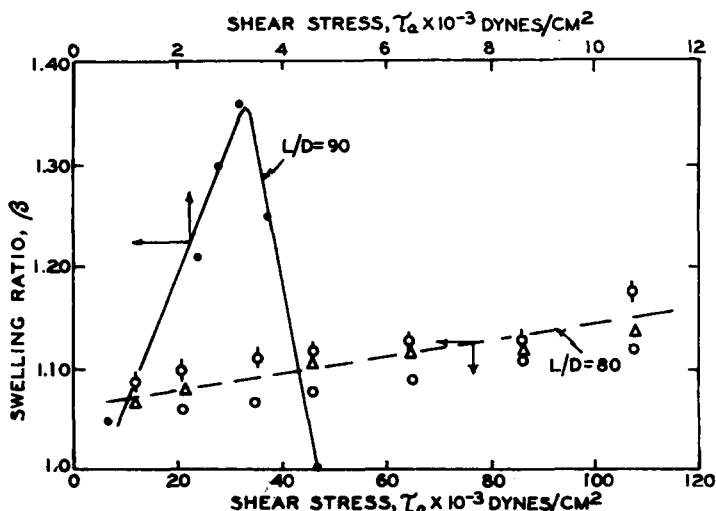

Fig. 10. Effect of shear stress on swelling ratio. Values are (●), 2% CMC; (O) Viscasil 100,000; (△) Viscasil 30,000; (◇) Viscasil 5,000.

TABLE II
Effect of Shear Stress on Swelling of Capillary Jets

L/R	Swelling ratio β	Shear stress $\tau_R \times 10^{-4}$ dyne/cm.$^{-2}$	Residence time t, sec.
	Viscasil 100,000		
80	1.06	2.16	18.6
	1.07	3.24	11.0
	1.08	4.31	8.2
	1.09	6.46	5.4
	1.11	8.62	4.7
	1.12	10.8	2.9
	1.13	12.9	2.3
140	1.04	1.23	43.0
	1.06	1.85	20.0
	1.08	2.46	15.2
	1.10	4.92	7.1
	1.11	6.15	5.2
	1.12	7.38	4.4
	Viscasil 30,000		
80	1.07	1.08	8.3
	1.08	2.16	3.1
	1.11	4.31	1.9
	1.12	6.47	1.2
	1.12	8.62	0.92
	1.14	12.9	0.54
140	1.04	0.615	19.6
	1.05	1.23	11.2
	1.06	2.46	5.3
	1.06	3.69	3.8
	1.08	4.92	2.7
	1.09	7.38	1.8
	Viscasil 5,000		
80	1.08	1.08	1.65
	1.10	2.16	0.83
	1.11	3.24	0.55
	1.12	4.31	0.40
	1.15	6.46	0.26
	1.15	8.62	0.19
	1.18	10.8	0.15
	1.17	12.9	0.10

man and Gavis[8] used aqueous solutions of carboxymethylcellulose (CMC) to study this phenomenon. The ratio of the maximum diameter of the free stream to the inside diameter of the capillary, β, was determined as a measure of the swelling. Both investigations showed that when the swelling ratio is plotted against the shear stress a maximum is reached. Figure 10 shows a typical set of data for a 2% CMC solution. Also shown are swelling data for three silicone fluids. The effect of shear stress on the

swelling is considerably less for the silicone fluids, and a qualitative comparison indicates that these fluids are only mildly viscoelastic under these conditions. This conclusion agrees with the overall results obtained from the entrance effects analysis. Table II gives additional swelling data and also lists the residence time of the fluid in the capillary for each run. Attempts to fit these data to a previously proposed viscoelastic model[7] were unsuccessful owing to insufficient data at short residence times.

CONCLUSIONS

1. At low pressures the silicone fluids obeyed the power law. However, at high pressures appreciable deviations from linearity were observed, especially for the capillaries with short L/R ratios. As L/R becomes large, both the flow index n and the consistency m approach the Newtonian values.

2. The entrance effects were successfully analyzed by the method proposed by Bagley. At low shear stresses the end correction is only dependent on the geometry of the apparatus. Only at relatively high shear stresses does the elastic part of the end correction become appreciable. A comparison with polyethylene at 190°C. shows that the silicones at 25°C. are less viscoelastic.

3. The swelling of capillary jets issuing from the tube increased slightly with increasing shear stress. A qualitative comparison with the behavior of a 2% CMC solution again indicates the mildly viscoelastic nature of the silicone fluids at 25°C.

References

1. Ryder, L. B., *SPE (Soc. Plastics Eng.) J.*, **17**, 1305 (1961).
2. *Am. Soc. Testing Mater. D-1238-S2T*.
3. *General Electric Silicones Product Data*, Silicone Product Department, Waterford, New York.
4. Bagley, E. B., *J. Appl. Phys.*, **28**, 624 (1957).
5. Bagley, E. B., *J. Appl. Phys.*, **31**, 1127 (1960).
6. Reiner, M., *Deformation, Strain and Flow*, Interscience, New York–London, 1960, p. 245.
7. McIntosh, D. L., Sc.D. Thesis, Washington Univ., St. Louis, Mo., 1960.
8. Middleman, S., and J. Gavis, *Phys. Fluids*, **1**, 963 (1961).

Synopsis

The non-Newtonian flow of silicone fluids in capillaries was investigated with special emphasis on the viscoelastic nature of entrance and exit effects. At low pressures the power law was obeyed, while at high pressures considerable deviations were observed, particularly with short capillaries. For capillaries with large length-to-radius ratios, the flow index and consistency approached the Newtonian values. Entrance effects were successfully analyzed by the method proposed by Bagley. At low shear stresses the end correction was dependent only on the geometry of the apparatus. An elastic

contribution to the end correction was observed only at high shear stress, indicating a relatively mild viscoelastic behavior. Additional evidence indicating small elastic effects was obtained from swelling measurements of capillary jets.

Résumé

On a étudié l'écoulement non-Newtonien de silicones liquides, spécialement du point de vue de la nature viscoélastique des effets d'entrée et de sortie. A basse pression, la loi de l'énergie est respectée tandis qu'à haute pression il y a des écarts considérables surtout avec de courts capillaires. Pour des capillaires à grand rapport L/R, l'index d'écoulement et la viscosité sont proches des valeurs Newtoniennes. Les effets d'entrée ont été successivement analysés par la méthode proposée par Bagley. Pour de faibles tensions de cisaillement, la correction finale dépend seulement de la géométrie de l'appareil. Une contribution élastique à la correction finale est seulement observée pour de fortes tensions de cisaillement, indiquant un comportement viscoélastique relativement peu important. Une preuve supplémentaire des faibles effets élastiques est fournie par les mesures de gonflement des jets capillaires.

Zusammenfassung

Das nicht-Newtonsche Fliessen flüssiger Silikone in Kapillaren wurde mit besonderer Berüchsichtigung der viskoelastischen Natur von Ein- und Austrittseffekten untersucht. Bei niedrigem Druck erwies sich das Potenzgesetz als gültig während bei hohem Druck besonders in kurzen Kapillaren beträchtliche Abweichungen auftraten. In Kapillaren mit hohem L/R-Vehältnis näherten sich Fliessindex und Konsistenz den Newtonschen Werten. Eintrittseffekte konnten mit der von Bagley vorgeschlagenen Methode mit Erfolg erfasst werden. Bei kleiner Schubspannung hing die Endkorrektur nur von der Geometrie des Apparates ab. Ein elastischer Beitrag zur Endkorrektur konnte nur bei hoher Schubspannung beobachtet werden, was für ein relativ schwaches viskoelastisches Verhalten spricht. Zusätzliche Hinweise auf kleine elastische Effekte wurden aus Kapillarstrahl-Quellungsmessungen erhalten.