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An Instability in the Flow of Molten Polymers

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With 7 Figures and 1 table

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I. Introduction

In the flow of molten high polymers through capillaries, a striking effect occurs at shear stresses near 10^6 dynes/cm². The contour of the emerging stream changes abruptly from a cylinder to an irregular shape. As the shear rate is increased beyond the critical rate at which the change in shape occurs, the degree of irregularity of the emerging stream increases. The effect is illustrated by specimens of polymethyl methacrylate in fig. 1.

Several different explanations of the phenomenon illustrated in fig. 1 have been proposed (1–4). Those which are discussed herein are *Reynolds'* turbulence, buckling of the emerging stream, and fracture or rupture of the molten polymer during flow.

Reynolds' turbulence involves the ratio of inertial transfer to viscous dissipation of energy. In the turbulent range of flow, inertia carries energy into small disturbances faster than viscosity dissipates it.

The buckling hypothesis involves differential elastic recovery between the inner and outer layers of the emerging stream. It is suggested that the larger recovery of the highly strained outer layers results in buckling when the strain is greater than a critical value.

The fracture hypothesis involves the strength of a viscoelastic, polymer liquid. It is proposed that when the applied stress exceeds the strength of such a liquid, failure by rupture or fracture occurs.

The particular effect illustrated in fig. 1 is not the only type of surface irregularity observed in flow of molten polymers. Another type of irregularity, of wavelength much smaller than the radius of the polymer stream, has been noted (5). The discussion herein is limited to irregularities of the type illustrated, of wavelength comparable to the radius of the strand.

II. Discussion

A. Reynolds' Turbulence

Turbulent flow occurs when the value of a dimensionless parameter, the *Reynolds'* number, exceeds a critical value usually between 1000 and 1500. The *Reynolds'* number, *Re*, is

$$Re = V \varrho R / \eta$$

where V is the mean velocity of flow in a tube of radius R of a fluid of viscosity η and

Table 1

Reynolds' number at onset of melt fracture (3)

Material	Temp. (°C)	Capillary Dimensions*) Radius cm	Length cm	Apparent Viscosity**) (poises)	Data at Onset of Fracture: Shear Rate $4\,Q/\pi R^2$, sec⁻¹	Flow Rate (cc/sec)	*Reynolds'* Number
Polytetra-fluoroethylene	350	0.216	0.432	$\sim 10^{10}$	2×10^{-4}	1.6×10^{-6}	4.7×10^{-16}
Polyethylene	125	0.079	0.158	1.1×10^{5}	1×10	3.9×10^{-3}	1.4×10^{-7}
Polymethyl-methacrylate	200	0.040	1.27	5×10^{4}	1×10^{2}	4.8×10^{-3}	7.7×10^{-7}
66 Nylon	275	0.040	0.127	3.2×10	2.8×10^{5}	1.4×10	3.9

*) Short capillaries are often used since the degree of irregularity of the emerging stream is larger than with long capillaries. The critical shear rate is substantially independent of the length to radius ratio for values of the ratio 0.4 to 40 (1).

**) Apparent Viscosity $= (PR/2\,L)/(4\,Q/\pi R)$ where: P is pressure; R and L, capillary radius and length, respectively; and Q, volume rate of flow.

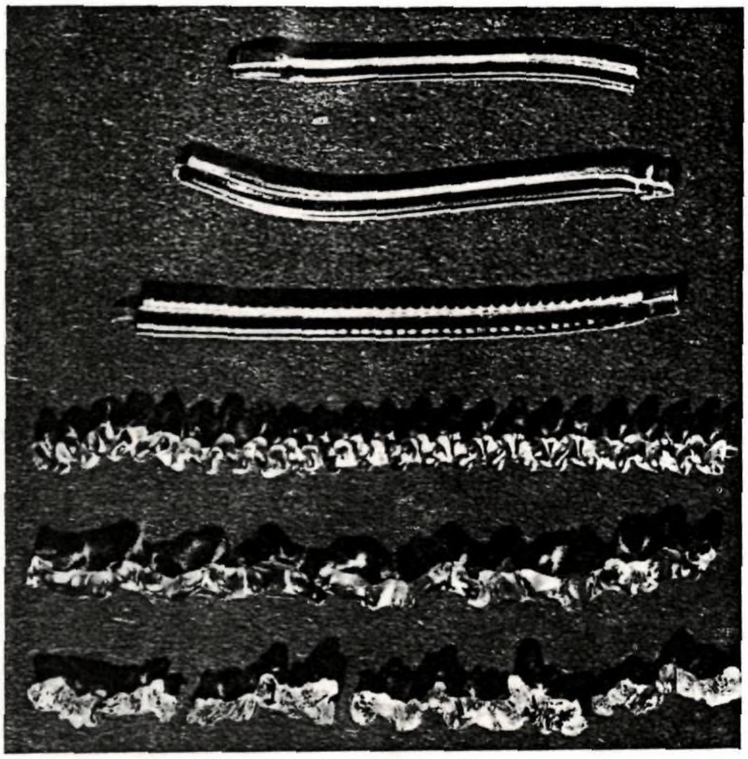

Fig. 1. Polymethyl methacrylate specimens (1). Conditions: 0.060 cm radius; 0.020 cm long capillary; 170°C. The first irregularity occured at 4.8 × 10^6 dynes/cm² stress. The bottom specimen was broken in handling

density ϱ. The *Reynolds'* number may also be written in terms of the volume flow rate Q:

$$Re = (Q/R\eta)(\varrho/\pi).$$

Applicability of the *Reynolds'* turbulence criterion to onset of the flow instability may be considered from three viewpoints: (a) the magnitude of the *Reynolds'* number at onset of the phenomenon; (b) the relation between the critical flow rate and capillary radius at fixed viscosity; (c) the relation between the critical flow rate and viscosity at fixed radius.

Values of the *Reynolds'* number at onset of the flow instability vary from 4.7×10^{-16} to 3.9 (table 1). These *Reynolds'* numbers are very small relative to 1000–1500. Indeed, the inertia involved in flow of polytetrafluoroethylene at onset of the flow instability is so small as to be negligible; the flow rate is about one-millionth cc/sec for a capillary of 0.216 cm radius.

For fixed viscosity, the *Reynolds'* turbulence criterion predicts that the critical flow rate is proportional to the capillary radius. This is not observed: flow rate at the onset of the instability increases as the third power, rather than as the first power of the capillary radius. This is illustrated for a thirty-fold variation of capillary radii in fig. 2.

Finally, the *Reynolds'* criterion predicts that, for fixed radius, the critical flow rate is directly proportional to the viscosity.

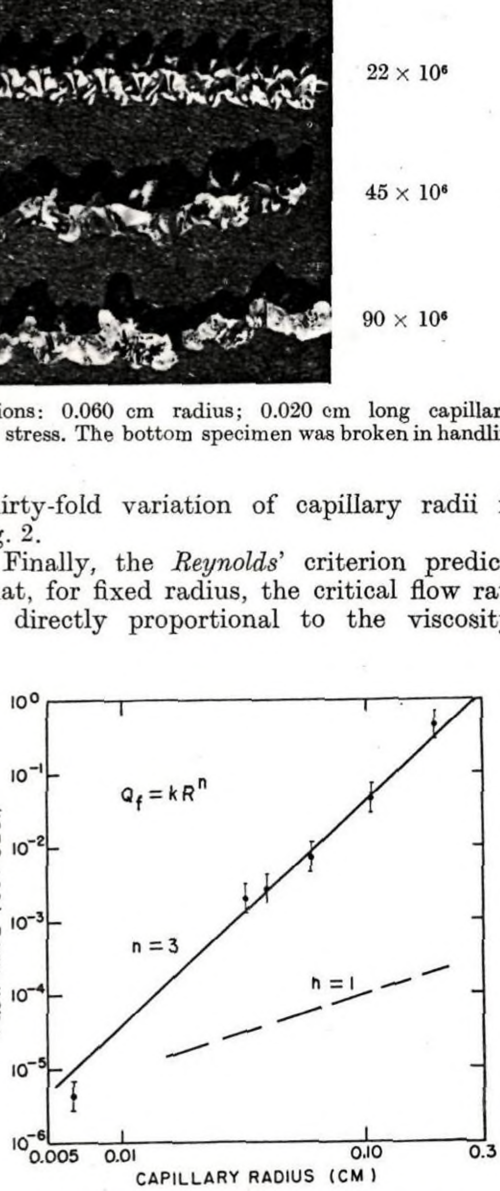

Fig. 2. Variation of the volume flow rate at onset of the flow instability with capillary radius (2). Data for "Alathon" 14 polyethylene resin (melt index 2.0, density 0.914) at 150°C.

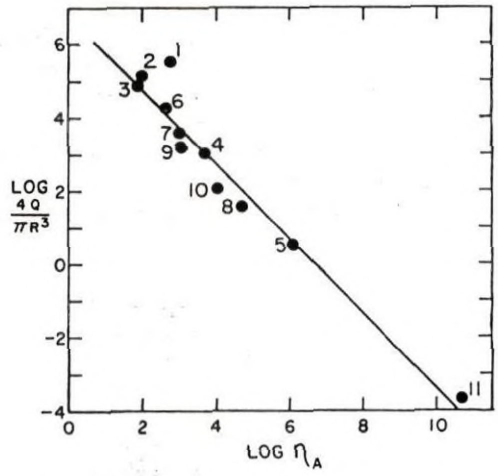

Fig. 3. Nominal shear rate *vs* apparent viscosity at onset of the flow instability. Polymers and temperature: 1. "Zytel" 101 nylon resin (66 nylon) 275°C; 2. "Akulon" K-2 (6 nylon) 240°C; 3, 4, 5. "Lucite" 140 acrylic resin (polymethyl methacrylate), respectively 280°, 220°, and 170°C; 6. "Delrin" 500 × acetal resin (polyformaldehyde), 185°C; 7, 8. "Alathon" 14 polyethylene resin (2.0 melt index, 0.914 $D^{23}{}_4$) 300° and 125°C; 9. "Styron" 475 polystyrene, 200°C; 10. Plastized polyvinyl butyral resin, 160°C; 11. "Teflon" TF-1 TFE-fluorocarbon resin (polytetrafluoroethylene), 350°C

Actually, the opposite is true; the critical flow rate is inversely proportional to the viscosity, as shown in fig. 3. The obvious conclusion is that *Reynolds'* turbulence is not involved in the observed flow instability.

B. Another Dimensionless Parameter

The *Reynolds'* number, which involves inertia, is written in terms of velocity, tube radius, viscosity, and density. Another dimensionless parameter, N_J, may be written involving elastic strain by introducing a compliance, J:

$$N_J = V \eta J / R.$$

In terms of the volume discharge rate, the expression is

$$N_J = (Q/\pi R^3)\, \eta J.$$

Functionally, N_J is equivalent to an amount of elastic strain.

If the flow instability occurs at a critical value of N_J, then the critical flow rate should vary as R^3. Also, $Q/\pi R^3$, or $4\,Q/\pi R^3$ at onset should vary inversely as the product ηJ. The first two of the three requirements

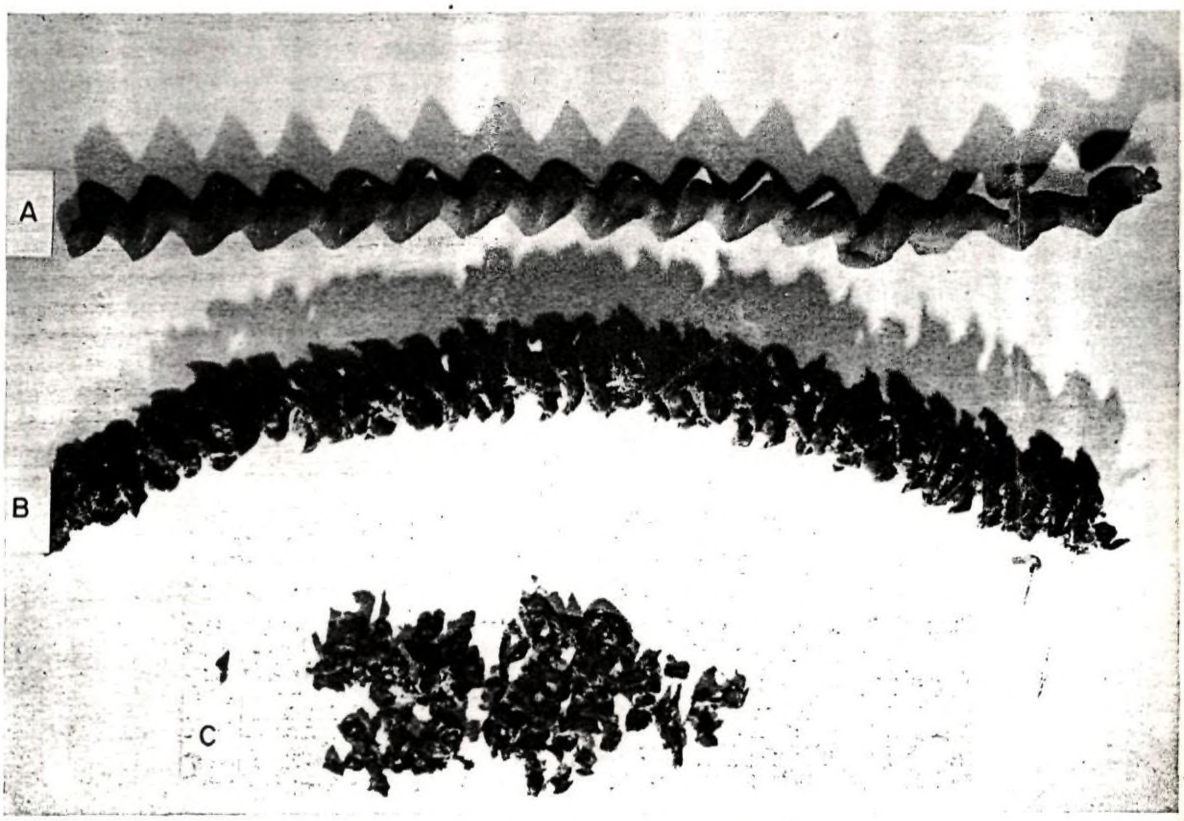

Fig. 4. Specimens of polytetrafluoroethylene extruded at successively higher stresses at 360°C (1)

are fulfilled as shown in fig. 2 and 3. The relation between $4\,Q/\pi\,R^3$ and η at onset of the flow instability is very nearly an inverse proportion for a wide variety of polymers. Surprisingly little variation of J would be required for a critical value of N_J to describe onset of the flow instability. This implies relatively little variation in the amount of strain at the onset of the flow instability.

Measurement of elastic compliance at high shear rates is difficult, and data are scarce. However, elastic recovery as manifest in extrusion swelling has been used to estimate elastic compliance. A constant value of a dimensionless number similar to N_J at onset of the flow instability was found for polystyrene (4). In this particular case, the swelling was constant at onset of fracture. However, the amount of swelling is strongly dependent on the length to radius ratio, and appears to be a complicated function of conditions at the entrance of the capillary, shear rate, and dwell time within the capillary. Consequently, extrusion swelling does not appear to be a suitable measure of elastic compliance.

C. *Buckling and Fracture*

Even though it appears that a critical value of N_J describes conditions at onset of the flow instability, this criterion affords little insight into the cause of the phenomenon. Certainly, no basis is provided for choosing between the fracture and buckling hypotheses. However, experimental evidence does appear to provide a basis of choice.

The buckling hypothesis may be eliminated on the basis of several observations. First, it is difficult to see how buckling could result in irregular, jagged emerging polymer streams, or in fragmentation of a stream. These effects are illustrated in specimens B and C in fig. 4. Second, buckling should not affect flow in the capillary system. However, at onset of the flow instability, the volume flow rate becomes irregular with time (fig. 5) and there is a change of slope of the shear-stress shear-rate curves (fig. 6).

The most severe criticism of the buckling hypothesis is that the site of the flow instability appears to be at the inlet to the capillary rather than at the outlet. This conclusion was reached from consideration of the shapes of extruded specimens (1) and from observation of flow in glass apparatus (3). Small particles of colored (black) polyethylene were incorporated in natural, branched polyethylene. The small black particles acted as visual tracers so that the flow pattern could be observed. Axially symmetric flow into and within the capillary was noted below the critical rate. Above the critical rate, appearance of the irregular emerging stream was accompanied by fluctuating, unsymmetrical flow in the capillary inlet.

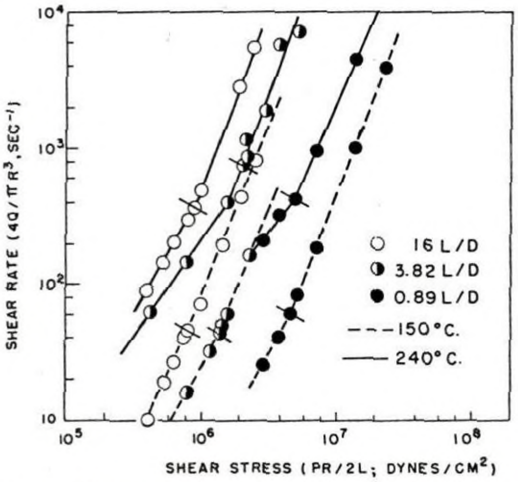

Fig. 6. Shear rate *vs* shear stress data for branched polyethylene (polymer 7, 8 in Fig. 3) showing change of slope of data at onset of the flow instability (1). (Short marks indicate points at which flow instability was detected.)

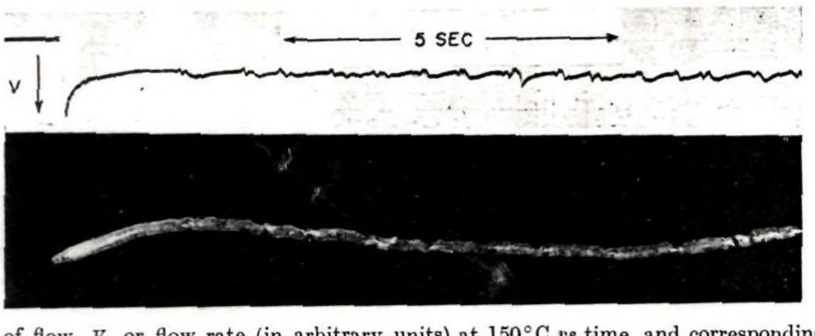

Fig. 5. Velocity of flow, V, or flow rate (in arbitrary units) at 150°C *vs* time, and corresponding polyethylene specimen (1). (Same polymer as 7, 8 in fig. 3)

The original work in glass apparatus involved short capillaries of length to radius ratio about 2. It appeared possible with such a short capillary, that outlet effects could propagate back to the inlet. Accordingly, similar observations of flow were made for a capillary having a length to radius ratio of 25. It is not likely that outlet effects propagate back to the inlet of *this* capillary. The results are illustrated in fig. 7. Fluctuating, unsteady flow occurred near the inlet of the capillary at shear rates above the critical rate. This critical rate was the same as that found with the shorter capillaries. No disturbance of flow within the capillary was noticeable.

The irregular shape of the emerging stream is the result of unsymmetrical flow at the capillary inlet, followed by elastic recovery at the outlet. Recovery partially restores the various volume elements to the relative position they had at the inlet. Thus, unsymmetrical flow at the inlet results in emerging streams of irregular shape.

The observations of flow in glass apparatus appear to demonstrate that buckling is not responsible for the irregularly shaped streams. However, these observations do not demonstrate plainly that fracture or rupture of the polymer liquid causes the flow instability. The conclusion that fracture or rupture is the cause may be approached in two complementary ways: first, from direct experimental evidence; second, from rheological considerations relative to flow of viscoelastic liquids.

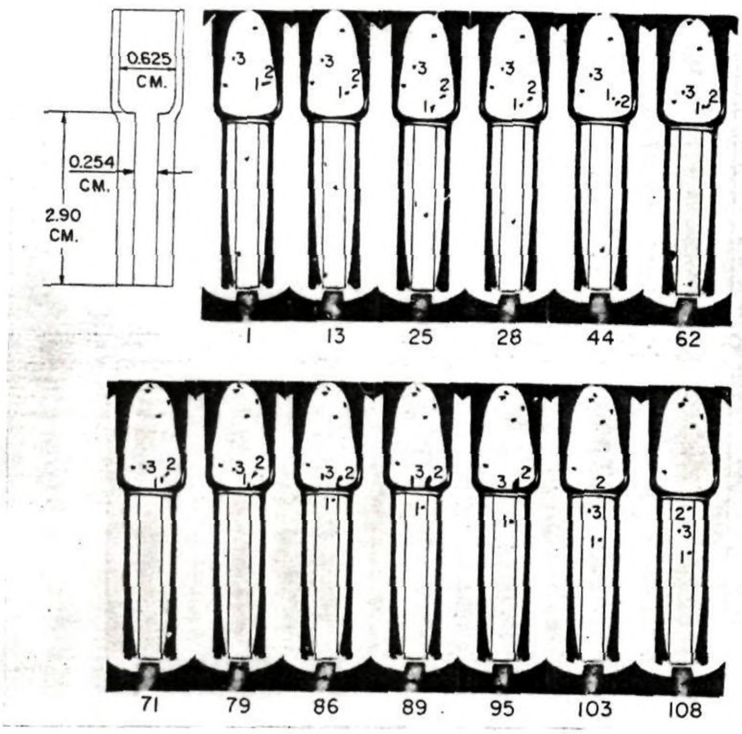

Fig. 7. Photographs of flow of polyethylene in glass apparatus showing irregular flow at the inlet to the capillary. The line drawing indicates the dimensions of the glass capillary and entrance tube. Three particles of pigmented polyethylene, identified respectively as 1, 2, and 3, illustrate the irregular flow at the capillary inlet. The numbers below each frame indicate the position of the frame in a sequence filmed at 64 f/sec. The polymer was "Alathon" 3 polyethylene resin (melt index 0.3, D^{25}_{4} 0.923). The temperature and shear stress were, respectively, 125°C and 2.7×10^6 dynes/cm². (Photographs were retouched to delineate the capillary bore.)

Experimentally, it appears that fracture or rupture of the polymer liquid does occur. Some extruded polymer streams have the appearance normally associated with fracture of elastic solids, i. e., jagged and rough surfaces—even separate fragments [fig. 2 and (2)]. Tearing noises are sometimes audible. The noise and the specimen shape strongly indicate fracture. For the case in which neither noise nor jagged shapes obtain, more flow and less extensive fracture seem to occur. However, the *type* of irregularity of the extruded streams is the same, but the *degree* of irregularity is less than that for more extreme cases of fracture.

The rheological considerations relative to occurrence of fracture involve the nature of a viscoelastic liquid. As the shear rate imposed on such a liquid is increased, the number of modes of motion whose retardation times are shorter than the time corresponding to the reciprocal of the shear rate decrease. The response of the liquid is more and more like that of an elastic solid: the fraction of the deformation that is viscous decreases while the fraction which is elastic increases. Orderly flow will not persist if the shear rate is increased indefinitely. Either turbulent flow of the liquid will set in or the limit of the elastic deformation will be reached—in which case rupture or fracture will occur.

The conclusion seems inevitable: neither *Reynolds'* turbulence nor buckling appear to be the cause of the flow instability. Rheological considerations and experimental evidence, indicate that fracture or rupture of the molten polymer is responsible for the flow instability. Orderly flow of the polymer at the capillary inlet is terminated by onset of fracture when the strength of the viscoelastic liquid is exceeded.

The suggestions of *W. E. Langlois* are gratefully acknowledged.

Summary

In the flow of molten high polymers through capillaries, an instability occurs at shear stresses near 10^6 dynes/cm². The instability results in emerging streams of irregular shape. Several explanations have been proposed: *Reynolds'* turbulence, buckling during elastic recovery of the emerging stream, and rupture or fracture of the molten polymer at the entrance to the capillary. The first two are found not to apply. The latter appears correct on the bases of experimental observations and rheological considerations.

Zusammenfassung

Das Fließen von geschmolzenen Hochpolymeren zeigt Instabilitäten der Scherspannung in der Nähe von 10^6 dyn/cm². Die Instabilitäten haben Irregularitäten in der Form der austretenden Stränge zur Folge. Verschiedene Erklärungen wurden vorgeschlagen: *Reynolds*sche Turbulenz, Aufkrümmung während der elastischen Erholung des Ausströmenden und Zerreißen oder Bruch des geschmolzenen Polymeren bei Eintritt in die Kapillare. Die ersten beiden kommen nicht in Frage, die letztere Erklärung scheint auf Grund der experimentellen Beobachtungen und der rheologischen Betrachtungen das Richtige zu treffen.

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Aus dem Institut für Mechanik, Techn. Hochschule Aachen

Polarisationsoptische und mechanische Ermittlung von Spannungszuständen in makromolekularen Flüssigkeiten am Beispiel des Acronal 4 F *)

Von W. Schürmann

Mit 29 Abbildungen in 35 Einzeldarstellungen und 1 Tabelle

(Eingegangen am 24. April 1958)

1. Einleitung

Die Scherbewegung von Stoffen mit nichtlinearer Zähigkeit läßt sich nach *Schultz-Grunow* (1) durch die Beziehung

$$\frac{\dot{\gamma}}{C} = f\left(\frac{\tau}{A}, \frac{\dot{\tau}}{GC}, \frac{t}{t^*}\right) \qquad [1,1]$$

darstellen, wo $\dot{\gamma}$ die Schergeschwindigkeit, τ die Schubspannung, t die Zeit, t^* eine Zeitkonstante, G den Schubmodul und A und C zwei Materialkonstanten bedeuten. In der vorliegenden Arbeit ist beabsichtigt, mit Hilfe optischer Methoden, insbesondere polarisationsoptischer Untersuchungen, die rheologischen Eigenschaften von Acronal 4 F, welcher Stoff zur Bestätigung von [1,1] meist herangezogen wurde (2), (3), weiter aufzuklären. Dabei interessieren die Abhängigkeiten der Doppelbrechung und des Auslöschungswinkels von der Deformationsgeschwindigkeit, da sich nach (4) daraus Rückschlüsse auf die Mikrorheologie der Substanz ziehen lassen und da sie als Eichkurven bei der Untersuchung ebener Strömungsfelder verwendet werden können. Weiterhin soll versucht werden, mit Hilfe der Strömungsdoppelbrechung Feststellungen über die Koaxialität des Spannungs- und Formänderungstensors zu machen.

2. Beschreibung der Versuchsanordnung

Die Meßanordnung, insbesondere die *Couette*-Apparatur wurde so gebaut, daß praktisch gleichzeitig optische und mechanische Größen in der Ringspaltströmung gemessen werden konnten. Im Gegensatz zu den sonst üblichen Apparaturen zur Messung

*) Die Arbeit wurde auf Anregung von Herrn Professor Dr. *Schultz-Grunow* im Institut für Mechanik der Techn. Hochschule Aachen durchgeführt.