

## Zusammenfassung

Eine gummiartige Flüssigkeit (definiert gemäß [1], [3]) wird einer homogenen stationären Scherströmung vom Geschwindigkeitsgefälle  $G$  von der Zeit  $t = -\infty$  bis  $t = t_1$  unterworfen. Die Spannung ist Null für  $t \geq t_1$ . Die Form wird als Funktion von  $t$  für  $t > t_1$  mit Hilfe numerischer Methoden für verschiedene Werte von  $G$  und des Parameters  $a, l$  in der Erinnerungsfunktion [3] berechnet. Trägheitskräfte werden vernachlässigt. Die Erholung ergibt sich als von der in Abb. 1 dargestellten Art mit gleichen seitlichen Ausdehnungen  $h_2, e_3$  und einem Schub; sie erhöhen sich insgesamt gleichmäßig mit der Zeit. Die hauptsächliche Erholung findet mit Unterbrechungen bei  $t = t_1$  statt. Der Schubholungs-winkel  $\varepsilon$  übersteigt nicht  $45^\circ$ .

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From the Centraal Laboratorium TNO Delft

## Comparison between Slit Viscometry and Cylindrical Capillary Viscometry

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With 11 figures and 1 table

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### 1. Introduction

The most widely used apparatus for measuring viscosity is the capillary rheometer. In this apparatus, the material is forced through small diameter cylindrical capillaries. The pressure required at given or measurable flow rates is recorded.

The shear stress at the wall ( $\tau_w$ ) for a long cylindrical capillary and the apparent shear rate ( $D_c$ ) are given by:

$$\tau_w = P \left( \frac{R}{2L} \right) \quad [1]$$

$$D_c = \frac{4Q}{\pi R^3}, \quad [2]$$

where  $P$  = driving pressure,  $R$  = radius of tube,  $L$  = length of tube,  $Q$  = volume output per second.

There is a unique relationship between  $\tau_w$  and  $D_c$  when

1. the requirement of no slip is met;
2. flow in the capillary is independent of the distance from the entrance (or exit). This implies that the capillary must be sufficiently long and pressure dependency of density and flow properties negligible.

For any liquid it is found experimentally, that at given apparent shear rate, the pressure is not proportional to  $(L/R)$  but rather to  $[(L/R) + n]$ , where  $n$  is a term which accounts for the entrance loss (change of velocity and streamlines upon entering the tube), and is independent of  $L$  at constant  $R$ .

For Newtonian liquids at low shear rates,  $n$  is called the Couette constant and various values between 0.57 and 0.82 have been quoted. These values are independent of the stress. For non-Newtonian materials, such as polymer melts,  $n$  is found to be much larger in general and dependent on  $\tau_w$ . For measurements of viscosity, the elimination of the end correction  $n$  is an inconvenience since a series of capillaries with different  $L/R$  must be used. It would be preferable to examine the pressure distribution along one capillary. Unfortunately, in view of the necessarily small dimensions of capillaries (small diameter to ensure an even temperature distribution throughout the melt; fairly short length because of attendant machining difficulties with small diameter tubes) this is not practical yet.

In a rectangular slit capillary, however, one has the possibility of measuring the pressure distribution along its length. On the longer side of the rectangle, smooth fitting pressure gauges can be mounted. The smallness of the other side of the rectangle then ensures an even temperature distribution throughout the liquid.

The flow of Newtonian liquids through rectangular channels has already been theoretically analysed; see for instance ref. 1. It is found that, for these liquids at least, the breadth/width ratio of the rectangular cross section of the slit has to be greater than 10/1

to give an error smaller than 7% in the calculated viscosity, when the slit is treated as ideal (that is of finite breadth and infinitely small width).

The flow of real non-Newtonian fluids of any kind has never been treated theoretically for anything but ideal slits. Polymer melts show a more plug like flow through cylindrical capillaries. It is therefore thought that with slits of breadth/width ratio greater than 10/1 ideal slit flow behaviour should occur to a better approximation than with Newtonian liquids.

The intent of this investigation was to compare the results of measurements carried out with slits of different breadth/width ratios, as well as with different cylindrical capillaries. A series of different polyethylene grades was investigated in this way. All measurements were made in the region where the extrudate was smooth.

The equations for the ideal slit, replacing equations (1) and (2) for the capillary are:

$$\tau_w = (a/2) (P/L) \quad [3]$$

$$D_s = \frac{6Q}{b a^2}, \quad [4]$$

where  $a$  = (short) width of slit

$b$  = (long) breadth of slit

$D_c$  = apparent rate of shear.

In Newtonian flow the quantities  $D_c$  and  $D_s$  are the real rates of shear at the wall, in non-Newtonian flow they are related to the real rate of shear ( $q$ ) by the relations [*Rabinowitsch* (2)].

$$q = \frac{D_c}{4} \left[ 3 + \frac{d(\log D_c)}{d(\log \tau_w)} \right] \quad [5]$$

$$q = \frac{D_s}{3} \left[ 2 + \frac{d(\log D_s)}{d(\log \tau_w)} \right]. \quad [6]$$

These equations are valid under the same conditions as equations (1) and (2).

## 2. Materials

The materials used were all polyethylenes. They were supplied by the manufacturer in the form of pellets, and were directly used as such.

- A Alkathene WJG 11 – low density of melt index 2.
- B Marlex 6050 – high density of melt index 5.
- C Marlex 6002 – high density of melt index 0.25.

The normal investigation temperature was 190 °C. However, some cylindrical capillary measurements were taken at 170 °C as well.

## 3. Experimental

The central feature of the experimental arrangement is the ram extruder. This apparatus has a variable speed piston and has already been described by *Eswaran, Janeschitz-Kriegl and Schijff* (3). It can be used for either slit or capillary experiments in the range 1–200 sec<sup>-1</sup>. New features with respect to the above mentioned apparatus are:

1. Use of new membraneless electronic pressure gauges developed in this laboratory; two kinds of which were used in the course of the investigation:

- a) a water cooled;

- b) an uncooled set which were both insensitive to changes in operating temperature.

The readings from the gauges were displayed on a 4 band chart recorder.

2. Use of pelletised material, the conical shape of the piston aiding exclusion of air from the extrudate.

Filling of the reservoir was done by hand. The reservoir was slowly filled, care being taken to tamp the polymer hard down whilst carrying out this operation. After filling, about five minutes was allowed before running the apparatus; longer intervals of up to 1 hr were also tried with no change in results.

### 3.1. Slit

As in ref. 3, the slit is formed from two parts, a channel with rectangular cross section being milled into the surface of the one, the other being left flat. The slit used on the ram viscometer was of length 110 mm, width 0.5 mm and breadth 10 mm, i. e. breadth/width = 20/1. Pressure measuring points were at 15, 55 and 95 mm from the exit, and also one within the reservoir. The protrusion of the pressure gauges into the viscometer channel was no greater than 0.02 mm. The two halves of the slit are clamped together with a large number of heavy screws. Two keys ensure the just positioning of the halves.

Two other slits of similar construction were also used, the breadth/width ratios of these were 10/1 and 30/1 (exactly: 12 mm/1.2 mm; 20 mm/2 mm and 18 mm/0.6 mm). However, these slits were only suitable for use with a screw extruder. Their outputs were only measurable in the form weight per second. To convert to volume output, the density of the polymers at 190 °C as a function of pressure was determined by weighing the ram viscometer output.

### 3.2. Capillary

Two series of capillaries were used. The first series, used in conjunction with a screw extruder, consisted of capillaries of lengths 0, 2, 8 and 16 mm and radii 0.5 mm. The second series used in conjunction with both the ram and screw extruders, consisted of capillaries of lengths 0, 10, 20 and 40 mm and radii 1 mm. The zero length capillaries had conical exits. The 1 mm radius series all had flat entrances. The 0.5 mm radius series was doubled in number so as to include both conical and flat entrances.

In the ram viscometer a pressure gauge was mounted near the entrance of the capillaries, as in ref. 3.

## 4. Results and Discussion

The pressure distributions for the slits 10/1, 20/1, and 30/1 are qualitatively very similar. To give an impression, the measurements on the slit 20/1 at 190 °C are given in figs. 1–3.

The slit results show good linearity near the exit, and because of the unknown effects of compressibility and entrance perturbations, the shear stress ( $\tau_w$ ) at the wall was evaluated in this region with the aid of formula (3) by equating the inclination of the lines near the exit to  $(P/L)$ . It can be seen from figs. 1–3 that especially at high speeds the pressure distri-

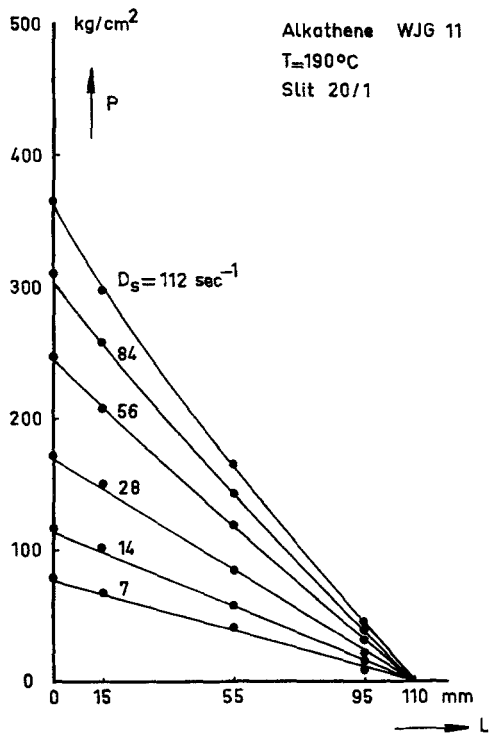


Fig. 1. Pressure distribution down 20/1 slit for Alkathene WJG 11 at 190 °C. The associated apparent shear rates ( $D_s$ ) are indicated

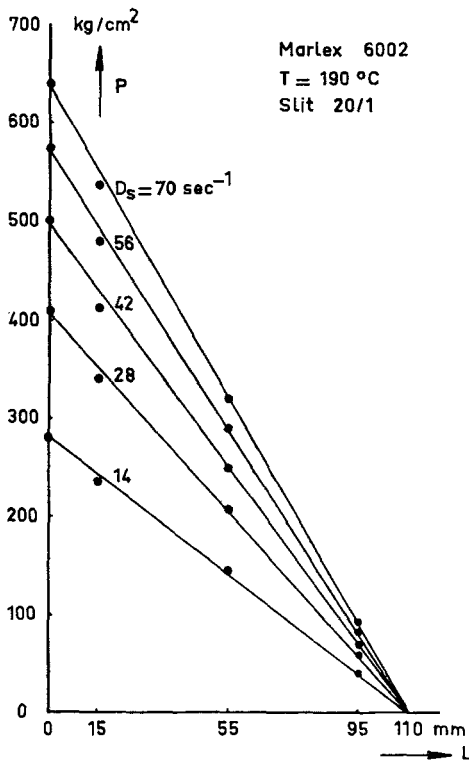


Fig. 3. As fig. 1 only with Marlex 6002

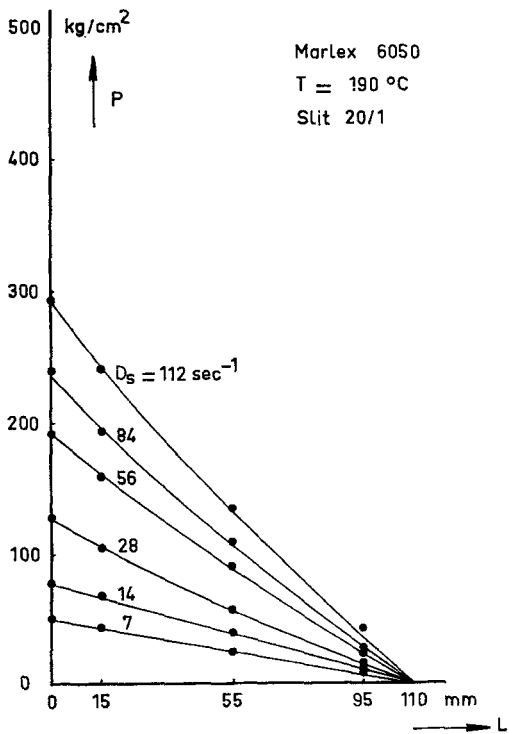


Fig. 2. As fig. 1 only with Marlex 6050

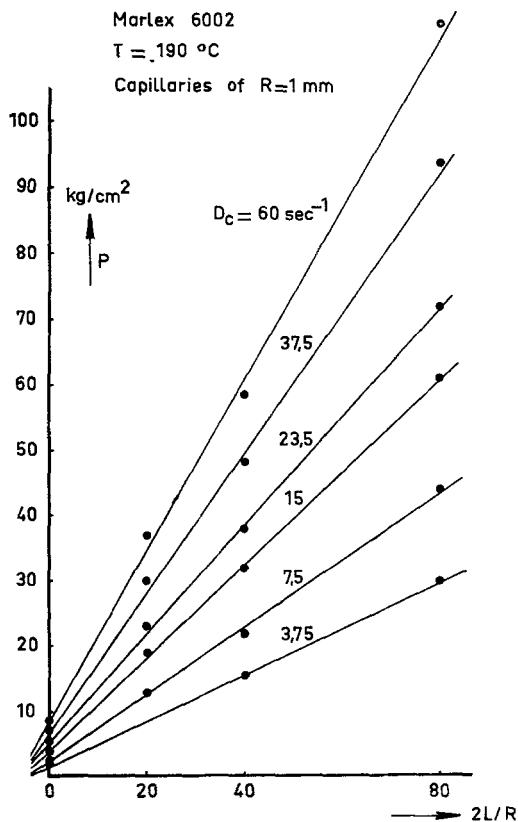


Fig. 4. Pressures for 1 mm radius capillaries for Marlex 6002 at 190 °C. The associated apparent shear rates ( $D_c$ ) are indicated

bution is not always linear over the whole length of the viscometer channel.

Fig. 4 shows the pressure plotted against  $2L/R$  for the 1 mm radius capillaries for Marlex 6002. It is clear from fig. 4 that the driving pressure of a zero length capillary accounts for the end correction: it is also to be noted that none of the capillary experiments were conducted in the pressure region where pressure (compressibility) effects would be noticeable. The stresses at the capillary wall ( $\tau_w$ ) were evaluated as the slopes of the lines shown.

It was found that neither  $n$ , the entrance correction nor  $\tau_w$  the shear stress, were influenced by changing from flat to conical entrances. It should be noted that Alkathene WJG 11 was not examined with the 0.5 mm series.

Different slits are compared for the three polyethylenes in figs. 5-7 (not the 30/1 slit with Marlex 6002; in fact, with the latter slit the pressures obtained with this material would be sufficiently high to damage the extruder screw). The pressure ( $P$ ) is plotted against  $D_s$  for each slit at the same value of  $L/a$  (or the same reduced distance from the exit (cf. equation [3])). An inspection of all the graphs reveals no significant change with slit occurring; except perhaps with Marlex

6050, where the 30/1 results are to the right of the 10/1 and 20/1.

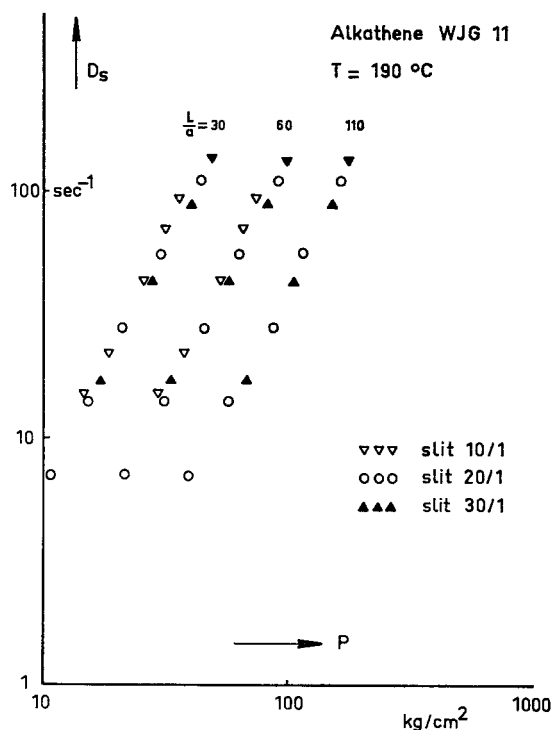


Fig. 6. As fig. 5 only with Marlex 6050

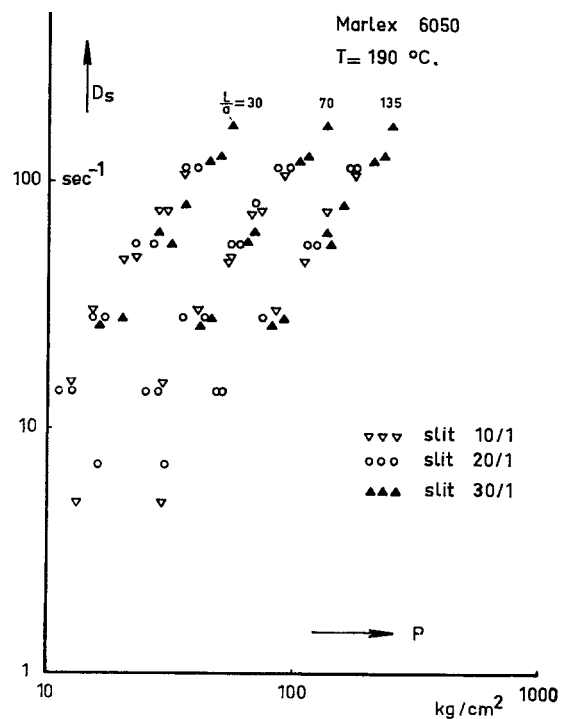


Fig. 5. Shear rate ( $D_s$ ) plotted against pressure ( $P$ ) at three different values of the reduced distance from the exit of the slit for Alkathene WJG 11 at 190 °C

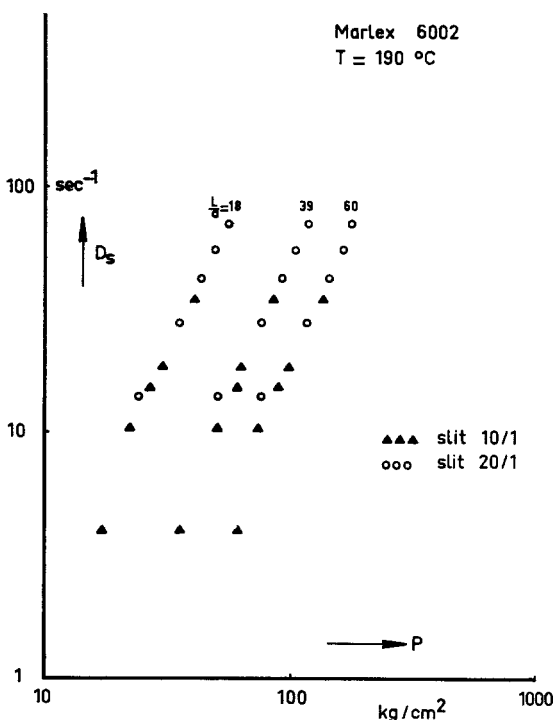


Fig. 7. As fig. 5 only with Marlex 6002 (not 30/1 slit, however)

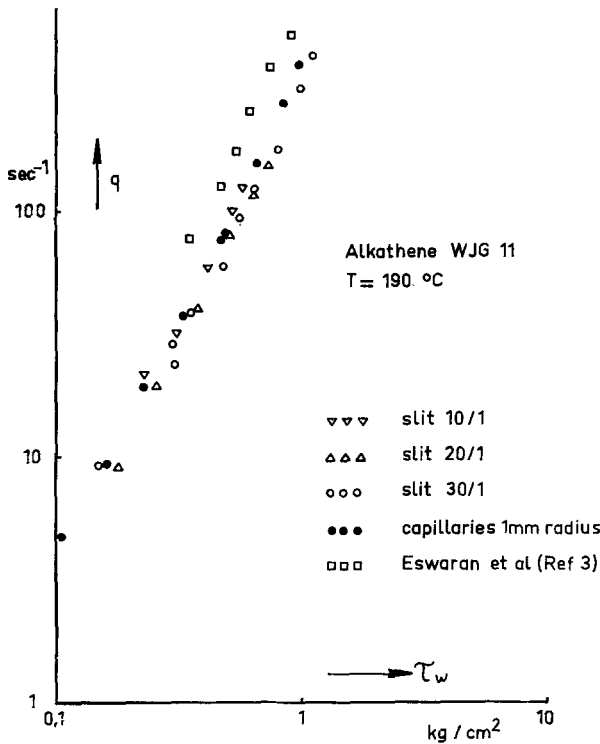


Fig. 8. Shear rate  $q$  plotted against shear stress  $\tau_w$  for slits and capillaries for Alkathene WJG 11 at 190 °C

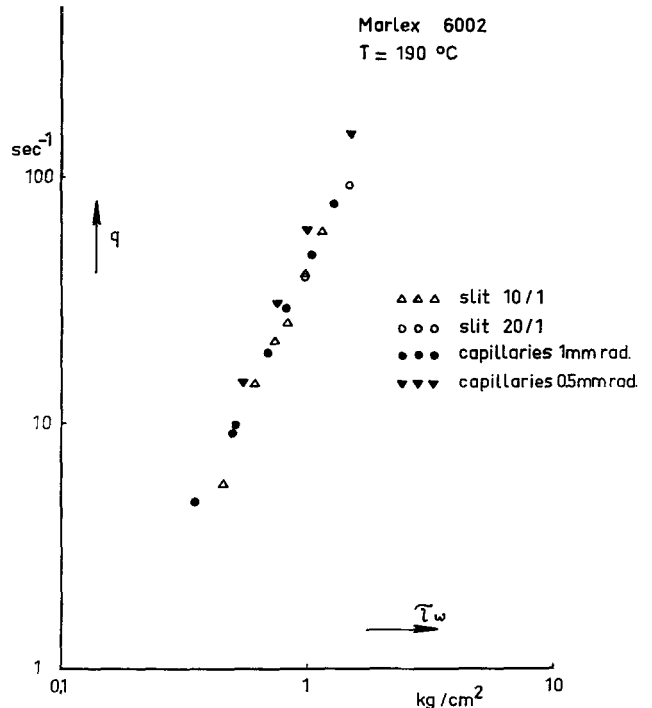


Fig. 10. As fig. 8 only with Marlex 6002

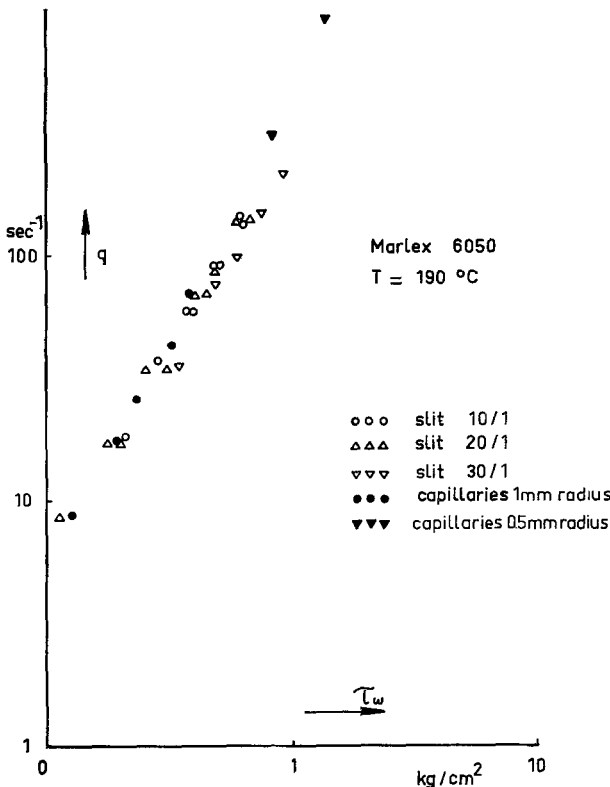


Fig. 9. As fig. 8 only with Marlex 6050

The cylindrical capillaries and the slits are compared in figs. 8-10.  $q$  as evaluated by formulae [5] and [6] is plotted against  $\tau_w$ . There may be a slight tendency for the slit to give higher  $\tau_w$  values than the capillaries, but the difference is certainly not so large as had been found for Alkathene in an earlier publication (3) (the earlier publication's slit results for this material completely agreed with those of this investigation, the capillary results seem to be incorrect).

In fig. 11 are plotted the end corrections,  $n$ , as a function of  $\tau_w$ , from measurements with the 1 mm radius capillaries. Agreement is obtained with the result of Bagley (4, 5) that for low melt indices  $n$  tends to 2 as  $\tau_w$  tends to 0, apparently irrespective of the degree of branching. For higher melt indices  $n$  approaches a much lower limiting value more in agreement with the Couette correction for Newtonian liquids. Not enough speeds were, however, evaluated to give certainty to the linear extrapolation to  $\tau_w = 0$ .

For comparison, data of Arai and Aoyama (6) on the same materials (only at 155 °C) are included. The rather strange variation of  $n$  with melt index, is perhaps reflective of the uncertain nature of  $n$  itself.

The effect of pressure on the materials as obtained by calculation from the 20/1 slit

results are given in table 1. The values of density at atmospheric pressure ( $\rho_0$ ), and fractional increase in density per unit increase in pressure ( $\frac{d\rho}{dP}$ ), have been calculated. A linear relation between  $P$  and  $\rho$  was assumed, and the line of regression of  $\rho$  upon  $P$  was found. The standard deviation (S.D.) of  $\rho_0$  and of ( $\frac{d\rho}{dP}$ ) have also been found. The compressibility ( $\beta$ ) is then given as  $\frac{1}{\rho_0} \frac{d\rho}{dP}$ . Values of this quantity are given in table 1.

The accuracy of this method of measuring  $\beta$  is not very good. More experiments would doubtlessly improve the results, especially in the case of Marlex 6050; with this latter material the statistical analysis was based on fewer experimental points than with Alkathene WJG 11 and Marlex 6002.

Only two, rather old now, papers are known to the authors concerning the compressibility of polyethylenes at this high temperature. *Parkes and Richards* (7) obtained a value of  $1.4 \times 10^{-10}$  cm<sup>2</sup>/dyne (on extrapolation to 190 °C) and *Spencer and Gilmore* (8) obtained a value of  $1.0 \times 10^{-10}$  cm<sup>2</sup>/dyne. These values are in fair agreement with the values in table 1. The only other check is on the density of Alkathene WJG 11 at atmospheric pressure by *D.T.F. Pals* (9), whose value of 0.761 gram/cc is in good agreement with the one given.

In conclusion: The important result of this study is to negate the finding of the earlier investigation (ref. 3.) on one polyethylene by showing that shear stress/shear rate plots of three different grades of polyethylene are essentially the same under cylindrical capillary and (three different) rectangular slit conditions. It is noted, however, that the slit measurements in ref. 3 are in excellent agreement with those in this investigation.

Table 1

Densities and compressibilities of the three polyethylenes used at 190 °C

Material	$\rho_0$ grams/cm <sup>3</sup>	$\frac{d\rho}{dP}$ sec <sup>2</sup> /cm <sup>2</sup>	$\beta$ cm <sup>2</sup> /dyne
Marlex 6002	0.745 S.D.=0.006	$9.8 \times 10^{-8}$ S.D.= $1.2 \times 10^{-8}$	$\sim 1.3 \cdot 10^{-10}$
Marlex 6050	0.752 S.D.=0.014	$13.4 \times 10^{-8}$ S.D.= $7.2 \times 10^{-8}$	$\sim 1.8 \cdot 10^{-10}$
Alkathene WJG 11	0.763 S.D.=0.007	$8.6 \times 10^{-8}$ S.D.= $2.7 \times 10^{-8}$	$\sim 1.1 \cdot 10^{-10}$

where  $\rho_0$  = density at 1 atmosphere  
 $P$  = pressure  
 $\beta$  = compressibility at 1 atmosphere  
 S.D. = standard deviation.

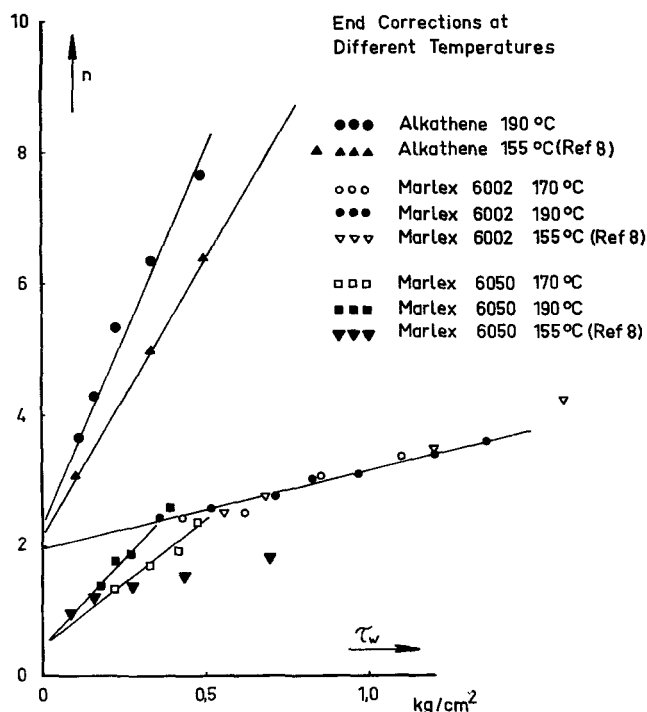


Fig. 11. End correction ( $n$ ) from capillary experiments for Marlex 6050, Marlex 6002, and Alkathene WJG 11 as a function of  $\tau_w$  and temperature

### Acknowledgements

Acknowledgements are gratefully given to the Dutch State Mines for supplying us with some of the materials and for publication permission, to *J. Schijf* and *F. Geradts* who assisted with the experimental work, to *F. R. Schwarzl* for valuable discussions and finally to *D.T.F. Pals* for supplying us with some of his data.

### Summary

A comparative study has been carried out on the flow behaviour (shear rate v. shear stress analysis) of some different polyethylene melts. For the purpose, viscometers of the cylindrical capillary and of the rectangular slit type were used. Comparison has been made between rectangular slits of breadth/width ratio 10/1, 20/1, 30/1 with (A) each other, and (B) with the cylindrical capillaries.

It is concluded that under these differing conditions the flow behaviour for the rectangular slits is compatible with that for the cylindrical capillaries.

It was also found possible to estimate the isothermal compressibilities of the materials examined.

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## Book Reviews · Buchbesprechungen

**Rheo-optics of Polymers.** (Journal of Polymer Science, Part C, Polymer Symposia, No. 5.) Herausgegeben von *Richard S. Stein-Amherst/Mass. (USA)*. VII, 192 Seiten mit zahlreichen Abbildungen. (Easton/Pa., London and New York 1964, Interscience Publ., John Wiley & Sons). Preis: kart. 60/—.

Der hier vorliegende Bericht über das zu dem Gegenstande von der Abteilung der Hochpolymerenphysik der American Physical Society gemeinsam mit dem Polymer Research Institute der University of Massachusetts abgehaltene eintägige Symposium besteht im wesentlichen aus den 14 vorgelegten Mitteilungen ohne die gewiß lebhaft gewesenen Diskussionen. Es handelt sich um eine wesentlich US-amerikanische Konferenz, zu welcher nur eine Arbeit aus einem englischen Institut, zwei Mitteilungen aus japanischen Instituten kamen. Bei der Fülle des vorgetragenen Tatsachenmaterials ist ein näheres Eingehen auf Details der diskutierten Probleme nicht möglich, nur eine Besprechung in großen Zügen mag zur Orientierung des Lesers erwünscht sein.

Ganz so neu, wie der Herausgeber annimmt, ist der Terminus der *Rheoptik* nun durchaus nicht. Vom Ref. wurde der Begriff mindestens seit dem zweiten internationalen Rheologen-Congress (Oxford 1953) immer wieder gebraucht und auf die quantitativ-optischen Untersuchungen bei rheologischen Vorgängen an der Materie, also Fließ- und Deformationsgeschehen, mannigfacher biologisch-medizinischer Objekte bezogen (Nachweis von Rheodichroismus, Rheoelastizität u. v. a.). In die Rheoptik gehört aber außer Strömungsdoppelbrechung und Fließdichroismus auch Rheodiffraktion, d. i. mit rheologischen Prozessen assoziierte Beugungspolarisation (Dityndallismus), ferner Beugung von Röntgenstrahlen, *H. Ziegen-specks* Difluoreszenz, Streuung von Lichtstrahlen aller Wellenlängen und Polarisationszustände, soweit sie sich für ein bestimmtes rheologisches Verhalten als charakteristisch erweisen. Manche dieser Arbeitsfelder konnten nach dem Stande unserer Einsicht noch gar nicht bei dem Symposium berücksichtigt werden.

Unter den 14 Konferenzbeiträgen stehen naturgemäß diejenigen der Strömungsdoppelbrechung oder überhaupt die mit polarisiertem Licht arbeitenden Methoden in vorderster Reihe. Hier geht es um die Ermittlung spannungsoptischer Koeffizienten (*Philippoff*), um den Vergleich im Verhalten von rein *Newton*schen Flüssigkeiten, kolloiden Lösungen und Polymeren (*Wayland*), um Messungen an einer Farbstoffsuspension des *Milling Yellow* mit Zylinderpolariskop (*Peebles et al.*), um Doppelbrechung zur Darstellung des dielektrischen Tensors als Funktion der Verformungsgeschichte (*Dill*), um die Relaxation der Spannungs-Deformations-Zeit polarisationsoptischen Verhaltens von

photo-elastischen Kunststoffen (*Amba-Rao*) und um die Temperaturabhängigkeit der Orientierungsdoppelbrechung von Polymeren in glasigem und kautschukartigem Zustande (*Andrews et al.*). Weiter wurde von *Read* die dynamische Doppelbrechung bei amorphen Polymeren, von *Yamada et al.* bei einigen Hochpolymeren zur Bestimmung komplexer Koeffizienten und des Elastizitätsmoduls, von *Sasaguri* und dem Herausgeber bei Olefinen und von *Takayanagi et al.* in Anwendung auf ein konstruiertes Modell neben der nicht-kristallinen Phase untersucht. Neben Arbeiten mit polarisiertem Lichte kamen auf der Konferenz auch solche der Lichtstreuung zum Vortrage, so etwa über die Teilchengröße an Dispersionen zweier flüssiger Phasen (*Lindsey et al.*), über die Relaxation in gedehnten dünnen Polyäthylenfilmen (*LeGrand et al.*) und stark eingeschränkte Kristallisation der Filme mittleren Molekulargewichts (*Moore et al.*) oder über Geschwindigkeiten der Sphärolithdeformation bei verlängerten und kontrahierten Proben von Polyäthylen und Poly-1-buten in Kleinwinkelstreuungsdiagrammen mittels Rubinlaser (*Erhardt et al.*).

Auch wenn andere Methoden an rheologisch beanspruchten Polymeren noch nicht behandelt werden konnten, beweist die Gesamtheit der Mitteilungen doch bereits die große Fruchtbarkeit dieses rheologischen Arbeitsfeldes. Das gut ausgestattete Büchlein enthält eine große Fülle grundlegender rheologischer Überlegungen, von denen sich alle Rheologen und nicht nur die mit ihren Untersuchungen auf das rheo-optische Verhalten der Materie eingestellten Forscher befassen sollten. Mit der dankenswerten Drucklegung der auf dem Symposium vorgetragenen Mitteilungen werden nicht nur die Teilnehmer beschenkt, sondern ist auch einem weiteren Kreise von Rheologen die Beachtung des Gebietes möglich. Nach dem Themenkreise werden dabei sowohl theoretisch interessierte Benutzer als auch experimentell auf die Anwendbarkeit ausgerichtete Leser auf ihre Kosten kommen. *H. H. Pfeiffer* (Bremen)

### Correction

of the paper

#### On the Use of Power Equations to Relate Shear-Rate to Stress in Non-Newtonian Liquids

By *G. W. Scott Blair* (Reading/England)

Rheol. Acta 4, No. 3, 53-55 (1965)

The middle sentence in the paragraph headed "shear thickening liquids" should read: "As shear rate increases, the duration of contact between the particles would decrease and hence, by an entirely different mechanism, there would also be a diminishing increase in  $n \dots$ "