

Studies of Time Effects in the Flow of Polymer Melts Using a Biconical Viscometer

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Synopsis

The variation of viscosity of various polymer melts under constant shear rate conditions has been investigated using a biconical viscometer, a cone-plate viscometer, and a capillary rheometer. The validity of the biconical viscometer edge-zone correction was investigated. Comparisons between the three types of viscometer showed that sample fracture at the material boundary contributed to the decrease of viscosity with time of shearing occurring in the cone-plate viscometer. Polymer melts are subjected to hydrostatic pressure within the biconical viscometer and fracture appears to be prevented. Shear stress-shear rate-time relationships were obtained for the materials studied with the biconical viscometer at shear rates up to a few reciprocal seconds. There was good agreement with capillary data at high shear rates and cone-plate data at low shear rates. A recoverable decrease of viscosity with time of shearing was found to occur. Both the fractional decrease in viscosity and the time taken to recover the original viscosity become smaller as the temperature is increased.

INTRODUCTION

Cone-plate viscometers have the fundamental advantage over other types of instrument that the strain rate is constant throughout the test specimen. Many workers have used this type of instrument to measure both the shear stress and first normal stress difference for molten polymers as functions of strain rate and time, and there is no reason to doubt the validity of such measurements at very low strain rates. However, as the strain rate rises, a number of effects may partially or wholly invalidate the measurements. Firstly, the sample may slip over the metal surfaces of the cone or the plate as suspected by, for example, Raha¹ and Vinogradov.² Secondly, the test piece may fracture near the edge so that its effective area is not known and the apparent shear stress is less than the true stress; this effect was discussed by Hutton³ in relation to silicone fluids and by Vinogradov² and others for polymer melts. A third source of error arises particularly in instruments used to measure normal as well as shear stresses since there is a likelihood that the cone and plate will separate slightly under the action of normal stresses as realized by several workers and emphasized by Meissner.⁴

It appeared to us that use of the biconical viscometer devised by Piper and Scott⁵ might reduce the probability of errors due to the above causes,

since the polymer is under hydrostatic pressure during the measurement and the surfaces confining the material are extremely rigid because no attempt is made to measure normal stress. Before results on this type of instrument can be considered valid, it is necessary to determine whether the rather larger torque contributed by the edge of the biconical rotor can be calculated sufficiently accurately, and in the section on results in this paper, we examine this problem in some detail. It is also necessary to prepare test pieces free from voids, and a special mold for this purpose is described in the experimental section.

There are two sources of error which may be expected to affect equally cone-plate and biconical measurements and which we consider in the section on time dependence. They are the possible temperature rise due to viscous generation of heat and the secondary (radial) flow which has been reported to occur in cone-plate instruments.

The errors enumerated above are likely to result in an apparent reduction of viscosity with time of shearing, and there has been uncertainty whether reported time variations were due to material behavior or instrumental defects or both. In this paper we attempt, by making measurements under virtually identical conditions of temperature and shear rate in biconical and cone-plate viscometers, to separate the material and instrumental contributions to the time dependence of viscosity.

DESCRIPTION OF VISCOMETERS USED

Biconical Viscometer

The biconical viscometer⁵ is a modification of the Mooney shearing disc viscometer.⁶ Polymer is sheared in the space between the wide-angled cones of a rotating biconical rotor and the flat top and bottom of a closed chamber and also between the rotor tip and chamber edge which have semicircular cross sections (Fig. 1). The two halves of the chamber are bolted onto steel platens which are heated by embedded resistance coils,

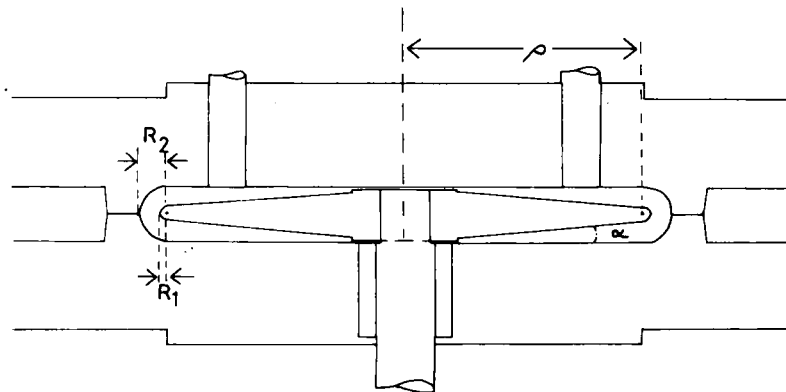


Fig. 1. Biconical viscometer rotor and chamber.

the temperatures of which are separately controlled by proportional temperature controllers. The temperature within the chamber is kept constant to within $\pm 0.1^\circ\text{C}$. The rotor is made in two pieces, the head being detachable from the stem. It is turned by a variable-speed d.c. motor and a four-speed gearbox, and the speed is monitored (to $\pm 0.1\%$) by a digital frequency meter. The torque required to rotate the rotor produces a backthrust on the worm drive to the rotor which in turn deflects a cantilever spring. The deflection of this spring, measured by means of a dial gauge or an inductance transducer connected to a graph plotter is proportional to the torque. In this type of instrument, it is essential that leakage of sample should be small where the rotor stem passes through the cavity wall. The necessary small clearance led to friction in the original Piper-Scott design unless alignment was extremely precise. A P.T.F.E. sleeve was let into the bearing surface of the cavity; this made alignment less critical, and very few subsequent results were rejected because of suspected friction. The torque due to friction between the rotor shaft and the P.T.F.E. sleeve is difficult to assess as it is likely to depend on the pressure within the chamber. It was measured by rotating a dummy shaft without a head in a polymer-filled chamber and was found to be less than 1% of the average level of torque during tests.

The shear rate is substantially constant in the material sheared between the conical and flat surfaces and equal to ω/α , where ω is the angular velocity of the rotor and α is the angle between the two surfaces. It is necessary to consider the material between the radiused rotor tip and radiused chamber outer edge called the edge zone, where the shear rate varies in a more complicated manner. On the basis of reasonable assumptions about the flow geometry in the edge zone, Piper and Scott derived the following expressions for the total torque on the rotor:

$$T = \frac{4}{3}\pi\rho^3s_u + 2\pi^2s_uX\alpha^{1/n}. \quad (1)$$

The first term arises from the uniform stress s_u assumed to exist to a radius ρ . The second term gives the edge contribution calculated assuming that the power law relationship $\dot{\gamma} = Ks^n$ (where $\dot{\gamma}$ is the shear rate and s is the shear stress within the fluid) adequately represents the flow law over the relatively small range of stresses which significantly contribute to the edge torque. The factor has been computed for a range of values of n for each

$$X = \rho^{2+1/n} \left(\frac{n-1}{R_1^{1-n} - R_2^{1-n}} \right)^{\frac{1}{n}} \left(1 + \frac{2(n-1)(2n+1)(R_1^{2-n} - R_2^{2-n})}{\pi n(n-2)\rho(R_1^{1-n} - R_2^{1-n})} \right) \quad (2)$$

geometry used; and since it does not vary rapidly with n , interpolation is simple. For the same reason, an approximate value of n derived from the slope of a graph of $\log \omega$ against $\log T$ (equivalent to assuming X is constant over a range of stresses) is sufficient to determine X , and thus it is possible to determine s_u from the total torque.

TABLE I
Rotor and Chamber Dimensions

Rotor	R_1 , cm	R_2 , cm	α , radians	ρ , cm	Special feature
1	0.10	0.36	0.087	3.00	
2	0.20	0.46	0.087	3.00	
3	0.10	0.47	0.123	3.00	
4	0.10	0.41	0.123	2.50	
5	0.10	0.47	0.123	3.00	grooved rotor and chamber

As far as we are aware, the above expression for the edge-zone torque has not previously been verified experimentally, and rotors and corresponding chambers having the dimensions given in Table I were constructed in order to investigate the validity of the assumptions made. The finite edge radius adopted by Piper and Scott was retained in preference to the sharp edge favoured by Best and Rosen,⁷ as this makes it possible to compare grooved and smooth rotors to check on slippage effects. Furthermore, the assumptions implicit in the derivation of eq. (1) are not valid for very small values of R_1/R_2 .

Weissenberg Cone-Plate Rheogoniometer

The instrument used was a standard R18 rheogoniometer manufactured by Sangamo Weston Controls Ltd. of Bognor Regis.⁸ This is a cone-plate instrument which has facilities for the measurement of shear stresses and normal forces. Two 2.50-cm-radius cones, the cone angles being 2.02° and 4.95°, and one 1.20-cm-radius cone of angle 8.04° were used. In each case the plate radius equalled that of the cone.

The shear stress s , first normal stress difference σ_1 , and shear rate $\dot{\gamma}$ were calculated from the standard formulae:

$$s = \frac{3T}{2\pi\rho^3} \quad (3)$$

where T is the torque required to rotate the plate and ρ is the cone and plate radius,

$$\dot{\gamma} = \frac{\omega}{\alpha} \quad (4)$$

where ω is the angular velocity of the rotating plate and α is the cone-plate angle, and

$$\sigma_1 = P_{11} - P_{22} = \frac{2F}{\pi\rho^2} \quad (5)$$

where F is the normal force exerted by the material.

Instron Capillary Rheometer

Two instruments were used both being standard Merz-Colwell extrusion rheometers manufactured by Instron Ltd.⁹ The instrument is a ram-

TABLE II
Capillary Dimensions

Instrument	<i>L</i> , cm	<i>R</i> , cm	<i>L/R</i>
Instron rheometer	7.64	0.064	119
	5.099	0.063	81
	2.546	0.063	40.5
Davenport rheometer	5.105	0.147	34.8
	1.905	0.197	9.7

driven rheometer, the force required to extrude polymer at a set rate through a capillary being measured on the ram.

The shear stress at the wall s_w corrected for viscous end effects by the factor ϵ was calculated from

$$s_w = \frac{\Delta P}{2 \left(\frac{L}{R} + \epsilon \right)} \quad (6)$$

where ϵ is determined by extrapolating to $\Delta P = 0$, a plot of ΔP versus (L/R) at constant flow rate and radius obtained from capillaries of various lengths; L and R are the capillary length and radius, respectively; and ΔP is the pressure drop through the polymer melt.

The $\dot{\gamma}_w$ was calculated using the Rabinowitch correction¹⁰

$$\dot{\gamma}_w = \frac{3 + b}{4} \left(\frac{4Q}{\pi R^3} \right) \quad (7)$$

where b is the slope of a log/log plot of $4Q/\pi R^3$ versus s_w , and Q is the volumetric flow rate. The dimensions of the capillaries used are given in Table II.

Davenport Capillary Rheometer

The instrument used was a standard rheometer manufactured by Davenport London Ltd., Welwyn Garden City, Herts, England, and is of the gas-driven type, the weight of polymer extruded through a capillary in a certain time being measured for a given gas pressure.

The s_w and $\dot{\gamma}_w$ values were calculated using eqs. (6) and (7), the capillary dimensions being given in Table II.

EXPERIMENTAL

Polymers Studied

The three materials principally used were obtained in powdered or granular form and were chosen to be chemically stable under test conditions. The materials were:

A low-density polyethylene "Alkathene" manufactured by I.C.I. Ltd. The viscosity at 122°C and shear rate of 0.01125 s⁻¹ was 2.25 × 10⁵ poise. According to the suppliers, the British Standard Nominal density was

0.917 g/cm³, and the melt flow index was 7 (BS. 2782 Method 105C). The number-average molecular weight for this grade was 28,000, branch points occur at intervals of 25–100 chain carbon atoms; most of the branches being two or four carbon atoms long, some being very much longer. This polymer was referred to as LDPE.

A high-density polyethylene "Rigidex" manufactured by B.P. Ltd. The viscosity at 167°C and shear rate of 0.01125 s⁻¹ was 3.58 × 10⁵ poise. According to the suppliers, the British Standard Nominal density was 0.96 g/cm³, and the melt flow index was 0.9. The molecular weight M_z for this grade is 150,000; the ratio of M_w/M_n is 15. The degree of branching is approximately one per 1000 chain carbon atoms and is substantially methyl branching. This polymer was referred to as HDPE.

A copolymer, ethylene vinyl acetate, 18% vinyl acetate, manufactured by I.C.I. Ltd, of melt flow index 10, referred to as EVA.

Other polymers used were LDPE and HDPE of different melt flow indices, polystyrene, and poly(styrene/butadiene).

Sample Preparation

Biconical Viscometer. A major problem with this sample geometry is the production of test pieces free of entrapped air. The following procedure was adopted after extensive experimentation.

Polymer was molded around the rotor head using a specially designed vacuum mold (see Fig. 2) which produced a disc which was larger than that needed to fill completely the viscometer chamber. The pressure exerted on the polymer due to the vacuum within the mold helped prevent voiding occurring within the molding during cooling. The molding cavity was overfilled with powdered or granular polymer surrounding the rotor. The plunger platen was then replaced, the mold was placed within a press used solely for heating purposes, and the vacuum was applied by means of a rotary pump (~25 torr). The top platen raising-lowering bolts were unscrewed after several minutes, allowing the platen to exert pressure on the polymer due to the vacuum within the mold. The molding temperature was 135°C for LDPE; 145°C for HDPE, polystyrene, and poly(styrene/butadiene); and 130°C for EVA. The optimum molding temperature is decided by the viscosity of the melt. If the viscosity is too low the plunger platen travels down and makes contact with the molding cavity ring and

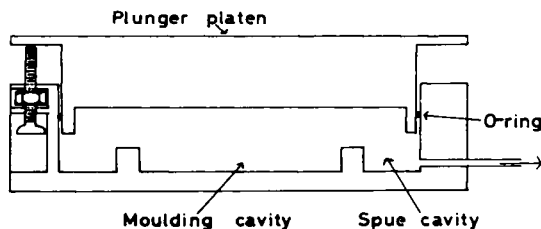


Fig. 2. Vacuum mold showing one of three raising-lowering bolts.

voids are formed within the polymer owing to lack of pressure from the plunger platen during cooling of the melt. If the viscosity is too high, then the process takes an excessive time. After 30 min, when the plunger platen was about 2 mm from the metal molding ring, the mold was allowed to cool slowly, rapid cooling of the molten polymer leading to voiding. When the polymer was below its melting point the mold was cooled rapidly by means of water cooling. The mold was opened by means of the three bolts and the polymer-encased rotor was taken out and placed on the rotor stem located within the viscometer chamber. The chamber was then closed forcing out excess polymer and expelling any air trapped between the polymer disc and chamber.

Tests with a thermocouple positioned within the chamber had shown that a uniform temperature was attained within 15 min of placing the rotor within it, and thus testing was commenced after waiting for that time.

Rhegoniometer. Samples to be sheared in the rhegoniometer were vacuum molded as discs, then inserted between the platens. Excess material was cleared away from outside the cone and plate. The sample was surrounded by an atmosphere of nitrogen throughout the test. Similar results were obtained using specimens premolded to the cone-plate gap dimensions.

Capillary Rheometers. Samples to be sheared were loaded as granules into the barrels of the capillary rheometers. Care was taken to exclude as much air as possible, and results were ignored if air bubbles were noticed in the extrudate.

COMPARISON OF EXPERIMENTAL RESULTS FOR DIFFERENT INSTRUMENT GEOMETRIES

Under the conditions of shear stress and shear rate used in these experiments (except where specifically mentioned), temperature rise effects due to viscous dissipation of energy were minimal and were ignored.

Results for HDPE at 147°C

Biconical Viscometer. Figure 3 is a logarithmic graph of viscosity against shear rate for HDPE at 147°C. Each point represents the mean result of several replicate tests with a given rotor, the viscosity being measured when it was no longer changing appreciably with time (see section on time dependence). Replicate tests with any one rotor normally agreed within $\pm 1\%$. Occasionally, fluctuating torque values were obtained due to the presence of air bubbles or fluctuating friction, and those were discarded. Four different rotors (rotors 1-4, Table I) were used; and as the spread of results ($\pm 2\%$) is no greater than can be expected from uncertainties in the dimensions of the rotors, it can be concluded that the Piper-Scott correction for edge torque is satisfactory for this material. The edge zone contributes between 25% and 37% of the total torque.

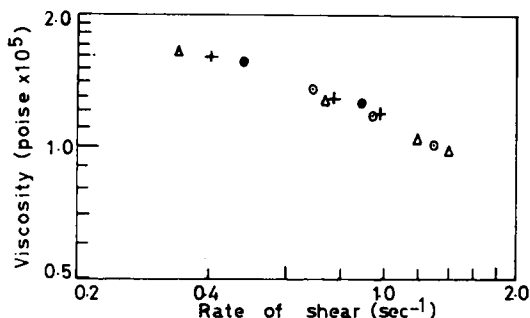


Fig. 3. Dependence of the viscosity of HDPE at 147°C upon shear rate. Biconical viscometer: (⊙) rotor 1; (Δ) rotor 2; (+) rotor 3; (⊗) rotor 4.

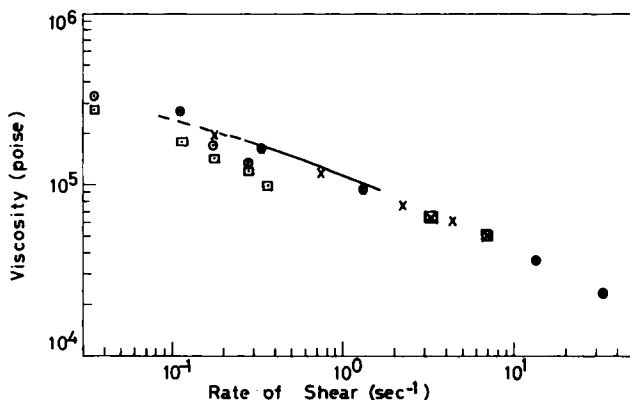


Fig. 4. Dependence of the viscosity of HDPE at 147°C upon shear rate. Cone-plate viscometer, 2° cone: (○) peak value; (⊠) final value. Biconical viscometer: full line, mean of data in Fig. 3; broken line, other data, rotor 2. Capillary rheometers: (×) Davenport; (⊗) Instron 1, (⊠) Instron 2.

Capillary Rheometer. The capillary data plotted in Figure 4, log viscosity against log shear rate, were obtained from replicate tests on the Davenport and Instron rheometers. The agreement to within 9% with the biconical data is satisfactory in view of the great difficulty in obtaining comparable test conditions (for example, a temperature difference of less than 3°C could account for the discrepancy) and gives us further confidence in the validity of the biconical viscometer results.

Rheogoniometer. The cone-plate data plotted as dots in Figure 4 were obtained using the rheogoniometer with 2° angle cone of radius 2.5 cm. The repeatability of replicate tests was of the order $\pm 5\%$. As shown later in this paper, the shear stress recorded at a particular shear rate generally rises to a peak and then falls with time. The magnitude of this peak depends of the material and the test conditions (temperature, shear rate, sample history). The results shown in Figure 4 were obtained by shearing at a particular low rate until an approximately constant shear stress was recorded and then shearing at the next higher shear rate until

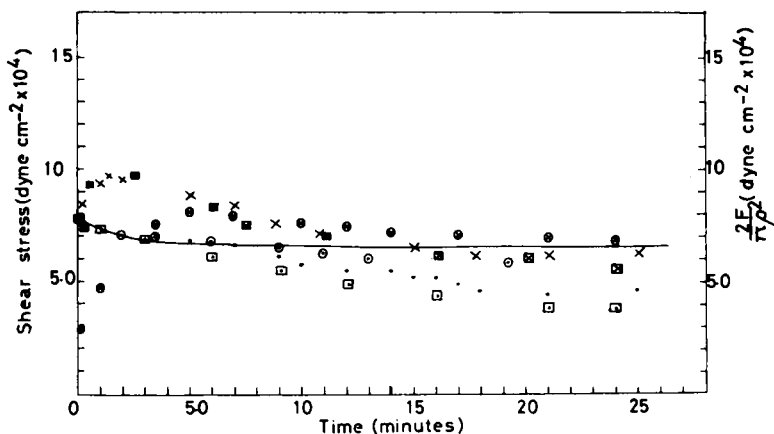


Fig. 5. Variation of shear stress and $2F/\pi\rho^2$ with time for HDPE at 147°C , shear rate 0.45 s^{-1} . Biconical viscometer rotor 3: full line, shear stress. Cone-plate viscometer: shear stress, (○) 2° cone, (◻) 5° cone; (·) 8° cone. $2F/\pi\rho^2$, (⊗) 2° cone; (⊠) 5° cone; (×) 8° cone.

the stress again became constant. However, at the higher rates the stress was still falling slowly and often fluctuating when the speed was increased. The points marked with circled dots in Figure 4 represent the peak values obtained at each speed under these conditions, while the squared dots represent the approximately constant final stress. The peak values shown are rather lower than those obtained with material not previously sheared. There is fair agreement between cone-plate viscosity values and capillary and biconical values at low strains, i.e., low shear rates and/or short times of shear, but nonagreement at higher strains. This points toward some instrumental rather than material effect causing the large stress decrease with time at constant shear rate in the rheogoniometer. When these low values of torque occurred, disturbances of the edge zone were noticed similar to those described by Hutton and Vinogradov. Since the torque produced from material sheared between a cone and plate is proportional to the cube of the radius of the material boundary, a slight disturbance in the edge conditions can have a significant effect on torque. Time effects are considered in greater detail in the next section.

Comparison of Biconical and Cone-Plate Results on Materials with Similar Shear Histories. Figure 5 shows the variation of both shear stress (dots) and first normal stress difference, σ_1 (crosses), with time at a constant shear rate of 0.45 s^{-1} , again for HDPE at 147°C . The tests were carried out using the rheogoniometer with 2° and 5° cones of radius 2.5 cm, with an 8° cone of 1.2 cm radius and also with the biconical viscometer using rotor 3. In all cases the samples were not sheared prior to testing, apart from the inevitable shearing associated with molding. The peak shear stress is very similar for all four systems, but after a few minutes all cone-plate stress values are lower than the corresponding biconical

stress values by varying amounts, and we must consider what instrumental effects may be responsible for the discrepancies.

It is well known¹¹ that the upper platen of the rheogoniometer moves upward under the action of normal force by $0.5 \mu\text{m}/\text{kg}$ force. Meissner added a stiffening column and reduced the upper platen movement to $\sim 0.1 \mu\text{m}/\text{kgf}$.

The theoretical maximum movement of the lower platen of his modified normal force-measuring system was $\sim 1 \mu\text{m}$ under maximum load. He observed that the variation of σ_1 with time was influenced by the cone angle used and ascribed the effect to such a movement. With the servo system in operation, the bottom platen of our instrument moved downward by $10 \mu\text{m}/\text{kgf}$, and remained displaced even though the cantilever returned to within $0.1 \mu\text{m}$ of its original position after only a few seconds of shearing, apparently because the driveshaft moved within the normal force pivot bearing. A movement of $2 \mu\text{m}/\text{kgf}$ was recorded on the bottom platen of another rheogoniometer. It is important to note that under these circumstances, replacement of the standard cantilever-servo system of normal force measurement by a stiff cantilever, as proposed by Meissner,⁴ would not reduce the movement of the lower platen if the same pivot bearing were used.

The separation of cone and plate due to the presence of normal stress will have two distinct effects. Firstly, the shear stress will decrease with time as the surfaces separate, and some part of the fall in shear stress with time in the cone-plate tests will be due to this phenomenon. To understand the second effect, let us imagine a material such that the normal stress difference is constant at a given strain rate. When shearing starts in the cone-plate viscometer, a large force is generated which forces the shearing surfaces apart. It is well known that alteration of the separation of two close surfaces separated by a viscous medium requires a large force, and the measured normal force will be only a small fraction of what would be measured with an absolutely rigid measuring system. The measured normal force will not reach a peak until the shearing surfaces have separated appreciably, and the delay will be much greater for cones of small angle and/or large radius.

In accordance with the above, Figure 5 shows that the normal force peak recorded with the 2° cone is retarded compared with the 8° cone and the peak value reached is lower.

Comparison of Instruments at Higher Temperatures

In Figure 6, viscosity is plotted logarithmically against shear rate for HDPE at 167°C using the same instruments as for Figure 4. Cone-plate peak values (circled dots) and values at a later time (squared dots) are again plotted. The biconical viscometer readings are those taken when the torque was not falling appreciably with time. Capillary rheometer data are also plotted. Again there is good agreement. There is relatively little fall of the rheogoniometer shear stress with time, and this is consistent

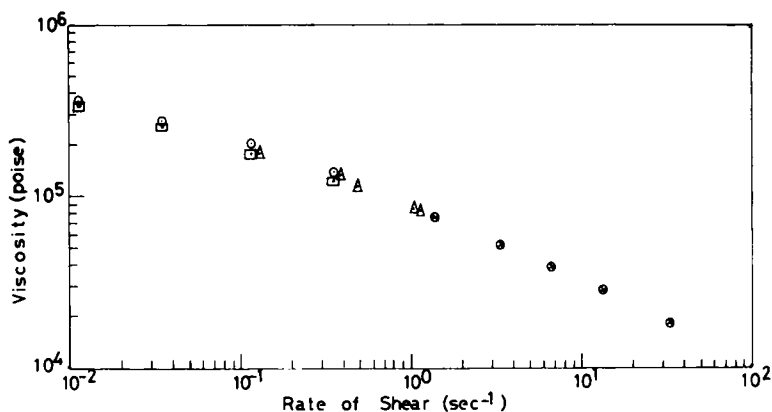


Fig. 6. Dependence of the viscosity of HDPE at 167°C upon shear rate. Cone-plate viscometer, 2° cone: (○) peak value; (◻) final value. (△) Biconical viscometer, rotor 2. (⊗) Instron 1 capillary rheometer.

with the observation that the severity and rapidity of material disturbances at the cone-plate edge were less at the higher temperatures.

Comparison of Instruments Using Other Polymers

Similar results to those reported above have been obtained with LDPE and EVA of various melt flow indices. Viscosity is plotted logarithmically against shear rate in Figure 7 for LDPE (MFI7) at 150°C, the shear rates being much higher than in the measurements reported above. The data were obtained from the biconical viscometer (rotor 3) and the rheogoniometer (8° cone, 1.2 cm radius). Also plotted are capillary data kindly supplied by I.C.I. Ltd. The peak values and those after 25 min when the viscosity was approximately constant are plotted for the biconical

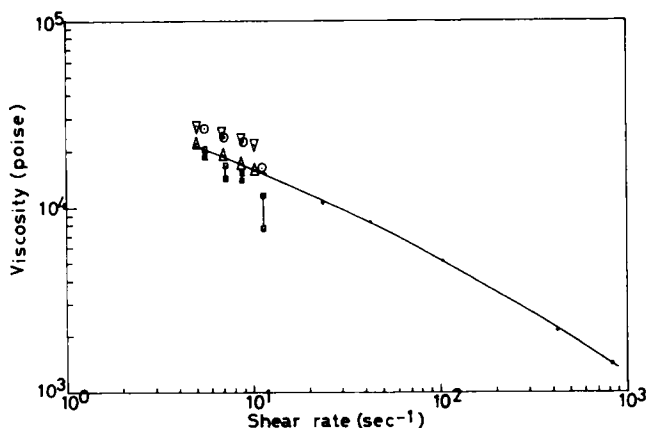


Fig. 7. Dependence of the viscosity of LDPE at 150°C upon shear rate. Biconical viscometer: (▽) peak value; (△) value after 25 min. Cone-plate viscometer: (○) peak value; (◻—◻) after about 6 min. (·) and solid line, I.C.I. capillary data.

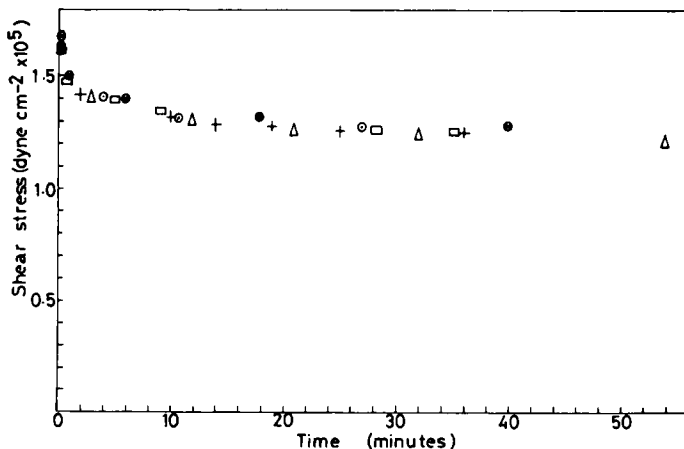


Fig. 8. Variation of shear stress with time for LDPE at 122°C, shear rate 1.78 s⁻¹. Biconical viscometer: (○) rotor 1; (Δ) rotor 2; (+) rotor 3; (⊙) rotor 4; (□) rotor 5.

viscometer. At these high shear rates and stresses, temperature rise effects due to shear heating may be significant with the biconical viscometer. (For rotor 3 at 10 s⁻¹ and shear stress of 2 × 10⁵ dynes/cm², calculations suggest a temperature rise within the melt of ~2°C.) The peak values and those after 6 min are plotted for the rheogoniometer. At this stage, the sample boundary conditions were not ideal; and oscillations in both normal force and torque, within the limits of the line drawn in Figure 7 were recorded, the magnitude increasing with shear rate. Such effects were less severe with LDPE than with HDPE at similar shear rates. Less comprehensive tests using polystyrene and poly(styrene/butadiene) in the cone-plate and biconical viscometers showed that these materials behaved similarly.

Dependence of Shear Stress/Time Plot on Grooving of Instrument Surfaces and Alteration of Dimensions

Figure 8 is a graph of shear stress against time for LDPE at 122°C and a shear rate of 1.78 s⁻¹ using the biconical viscometer and rotors 1-5. Rotor 5 has tapered radial grooves 1 mm deep at the rotor tip, the rotor angle being measured along the tops of the ridges. The agreement to within ±2.5% between the shear stress values derived from measurements with various instrument geometries, including a grooved system, gives us further confidence in the accuracy of the assumptions made in the analysis of the measurements, such as lack of slippage and the adequacy of the edge torque correction.

FURTHER STUDIES OF TIME DEPENDENCE

Effect of Resting

In order to elucidate further the nature of the time effects observed in biconical and cone-plate viscometry, a sample of LDPE at 122°C was

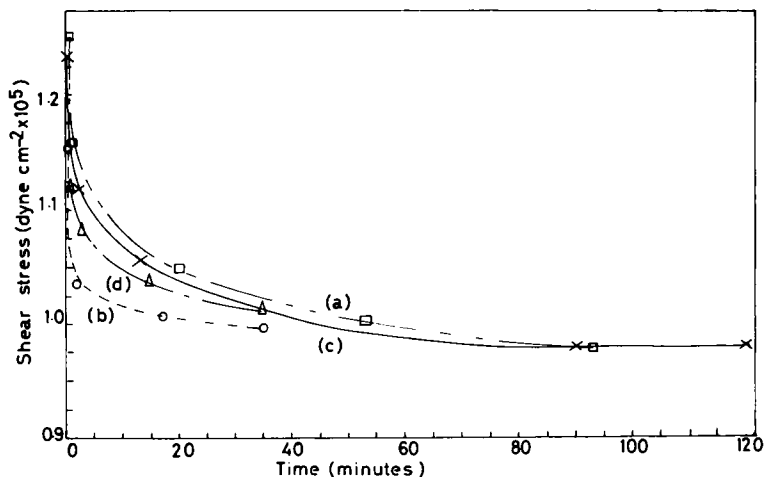


Fig. 9. Influence of shear history upon the variation of shear stress with time, for LDPE at 122°C , shear rate 1.18 sec^{-1} : (\square) fresh sample; (\circ) the same sample after shearing for 93 min and resting for 28 min; (\times) after further shearing for 36 min and resting for 180 min; (Δ) after further shearing for 120 min and resting for 75 min. In each case, the first plotted point represents the peak stress.

sheared at a constant rate of 1.18 s^{-1} in the biconical viscometer (rotor 3). Figure 9 shows how the shear stress varied with time of shearing (a) for a fresh sample; (b) for the same sample after shearing for 93 min and then resting for 28 min; (c) for the same sample after further shearing for 36 min and resting for 180 min; and (d) after further shearing for 120 min and resting for 75 min. It appears that if the material is sheared at a constant rate, a particular viscosity is approached in all cases. If the shearing is stopped for a time and then recommenced, the longer the rest time (up to 180 min for this material at this temperature), the more nearly is the original stress/time curve reproduced. Similar results within a shorter time scale were observed with HDPE.

The stress drop recorded with the rheogoniometer was also recoverable even if the material had been seen to fracture at the edge during shear, provided that the material had not been ejected from the gap.

Effect of Temperature and Differences Between Materials

The rates at which polymer melts approach a constant viscosity may conveniently be compared by plotting the ratio of viscosity to peak viscosity against time, as in Figure 10. All three curves were obtained using the biconical viscometer (rotor 3) at a strain rate of 1.18 s^{-1} . The viscosity of LDPE at 145°C reaches a constant value after about 10 min. The same material at a lower temperature (122°C) takes much longer to reach a steady viscosity and the fractional decrease in viscosity is greater. It was also found that longer resting times after shearing were necessary at the lower temperature in order to reproduce the original viscosity time curve.

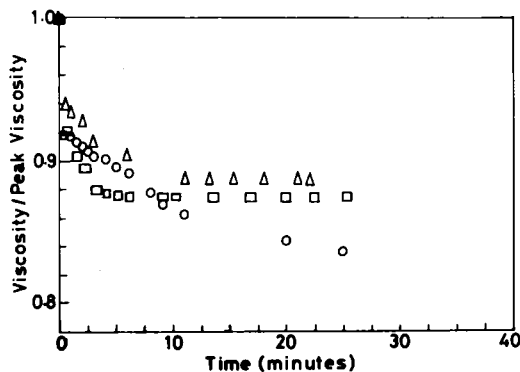


Fig. 10. The variation of the ratio viscosity/peak viscosity with time for LDPE and HDPE, biconical viscometer, shear rate 1.18 s^{-1} : (Δ) LDPE 145°C ; (\circ) LDPE 122°C ; (\square) HDPE 145°C .

The above behavior is consistent with a simple model associating the fall in viscosity with untangling and alignment of molecules with thermal agitation opposing the effects of shear. The third curve in Figure 10 shows that the HDPE sample tested at 145°C reached a steady viscosity much more rapidly than LDPE at the same temperature, even though more viscous, possibly because of the small amount of long-chain branching in HDPE. The viscosity of HDPE at 145°C was comparable with that of LDPE at 122°C .

Discussion of Time Dependence

Five instrumental effects were discussed in the introduction as possible contributors to a spurious fall in the measured viscosity of polymer melts and solutions during shear at a constant rate in cone-plate viscometers: (a) slippage of a highly viscous material over the metal shearing surfaces; (b) breakup of laminar flow near the cone edge resulting in a crack propagating inward an uncertain distance, perhaps with balls of polymer rolling between cone and plate; (c) variation in the spacing between cone and plate due to finite stiffness of the normal force measuring system; (d) a rise in fluid temperature due to viscous dissipation of energy in the material; (e) secondary flows causing radial movement of material to be superimposed on the main circumferential velocity.

We believe that in our experiments with the biconical viscometer, none of these effects contributed significantly to the observed time variation of viscosity and that a true material time variation was shown in Figures 5, 8, 9, and 10. We also believe that large time variations of viscosity found in our cone-plate viscometer measurements at higher strain rates are spurious and that in consequence similar results by other workers are suspect. If we are correct, it is presumably the defined edge conditions in the biconical viscometer together with the hydrostatic pressure in the sample which prevent effects (a) and (b) from occurring. Effect (c) will not occur, and

(d) will not be significant at the strain rates ($<2 \text{ s}^{-1}$) used in the majority of our measurements.

The evidence for our claim is primarily the self-consistency of results obtained with various rotors together with the agreement of these results with cone-plate results at very low shear rates and with capillary results at high shear rates. It seems unlikely in the extreme that effects (a), (b), or (e) would affect equally the calculated shear stress for all the five rotors used in obtaining the results in Figure 8 or for the four rotors used with a different material at a different temperature for the results in Figure 3. It is probably also significant that the cone-plate and biconical viscometer results begin to differ appreciably only above the strain rate at which severe edge disturbances become visible with the cone-plate system.

CONCLUSIONS

The first conclusion we draw from the results reported above is that the double cone viscometer provides a reliable means of obtaining shear stress-shear rate-time relationships for several molten polymers at shear rates up to a few reciprocal seconds. The previously published edge-zone correction formula appears to be valid. However, considerable care is necessary to obtain test specimens free from voids, and normal stress measurements cannot be made with the instrument in its present form.

The second conclusion is that a genuine decrease in viscosity with time of shearing takes place in HDPE and LDPE and that the original viscosity is recovered on resting. Both the fractional decrease in viscosity on prolonged shearing and the time taken to recover the original viscosity become smaller as the test temperature is increased. These conclusions apply at shear rates up to 1 or 2 s^{-1} ; but at these high rates, the decrease in viscosity with time of shearing is much less than is observed in a cone-plate viscometer testing the same material at the same temperature. We ascribe the difference to the usually visible breakup of the edge of the material in the latter instrument. Consequently, our conclusions are in qualitative agreement with those of many previous workers using cone-plate viscometers but can be relied on quantitatively to much higher shear rates.

It is of particular interest that, in the cone-plate viscometer, we observed severe fracture at the edge of the test piece and large time variations in stress only at strain rates above about 0.1 s^{-1} . Chen and Bogue,¹² working with LDPE at 160°C ; Mills,¹³ working with filled and unfilled polymers; and King,¹⁴ working with three polyethylenes at 190°C , have all reported that fracture first occurs at a rate of shear between 0.1 and 0.5 s^{-1} .

Hutton,³ working with poly(dimethylsiloxanes) of various molecular weights sheared in a cone-plate viscometer, showed that fracture occurs when the first normal stress difference exceeds a critical value given by the expression

$$P_{11} - P_{22} = \frac{N\Gamma}{\rho\alpha}$$

where Γ is the surface tension and N is a parameter found experimentally to be about 24. We might therefore expect that the extent to which the torque in cone-plate measurements at a given shear rate falls with time below the corresponding torque in the biconical viscometer would increase with $\rho\alpha$. Our results (Fig. 5) for HDPE at 147°C are in agreement with this conclusion, the most severe fall in torque being observed with the 5°, 2.5-cm radius cone ($\rho\alpha = 0.22$ cm), the fall with the 8°, 1.2-cm radius cone ($\rho\alpha = 0.19$ cm) being less severe and the 2°, 2.5-cm radius cone ($\rho\alpha = 0.07$ cm) showing relatively little fall in torque. In order to assess the applicability of Hutton's criterion to the fracture of molten polymers during cone-plate viscometry, we have attempted to calculate the parameter N in a number of cases, taking Γ as 36 dyn/cm. However, it is not easy to observe with certainty the minimum shear rate at which fracture occurs. King first noticed fracture in three high-density polyethylene melts at shear rates corresponding to values of N between 235 and 580. We observed fracture in LDPE at 122°C with a 2° cone when N was 120 and severe fracture with a 5° cone, after a considerable time, when N was 240. Other authors mention loss of material from the gap at particular rates of shear, and reasonable assumptions about their test conditions lead to estimates of N between 12 and 480. On the whole, it appears that N is much higher for polyethylene melts than for poly(dimethylsiloxanes) but fracture may well have started at much lower shear rates than those at which it was first noticed.

Cone-plate viscometers presumably measure both shear and normal stresses satisfactorily at low rates, provided that the normal force does not cause the cone and plate to separate. Meissner appears to emphasize this cone-plate separation as a source of error to the exclusion of either edge fracture or temperature rise. Using LDPE in a modified rheogoniometer at 150°C, he measured both torque and normal force with cones of the same radius with angles between 2° and 10° and selected an 8° cone as standard because the time variation of normal force was similar for 6°, 8°, and 10° cones but different for the 2° cone. He did not regard as significant the greater rate of decrease of torque with time observed with all cones having angles greater than 2°. Reference to Figure 5 illustrates this point. Results using a cone having the dimensions favored by Meissner show not only that the peak normal stress reading is reached rapidly but also that the shear stress decreases more rapidly with time than with the 2° cone. Although this decrease is only serious after several minutes, it must be remembered that the strain rate is only 0.45 s⁻¹, and our results show that fracture occurs very much more rapidly as this strain rate is exceeded. Clearly, great care is needed if the advantage of rapid achievement of peak normal force is not to be overwhelmed by the loss of torque and presumably normal force due to sample fracture. The 8° cone has a further disadvantage at very high shear rates that a serious temperature rise may occur in the testpiece. For example at the maximum shear stress recorded by Meissner, 1.0×10^6 dyn/cm² at a strain rate of 50 s⁻¹, the formulae of

Turian and Bird¹⁵ predict a temperature rise near the edge of the order of 10° or 20°C.

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