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Experimental observations on the pressure-dependent polymer melt rheology of linear low density polyethylene, using a multi-pass rheometer

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Dedicated to Prof. Dr. J. Meissner on the occasion of his retirement from the chair of Polymer Physics at the Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland

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Abstract We report experimental data for a linear low density grade of polyethylene at elevated temperatures using a newly designed Multi-Pass Rheometer. This rheometer is capable of measuring oscillatory viscoelastic data and steady shear capillary measurements on the same test fluid within an enclosed environment. Data presented in this paper show that at low pressures there is reasonable self-consistency between the Multi-Pass data and separate oscillatory data obtained by using a Rheometrics Mechanical Spectrometer and steady shear data

obtained from a Rosand capillary rheometer. In addition, we report experimental data on the pressure dependence for both viscoelastic and steady shear data over the range of 1–230 bar. The steady shear results appear to be consistent with previously published data. The apparent viscosity and the viscoelastic data both show a linear increase of about 20% over the pressure range tested.

Key words Multi-pass rheometer – melt rheology – polyethylene – pressure

Introduction

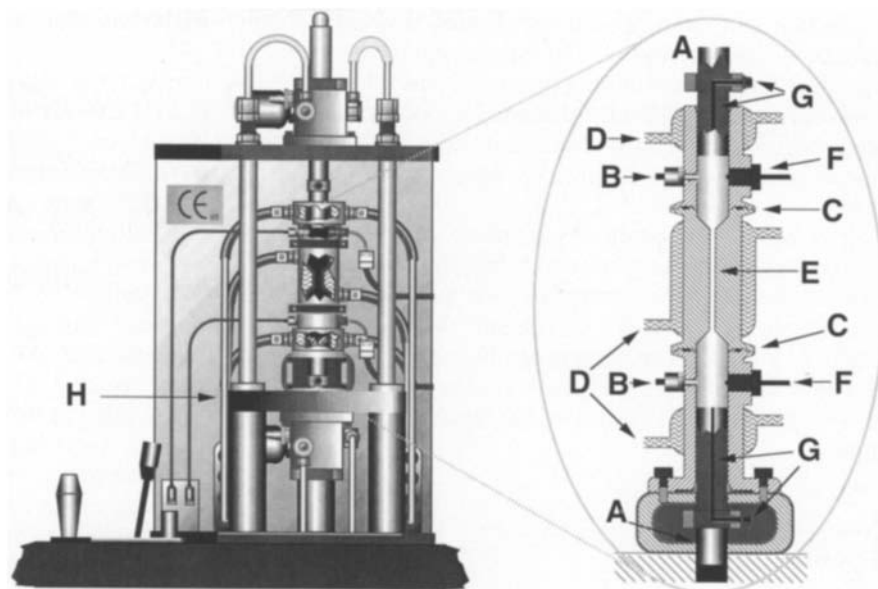
General background

In the past molten polymer behaviour has been characterised by a single parameter melt flow index (see for example Brydson (1981)) subsequently flow curves, where the apparent viscosity plotted as a function of apparent shear rate were used. The pioneering work of Meissner (1975), Laun (1978) and Wagner (1979) in the 1970s demonstrated a scheme where linear and non-linear viscoelastic data could be used to give a more complete viscoelastic description of polymers. This work sets the framework for the development of integral viscoelastic constitutive equations (see for example Wagner (1979)) which have been used, in the numerical prediction of complex engineering flows (Gouldhomme and Crochet (1993), Ahmed et al. (1995)). This development has directly linked viscoelastic data to engineering processing behaviour and in turn this has led to increased interest in high resolu-

tion experimental data that can enable subtle but important processing differences in different grades of polymers to be identified.

At present simple shear data is usually obtained from two separate apparatus. Steady shear flow curves are obtained from capillary devices such as the Rosand and Göttfert rheometers. Additional viscoelastic measurements are generally made from oscillatory data obtained from dynamic spectrometers such as the Rheometrics, Bohlin and Carrimed machines. In two previous papers a Multi-Pass rheometer was introduced (Mackley et al. (1994, 1995)). This apparatus is capable of obtaining both capillary and oscillatory viscoelastic data using the same machine. Moreover, both types of data can be obtained as a function of pressure. The apparatus consists of two hydraulically driven pistons which force material through a central test section which may be a tube or a capillary. The apparatus is shown schematically in Fig. 1. The idea of a two-piston capillary device is not new; Westover (1961), Karl (1979) and Kadijk and van den Brule (1993) carried out a series of capillary flow measurements using

Fig. 1 Schematic view upon the Multi-Pass Rheometer. A) Pistons, B) pressure transducers, C) flanges incorporating O-rings, D) cooling/heating jackets, E) capillary, F) thermocouples, G) drillways in pistons and bleed valves, H) hydraulic lift mechanism



a two-piston configuration in order to measure the pressure dependence of steady shear viscosity for certain polymer melts. The Multi-Pass rheometer that is described in this paper has the advantage that both constant velocity and oscillatory piston displacements can be made. A broad range of sequential experiments can be carried out on the same polymer within a fully enclosed environment.

The pressure dependence of the steady shear viscosity for a range of polymers has been considered by a number of research workers (see, for example, Westover (1961), Lord (1977), Cogswell (1981), Utracki (1985), Baker et al. (1993) and Kadijk et al. (1994)). The subject is of importance because most extrusion processes and injection moulding of molten plastics occurs at elevated pressure and consequently it is important to establish the effect of this variable on processing and rheology. Utracki (1983, 1985) has correlated observed pressure-dependent viscosities with free volume concepts. One of the objectives of this paper is to obtain both steady shear and viscoelastic data for a polymer melt as a function of applied mean pressure.

The Multi-Pass rheometer MPRII

The basic operation of the prototype Multi-Pass rheometer MPRI for polymer solutions and Newtonian fluids has been described in Mackley et al. (1995). The polymer melt experiments carried out at elevated temperature described in this paper were performed in a second development machine MPRII. The main new feature of this machine is its ability to hydraulically lower the bottom piston

assembly and the test section in order that the solid polymer pellets could be conveniently loaded into the apparatus. A schematic diagram of the apparatus is shown in Fig. 1, where both top and bottom pistons, test section and hydraulic lift mechanism can be seen.

The Multi-Pass Rheometers MPRI and MPRII were designed in Cambridge and have been built by Eland Test Plant, London. Both rheometers are capillary type rheometers which fully contain the test material. The top and bottom sections that contain the pistons and pressure transducers are made with a 12 mm diameter bore. The central test section can either be a plain tube or a capillary of any chosen diameter. The two pistons positioned at either end of the test section can be operated independently or together using high precision servo-hydraulic control. The pistons can drive test material through the test section while maintaining a set mean hydraulic pressure. Temperature and pressure are measured at either side of the test section. Temperature control is achieved using

Table 1 Specifications of Multi-Pass Rheometer II

Pressure	1 – 250 bar
Temperature	10 – 190 °C
Sample volume	10 – 20 ml
<i>(Multi-Pass) steady mode:</i>	
Piston velocity	0.05 – 300 mm/s
Wall shear rate	$10^{-1} - 2 \cdot 10^5 \text{ s}^{-1}$ *
<i>Oscillatory mode:</i>	
Frequency	0.01 – 200 Hz
Piston stroke	0.05 – 7 mm
Wall strain	$6 - 10^6\%$ *

* Depending on the capillary diameter (1, 8 or 12 mm)

a constant temperature bath with hot oil flowing through jackets around the barrel. The whole system is controlled by a microcomputer running programs written with LAB-view software specifically designed for controlling and data acquisition. Data acquisition consists of reading piston positions and the pressure traces from both transducers.

The MPRII rheometer is mounted on a table which can be lowered for easy access. When the polymer is fully contained within the machine, one piston can be advanced in order to reach a set pressure. When this pressure has been achieved the pistons can be moved together and constant volume displacements are then carried out.

The Multi-Pass Rheometer has been run in two basic modes:

a) The Multi-Pass steady mode

The pistons force material through a test section with a constant velocity keeping the volume constant. Unlike more usual single shot capillary rheometers the material can be forced back performing another measurement. As a consequence, many measurements are possible with a very limited amount of material. The apparent viscosity is given by (Mackley et al., 1995),

$$\eta = \frac{a^4 \Delta P}{8LR^2 v_p} \quad (1)$$

where L and a are the length and the radius of the capillary respectively, v_p the piston velocity and R the piston radius. The pressure difference across the capillary is given by ΔP .

b) The oscillatory mode

The pistons can move sinusoidally and a harmonic pressure response will be observed generating a differential pressure ΔP , and a phase angle δ , which is the phase angle between the applied displacement and the measured pressure signal. Using a cross-correlation method (Smits et al., 1992; Mackley et al., 1995) it is possible to obtain the phase angle δ with a high degree of precision. In this way the storage G' and loss G'' modulus for the material can be readily determined,

$$G' = \frac{a^4 \Delta P_{\max}}{8LR^2 x_{\max}} \cos \delta \quad \text{and} \quad G'' = \frac{a^4 \Delta P_{\max}}{8LR^2 x_{\max}} \sin \delta, \quad (2)$$

where x_{\max} is the centre to peak amplitude of oscillation for a chosen angular frequency.

Materials and methods

The test material used was linear low density polyethylene (LLDPE) provided by BP chemicals. The material has a density of 920 kg/m^3 and a melt flow index (MFI) of 0.09. Experiments on the linear low density polyethylene (LLDPE) were carried out at 180° and 190°C and we estimate a temperature variation within the test section of not greater than 1°C when no flow is present. Loading of the sample was achieved by introducing pellets of polymer into the test section and melting them at high temperatures. After this the top piston was advanced. The final removal of any trapped air was achieved using a bleed valve in both the top and the bottom piston. Once loaded, the sample was pressurised to the required test pressure by the movement of one or both pistons. Once this was achieved both the pistons were moved together from the same driving signal.

Linear viscoelastic and steady shear data were obtained by using a single test section of 12 mm diameter. Since in this case there is no change in cross-sectional area within the system, entry effects are not present. The test section was 56 mm in length, giving a distance of 82 mm between each pressure transducer. Entran pressure transducers with a range up to 1–350 bar were used for all measurements.

Experimental results

The self-consistency of the MPRII with the Rheometrics RDSII

We report data on a linear low density polyethylene. In order to compare results with the MPR we have carried out some experiments using a Rheometrics RDSII mechanical spectrometer operating with parallel plates at a 1 mm gap. Additional steady shear data obtained from a Rosand capillary rheometer is also presented. All MPRII and Rheometrics experiments were carried out at 180° and 190°C .

Steady flow Multi-Pass data were obtained on the MPR by driving the pistons at a constant velocity for a specified time; then holding the pistons for a chosen delay time and then reversing the motion. This experiment can be continued for many passes and an example is shown in Fig. 2. The continuous line shows that displacement of the top piston; both pistons will move in the same way. The dotted line shows the measured differential pressure difference. This shows that during piston movement there is a rapid build up in pressure and a near steady flow pressure is achieved. On cessation of each piston movement, pressure relaxation occurs during each delay period and the pressure approaches a zero differential pressure. Figure 2 shows that the data has a high level of reproduc-

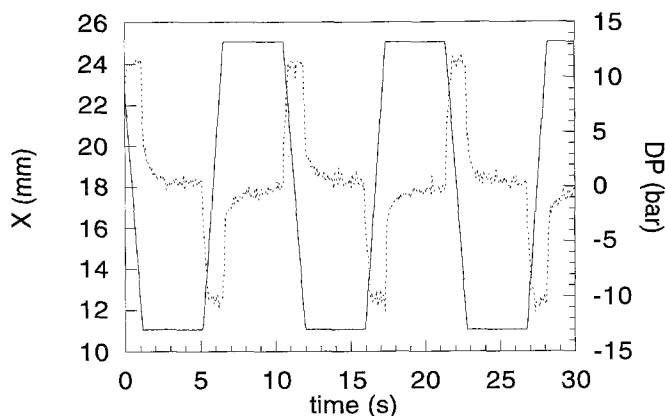


Fig. 2 Multi-Pass steady experiments on LLDPE at 180 °C. The piston position, X , is given by the solid line, the resulting differential pressure, DP, with the dotted line. Barrel diameter of 12 mm over the whole length between transducers. The distance between pressure transducers was 82 mm. Piston displacement was 14 mm, piston velocity 10 mm/s, pressure transducers 350 bar, no prior pressurisation

ibility for each successive “Multi-Pass”. Details of the stress build up and relaxation in the Multi-Pass steady mode are shown in Fig. 3. In these experiments different delay times of 0, 2 and 4 s were chosen between each piston movement. Rather surprisingly for the material tested, the stress build up appears to be independent of the delay time chosen. The longer delay times gave, as expected, more time for pressure relaxation. The results show however that, for steady flow, the measured pressure difference was independent of the selected delay time between each flow reversal.

Figure 4 shows the corresponding oscillatory data for the same polymer. The continuous line records piston displacement and the dotted line the differential pressure. The noise seen on the pressure data in this case is due to the relatively low differential pressure signal being monitored. The data is however very reproducible and it is not difficult to obtain both a peak pressure difference and phase angle. In addition, both signals are close to being harmonic.

Using data of the type described in Figs. 2–4, coupled with the equations given in the previous section, it is possible to derive viscometric and viscoelastic measurements for the polymer under test. Figure 5 shows an oscillatory strain sweep for the test material and this is also compared with a strain sweep obtained using the Rheometrics RDSII. For the chosen fixed frequency, it can be seen that the two sets of data for G' and G'' overlap with reasonable consistency. Both systems indicate that the LLDPE has a linear region and that the material starts to exhibit non-linear behaviour at a strain of about 30%.

Figure 6 shows a frequency sweep for the material using both MPR and Rheometrics. Again the data shows

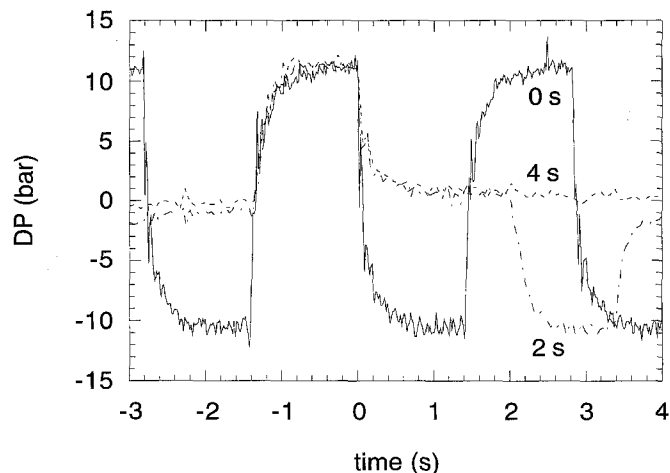


Fig. 3 The differential pressure, DP, for Multi-Pass steady experiments on LLDPE at 180 °C. In the experiments shown the dwell time between passes was 4, 2 and 0 s. Barrel diameter of 12 mm over the whole length. The distance between pressure transducers was 82 mm. Piston displacement was 14 mm, piston velocity 10 mm/s giving an apparent wall shear rate of 6.7 s^{-1} , pressure transducers 350 bar, no prior pressurisation

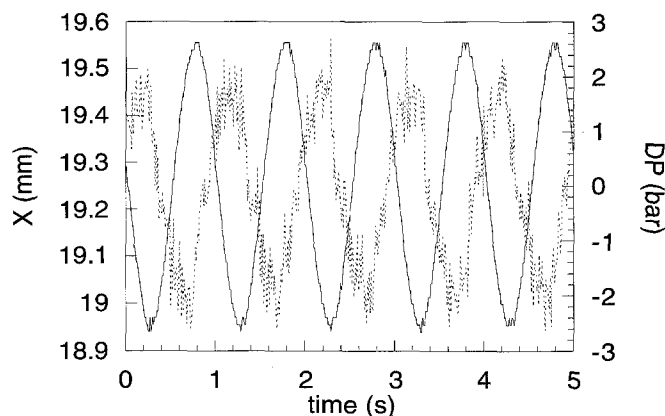


Fig. 4 Multi-Pass oscillatory measurements on LLDPE at 180 °C. The solid line corresponds to the piston position and the dotted line to the pressure difference. Barrel diameter of 12 mm over the whole length. The distance between pressure transducers was 82 mm. Centre to peak piston amplitude 0.3 mm, maximum wall strain 10%, frequency 6.28 rad/s, pressure transducer 350 bar, no prior pressurisation

reasonable consistency. The absolute values of the MPR data are lower than the Rheometrics results. At this stage we are not exactly sure of the reason for this discrepancy, although it could be due to incorrect temperature calibration of the pressure transducers in the MPR. The trends of both the phase angle and the relative increase of G' and G'' with increasing frequency, give us confidence that the data is reasonable within an accuracy of 20%. Two sets of MPR data are shown on the figure which do not differ very much.

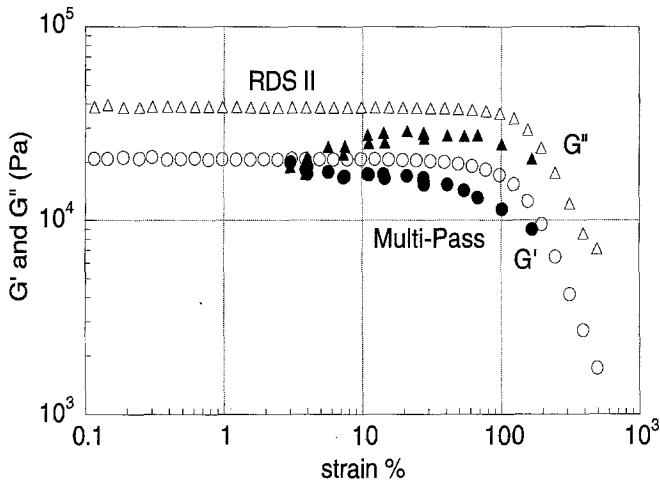


Fig. 5 Oscillatory measurements on LLDPE at 180 °C, G' and G'' as a function of strain. Open symbols correspond to RDS and solid to Multi-Pass data, G'' , triangles, G' , circles. MPR Frequency = 6.28 rad/s, pressure transducers 350 bar. RDS 2.5 cm dia parallel plates with 1 mm spacing

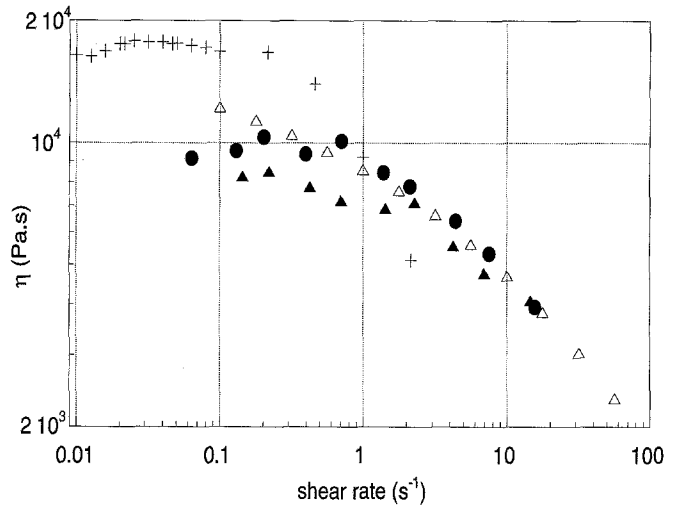


Fig. 7 Steady shear measurements on LLDPE, η as a function of shear rate. RDS 180 °C, crosses, MPR 180 °C, solid circles, Rosand 190 °C, open triangle, MPR 190 °C, solid triangle, MPR pressure transducers 350 bar. RDS, 2.5 cm dia parallel plates with 1 mm spacing

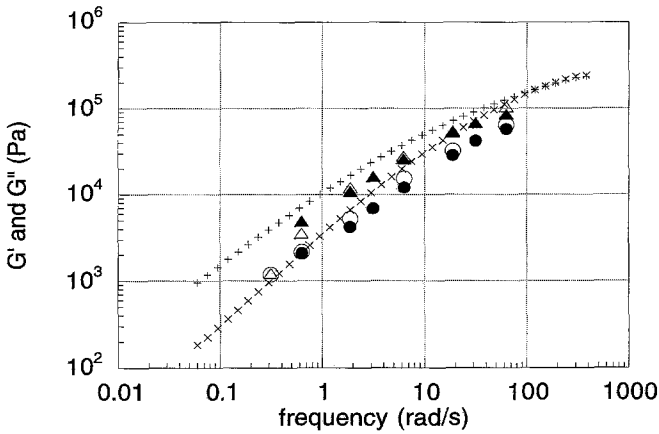


Fig. 6 Multi-Pass oscillatory measurements on LLDPE at 180 °C, G' and G'' as a function of angular frequency. RDS G'' (+), G' (×). Multi-Pass measurements at 50 bar solid symbols and at 1 bar open symbols, G'' triangles and G' circles. Wall strain 27%, pressure transducers 350 bar

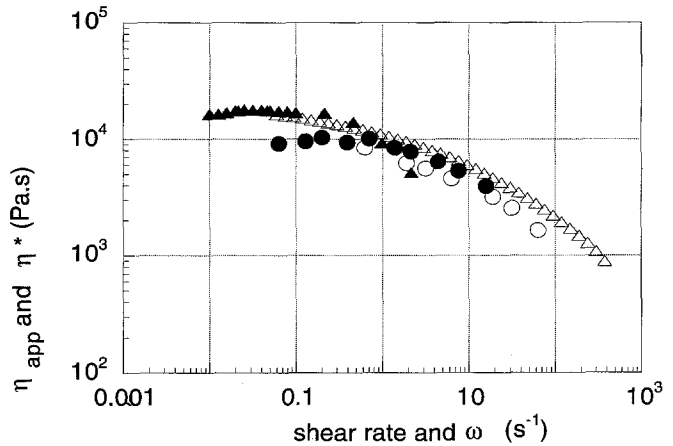


Fig. 8 Apparent viscosity η_{app} as a function of shear rate, solid symbols, and complex viscosity, η^* as a function of frequency, open symbols, of LLDPE at 180 °C. RDS, triangles; MPR, circles. The MPR barrel had a diameter of 12 mm over the whole length. The distance between pressure transducers was 82 mm. Pressure transducers 350 bar. RDS, 2.5 cm dia parallel plates with 1 mm spacing

In addition to oscillatory data, it is possible to use the MPR to obtain steady shear values and these results are shown in Fig. 7 where the apparent steady shear viscosity is plotted as a function of shear rate. Four sets of data are plotted. Two using the MPR, one from a Rosand capillary rheometer and one from the Rheometrics in steady shear mode. Both Rosand and MPR data have been Rabinovitch corrected. In general, the agreement between the three machines appears reasonable, although the low shear rheometrics data seems to be higher. The MPR data reported here covers a range of shear rates between 0.1 to 10 s⁻¹. By using smaller diameter capillary sections it

would be possible to greatly increase the range up to 10⁶ s⁻¹.

The connection between the steady shear and oscillatory MPR data is shown in Fig. 8. In this graph both the oscillatory complex viscosity $\left(\eta^* = \frac{1}{\omega} \sqrt{G'^2 + G''^2}\right)$ and the apparent viscosity η_a are plotted as a function of angular frequency, ω , and shear rate respectively. It can be seen that the Cox Merz rule appears to hold for this material and the results give us further confidence in rela-

tion to the values of both the oscillatory and the steady shear data.

The effect of pressure on viscometric and viscoelastic data

One of the strategic benefits of the MPR is its ability to operate at a set mean pressure. This is achieved by moving one piston to give the required mean pressure and then performing either Multi-Pass steady or oscillatory measurements at that pressure. Polyethylene has been the subject of several studies on viscosity measurements at elevated pressures by Westover (1961), Cogswell (1972), Christmann et al. (1974), Karl (1979), Baker (1993), but we are not aware of any published viscoelastic data.

Figure 9 shows the dependence of G' and G'' at two angular frequencies plotted as a function of the absolute mean pressure. There is a small linear increase in the values of both G' and G'' over the pressure range tested of 1–230 bar. Significant volume compressibility occurs over this range of pressure. One piston for example will have moved by a distance of order 4 mm in order to establish the required pressure; however little change in viscoelastic response was detected.

Figure 10 shows both the apparent viscosity η_a at 0.27 s^{-1} and η^* plotted as a function of pressure. This is a linear plot and a 20% change of viscosity can be seen over the range tested. This level of viscosity change is consistent with previously published Westover (1961) data. In addition our viscosity data shows a linear dependence on pressure. Our viscoelastic data also closely follows a linear dependence.

In Fig. 11 we compare our own apparent viscosity data with that of other published work, namely data of West-

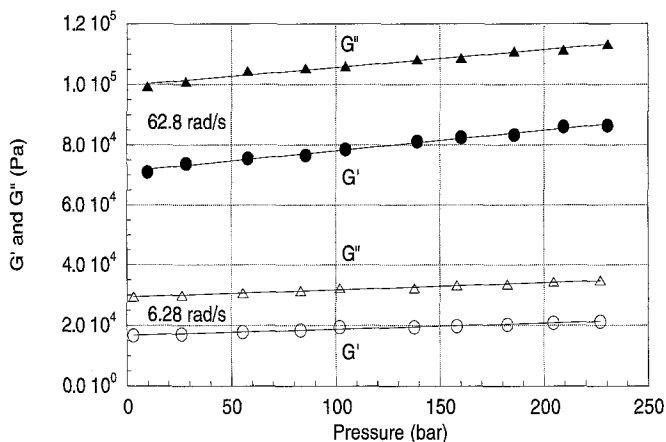


Fig. 9 Pressure dependence of G' and G'' of LLDPE at 180°C , frequencies 6.28 rad/s (1 Hz) and 62.8 rad/s (10 Hz), maximum wall strain 27%. Lines show best fit linear plots

over (1961), Choi (1968), Cogswell (1972) and Christmann et al. (1974). The absolute value of the viscosity will be very dependent on the molecular mass distribution of each sample that has been used. However, the data does show a similar trend in terms of pressure dependence although the data of Cogswell, Choi and Westover are over a greater range than our results.

Time-dependent rheological measurements

The MPRII has useful potential as a machine that can determine the time-dependent behaviour of a material

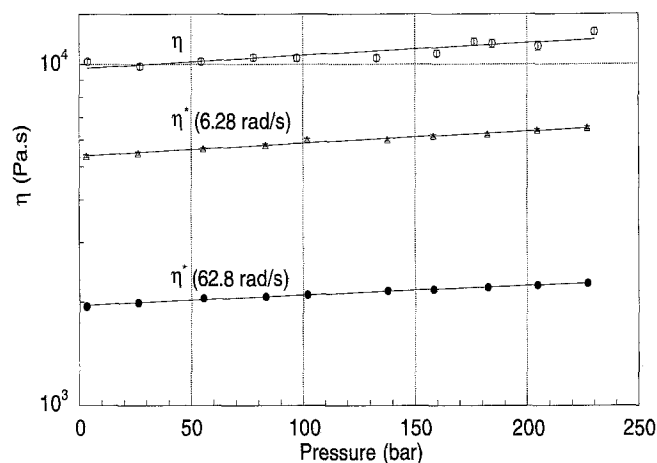


Fig. 10 Pressure dependence of the steady shear apparent and oscillatory complex viscosity of LLDPE at 180°C , apparent viscosity taken at a shear rate of 0.27 s^{-1} . Complex viscosities taken at 6.28 and 62.8 rad/s

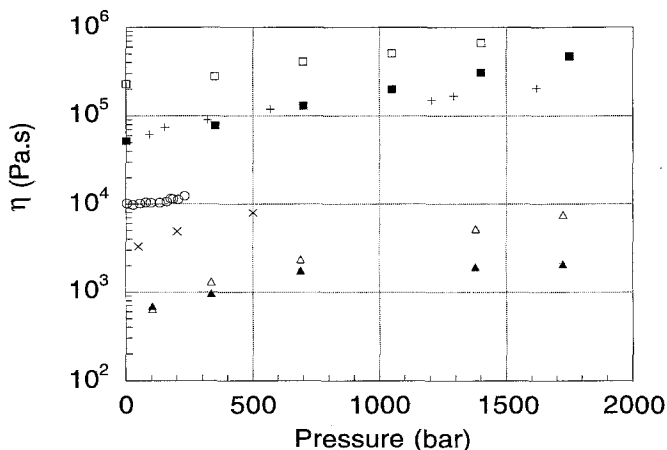


Fig. 11 Comparison between reported data on the pressure dependence of the polyethylene melt viscosity. Triangles: Westover (1961) diameters of dies solid: 1.27 cm, open: 2.29 cm; squares: Cogswell (1972) open: HDPE, solid: LDPE, pluses: Choi, crosses: Christmann. Open circles are the data on LLDPE reported here

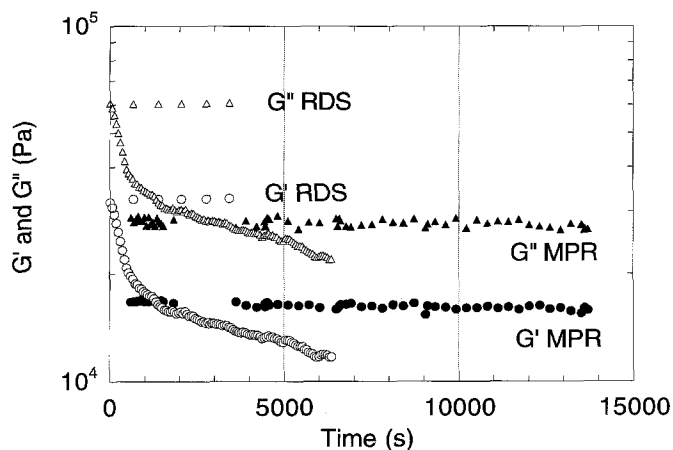


Fig. 12 The time dependence of the dynamic moduli of LLDPE at 180°C. MPR data taken at 6.28 rad/s maximum wall strain 27%. RDS data taken at 6.28 rad/s, the near horizontal lines corresponding to 10% strain and the data that progressively decays with time corresponding to 30% strain

whilst being subject to shear within a fully constrained environment. In Fig. 12 we present the time-dependent data of the LLDPE test material obtained both from the MPRII and the Rheometrics RDSII. The time-dependent change in G' and G'' is shown for Rheometrics data obtained at 10% and 30% strain. At lower strain values, the data is seen to be essentially independent of time; however at larger strains there is a significant decrease in the values of the moduli. The higher strain decrease correlates with the observation that at this strain level the polymer is observed with time to slowly squeeze out between the plates of the rheometer, whereas at lower strain this does not occur. The effect of polymer "leaving the gap" is well known and generally occurs for combinations of high strains and highly elastic liquids.

Time-dependent G' and G'' data are also shown for the MPRII and it can be seen from this data that the result although measured at high strains, are independent of time. Because the MPRII is fully constrained, there is nowhere for the polymer to go, other than being forced through the test section by the two pistons. Clearly the MPRII offers further potential for the study of materials such as PVC and low density polyethylene, where genuine time-dependent rheological changes can be expected with the imposition of shear.

Conclusion

The experimental results reported in this paper are on polyethylene melts using an MPR and support our previous observations on Newtonian fluids and polymer solutions (Mackley et al., 1995). The combined data demonstrates that the MPR is capable of determining both steady shear capillary data and oscillatory linear viscoelastic data. At present the precision of the MPR steady flow data is capable of matching that of existing capillary rheometers. The linear viscoelastic data generated by the MPR is close to, but not in exact agreement with the mechanical spectrometers and at present the frequency range that has been explored does not yet match that of most parallel plate spectrometers.

The fact that the MPR is a fully enclosed system does offer certain experimental advantages and this has been demonstrated by generating both steady and linear viscoelastic data for LLDPE over a pressure range of 1–230 bar. Our steady shear data behaves in a similar way as reported by others. The viscoelastic data reported here also follow a similar trend, in that the response is close to a linear relationship and the overall increase in moduli is of the order of 20% for the pressure range tested.

The MPR has considerable potential in exploring the effect that shear has on certain time-dependent rheological behaviour. In the case of LLDPE, we have found that the material is not sensitive to successive 30% strain oscillations, whereas a parallel plate rheometer does show changes which are almost certainly related to material squeezing out of the free surface between the plates.

It is our belief that the MPR offers a real advantage over many other machines in characterising the viscoelastic behaviour of rheologically difficult materials. At present this potential advantage has to be offset with the not so inconsiderable difficulties experienced in cleaning the apparatus when switching over from one material to another.

Acknowledgments This paper is submitted to *Rheologica Acta* as one of a set that will acknowledge the contribution that Professor Joachim Meissner has made to polymer melt rheology. We are delighted to participate in this celebration and congratulate him on his meticulous and consistent study on the importance of extensional flow on both the characterisation and processing of polymer melts. We would also like to thank EPSRC for funding work related to this project. In addition we thank BP Chemicals for providing both polymer samples and some data, Eland Test plant for expertly manufacturing the MPRII and Robert Marshall for assistance with some of the drawings.

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