

Measurements of the rheological properties of standard reference material 2490 using an in-line micro-Fourier rheometer

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(Received September 15, 2004; final revision received November 26, 2004)

Abstract

The control of the rheological properties of a fluid during processing is important and can determine the efficiency of the production in addition to the performance of the final product. The vast majority of process fluids are viscoelastic, hence an instrument that measures both the viscous and elastic properties of the material during processing would be of great practical use. However, most in-line instruments commercially available to date are only capable of measuring viscosity at a single shear rate. An in-line rheometer that measures both the viscous and elastic properties of fluids over a wide range of shear rates simultaneously has been described in a previous publication (Glasscock *et al.*, 2003) in which the results of measurements on flowing sunflower oil were presented. Before this instrument can be used in an industrial situation, it must be demonstrated that the generated results are the same as, or bear some fixed relationship to, the results obtained by conventional off-line rheometers. To this end, the present investigation describes the measurements of a standard reference fluid, polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane, labelled SRM2490 by the National Institute of Standards and Technology (NIST) in the USA. The results obtained using the in-line rheometer show remarkably good correlation for viscosity, using a modified Cox-Merz rule, with the results supplied with the reference material from NIST.

Keywords : in-line rheometer, Cox-Merz rule, standard reference material

1. Introduction

To date, the control of the properties of process flows has been achieved (to varying levels of success) by the use of capillary viscometers/rheometers (Chiu and Pong, 1998; Covas *et al.*, 2000), vibrating plate viscometers, and slit rheometers (Kalyon *et al.*, 1997; Pabedinskas *et al.*, 1991). In-line viscometers by their very nature yield only viscosity data, and hence provide an incomplete analysis of viscoelastic fluids. All of the instruments mentioned above operate only at a single shear rate, thereby potentially limiting the usefulness of the data. If more detailed knowledge of the viscoelastic properties of the fluid is required to control the properties, quality, and reproducibility of the product, test volumes must be removed from the process stream and measured off-line using an instrument such as a controlled strain rheometer. However, this is a time consuming procedure that may require the process line to be shut down until the results are available to confirm, or otherwise, the quality of the product. Alternatively, the process flow may continue with the potential loss of product. In some cases, the volume of lost fluid could be large and this

could be particularly problematic when processing high-value materials (such as pharmaceuticals) or products that cannot be reprocessed or products that incur a disposal cost (for example, an environmental levy). Thus a genuine in-line rheometer (ILR) which can measure the viscoelastic properties in a flow environment and in real time has the potential to improve product quality and reduce processing costs. The instrument used in the present investigation is based on the squeeze flow method which is quite different from the controlled-strain instruments commonly employed off-line for quality control. Before an instrument based on a new technology can be introduced into an industrial environment, it is necessary to ensure that the results obtained can be correlated with those obtained from the commonly used off-line instruments. The purpose of this paper is to demonstrate using a viscoelastic reference fluid that the ILR produces results for complex viscosity which correlate very well with those from a controlled strain instrument.

2. Experimental apparatus

The in-line rheometer has been described in detail in a previous publication (Glasscock *et al.*, 2003) and has been patented (O'Brien, 2002). However, for completeness, a brief description of the rheometer will be given here. The

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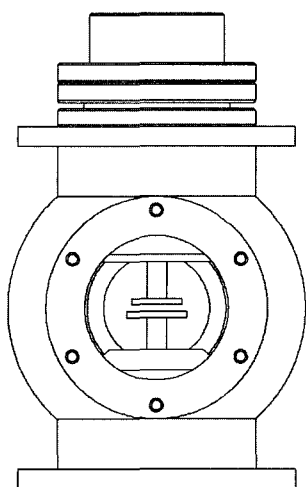


Fig. 1. Schematic of the in-line micro-Fourier rheometer construction.

equipment is based on the technology integral to the micro-Fourier rheometer (Field *et al.*, 1996; Swain, 1995), a laboratory instrument now commercially available from GBC Scientific Equipment [GBC Scientific Equipment Pty Ltd, 12 Monterey Rd, Dandenong VIC, 3175, Australia]. Fig. 1 shows a schematic diagram of the in-line micro-Fourier rheometer which consists of two parallel plates situated coaxially in a stainless steel body which may be bolted into a pipe of diameter ≥ 7 cm containing the process flow.

The top plate is used to impress a multi-frequency signal via a piezoelectric stack onto the fluid sample contained between the plates. The lower plate is connected to an ac load cell which detects the resultant signal transmitted through the process fluid. When no measurements are being made the plates are kept some 2–3 cm apart so as not to impede the process flow. Immediately before a measurement is made, the plates are brought together to a pre-determined gap defined by a spacer ring. The gap is chosen in order to optimise the signal-to-noise ratio and to prevent flow between the plates when measuring a particular fluid. The chosen gap, and hence the generated forces, are dependent on the viscoelastic properties of the fluid. Twenty measurements (lasting a total of 20 seconds) are made and averaged to maximise the signal-to-noise ratio. When the measurements are complete the plates are again separated to allow the sample fluid to be flushed out ready for the next measurement. Moving the plates together and apart to make measurements is not expected to produce a significant pressure drop within the process line. Fourier transforms of the applied and transmitted signals are calculated and from this analysis the values of storage modulus G' , loss modulus G'' , and the complex viscosity η^* are calculated. A more detailed explanation of this analysis can be found in other publications (Phan-Tien, 1980; Phan-Tien *et al.*, 1996; See, 2001).

3. Experimental results

All of the measurements reported in this publication have been made in the static mode i.e. without flow, as the volume of the standard fluid available is too small to allow a pumping rig to be used. It has been demonstrated previously (Glasscock *et al.*, 2003) that surrounding the plates with fluid and operating under in-line/on-line conditions produces insignificant changes to the measured rheological properties. As discussed previously (Glasscock *et al.*, 2003), the in-line rheometer must be calibrated using a standard reference oil of known viscosity. Although counter-intuitive the Newtonian reference oil can be used to calibrate both the “viscous” and “elastic” responses of the instrument. The calibration works equally well using a purely elastic spring with a known stiffness (Field *et al.*, 1996; Phan-Tien *et al.*, 1996). In the present case S8000 oil (Cannon Certified Viscosity Standard) having a viscosity of 34.1 Pa·s at 20 °C was used as the reference material. A quantity of oil sufficient to cover the bottom plate was placed in the rheometer and the top plate was lowered and clamped to the spacer ring giving a gap of 0.901 mm. Where necessary, additional oil was added so as to form a uniform meniscus between the two plates. The reference oil was then measured twenty times and averaged to increase the signal-to-noise ratio and the data stored as a reference file for use in the measurement of the standard reference material (SRM) sample. A number of measurements of the standard oil were made using oscillation amplitudes of 2 μm , 6 μm and 9 μm . The duration of each set of measurements was 20 seconds.

The plates were then separated and cleaned to remove all traces of the reference oil and the SRM sample then loaded and the plates moved to produce the measurement gap. Where necessary more of this sample was added to ensure that a uniform meniscus was formed around the whole periphery of the plates. The standard fluid SRM2490 is a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane, and was purchased from the National Institute of Standards and Technology (NIST). A NIST special publication (Schultheisz and Leigh, 2002) contains SRM2490 rheological data measured using a controlled strain rheometer. These data were later compared to data measured using the in-line rheometer.

Compressing the SRM sample between the plates might be expected to change its rheological properties as the magnitude of shear used might exceed the limit of the linear viscoelastic region. Hence measurements were made over a period of 50 minutes at 10 minute intervals to determine how long it takes for the sample to recover. The results of these measurements in the form of the rheological parameters G' and G'' at a frequency of 10 Hz plotted with respect to time are shown in Fig. 2. These results are typical of those for all frequencies however at low fre-

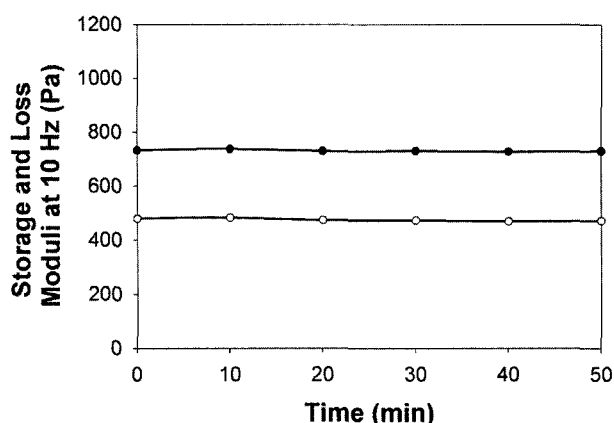


Fig. 2. Recovery of SRM2490 as shown by the storage modulus G' (represented by symbol ●) and the loss modulus G'' (represented by symbol ○) at a frequency of 10 Hz as a function of time after loading the sample.

quencies the rheological properties are more sensitive to changes within the molecular structure. It is clear from these data that compressing the SRM2490 between the plates causes no change to the fluid since the values of G' and G'' vary by less than 1% over the 50 minute measurement period.

The SRM2490 was then measured using oscillation amplitudes of 2 μm , 6 μm and 9 μm to determine the linear viscoelastic region of the material. The storage and loss moduli and the complex viscosity as a function of frequency at each oscillation amplitude are shown in Figs. 3, 4 and 5 respectively. Fig. 6 shows the storage and loss moduli at a frequency of 10 Hz as a function of oscillation amplitude. Over the amplitude range of 2 μm to 9 μm , the magnitudes of G' and G'' across the whole frequency range remain constant indicating that the fluid is being measured within the linear viscoelastic region. Since the signal-to-

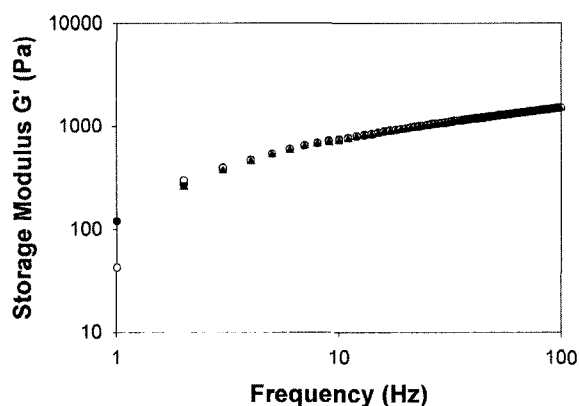


Fig. 3. Three measurements of the storage modulus G' of SRM2490 using an oscillation amplitude of 2 μm (represented by symbol ●), 4 μm (represented by symbol ○) and 9 μm (represented by symbol ▲).

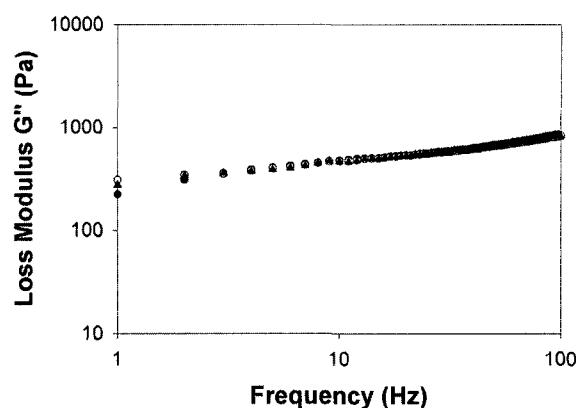


Fig. 4. Three measurements of the loss modulus G'' of SRM2490 using an oscillation amplitude of 2 μm (represented by symbol ●), 4 μm (represented by symbol ○) and 9 μm (represented by symbol ▲).

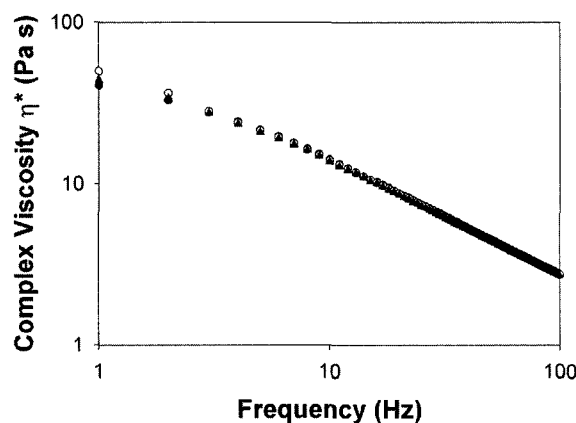


Fig. 5. Three measurements of the complex viscosity η^* of SRM2490 using an oscillation amplitude of 2 μm (represented by symbol ●), 4 μm (represented by symbol ○) and 9 μm (represented by symbol ▲).

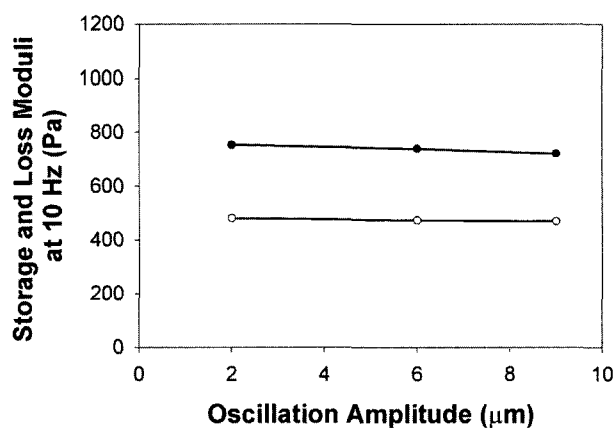


Fig. 6. Linear viscoelastic region of SRM2490 as shown by the storage modulus G' (represented by symbol ●), and the loss modulus G'' (represented by symbol ○) at a frequency of 10 Hz as a function of oscillation amplitude.

noise ratio is highest at the largest oscillation amplitude of 9 μm , these results will be used in the following discussion.

4. Discussion

A number of authors have compared measurements of viscosity under both dynamic and steady shear (Berland and Launey, 1995; Cox and Merz, 1958; Ferry, 1980; Morris *et al.*, 1981; Onogi *et al.*, 1966). Cox and Merz (Cox and Merz, 1958) found an empirical relationship between the shear rate dependence of steady-shear viscosity η and the frequency dependence of the modulus of complex viscosity η^* at equal values of angular frequency ω and shear rate $\dot{\gamma}$ as given by Eq. 1, where $\omega = \dot{\gamma}$.

$$(\eta^*(\omega)) = \eta(\dot{\gamma}) \quad (1)$$

This relationship has been confirmed for a number of synthetic polymers (Ferry, 1980; Onogi *et al.*, 1966) and for random-coil polysaccharides (Morris *et al.*, 1981). In a number of cases, polymers follow a similar behaviour but with a need to scale the frequency axis by a constant factor k , giving Eq. 2 known as the modified Cox-Merz rule.

$$(\eta^*(k\omega)) = \eta(\dot{\gamma}) \quad (2)$$

This modified or extended Cox-Merz rule has been found to apply to some food materials such as wheat flour dough and tomato paste (Berland and Launey, 1995; Rao and Cooley, 1992). In some cases more complicated relationships may hold as discussed by Doraiswamy and others (Doraiswamy *et al.*, 1991). However, it is still not explicitly known why the Cox-Merz rule (or modification) applies for some materials and not for others. All mea-

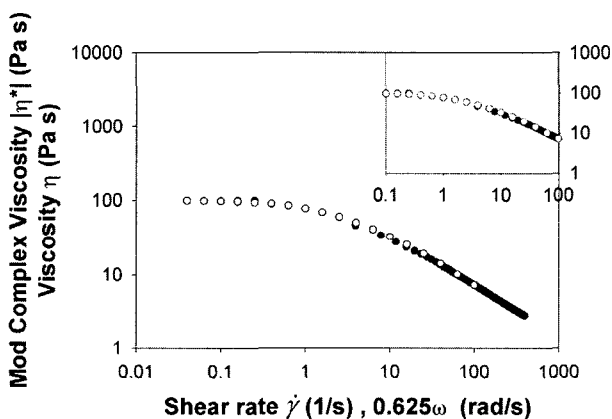


Fig. 7. The modulus of the complex viscosity $|\eta^*|$ of SRM2490 as measured by the in-line rheometer is represented by symbol \bullet and the viscosity η as measured by NIST using a controlled strain rheometer is represented by symbol \circ . The inset graph shows only the region of overlapping data.

surements made by NIST used a Rheometric Scientific, Inc. ARES controlled-strain rheometer. The NIST results for the viscosity measurements were measured at 25 °C using a cone and plate geometry whereas the loss and storage moduli reported here were measured at 20 °C using a parallel plate geometry. It is clear from a comparison of the $(\eta^*(k\omega))$ data measured using the ILR and the NIST data for $\eta(\dot{\gamma})$, that the Cox-Merz rule does not apply. However, by applying the modified Cox-Merz rule to the ILR data using a shift factor $k = 0.625$, a very good correlation can be obtained between the two curves of (η^*) plotted against $k\omega$ and η plotted against $\dot{\gamma}$ as shown in Fig. 7. In fact plotting the two sets of data against one another yields a straight line of slope 0.95 and a correlation factor $R^2 = 0.999$ which demonstrates the excellent agreement between the two sets of data. Although the data can be brought into good agreement using a k value of 0.625 a somewhat different value would have been found if the in-line rheometer measurements were undertaken at 25 °C.

5. Conclusions

Measurements were made on a standard reference fluid SRM2490 using an in-line rheometer based on the squeeze flow technique. These results were compared with those measured by NIST (Schultheisz and Leigh, 2002) using a controlled-strain rheometer. A comparison of the complex viscosity as a function of frequency measured by the ILR with the steady shear viscosity measured by NIST demonstrates a remarkably good correlation when a modified Cox-Merz rule is applied to the present data. This suggests that results obtained with the ILR in an in-line application could be used in place of those from an off-line controlled-strain rheometer for process and quality control. Clearly the correlation between the two sets of data would have to be established for each fluid application, as a different shift factor is expected for different materials. The exact correlation would of course depend on the fluid under test and might well be less simple than the modified Cox-Merz rule used here. The fact that the modified Cox-Merz relationship is dependent on the fluid being measured (i.e. a different shift factor is required) does not limit the usefulness of this instrument. This rheometer is designed to operate as a quality control tool and hence sensitivity to relative changes is highly important rather than absolute values. Use of the modified Cox-Merz rule demonstrates that the rheological data measured by the in-line rheometer can be correlated to those measured by conventional off-line controlled-shear instruments commonly used as off-line quality control rheometers, hence existing process specifications could be used. The ability of the ILR to measure the viscoelastic properties of a fluid over a range of frequencies in a very short time makes it an ideal instrument for real time process control.

References

- Berland, S. and B. Launey, 1995, *Cereal Chemistry* **72**, 48.
- Chiu, S. H. and S. H. Pong, 1998, *Polymer Degradation and Stability* **64**, 239.
- Covas, J., J. Nobrega and J. Maia, 2000, *Polymer Testing* **19**, 165.
- Cox, W. and E. Merz, 1958, *Journal of Polymer Science* **28**, 619.
- Doraiswamy, D., A. Mujumdar, I. Tsao, A. Beris, S. Danforth and A. Metzner, 1991, *Journal of Rheology* **35**, 647.
- Ferry, J., 1980 *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York), 3rd edition.
- Field, J., M. Swain and N. Phan-Tien, 1996, *Journal of Non-Newtonian Fluid Mechanics* **65**, 177.
- GBC Scientific Equipment Pty Ltd, 12 Monterey Rd, Dandenong VIC, 3175, Australia.
- Glasscock, J., R. Smith, J. Vanajek and J. Winter, 2003, *Review of Scientific Instruments* **74**(11), 4925.
- Kalyon, D., H. Gokturk and I. Boz, 1997, *SPE ANTEC Technical Papers*, 2283.
- Morris, E., A. Culter, S. Ross-Murphy and J. Price, 1981, *Carbohydrate Polymers* **1**, 5.
- O'Brien, V., 2002, Patent No. PCT/AU02/00484.
- Onogi, S., H. Kato, S. Ueki and T. Ibaragi, 1966, *Journal of Polymer Science*, 481.
- Pabendinskas, A., W. Cluett and S. Balke, 1991, *Polymer Engineering and Science* **31**(5), 365.
- Phan-Tien, N., 1980, *Journal of the Australian Mathematical Society (Series B)* **32**(22).
- Phan-Tien, N., J. Field and M. Swain, 1996, *Rheologica Acta* **35**, 410.
- Rao, M. and H. Cooley, 1992, *Journal of Texture Studies* **23**, 415.
- Schultheisz, C. and S. Leigh, 2002, *Certification of the Rheological Behaviour of SRM 2490, Polyisobutylene Dissolved in 2,6,10,14-Tetramethylpentadecane*, Technical Report Technical Report 260-143, National Institute of Standards and Technology.
- See, H., 2001, *Korea Australia Rheological Journal* **13**(2), 67.
- Swain, M., 1995, US Patent No. 5750884.