DEVELOPMENT OF A SLIDING PLATE RHEOMETER TO MEASURE THE HIGH FREQUENCY VISCOELASTIC PROPERTIES OF POLYMER MELTS

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ABSTRACT:
A newly designed and constructed sliding plate rheometer is used to measure the high frequency (210 Hz) linear viscoelastic properties of two model polymers: polybutene (PB) and polydimethylsiloxane (PDMS). Using well-known rheological models, extrapolations of the viscoelastic measurements obtained on a rotational parallel plate rheometer to a frequency of 210 Hz are used to assess the performance of the high frequency sliding plate rheometer. Good agreement between the extrapolated and measured data demonstrates the ability of the sliding plate rheometer to measure the high frequency rheological properties of both Newtonian and shear-thinning materials.

ZUSAMMENFASSUNG:
Ein neu entworfenes und konstruiertes Plattenrheometer wird verwendet, um die linear-viskoelastischen Eigenschaften von zwei Modellpolymeren bei hoher Frequenz (210 Hz) zu messen: Polybuten (PB) and Polydimethylsiloxan (PDMS). Mit Hilfe bekannter rheologischer Modelle wurde die Extrapolation auf eine Frequenz von 210 Hz von viskoelastischen Messungen verwendet, die mit einem Rotationsplattenrheometer erhalten wurden, um die Güte des Hochfrequenz-Plattenrheometers zu ermitteln. Die gute Übereinstimmung zwischen den extrapolierten und den gemessenen Daten verdeutlicht die Fähigkeit des Plattenrheometers, die rheologischen Eigenschaften bei hohen Frequenzen von sowohl Newtonschen als auch scherverdünnenden Materialien zu messen.

RÉSUMÉ:
Un nouveau rhéomètre à plaque glissante a été conçu et fabriqué pour mesurer les propriétés visco-élastiques linéaires à haute fréquence (210 Hz) de deux polymères: polybutène (PB) et polydimethylsiloxane (PDMS). A l'aide des modèles rhéologiques, les mesures visco-élastiques obtenues sur un rhéométrè rotationel plan-plan ont pu être extrapolées à des fréquences de 210 Hz pour établir le bon fonctionnement du nouveau rhéomètre. La concordance entre les extrapolations et les résultats du nouveau rhéomètre démontre sa capabilité de mesurer les propriétés rhéologiques des fluides Newtoniens ou rhéofluidifiants.

KEY WORDS: high frequency, rheology, sliding plate rheometer

1 INTRODUCTION

The rheological behaviour of molten polymers is of prime importance as it relates to their microstructure and governs their processing characteristics [1]. Rotational rheometers are routinely used to characterize the linear viscoelastic properties of polymer melts through small amplitude oscillatory shear experiments [1–3], and sliding plate rheometers are used to measure the nonlinear viscoelastic properties polymer melts using large amplitude oscillatory shear (LAOS) measurements [4, 5].

The measurement of viscoelastic properties using rotational and sliding plate rheometers is generally limited to frequencies ≤ 30 Hz as inertial effects are known to become significant at high frequencies [1–3]. Extension of the frequency range to higher frequencies (≥ 30 Hz) by means of time-temperature superposition (TTS) is not always possible, especially for semi-crystalline polymers such as polypropylene, as the highest frequency attainable in TTS is limited by the melting point of the polymer [1, 6].

In recent years, several high frequency rheological techniques have been developed to characterize the linear viscoelastic behaviour of complex fluids. Torsional resonators, like the ones developed by Willenbacher [7] and Ballauff [8], are capable of measuring in the kHz range, but only at discrete frequencies. Optical microrheo-

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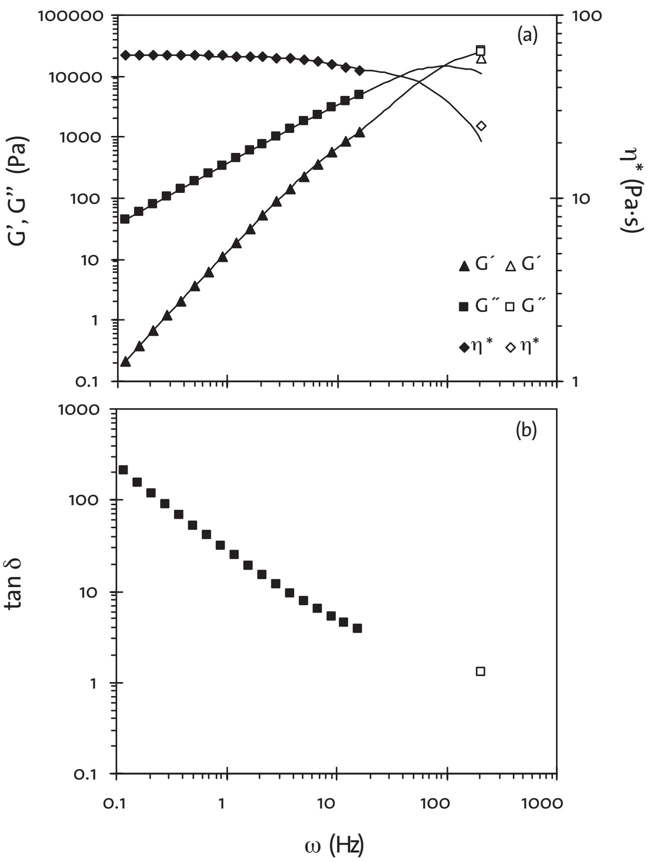

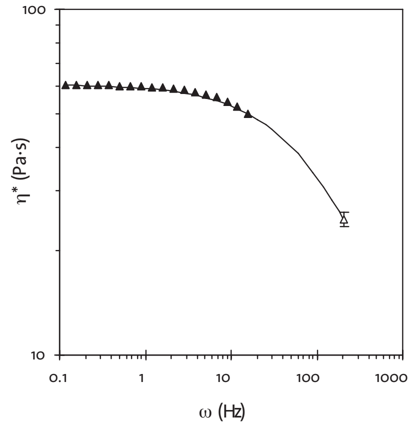

i	G_i (Pa)	λ_i (s)
1	29115	$1.666 \cdot 10^{-3}$
2	582.8	$1.863 \cdot 10^{-2}$
3	4.8	$1.445 \cdot 10^{-1}$

Figure 8 (left):
a) Storage modulus, G', loss modulus, G'', complex viscosity, η, and*
b) loss tangent, tan δ, as a function of angular frequency, ω, for PDMS measured on the parallel plate rheometer (filled symbols) and HF-SPR (unfilled symbols). Solid lines are the generalized Maxwell model extrapolated to 210 Hz.

Figure 9:
Complex viscosity data as a function of frequency for PDMS measured on the parallel plate rheometer (filled symbols) and the HF-SPR (unfilled symbols). Solid line is the Cross model extrapolated to 210 Hz.

Table 1:
Discrete relaxation spectrum for PDMS

parallel plate rheometer, indicate that PDMS is a non-Newtonian material as η^* displays shear-thinning behaviour. Expansion of the frequency range by time-temperature superposition was not possible as the rheometers used in this work do not have the capability to measure at the sub-ambient temperatures required to reach the frequency of interest. The low frequency *G'* and *G''* data were fit with the generalized Maxwell model [1], Eqs. 19 and 20, where G_i is the relaxation strength, and λ_i is the relaxation time of Maxwell elements *i* to *N*. The parameters (G_i, λ_i) were determined using a nonlinear optimization program following the algorithm developed by Baumgaertel and Winter [16]. Employing this program results in the calculation of the least number of (G_i, λ_i) parameters (Parsimonious spectra). Excellent agreement between the generalized Maxwell model and the low frequency data (i.e. 0.12 to 16 Hz) obtained on the parallel plate rheometer is observed as shown in Figure 8. Table 1 shows the discrete relaxation spectrum calculated for PDMS.

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2} \tag{19}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)}{1+(\omega\lambda_i)^2} \tag{20}$$

The slight deviation between the *G'* and *G''* values measured on the HF-SPR and the extrapolations based on the generalized Maxwell model extrapolations is believed to be due to the fact that the generalized Maxwell model was fitted using experimental data obtained from frequencies of 0.12 to 16 Hz. One or more additional Maxwell elements, which are not experimentally accessible, would most likely be needed to obtain good predictions at 210 Hz.

As shown in Figure 9, the Cross model, Eq. 21, was also used to extrapolate the low frequency η^* measurements obtained on the parallel plate rheometer to a frequency of 210 Hz, where η^* is the complex viscosity, η_o is the zero-shear complex viscosity, λ is the relaxation time and *n* is the power-law index [1].

$$\eta^* = \frac{\eta_o}{1+|\lambda\omega|^{1-n}} \tag{21}$$

Good agreement between the Cross and generalized Maxwell model extrapolations of the low frequency parallel plate rheometer data and η^* measured on the HF-SPR, demonstrates the ability of the HF-SPR to measure the high frequency viscosity of shear-thinning materials.

A significant limitation of the HF-SPR is its inability to measure the viscoelastic properties of polymer melts over a range of frequencies. As mentioned previously, the HF-SPR can only operate at one frequency due to power restrictions of the vibration welder. However, the intended use of the HF-SPR is to measure the viscoelastic properties of thermoplastic materials at the frequency and amplitudes typically employed in vibration welding (i.e. 210 Hz and 1 mm, respectively), to enable better modelling of the vibration welding process. In particular, the speed of the welding process is governed by the rate of viscous dissipation. Although the measurements conducted herein were done at ambient conditions, the HF-SPR can operate at temperatures as high as 200°C [17]. Therefore, attempts to expand the frequency range of the HF-SPR through the use of TTS is possible.

5 CONCLUSIONS

A newly constructed high frequency sliding plate rheometer (HF-SPR) was used to measure the high frequency linear viscoelastic properties of polymer melts. The capability of the HF-SPR to accurately measure the high frequency viscoelastic properties of Newtonian materials was demonstrated by the good agreement obtained between the viscoelastic properties measured for PB using the HF-SPR and those extrapolated from low frequency measurements obtained on a parallel plate rheometer. Although the low frequency generalized Maxwell model extrapolations for PDMS deviated slightly from the values measured for G' and G'' using the HF-SPR, the discrepancy is likely due to uncertainty in the generalized Maxwell model extrapolations rather than error in the measured values. However, good agreement between Cross model extrapolation and η^* measured using the HF-SPR for PDMS demonstrated the ability of the HF-SPR to measure the high frequency viscosity of shear-thinning materials.

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REFERENCES

[1] Dealy JM, Wissburn KF: Melt Rheology and its Role in Plastics Processing, Van Nostrand Reinhold, New York (1990).
[2] Walters K: Rheometry, Wiley, New York (1975).
[3] Han CD: Rheology in Polymer Processing, Academic Press, New York (1976).
[4] Reimers MJ, Dealy JM: Sliding Plate Rheometer Studies of Concentrated Polystyrene Solutions: Large Amplitude Oscillatory Shear of a Very High Molecular Weight Polymer in Diethyl Phthalate, J. Rheol. 40 (1996) 167-186.
[5] Chopra D, Vlassopoulos D, Hatzikiriakos SG: Non-Linear Rheological Response of Phase Separating Polymer Blends: Poly(Styrene-Co-Maleic Anydride)/Poly(Methyl Methacrylate), J. Rheol. 44 (2000) 27-45.
[6] Ferry JD: Viscoelastic Properties of Polymers, Wiley, New York (1980).
[7] Fritz G, Pechhold W, Willenbacher N, Wagner NJ: Characterizing Complex Fluids with High Frequency Rheology using Torsional Resonators at Multiple Frequencies, J. Rheol. 47 (2003) 303-319.
[8] Crassous JJ, Regisser R, Ballauff M, Willenbacher N: Characterization of the Viscoelastic Behaviour of Complex Fluids using the Piezoelastic Axial Vibrator, J. Rheol. 49 (2005) 851-863.
[9] Gardel ML, Valentine MT, Weitz DA: Microrheology, in Microscale Diagnostic Techniques, Breuer KS (Ed.), Springer Verlag, (2000) 1-50.
[10] Longin PY, Verdier C, Piau M: Dynamic Shear Rheology of High Molecular Weight Polydimethylsiloxanes: Comparison of Rheometry and Ultrasound, J. Non-Newton. Fluid. 76 (1998) 213-232.
[11] Lionetto F, Montagna F, Maffezzoli A: Ultrasonic Dynamic Mechanical Analysis of Polymers, Appl. Rheol. 15 (2005) 326-335.
[12] Alig I, Stieber F, Bakhramov AD, Manucarov YS, Solovyev VA: Ultrasonic Absorption and Dynamic Shear Properties of the Transition from Dilute Solution to the Melt for Polybutadiene, Polymer 30 (1989) 842-848.
[13] Bates PJ, MacDonald J, Sidiropoulos V, Kontopoulou M: Comparison of Experimental and Analytical Vibration Welding Meltdown-Time Profiles for Nylon 66 and Polypropylene, Polym. Eng. Sci. 45 (2005) 789-797.
[14] Stokes VK: Vibration Welding of Thermoplastics. Part 1: Phenomenology of the Welding Process, Polym. Eng. Sci. 28 (1988) 718-739.
[15] Fetters LJ, Lohse DJ, Colby RH: Chain Dimensions and Entanglement Spacings, in Physical Properties of Polymers Handbook, Mark JE (Ed.), Springer Verlag (2007) 445-452.
[16] Baumgaertel M, Winter HH: Determination of Discrete Relaxation and Retardation Time Spectra from Dynamic Mechanical Data, Rheol. Acta 28 (1989) 511-519.
[17] Braybrook CA, Lee JA, Bates PJ, Kontopoulou M: Measurement of the High Frequency Viscoelastic Properties of Polypropylene using a Sliding Plate Rheometer, SPE ANTEC Tech. Papers 65 (2007) 1970-1974.

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