Creeping Sphere-Plane Squeeze Flow to Determine the Zero-Shear-Rate viscosity of HDPE Melts

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Abstract:
A creeping squeeze flow apparatus [1 - 2] was modified with a Fizeau interferometer optical motion transducer and equipped with a high-temperature, high-vacuum enclosure. Long-term squeeze flow experiments were done on a broad-MW, 1 melt-flow index commercial HDPE at 190°C, with runs covering about a week. Over this period, no thermal degradation of the polymer was observed, and the geometry of the apparatus was stable. Low-shear-rate viscosities were measured within the maximum shear rates from 1.7×10^{-5} to 7.6×10^{-5} 1/s (stress ~ 1.7 to 8 Pa), resulting in an two-decade expansion in the experimental window for this difficult-to-characterize HDPE resin with long relaxation times.

Zusammenfassung:
Eine Apparatur, welche Kriech- und Quetschströmung kombiniert [1-2] wurde durch einen optischen Bewegungssensor, der auf einem Fizeau Interferometer basiert, erweitert und in einer Hochtemperatur und Hochvakuum Zelle installiert. Langzeit Quetschströmversuche über eine Woche wurden an einer komerziellen HDPE Schmelze mit breiter Molekulargewichtsverteilung und Schmelzbruchindex 1 bei 190°C durchgeführt. Über diesen Zeitraum wurde keine thermische Zersetzung des Polymers beobachtet, und die Geometrie des Apparates war stabil. Nullviskositäten wurden im Bereich der grössten realisierbaren Scherraten, zwischen 1.7×10^{-5} und 7.6×10^{-5} 1/s (Spannung ~ 1.7 - 8 Pa) gemessen und erlaubten, für dieses messtechnisch schwierig behandelbare HDPE Harz mit langen Relaxationszeiten, eine Erweiterung des Messbereiches um zwei Dekaden.

Résumé:
Un appareil d'écoulement en écrasement à imposition de contrainte [1-2] a été modifié à l'aide d'un transducteur de mouvement à interféromètre optique de type Fizeau, et a été équipé d'un compartiment haute température sous vide. De longues expériences d'écoulement en écrasement ont été faites à 190°C pendant environ une semaine avec un HDPE commercial possédant une large MW et un indice d'écoulement fondu 1. Durant cette période, nous n'avons pas observé de dégradation du polymère, et la géométrie de l'appareil fut stable. Les viscosités à basses vitesses de cisaillement ont été mesurées pour des vitesses de cisaillement maximales allant de 1.7×10^{-5} à 7.6×10^{-5} 1/s (contraintes ~1.7 à 8 Pa), ce qui revient à une augmentation de deux décades de la fenêtre expérimentale disponible pour cette résine de HDPE difficile à caractériser du fait des ses longs temps de relaxation.

Key Words: squeeze flow, Fizeau interferometer, HDPE, zero-sher-rate viscosity

1 INTRODUCTION

The rheological characterization of polyolefins in the terminal region, via the measurement of low-frequency viscoelastic properties, remains a challenge in rheometry. This is particularly true for low melt-flow index (MI) commercial extrusion-grade polyethylene resins having broad molecular weight distributions (MWD) with significant high-molecular-weight tails. Because the time-temperature shifts for polyethylene are small due to their low glass-transition temperatures, time-temperature superposition is of little value for expanding the experimental window to lower frequencies [3]. Thus, the only recourse is to combine interconverted viscoelastic data obtained by different measurements. For low frequency or long time information, creep is often the method of choice, particularly when the steady shear viscosity is needed.

measured viscosities illustrated in Fig. 12 is one of the few available for HDPE.

For the calculation of the shear rates, absolute gaps were needed. As before, the final gap served as the reference. The final gap while the sample was in the melt state was determined by measuring the sample contraction during cooling up to its crystallization temperatures using the same fringe counting technique; the sample contraction was then added to the measured center thickness of the cooled sample. The uncertainty in the estimation of the shear rates for a final gap of 180 μm is 5.5% because of uncertainties in the thermal contraction of the solid after crystallization and the measurement of the recovered sample.

The limited size of the bottom plate constrained samples to a maximum diameter of 25 mm. Because of this constraint, the sample featured a meniscus-shaped fluid-air interface. In view of this, it was necessary to account for the effect of Laplace's pressure [1, 2, 11]. This adhesive wetting force is given by

$$F_{wet} = 4\pi R\gamma\cos\theta\left(1+\frac{2hR}{r_{wet}^2}\right)^{-1} \qquad (4)$$

where r_{wet} is the wetted radius, γ is the surface tension of PDMS in air, and θ is the contact angle the polymer makes with the glass [12]. The HPDE surface tension used was 22.29 dyne/cm (0.02229 N/m) [13]. The wetted radius (r_{wet} = 17 mm) and the average contact angle (~ 60°) were measured from the cooled sample after each run. Calculation of the wetting force in this case yielded 10.6 mN, which is 16.8% of the weight (63.2 mN) of the lens. The force F_{wet} from Eq. 4 was added to the weight of the lens, W in Eq. 1 to obtain the corrected viscosities, as it tends to pull the glass surfaces together.

4 CONCLUSION

PDMS gum (GE™ SE-30) and a broad MWD, 1.04 MFI HDPE with a significant high - M_W tail (Phillips Petroleum) were characterized using squeeze flow between a spherical lens and an optically flat plate. Using a Fizeau interferometer to measure the decreasing gap between the two surfaces, the viscosities of the two resins were calculated with Taylor's relation, which describes the squeeze flow of Newtonian fluids between a sphere and plane. Maximum shear rates as low as 1.7 x 10^{-5} to 7.6 x 10^{-5} s^{-1} were obtained.

While at this point it is not possible to state whether the viscosities for HDPE obtained through squeeze flow or any of the model extrapolations are the correct ones, it is evident that long-time data from such an experiment are valuable for establishing the behavior of high molecular weight melts. The successful outcome of results with difficult-to-characterize low-MI HDPE with the Fizeau-interferometer-equipped squeeze flow apparatus equipped with the high-temperature, high-vacuum cell established the suitability of the present device for conducting long-time experiments with extreme stability. In fact, there have been very few successful attempts to measure melt rheometry in melts at high temperatures over the periods of time (~ 1 week) covered in these experiments. The results indicate clearly that such experiments can be done.

Aside from vacuum conditions, the cell can be evacuated and back-filled with pressurized inert gas (e.g., CO_2, propane), which can act as a diluent. This would be advantageous in the characterization of polyolefins with very large relaxation times and low-LCB levels, as suggested, for example, by McLeish and coworkers [14].

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