Single-point Determination of Nonlinear Rheological Data from Parallel-Plate Torsional Flow

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Abstract:
Of the torsional drag-flow experiments, the hands-down winner for simplicity and ease of use is that using parallel-plate fixtures. This geometry is highly flexible, allowing custom modification of plate size and material, and is easily adaptable for optical use and the application of electric fields. However, its nonuniform flow is a major encumbrance for measuring nonlinear response. In 1987, Cross and Kaye offered a simple and clever solution for this problem, which essentially states that one assumes the sample is Newtonian, but the shear rate assigned to the observed "Newtonian" viscosity is 3/4ths of the rim shear rate . This shift factor arises from the use of Gaussian integration over radius of the nonlinear stress profile. Recent re-examination of the Cross-Kaye rule indicates that there may be a more accurate rule of thumb with the shift factor being 0.8 instead of 0.75 (4/5 instead of 3/4). However, for complex materials, the real question is how much useful information is covered up by this approach vs. the traditional differentiation of the integral to account for the stress profile. We have attempted to answer this question using a selection of nonlinear measurements on an AB block copolymer solution that is rheologically complex.

Zusammenfassung:
Bei den Torsions-Drag-Fliessexperimenten mit kommerziellen Geräten ist die Anwendung von parallelen Platten-Einrichtungen hinsichtlich Einfachheit und Handhabung am erfolgreichsten. Diese Geometrie ist sehr flexibel, erlaubt eine Modifikation der Plattengrösse und des Materials, und kann einfach für optische Messungen und die Anwendung von elektrischen Feldern angepasst werden. Jedoch ist ihre inhomogene Strömung eine grössere Behinderung, um die nichtlineare Antwort zu messen. 1987 haben Cross and Kaye eine einfache und intelligente Lösung für dieses Problem aufgezeigt, die im wesentlichen beinhaltet, dass man annimmt, dass sich die Probe newtonsch verhält, aber die Schergeschwindigkeit, die der beobachteten Newtonschen Geschwindigkeit zugeschrieben wird, 3/4 der Schergeschwindigkeit am Rand beträgt. Dieser Verschiebungsfaktor resultiert aus der Anwendung der Gaussschen Integration über den Radius des nichtlinearen Spannungsprofils. Neuere Betrachtungen der Cross-Kaye-Regel deuten an, dass möglicherweise eine genauere Daumenregel mit dem Verschiebungsfaktor 0.8 anstelle von 0.75 existiert. Jedoch ist für komplexe Materialien die wahre Frage, wieviel sinnvolle Information mit diesem Ansatz gegenüber der herkömmlichen Differentiation des Integrals abgedeckt wird, um das Spannungsprofil miteinzubeziehen. Wir haben versucht, diese Frage zu beantworten mit Hilfe einer Auswahl von nichtlinearen Messungen an einer AB-Blockcopolymerlösung, die rheologisch komplex ist.

Résumé:
Parmi les expériences en écoulement de rotation, la préférée en termes de simplicité et facilité d'utilisation est celle qui utilise des géométries plan-plan. Cette géométrie est très flexible, permettant la modification à volonté de la taille du plateau ainsi que du matériau qui le constitue. De plus elle est facilement adaptable à des montages optiques ou à l'application de champs électriques. Cependant, son écoulement non uniforme représente l'embarras principal pour la mesure de réponses non linéaires. En 1987, Cross et Kaye ont propose une solution simple et intelligente à ce problème. Elle consiste principalement à supposer que l'échantillon est Newtonien, mais que la vitesse de cisaillement correspondant à la viscosité Newtonienne observée est 3 quarts de celle mesurée au périmètre. Ce coefficient vient de l'utilisation d'une intégration Gaussienne sur le rayon du profile de la contrainte non linéaire. Un re-examen récent de la loi Cross-Kaye indique qu'il pourrait exister une correction plus précise ayant pour valeur 0.8 au lieu de 0.75 (4/5 au lieu de 3/4). Cependant, pour des matériaux complexes, la vraie question qui se pose est quelle est la quantité d'information utile qui est recouvrée par cette approche par rapport à l'intégration traditionnelle qui justifie le profile de la contrainte. Nous avons tenté de répondre à cette question en utilisant une sélection de mesures non linéaires obtenues avec une solution de copolymère en block de type AB qui est rhéologiquement complexe.

Key words: Single-point method, Cross-Kaye correction, AB block copolymer, parallel-plate fixtures

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gives the expected result:

$$G(t; \tfrac{4}{5}\dot{\gamma}_R) = \frac{2M(t; \dot{\gamma}_R)}{\pi R^3 \dot{\gamma}_R} = G_A(t) \qquad (25)$$

where $G_A(t)$ is the apparent linear relaxation modulus, and $\dot{\gamma}_R$ is the strain at the rim of the plates ($\dot{\gamma}_R = \Omega Rt/H$, where H is the total gap).

3.3 STRAIN SWEEP, OSCILLATORY SHEAR

The next example is a strain sweep on the same solution. These sweeps start at low strain where the solution has gelled, and advance to strains corresponding to a semi-solid. The response shows a well-defined inflection, which is convenient for comparing the P-P and C&P fixtures. As expected, the P-P strain sweep has to be brought to higher apparent strains to explore the nonlinear effects, and the 4/5^{ths} shift gives as satisfactory estimate of this strain (Fig. 7, right panel). However, the P-P data shows less abrupt strain softening, which is undoubtedly a rounding effect due to the range of strains in this fixture, as was also observed with the transient data. As can be seen from the original data, the agreement of the modulus values at low strains is reasonable, although both *G'* and *G"* from the C&P fixtures are somewhat higher than from the P-P. This was also the case for the linear data in steady shear, implying that there is a systematic difference between these fixtures even in the linear regime. This is perhaps due to an error in the geometry of either set, or a systematically faulty setting of the truncation gap for the C&P.

CONCLUSIONS

The attractions of the parallel-plate (P-P) fixtures are negated somewhat by the difficulty of extracting nonlinear material functions from the observations. Several single-point methods that avoid the complicated and error-prone conventional correction are available. An apparently new one, coined the 4/5^{ths} correction, has been presented – it is based on the third moment Gaussian approximation of the integral expression for torque. (It is called the 4/5^{ths} correction because one simply assigns the apparent viscosity reported by most instruments to 4/5^{ths} of the rim shear rate.) Exact solutions for special cases of analytical GNF functions show that the 4/5^{ths} correction and the Cross-Kaye 3/4^{ths} corrections bracket the correct viscosity function, and thus the limits of the error can be estimated accurately. For viscosity functions with inflections (e.g. the Carreau function) this is not quite the case. For this function, however, the 4/5^{ths} correction shows < 1% error up to shear rates well into the transition between Newtonian and power-law behavior, while the 3/4^{ths} correction has up to 3% error in the same range. Single-point methods based on the exact solution for power-law fluids were found to provide less accurate estimates of the behavior of the more realistic GNF fluids featuring Newtonian behavior at low shear rates. The correction suggested by Schümmer and Worthoff [6] is virtually indistinguishable from the 4/5^{ths} rule.

A test material comprising an SEP block copolymer solution in squalane was used to compare corrected P-P data with that gathered using the cone and plate (C&P) fixtures. For steady shearing, the single-point corrections worked quite well, with perhaps a slight advantage for the 4/5ths correction. For strain sweeps of dynamic data, the results were not as favorable: the P-P fixtures reduced the sharpness of the transition from linear to nonlinear behavior. A similar problem occurred with the stress growth in the nonlinear regime. Oddly enough, for both the dynamic and steady measurements, significantly higher stresses were observed for the C&P in the linear regime in spite of attempts to block out any systematic differences (matched fixtures, matched rim gaps, alternating repeat runs). The source of this discrepancy could be an error in the fixture geometry, or a systematic problem with setting the gap of either fixture. In particular, the parallel-plate fixtures must have perfect axial alignment, or the recorded viscosity will be too low.

The single-point methods offer a huge savings of labor over the tedious differential methods, and can provide even higher precision. Obviously, they are the only recourse for estimating the viscosity from a single run and one shear rate. They certainly provide a vastly superior answer than the frequently used Newtonian equations applied to experimental data gathered with parallel plate or capillary rheometers.

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