

CHARACTERIZATION OF COMPLEX FLUIDS AT VERY LOW FREQUENCY: EXPERIMENTAL VERIFICATION OF THE STRAIN RATE-FREQUENCY SUPERPOSITION (SRFS) METHOD

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ABSTRACT:

Strain rate frequency superposition (SRFS) has been suggested as new method to extend the frequency range for assessment of the complex storage modulus G^* of soft glassy materials to lower frequencies. The basic idea is that relaxation processes in such fluids are accelerated by an external shear field, analogous to the effect of a temperature shift in polymer melts and solutions. Master curves for G' and G'' are constructed from the apparent modulus data determined from non-linear oscillatory shear experiments. Here we validate the SRFS principle for the first time by independent experiments and also demonstrate its limitations. We compare SRFS results to directly measured G' , G'' at frequencies down to 10^{-3} rad/s and creep experiments lasting up to 10^4 s for a variety of gel-like fluids, including polymeric thickener solutions, a highly concentrated w/o-emulsion, and worm-like micellar surfactant solutions, as well as a weakly viscoelastic non-Brownian suspension of glass beads. Good agreement between SRFS data and directly measured G' , G'' values for the thickener solutions, the emulsion as well as the suspension. Apparent viscosity data obtained from creep experiments and absolute values of the complex viscosity in the low frequency limit agree fairly well for these fluids. But the method fails for the worm-like micellar solutions and this could be due to non-uniform flow or due to flow-induced structural changes. Finally, we demonstrate that the combination of SRFS, rotational rheometry, and advanced high frequency rheology methods allows for a broad bandwidth characterization of complex fluids spanning an unprecedented frequency range of about eleven decades.

ZUSAMMENFASSUNG:

Die Scherraten-Frequenz-Superpositions Methode (SRFS) wurde zur Ausdehnung des experimentell zugänglichen Frequenzbereiches für elastische, gelartige Materialien speziell zu kleinen Frequenzen hin vorgestellt. Die Grundidee der SRFS besteht darin, dass die Relaxationsprozesse in solchen Materialien durch ein äußeres Scherfeld beeinflusst werden können, analog zum Einfluss einer Temperaturänderung auf die Relaxation von Polymerschmelzen und -lösungen. Masterkurven für die linearviskoelastischen Funktionen G' und G'' werden aus scheinbaren G' und G'' Daten konstruiert, die aus oszillatorischen Scherexperimenten im nicht-linearen Bereich ermittelt werden. Hier validieren wir erstmals das SRFS Prinzip durch unabhängige Experimente und demonstrieren ebenso die Grenzen. Die SRFS Ergebnisse von verschiedenen gelartigen Fluiden, darunter Verdickerlösungen, eine hochkonzentrierte w/o Emulsion, Lösungen wurmartiger, zylindrischer Tensid-Mizellen, und eine schwach viskoelastische, nicht-brownsche Suspension von Glaskugeln in Silikonöl, werden mit direkt messbaren G' und G'' im linear viskoelastischen Bereich bis zu Frequenzen von 10^{-3} rad/s, sowie mit Kriechversuchen (bis zu 10^4 s) direkt verglichen. Die SRFS Daten und die direkt ermittelten G' , G'' stimmen bei den Verdickerlösungen, der Emulsion sowie bei der Suspension gut überein. Die aus Kriechversuchen ermittelten scheinbaren Viskositätsdaten und die absoluten Werte der komplexen Viskosität im niedrigen Frequenzbereich stimmen recht gut überein. Allerdings versagt die SRFS Methode für die Tensidlösungen. Dies könnte auf einer inhomogenen Scherdeformation oder auf einer scherinduzierten Strukturänderung beruhen. Abschließend demonstrieren wir, dass die Kombination von SRFS, Rotationsrheometrie und Hochfrequenz-Rheologie Methoden eine Charakterisierung von komplexen Fluiden über einen bisher unerreichten Frequenzbereich von elf Dekaden ermöglicht.

RÉSUMÉ:

Le principe de superposition vitesse de déformation fréquence (SRFS) a été proposé comme nouvelle méthode pour déterminer le module complexe de cisaillement G^* des matériaux viscoélastiques élargi aux basses fréquences. Pour de tels fluides les processus de relaxation sont accélérés par un champ de cisaillement externe, comparable à l'effet de la température dans les fondus et solutions de polymères. Des courbes maîtresses pour G' et G'' sont déterminées à partir du module apparent obtenu par des mesures de cisaillement en oscillation non linéaires. Dans cette étude, nous validons pour la première fois le principe de SRFS par des expériences indépendantes et démontrons également ses limites. Nous comparons les données de SRFS aux valeurs de G' et G'' obtenues à des fréquences allant jusqu'à 10^{-3} rad/s et à des expériences de fluage allant jusqu'à 10^4 s pour une

In this study we have applied the SRFS concept to a variety of strongly viscoelastic complex fluids including a set of polymeric thickener solutions, a highly concentrated emulsion and worm-like micellar surfactant solutions, but also a weakly viscoelastic non-Brownian suspension of glass beads in silicon oil. Similar as in the previous work of Wyss et al. [1], Mohan and Bandyopadhyay [8], and Erwin et al. [11] SRFS reveals a terminal flow regime for the thickener solutions and the emulsion. But in contrast to the fluids used in previous work, the thickener solutions used here have been chosen such that the onset of the terminal regime, in particular the crossover frequency ω_c is directly accessible with small amplitude oscillatory shear experiments at frequencies close to 10^{-3} rad/s. Good agreement is found between SRFS data and G' , G'' values directly measured in the linear response regime and in particular the ω_c values coincide very well. It should be noted that the high frequency data obtained in the linear response regime have to be removed carefully from the frequency sweep measurements at constant strain rate amplitude in order to avoid scatter in the master curves as reported earlier [1]. Furthermore, the existence of a terminal flow regime has been confirmed by independent long-term creep experiments revealing that a steady state viscosity is reached within about 10^4 s and that this viscosity is essentially independent of the applied stress. These values for the zero shear viscosities agree with the low frequency limiting absolute values of the complex viscosity within a factor of two. Taking into account the experimental uncertainties, we consider this fair agreement and SRFS is a fast and reliable tool to characterize the terminal flow behavior of such solutions.

In the case of the highly concentrated w/o-emulsion, SRFS again reveals a terminal flow regime. In this case ω_c is not directly accessible by small amplitude oscillatory shear experiments, but SRFS data agree very well with directly determined G' , G'' values in the frequency range down to 10^{-3} rad/s. Furthermore, the limiting low frequency absolute value of the complex viscosity lies in the same range as the apparent viscosities obtained in creep tests. But it has to be kept in mind that a true constant viscosity value is not yet reached even within 10^4 s and that the emulsion's response is extremely sensitive to the applied stress, so that a Newtonian plateau

seems not to be accessible. Nevertheless, the SRFS concept provides a reasonable estimate of the low shear flow behavior of such an emulsion. For the weakly viscoelastic suspension of glass beads in silicon oil again good agreement is found between SRFS data and G' , G'' data directly obtained in the linear response regime. In this case the terminal flow behavior is already accessed by small amplitude oscillatory shear measurements and due to the weak non-linearities SRFS does not offer a substantial extension of the accessible frequency range.

For the surfactant solution the SRFS concept obviously fails completely and this is presumably either due to non-uniform flow or structural changes, which may appear at large shear deformations. The occurrence of these phenomena is well-documented in the literature [22–24]. Finally, we have combined the SRFS concept with classical small amplitude oscillatory shear experiments and advanced high frequency rheometry techniques like oscillatory squeeze flow and torsional resonance oscillation. For an acrylic thickener solution we have demonstrated that this combination allows for a characterization of the linear viscoelastic behavior of such complex fluids over an unprecedented frequency range of about eleven decades spanning from $5 \cdot 10^{-6}$ to $3.6 \cdot 10^5$ rad/s.

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