Aging, Rejuvenation and Thixotropy in Complex Fluids: Time-dependence of the Viscosity at Rest and under Constant Shear Rate or Shear Stress(1)

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Abstract:

Complex fluids exhibit time-dependent changes in viscosity that have been ascribed to both thixotropy and aging. However, there is no consensus for which phenomenon is the origin of which changes. A novel thixotropic model is defined that incorporates aging. Conditions under which viscosity changes are due to thixotropy and aging are unambiguously defined. Viscosity changes in a complex fluid during a period of rest after destructuring exhibit a bifurcation at a critical volume fraction ϕ_{c2}. For volume fractions less than ϕ_{c2} the viscosity remains finite in the limit $t \longrightarrow \infty$. For volume fractions above critical the viscosity grows without limit, so aging occurs at rest. At constant shear rate there is no bifurcation, whereas under constant shear stress the model predicts a new bifurcation in the viscosity at a critical stress σ_B, identical to the yield stress σ_y observed under steady conditions. The divergence of the viscosity for $\sigma \le \sigma_B$ is best defined as aging. However, for $\sigma > \sigma_B$, where the viscosity remains finite, it seems preferable to use the concepts of restructuring and destructuring, rather than aging and rejuvenation. Nevertheless, when a stress $\sigma_A(\le \sigma_B)$ is applied during aging, slower aging is predicted and discussed as true rejuvenation. Plastic behaviour is predicted under steady conditions when $\sigma > \sigma_B$. The Herschel-Bulkley model fits the flow curve for stresses close to σ_B, whereas the Bingham model gives a better fit for $\sigma >> \sigma_B$. Finally, the model's predictions are shown to be consistent with experimental data from the literature for the transient behaviour of laponite gels.

Zusammenfassung:

Komplexe Fluide weisen zeitabhängige Viskositätsänderungen auf, die als thixotropes Verhalten und Alterung bezeichnet werden. Jedoch existiert kein Konsens über die Ursachen dieser Phänomene. Ein neues thixotropes Modell wird hier vorgestellt, das die Alterung miteinbezieht. Die Bedingungen, bei der Viskositätsänderungen aufgrund von Thixotropie und Alterung stattfinden, sind eindeutig definiert. Viskositätsänderungen in einem komplexen Fluid während einer Ruheperiode nach einer Strukturauflösung weisen eine Bifurkation bei einem kritischen Volumenanteil ϕ_{c2} auf. Für Volumenanteile unterhalb von ϕ_{c2} bleibt die Viskosität im Grenzfall $t \longrightarrow \infty$ endlich. Für Volumenanteile oberhalb des kritischen Wertes wächst die Viskosität unbeschränkt, so dass eine Alterung in der Ruheperiode stattfinden kann. Bei einer konstanten Schergeschwindigkeit entsteht keine Bifurkation, während aber unter konstanter Scherspannung das Modell eine neue Bifurkation in der Viskosität bei einer kritischen Scherspannung σ_B aufweist, die identisch mit der Fließspannung σ_y bei stationären Bedingungen ist. Die Divergenz der Viskosität für $\sigma \le \sigma_B$ kann als Alterung bezeichnet werden. Jedoch scheint es für $\sigma > \sigma_B$, wo die Viskosität endlich bleibt, sinnvoll zu sein, die Konzepte der Restrukturierung und der Strukturauflösung zu verwenden im Gegensatz zur „Alterung" und „Verjüngung". Falls jedoch eine Spannung $\sigma_A(\le \sigma_B)$ während der Alterung wirkt, resultiert ein langsameres Altern, dass als wahre Verjüngung beschrieben wird. Unter stationären Bedingungen mit $\sigma > \sigma_B$ wird ein plastisches Verhalten vorausgesagt. Das Herschel-Bulkley-Modell beschreibt die Fließkurve für Spannungen nahe bei σ_B, während das Bingham-Modell eine bessere Beschreibung für $\sigma >> \sigma_B$ liefert. Die Vorhersagen des Modells sind ebenfalls konsistent mit experimentellen Literaturdaten für das transiente Verhalten von Laponitgelen.

Résumé:

Un modèle thixotrope qui décrit la viscosité $\eta(t)$ au cours d'une période de repos, consécutive à une déstructuration, prédit l'existence d'une bifurcation pour une fraction volumique critique ϕ_{c2}. Pour $\phi < \phi_{c2}$, la limite $\eta(t \longrightarrow \infty)$ reste finie tandis que pour $\phi \ge \phi_{c2}$, la viscosité croît sans limite. C'est dans ce second domaine qu'a lieu le vieillissement. A l'inverse de l'absence de bifurcation lorsque le système est sous vitesse de cisaillement constante, le même modèle prédit l'existence, sous contrainte constante σ, d'une nouvelle bifurcation de $\eta(t)$ pour une contrainte critique σ_B qui s'identifie au seuil de contrainte σ_y observé en régime stationnaire. La divergence de $\eta(t)$ lorsque $\sigma \le \sigma_B$ est de nouveau associée au vieillissement, mais il semble préférable d'utiliser les concepts de restructuration et de déstructuration plutôt que de vieillissement et de rajeunissement dans le domaine $\sigma > \sigma_B$ où la viscosité reste finie. Néanmoins, lorsqu'on applique une contrainte σ_A à un système en cours de vieil-

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8 CONCLUSIONS AND FUTURE PROSPECTS

In conclusion, both for systems at rest and under controlled stress, the NLS-model of thixotropy has been shown to give satisfactory modelling of aging and, to some extent, shear-induced rejuvenation. This result has been obtained through giving prominence to bifurcations in the time-evolution of viscosity. At rest, different domains of volume fraction have been found, that depend on the initial structure, i.e. the previous history of the material. This has led to distinguish fluid and paste domains, the latter being divided into two states: hard and soft pastes. At constant shear rate, the model predicts neither aging nor rejuvenation. Only shear-induced restructuring or destructuring occurs, depending on initial state of the material.

On the contrary, under constant shear stress, there is a viscosity bifurcation at a critical stress. The critical value has been found to be the plastic yield stress, which depends on the volume fraction. As the latter is usually described by the empirical Herschell-Buckley law with constant yield, some progress can be expected by using instead the present, physically based modelling. The importance of distinguishing aging and rejuvenation from simple structural changes, restructuring or destructuring, either due to thixotropy alone or also in the presence of shear has been emphasized. This need has been illustrated by a satisfactory comparison of model predictions with data on laponite submitted to shear rate steps and under steady conditions. Finally, as the model works under all types of transient conditions, further testing can be done using stress relaxation and hysteresis cycles.

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FOOTNOTES

(1) Most of this paper has been previously published as [28].

(2) Clearly, this quadratic asymptotic behaviour is due to the form of Eq. 1 with an exponent of - 2. Changing to an exponent of - q will lead automatically to an asymptotic behaviour in t^q.

(3) For S_{init} = 0 (i.e. if the agitation completely breaks down the structure) S and therefore η should increase starting from its minimal value η_∞ (Eq. 4).

(4) This corresponds to the abrupt fall of the restructuring rate shown in Figure 3.

(5) It would be the same if the system had been left under any stress such as $\sigma_o < \sigma_B$. The special case σ_o = 0 is here considered in order to simplify the discussion. This choice does not reduce the generality of the results.

(6) For instance (Figure 10) the relative error in σ_y is less than 2 % for $0 < \dot{\gamma} < 200$ s^{-1}.

(7) Keeping the other NLS parameters unchanged (ϕ_m = 0.637, η_F = 1 mPa·s, φ = 0.637) but with S_{init} = 0.

(8) Figures 1 and 3 from [11] were not used as they concern complex viscosity that is not considered here.

(9) With the same parameter values as in Figure 11a.

(10) Curve a is identical to curve a of Figure 11.

(11) With interactions of the “soft sphere” type at low I [26]).

(12) A similar definition has already been used to model montmorillonite suspensions [27].

(13) Larger values such as $0.5 \geq \phi_{AF} \geq 0.37$ could be obtained using the size $2a_{eff}$ = 35 nm observed in [24].

(14) A hypothesis that is valid for fractal mesostructures.

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