

CONTINUUM MODELS WITH RUPTURED/HEALED MICROSTRUCTURE

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ABSTRACT

A continuum approach based on qualitative micro-structural physics and thermodynamic arguments has been elaborated for modeling of such interactive phenomena as yielding, thixotropy, nonlinear viscoelasticity, frozen memory, and stress localization. This type of modeling has been successfully applied to various systems, such as coagulating suspensions, highly filled polymers, concentrated solutions of surfactants, and elasto-viscoplasticity in metals. The mutual feature in these systems is the presence of a specific “structure” at rest, which can be destroyed at higher stresses and restored again after any type of unloading. Examples of this type modeling are presented in this paper. Several comparisons of calculations with experimental data will also be demonstrated in presentation.

KEYWORDS

Stress, strain, de-bonding, viscoelasticity, viscoplasticity, relaxation, yield, thixotropy.

INTRODUCTION

Many two-phase systems with small attractive colloidal particles display a peculiar mechanical behavior when the particle concentration is above a certain “gelation” (or a percolation) threshold. A simplest class of such systems is *dispersions* where solid colloidal particles with inter-particle attractive interaction are dispersed in a low molecular weight fluid. Many of them, such as lubricating greases, inks, pastes, foodstuffs, coal-water, and clay-water systems are of considerable industrial significance. Because of the attractive interactions, dispersions can create a particulate network, which is usually ruptured in flow with formation of “flocs”, and restored again at rest. The general approach presented below, was successfully applied to dispersed systems in [1]. The *filled polymers* represent another example of such a system. They include a broad variety of cured and uncured rubber compounds employed in rubber and tire industries, as well as the micro-gels used in electronics. Here, depending on the type of polymer and filler, a dominant physical bonding can happen either between small particles of filler or between filler and polymer matrix. Again, this secondary network existing at rest can be destroyed by stresses, with a long restoration after unloading. Examples of our modeling of uncured systems are given in [2,3]. The third class of the

phenomena to which the general approach has been applied is the *elasto-viscoplasticity in metals* [4]. Here, beyond a critical (yielding) level of stresses, a sharp and time dependent transition from elastic behavior to plastic flow occurs in active loading, caused by the sliding of metallic “grains” along multiple dislocation lines. Also, a long time stress-strain relaxation with restoration of structure, its hardening, stress localization, and frozen memory effects happen in metals. Finally, the same approach with few modifications can also be employed to describe the rheological behavior of the concentrated solutions of *worm-like micelles*. Here, the long chains of micelles with relatively strong but still secondary inter-micelle forces present the structure. At low stresses, the system behaves as a polymer-like viscoelastic liquid, but at higher stresses, the chains of micelles are destroyed being restored again in any type of unloading [5]. No yielding exists in this system.

BODY OF PAPER

We demonstrate below the basic principles of the approach and its applications to the above four systems. For the sake of simplicity only the case of simple shearing with small viscoelastic deformations is considered. The general 3D approach with a complete geometric nonlinearity has also been developed and presented in the cited papers, where the comparison was made between calculations and data.

Basic Principles and Formulation

It is easy to illustrate the basic principles of the approach on the example of colloidal suspensions in viscous or viscoelastic liquid with interparticle attractive interactions. These interactions are of two major types.

(i) *Direct attractive interactions*, which create the particulate network and flocs. These interactions being elastic before yield and viscoelastic beyond it produce a specific macroscopic viscoelastic shear sub-stress $\sigma_p = G_p \gamma_p$. Here G_p is the elastic modulus and γ_p is the small (visco-) elastic strain. Two relaxation times are important here: a lifetime of flocs θ_p , and a restructuring time θ_o ($\theta_o \geq \theta_p$) during unloading.

(ii) *Hydrodynamic interaction* between the flocs, as in a suspension of *inactive* particles, produces another type of sub-stress, σ_m , which depends on the rheological properties of matrix and such important parameters of suspension as particle concentration φ and size d . If the suspending matrix is a low molecular liquid, then $\sigma_m = \eta_m \dot{\gamma}$, where $\eta_m(\varphi, d)$ is the suspension viscosity. The function $\eta_m(\varphi, d)$ is approximately known from the rheology of suspension of inactive particles (see discussion in [2]). If the suspending matrix is a polymer liquid, the sub-stress σ_m is of viscoelastic nature (see details in [2,3]).

The total macroscopic shear stress σ is then represented as the sum of σ_p and σ_m . These are viewed as the contributions in the stress arising from specific matrix and particulate sub-media, or “modes” [2]. For high concentrated colloidal suspensions in low molecular matrices, the contribution σ_m in the total stress is negligible. Then the approach in this limit will also valid for the case of the elasto-viscoplasticity of metals [4]. Additionally, the normalized *debonding factor* ξ ($0 \leq \xi \leq 1$) should also be introduced to characterize the process of rupture/restoration of flocs.

The formulation of the constitutive equations is then as follows [1,2]:

$$\sigma = G_p \gamma_p + \sigma_m \quad (\sigma_m = \eta_m \dot{\gamma}); \quad \dot{\gamma}_p + f(\xi) \gamma_p / \theta = \dot{\gamma}; \quad \theta_o \dot{\xi} + \xi = (1 - \xi) |\dot{\gamma}| \theta / \gamma_* \quad (1,2,3)$$

Here $\dot{\gamma}$ is the shear rate. Eqn.2 describes the evolution of elastic strain γ_p , and *kinetic equation 3* describes the evolution of the debonding factor ξ . The *mobility function* $f(\xi)$ in Eqn.2 describes the effect of the floc rupture/restoration on the rheological properties of particulate mode. The properties of $f(\xi)$ are assumed as follows:

$$f(\xi), f'(\xi) > 0; \quad f \rightarrow f_0, \quad \xi \rightarrow 0; \quad f \rightarrow f_1 (< \infty), \quad \xi \rightarrow 1. \quad (4)$$

When $f_0 = 0$ the behavior of $f(\xi)$ near $\xi = 0$ is assumed as:

$$f = \xi + o(\xi), \quad \xi \rightarrow 0. \quad (4a)$$

An example of (*ad hoc*) specification which captures the properties shown in Eqns.4 and 4a for $f(\xi)$, is proposed as:

$$f(\xi) = (f_o + k\xi) \exp(\beta\xi) \quad (k, \beta \geq 0). \quad (5)$$

Two asymptotic cases of Eqn.5, (i) $f_o \approx 1, k = 0$ and (ii) $f_o = 0, k = 1$, are considered below. The physical sense of Eqns.1-5 is easy to illustrate on the simple situation when contribution of the matrix mode in the stress is negligible, i.e. $\sigma \approx G_p \gamma_p$. This situation also describes the effects of elasto-viscoplasticity in metals and rheology of worm-like micelles.

1. The particulate mode in Eqns.1, 2 has a viscoelastic character, since it has elastic properties (due to attractive inter-particle interaction) and quasi-viscous properties (due to floc rupturing under stress action). The effective relaxation time in Eqn.2, $\theta^* = \theta / f(\xi)$, decreases with the increase in debonding factor ξ , i.e. with the floc rupture. Thus $f(\xi)$ should be an increasing function of ξ . In accordance with Eqn.4, parameter θ/f_1 has the sense of the ultimate viscoelastic relaxation time in the mode, when the flocs are completely ruptured. The parameter f_o in Eqn.4 reflects the importance of fluctuations in the floc network at rest. If $f_o \sim 1$, the system at rest has a viscoelastic character with initial relaxation time θ ($> \theta / f_1$). This can describe the rheology of worm-like micelles. On the contrary, if $f_o \ll 1$, the value of f_o can be neglected and the floc network can be considered as "rigid". This is the case of dispersed systems in low molecular matrices, filled polymers and elasto-viscoplasticity, with yielding and sharp transition from solid-like behavior to flow. To guarantee the occurrence of such a sharp transition with yield behavior, the assumption shown in Eqn.4a is made about the behavior of $f(\xi)$ in the vicinity $\xi = 0$.

2. The phenomenological equation 3 is proposed here to capture the essence of the process of flocs rupturing and restoration. Here γ_* is the critical value of γ_p at which the intensive de-bonding process starts. When Eqn.4a is applicable, the parameter γ_* is associated with the elastic deformation at yielding point. It is easy to prove that Eqn.3 preserves the constraint $0 \leq \xi(t) \leq 1$. In thermodynamic interpretation [2] of floc de-bonding/re-bonding, the factor ξ is proportional to the free energy stored in flocs, ξ / θ_o is proportional to the rate of dissipation due to de-bonding and the

right-hand side of Eqn.3 is proportional to the average rate of work done by fluctuating micro-stresses on critical deformation γ_* [1,2].

3. For filled polymers, the matrix mode is viscoelastic and contributes a lot in the stress. Two cases are important here.

3a) In the simplest case, where the filler/filler interactions predominate, one can use along with Eqns.1-4, the multi-mode viscoelastic constitutive equations (Ces) for polymeric matrix. In our simplified case, these are the sum of linear Maxwell type modes with the relaxation spectrum $\{\hat{\theta}_k, \hat{G}_k\}$. Since the matrix mode is treated as a suspension of inactive particles in a polymer melt (or elastomer), there is the scaling relation [2]

$$\{\hat{\theta}_k, \hat{G}_k\} = \{\theta_k, G_k \chi\}, \quad \chi = \chi(\varphi, d) \quad (6)$$

between the matrix's viscoelastic spectrum and that for the pure polymer, $\{\theta_k, G_k\}$. The SBR elastomer filled with surface treated silica particles is an example of such a system.

3b) When the particle/polymer interactions predominate, more complicated particle/polymer secondary network and related flocs arise in the compound. At any instant, the polymer chains are classified here as either free or trapped to the particles; the total stress in the compound being the sum of the stresses in the two types of chains. During flow it is assumed that there is a dynamic balance between two competing structural processes - the debonding trapped chains from the particles, and the entrapment of free chains to the filler particles. The hydrodynamic effects of flow around the particles are lumped as in the case 3a), in the response of the free chains. The well-known examples of such compounds are the carbon black filled elastomers compounds [3]:

$$\sigma_f = G\gamma_f(\alpha + \xi)/(1 + \alpha); \quad \sigma_t = G\gamma_t(1 - \xi)/(1 + \alpha); \quad (7)$$

$$\sigma = \sigma_f + \sigma_t, \quad \dot{\gamma}_f + \gamma_f/\theta = \dot{\gamma}; \quad \dot{\gamma}_t + f(\xi)\gamma_t/\theta = \dot{\gamma}. \quad (8)$$

Here σ_f (or σ_t) and γ_f (or γ_t) are stresses and elastic strains for free (trapped) chains. Also, the kinetic equation 3 with $\theta_o = \theta$ was assumed to be valid for every relaxation mode, with parameter γ_* being mode independent. The total stress is then represented as the sum of stresses over all the relaxation modes. Comparisons between calculations based on a completely nonlinear formulation and some data for uncured rubber compounds have been made [3].

Qualitative Predictions

We now illustrate the basic predictions of the approach on the simple example of the Eqns.1-3 with the use of Eqn.5, when the matrix sub-stress is negligible, i.e. when $\sigma \approx G_p\gamma_p$.

1. *Steady shearing.* Here $\dot{\gamma} = \text{const}$ and the solution of Eqns.2, 3, 5 can be found as follows:

$$\xi = \frac{z}{1+z}, \quad \hat{\sigma} = \frac{z(1+z)}{f_o(1+z) + kz} \exp\left(-\beta \frac{z}{1+z}\right), \quad z = \frac{\dot{\gamma}\theta}{\gamma_*}. \quad (9)$$

Here $\hat{\sigma} = \sigma/(G_p\gamma_*)$. Eqn.9 displays a non-dimensional flow curve $\hat{\sigma}(z)$. Its non-Newtonian character is due to the floc rupture. Consider now two cases have been discussed above.

(i) When $f_o = 1$, $k = 0$, the asymptotic behavior of the flow curve at both the small and large shear rates is Newtonian. The maximum viscosity, $\eta_o = G_p \theta$, is reached at $\dot{\gamma} \rightarrow 0$, and minimum viscosity, $\eta_\infty = \eta_o e^{-\beta}$, at $\dot{\gamma} \rightarrow \infty$. If the numerical parameter β is large enough ($\beta > 2$), the flow curve is non-monotonous, which predicts the occurrence of the stress localization. This behavior is similar to that known for worm-like micelles [5].

When $f_o = 0$, $k = 1$, the asymptotic behavior of the flow curve at $\dot{\gamma} \rightarrow 0$ is *viscoplastic*, i.e.: $\hat{\sigma} = 1 + (1 - \beta)z + O(z^2)$, with the yield value, $Y = G_p \gamma_*$, and the Bingham plastic viscosity, $\eta_p = (1 - \beta)G_p \theta$. When $\dot{\gamma} \rightarrow \infty$, the asymptotic behavior of flow curve is Newtonian with the limit viscosity, $\eta_\infty = G_p \theta e^{-\beta}$. When $\beta > 1$, this model also predicts the occurrence of the stress localization near the yield stress. This behavior is similar to that known for dispersed systems [1]. Thus this analysis shows that the model predicts the occurrence of yield value without any yield criteria. The mechanism for this has been demonstrated in [1,2,4] and will be discussed in detail in Subsection 4 below.

2. *Start up shearing from the rest state.* Here the shear rate $\dot{\gamma}$ is constant at $t > 0$. A cumbersome transient solution for $\sigma(t)$ displays the well-known stress overshoot whose intensity increases and time location decreases with $\dot{\gamma}$ increasing. This demonstrates the effect *thixotropy*.

3. *Stress relaxation.* We assume that an active loading was applied at $t < 0$ and at the instant $t = 0$ the stress and de-bonding factor reached the values σ_o and ξ_o . For the more interesting case (ii), the model prediction of relaxation is:

$$\xi = \xi_o e^{-t/\theta}; \quad \sigma = \sigma_o \exp \left\{ \frac{-\theta}{\beta \theta} [\exp(-\beta \xi_o e^{-t/\theta_o}) - e^{-\beta \xi_o}] \right\}. \quad (10)$$

Eqn.10 demonstrates the effect of incomplete relaxation (or “frozen memory”) at $t \rightarrow \infty$. It is seen that the residual stress σ_∞ decreases with the increase in ξ_o . It happens since the rate of relaxation is higher when the flocs are more ruptured.

4. *Creep.* We consider here only interesting case (ii), when a constant stress σ_o is applied at $t > 0$ to the elasto-viscoplastic body initially at rest. Eqns.2, 3, 5ii always have the *static solution*:

$$\dot{\gamma} = 0, \quad \gamma = \gamma_p = \sigma_o / G_p, \quad \xi(t) = 0. \quad (11)$$

It corresponds to the solid-like behavior. Another solution, describing the plastic behavior, may also exist. To find it, $\dot{\gamma}$ is expressed at $t > 0$ from Eqn.2 as: $\dot{\gamma} = \sigma_o e^{\beta \xi} \xi / (G_p \theta)$ and substituted into Eqn.3. Then the problem is reduced to the initial problem for the kinetic equation 3 rewritten in the form:

$$\theta_o \dot{\xi} = \xi(1 - \xi)[e^{\beta \xi} \hat{\sigma} - 1 / (1 - \xi)], \quad \xi_o \equiv \xi(0) = 1 - e^{-r \hat{\sigma}}. \quad (12)$$

Here $r = \theta / \theta_o < 1$, $\hat{\sigma} = \sigma_o / Y$, and $Y = G_p \gamma_*$ is the yield stress. Analysis of this problem reveals that depending on the value of parameter $\delta = e^{\beta \xi_o} \hat{\sigma}$, the following behavior of $\xi(t)$ happens at

$t \rightarrow \infty$. (i) If $\delta < 1$, $\xi(t) \rightarrow 0$, and (ii) if $\delta > 1$, the solution goes at $t \rightarrow \infty$ to a steady solution shown by Eqn.9. The case (i) is related to solid like behavior, and the case (ii), to the flow, and the transition between these is of a *bifurcational type*. In the realistic case $r \ll 1$, $\delta \approx \hat{\sigma}$. It means that the bifurcation happens when the stress in creep is closed to the yield value, i.e. $\sigma_o \approx Y$.

CONCLUSION

The approach presented in this paper, demonstrates many mutual features peculiar for such different systems as colloidal dispersions, filled polymers, worm-like micelles and metals. It was shown that in these systems, a simple and flexible kinetic model could capture common rheological effects, such as yielding, thixotropy, viscoelasticity, frozen memory, and stress localization. The key element in this model is the coupling between a specific kinetic equation, which describes the rupture/restoration of a “structure”, and the equation of viscoelastic type for stress evolution. The remarkable feature of this approach is that it describes yielding as a bifurcation in the transition from solid-like behavior to flow. This gives this approach a computational advantage over those which employ an algebraic yield criterion, especially when solving complicated 3D problems.

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