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Materials Science and Engineering A 393 (2005) 223–228

ENGINEERING A

www.elsevier.com/locate/msea

Rheological model for short duration response of semi-solid metals

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Received 28 May 2004; accepted 17 October 2004

Abstract

A thorough understanding of the rheological behavior of the semi-solid metal (SSM) alloys is of utmost importance for modeling and simulation of rheocasting and thixoforming processes. Since the duration of these processes is very short—fraction of a second—the primary focus should be on fast transient flows. We present here a relatively simple engineering model for unsteady state shear stress of semi-solid metal suspensions. The time dependent character of thixotropic semi-solids is introduced through scaling by a structural parameter, which represents the degree of connectivity or aggregation of particles in the fluid. The kinetic equation for change in structural parameter as a function of time incorporates both breakage and agglomeration of suspended entities. The proposed model simulates the fast transient, tracks the evolution or healing of structure with holding time in absence of applied shear, and computes the steady state structure for a given shearing rate after long shearing time. Moreover, it explicitly incorporates the shear yield stress as well as is in agreement with important rheological characteristics of semi-solid materials, namely, shear thickening behavior under isostructural conditions and power law relationship between steady state viscosity and shear rate. The model is validated with published data for short time measurements of Sn–15%Pb thixotropic systems with near step change in shear rate and steady state shear viscosity. It could have practical utility in simulation of flow of semi-solid materials in different die cavities.

Keywords: Rheocasting and thixoforming of semi-solid metals; Slurry rheology; Structural parameter; Thixotropy

1. Introduction

Casting and forming of metal alloys in a semi-solid state is by now a well established manufacturing technique, which encompasses rheocasting at low solid fractions and thixoforming at higher solid fractions. The flow of metal in a die cavity in semi-solid metal (SSM) processing is determined primarily by the rheological characteristics of semi-solids which, in turn, depend on many variables, such as temperature, holding time, shape and size of particles in the slurry, connectivity of particles, etc. Because of the commercial importance of this shaping route, considerable research has been devoted to measurement and analysis of the flow behavior of semi-solid metals [1–3]. While models for the rheology of suspensions in a steady state has been presented by many workers [4–9], only a limited body of modeling work exists on the time dependence of rheology, that is, thixotropy [10–16]. Moreover, the available models in latter case are largely phenomenological in nature [12–16], although a few researchers have attempted to approach the problem from more fundamental principles [10,11].

Even though a thorough understanding of the thixotropic behavior of semi-solids is of critical importance from the perspective of shaping technology, the experimental data available in the literature on time dependent rheology is limited. Moreover, the data are invariably measured and modeled for time durations of the orders of few minutes, presumably because of experimental difficulties in measuring the viscosity transients over shorter time scales. However, both rheocasting as well as thixoforming processes occur in fractions of a second—and as such only the short duration unsteady state flow behavior is of significance in such situations. A notable exception is the work of Liu et al. [16] who measured the rheology of semi-solid metal suspensions for very short du-

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doi:10.1016/j.msea.2004.10.028

rations (up to 1 s) with fine granularity of time. The measurements captured the behavior of suspension in a time frame that is certainly more relevant to the SSM processing. The model employed by these authors relates the variation in viscosity to a step change in the shear rate as follows:

$$\frac{\sigma - \sigma_\mathrm{f}}{\sigma_\mathrm{i} - \sigma_\mathrm{f}} = \frac{\eta - \eta_\mathrm{f}}{\eta_\mathrm{i} - \eta_\mathrm{f}} = \mathrm{e}^{-t/\tau} \tag{1}$$

where σ and η represent shear stress and viscosity, respectively; t, time; τ, characteristic time and subscripts i and f denote initial and final states, respectively. This model, however, is applicable to the special case of jump experiments and is not suitable in the existing form for simulating flows in different situations.

Theoretical analysis and modeling of the rheology of cold suspensions of non-colloidal and colloidal particulate solids have a rather long history. This body of research has been summarized and reviewed extensively in the literature, for example [17,18]. Modeling of thixotropic suspensions is discussed in [19] and [20], among others. Understandably, the progress made in analyzing the complex flow behavior of cold suspensions has contributed significantly to modeling thixotropic semi-solid suspensions of metals at elevated temperatures. In this paper, we formulate within the framework of dense particulate suspensions a relatively simple engineering model for steady state and transient shear stress of hot metal suspensions over very short time durations with varying shear rate. The effect of network structure in the suspension, including its evolution or healing with holding time, as well as presence of shear yield stress are explicitly incorporated in the model. The model is validated with published short time measurements pertaining to Sn–15%Pb thixotropic systems subjected to near step change in shear rate under isothermal conditions. It could have practical utility in simulation of SSM processing, where the material may go through sharp rise and drop in shear rate within a matter of a few seconds.

2. Model framework

The semi-sold metal slurries are known to exhibit thixotropy [1]. The resulting time dependency is usually introduced through scaling by an aggregation index or structural parameter $s(t)$, which represents the degree of connectivity or aggregation of particles in the fluid. The magnitude of $s(t)$ ranges from zero (a fully deagglomerated state) to unity (a fully agglomerated state) where all particles are connected in a space filling network [21], provided the solid fraction in the suspension exceeds a threshold volume. Under an imposed shear rate the suspended entities continuously undergo aggregation/agglomeration and breakage. As a consequence, the connectivity varies with time and eventually reaches a dynamic steady state. Even when at rest, the system continues to evolve towards higher connectivity by some sort of a complex 'healing' process (or processes). Besides being thixotropic, the semi-solid metal suspensions exhibit shear yield stress [1,22], which is closely related to the degree of aggregation prevailing in the suspension. Based on a model of the effect of shearing time on shear yield stress of red mud [19], the shear yield stress of semi-solids is also scaled by a structural parameter. Considering these characteristics, it is assumed that the time dependent shear stress is scaled by a structural parameter and the shear stress of a semi-solid suspension $\tau(t)$ may be expressed in the form similar to Herschel–Bulkley fluid in following manner [12,13]:

$$\tau(t) = (\tau_\mathrm{y}(\phi, x, \ldots) + K(\phi, x, \ldots)\dot{\gamma}^m)s(t) + \eta_0\dot{\gamma} \tag{2}$$

where τ_y is shear yield stress of the suspension; K, consistency coefficient; m, consistency exponent and $\dot{\gamma}$, shear rate. The parameters τ_y and K pertain to fully agglomerated state and are functions of solid volume fraction ϕ, mean particle diameter x and other possible dependencies, such as particle shape, size distribution, properties of alloying elements, etc. η_0 is asymptotic viscosity of suspension at very high shear rates when solid particles are no longer able to form agglomerates. The system now behaves like a suspension of hard spheres, whose viscosity can be represented by the well-known equation of Krieger–Dougherty [17]:

$$\eta_0 = \eta_\mathrm{l}\left(1 - \frac{\phi}{\phi_\mathrm{max}}\right)^{-[\eta]\phi_\mathrm{max}} \tag{3}$$

where η_l is the liquid viscosity; ϕ_max, maximum possible solid packing and $[\eta]$ is intrinsic viscosity.

Many investigators have attempted to model the kinetics of structural changes in thixotropic fluids. These models seek to relate the rate of change of number of agglomerates to applied shear rate and the current state of aggregation. In case of semi-solid materials, it is convenient to represent the degree of agglomeration by a normalized continuous number or structural parameter, $0 \leq s(t) \leq 1$ [21]. The rate of change of s(t) with time may be expressed as [10–13,19]:

$$\frac{\mathrm{d}s(t)}{\mathrm{d}t} = -k_\mathrm{b}(\dot{\gamma}, \phi, x, \ldots)s(t) + k_\mathrm{r}(\dot{\gamma}, \phi, x, \ldots)(1 - s(t))^2$$
$$s(0) = s_\mathrm{o} \tag{4}$$

where the first term on right hand side of the equality arises from breakage of agglomerates and the second term reflects reformation of agglomerates. k_b and k_r are specific rate constants for breakage and agglomeration, respectively. It will be seen that while the rate of breakage is proportional to the current state of agglomeration, the rate of reformation is proportional to the square of $(1 - s)$. Other models [10–13] have assumed a reformation rate that is proportional to $(1 - s)$. However, based in part on the arguments presented in similar context elsewhere [19], it is felt that the dependence on $(1 - s)^2$ is more realistic from the point of view of the population balance of entities in suspensions subjected to shear [20].

The breakage rate is given by the product of collision frequency and probability of breakage. Since collision frequency is proportional to shear rate [4], it is permissible to express the breakage rate constant as follows:

$$k_b(\dot{\gamma}, \phi, x, \ldots) = \bar{k}_b(\phi, x, \ldots)\dot{\gamma} \quad (5)$$

The reformation rate reflects a more complex dynamics. The probability of reformation should be proportional to the number of collisions and inversely proportional to the duration of collision. Besides, reformation or “healing” of suspension occurs by Brownian motion, particle growth and coalescence even when the semi-solid is nominally at rest. Fan and Chen [4] assumed the following functional form for k_r:

$$k_r = \frac{r_0 + k_r'\dot{\gamma}}{1 + k_r''\dot{\gamma}} \quad (6)$$

The rate parameter in this function rises monotonically from a low value r_0 at rest—when Brownian motion and ripening prevails—to an asymptotic value k_r'/k_r'' at high shear rates. However, a detailed analysis of the data suggests that the reformation rate constant should go through a maximum. In other words, with increasing shear rate it should initially increase in step with increasing collision frequency and the enhanced probability of aggregation. At still higher shear rates, due to significant reduction in the duration of collision as well as the probability of agglomeration, the rate parameter should drop and eventually go to zero asymptotically. This trend can be captured by modifying Eq. (6) in the following manner:

$$k_r = \frac{r_0 + k_r'\dot{\gamma}}{1 + k_r''\dot{\gamma}^{\rho}}; \qquad \rho > 1 \quad (7)$$

where parameters ρ, r_0, k_r' and k_r'' are functions of solid volume fraction, particle size and distribution, etc. The final form of the kinetic equation for structural parameter becomes:

$$\frac{ds(t)}{dt} = -\bar{k}_b\dot{\gamma}s(t) + \frac{r_0 + k_r'\dot{\gamma}}{1 + k_r''\dot{\gamma}^{\rho}}(1 - s(t))^2 \quad (8)$$

2.1. Steady state viscosity

Setting the left hand side of equality in Eq. (8) to zero and solving the resulting quadratic equation for structural parameter yields the steady state structure $\bar{s}$ at constant shear rate:

$$\bar{s} = 1 + \left(\frac{k_b}{2k_r}\right) - \sqrt{\left(\frac{k_b}{2k_r}\right)^2 + 2\left(\frac{k_b}{2k_r}\right)} \quad (9)$$

It is readily shown from the dependence on shear rate that the term $2k_r/k_b$reduces to a low value, approaching zero at sufficiently high shear rate as the rate of reformation decreases while the breakage rate increases. Hence, the steady state structure can be approximated by a series expansion of the square root term in Eq. (9):

$$\bar{s} = \left(\frac{4k_r}{k_b}\right) + O\left(\frac{4k_r}{k_b}\right)^2 \quad (10)$$

where the second term on the right side represents the second order terms, which are small in magnitude and can be neglected. By substituting Eqs. (5) and (7) in the above equation, it can be shown that the steady state structure at sufficiently large shear rates becomes approximately proportional to $\dot{\gamma}^{-\rho}$. This implies that the steady state shear viscosity is approximately proportional to $\dot{\gamma}^{m-1-\rho}$. These results are in agreement with previous studies [8,9] which employs a power function to describe the relationship between shear rate and steady state viscosity with an exponent in the range of −0.8 to −1.5.

2.2. Evolution of structure at rest

At zero shear rate, only aggregation occurs at a specific rate constant r_0. From Eq. (8) evolution of the structure at rest or the healing path is given by:

$$s(t) = \frac{r_0(1 - s_0)t + s_0}{r_0(1 - s_0)t + 1} \quad (11)$$

It will be seen that structural parameter increases with time from initial value of s_0 and approaches unity in the limit. It turns out that Eq. (11) permits simulation of the development of the structure over wide ranging conditions including the rest state.

2.3. Model implementation and validation

The model was applied to the experimental data of Liu et al. [16] for Sn–15%Pb semi-solid systems published in both graphical and tabulated formats. The data includes temporal history of shear rate and shear stress for a number of cases in which shear rate jumps from 0 to 100 s^{-1} after different holding times and jumps from a steady state at shear rate of 1–200 s^{-1}. The importance of the data lies in the fact that it covers short durations of 1–1.5 s, which of course is of primary interest in SSM processing. Though the data is available for two solid volume fractions, namely, $\phi = 0.36$ and 0.5, the present study is restricted to solid fraction of 0.36 and to those cases where complete history is available.

2.4. Estimation of model parameters

Simulated Annealing, a global optimization algorithm, was employed to estimate model parameters from the data of Liu et al. [16]. The error norm used was the usual sum of squares of errors between the model and the measured shear stress values. The optimizer searched over the domain of parameters k_b, r_0, k_r', k_r'', ρ, K, m and s_0 to arrive at a minimum error. The search was subjected to a number of constraints. All parameters were assumed to be positive and, moreover, subjected to the stipulations that $m > 1$, $\rho > 1$ and $0 \le s_0 \le 1$. The structure at rest after the holding period (the beginning of the application of shear) was computed by substituting initial state of agglomeration s_0 and holding time in Eq. (11). As stated earlier, Eq. (10) implies that steady state shear viscosity

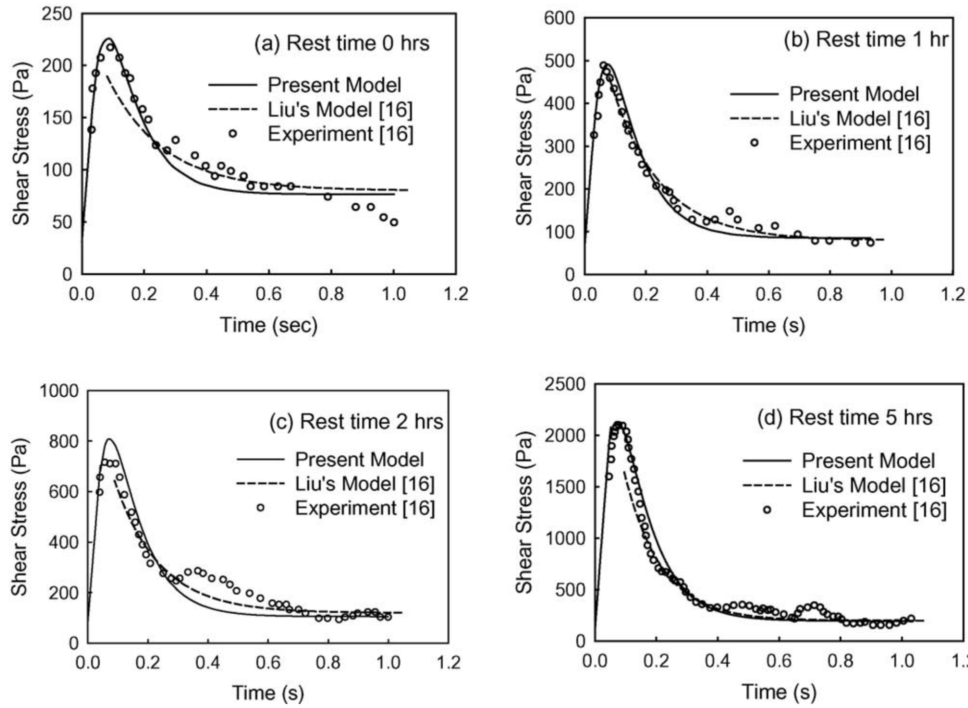

Fig. 1. Simulation of shear rate jumps from 0 to 100 s^{-1} compared with experimental data for different rest times (a) 0 h, (b) 1 h, (c) 2 h and (d) 5 h.

at high shear rates is approximately proportional to $\dot{\gamma}^{m-1-\rho}$. The fit of the Cross model [8] to steady state viscosity data showed that at high shear rates viscosity is approximately proportional to shear rate raised to an exponent equal to −1.3 for Sn–15%Pb systems. Hence, an additional constraint was imposed as follows:

$$m - 1 - \rho = -1.3 \qquad (12)$$

The parameters $\phi_{\max}$ and $[\eta]$ were assigned standard values of 0.64 and 3.28, respectively [17]. The viscosity η_l of molten Sb–15%Pb system is approximately 0.0025 Pa s, which lead to $\eta_0 = 0.014$. Preliminary simulations showed that the shear yield stress τ_y had only marginal effect on the suspension viscosity for the conditions examined in this work. Hence, following McLelland et al. [9], it was assigned a constant value of 100 Pa for solid volume fraction of 0.36.

Four sets of data were examined as shown in Fig. 1. A few comments on parameter estimation are in order here. Minimization by simulated annealing using individual sets of data lead to estimates of four parameter sets each comprising k_b, r_0, k_r', ρ, k_r'', s_0, K and m. The sets differed from each other in a narrow range with the exception of K. In view of this observation, in the final validated model presented here we chose to employ a single set of parameters with the exception of K obtained by fitting all data, even though some compromise had to be made in the quality of fits. The consistency parameter K varied with holding time. This is perhaps understandable as increase in particle size and changes in morphology could alter K significantly. Thus K was estimated by minimizing the error after fixing a common set of remaining parameters.

2.5. *Simulation I: Jump from rest state to 100 s^{-1} shear rate*

Fig. 1 shows that the model is able to track the experimental data quite realistically in all four cases. Also shown is the fit obtained by Liu et al. [16] who assigned different values to three parameters in their model equation in each of the four cases for a total of 12 parameters values. Our model, on the other hand, has 8 parameters (including τ_y), which are invariant across the four sets, and one parameter K that varies with rest time. Moreover, whereas the model tracks the entire transient triggered by a shear rate jump, the equation of Liu et al. [16] is restricted to data for one second after the shear rate reaches 90% of its final value, that is, mostly on right side of the curve peak. Table 1 lists values of the parameters employed in the model equation.

Fig. 2 shows the estimated K as a function of rest time. From the functional form of the fitted curve given in the figure, it would seem that K increases exponentially with rest time. Further work is required to develop a phenomenological or fundamental model for its evolution.

Table 1
Values of model parameters

τ_y	100
m	1.2
k_b	0.1 s
r_0	9.30×10^{-5}
k_r'	0.029
k_r''	0.008
ρ	1.5
s_0	0.163

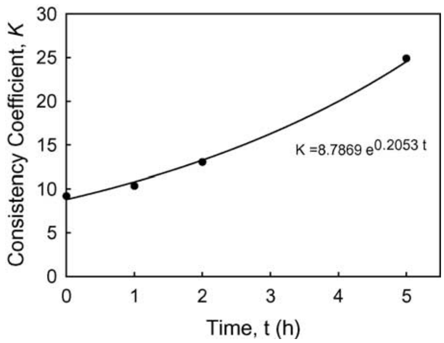

Fig. 2. Variation of consistency coefficient, K with rest time.

2.6. Simulation II: Jump from steady state at 1–200 s^{-1} shear rate

The parameters in Table 1, which were used to simulate the shear jump from rest to 100 s^{-1} in Fig. 1, were employed to predict the shear stress transient when shear rate jumps from steady state at 1–200 s^{-1}. The K value was taken as that for zero rest time and the initial structure before change of shear rate, s_0, was computed from the steady state structure relationship in Eq. (9) with 1 s^{-1} shear rate. Fig. 3 shows that the model predicted curve is in good agreement with experimental results of Liu et al. [16] for a jump to a high shear rate from an initial steady state at low shear rate.

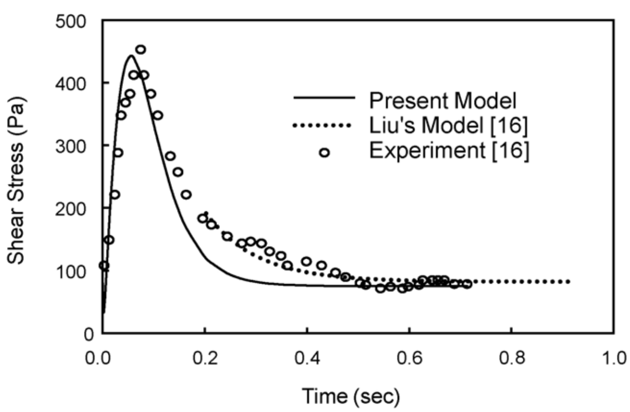

Fig. 3. Simulation of shear rate jumps from 1–200 s^{-1} compared with experimental data.

The steady state viscosities attained under various initial conditions of rest period and shear rate jumps were computed from Eqs. (2) and (7) and compared with the measured data provided by Liu et al. [16] in their Tables 1 and 2. Fig. 4 shows that a majority of points fall within the ±20% band.

3. Discussion

The exponent $m = 1.2$ implies that the material is likely to exhibit shear thickening behavior under isostructural conditions. This is in agreement with the phenomenon as it is presently understood. Fig. 5 shows variation of aggregation rate parameter k_r with shear rate. As discussed earlier, it increases with increasing shear rate, reaches its maximum at about 40 s^{-1} shear rate and then drops gradually. From Eq. (7), it is obvious that shear rate at which the peak occurs depends on k_r' and k_r''. It will go to zero only at very high shear rates when in theory at least a fully deagglomerated suspension should exist. Interestingly, the model has greater sensitivity to the ratio k_r'/k_r'' than individual parameters therein. This may be attributed to the fact that the shear rate rises abruptly in the set of experiments examined, and at higher shear rates the shear rate terms dominate in Eq. (7) for reformation rate. However, at very low shear rates, the magnitude of k_r' would become quite significant.

The evolution of structural parameter with rest time for this system was computed from Eq. (11) for various initial conditions s_0 and plotted in Fig. 6. It increases rapidly in the beginning and thereafter more slowly, eventually attaining the maximum value of one for a fully networked structure. It is obvious that the healing path depends on s_0 which can be altered by the prior history of the semi-solid (time-temperature, shear cycle, etc).

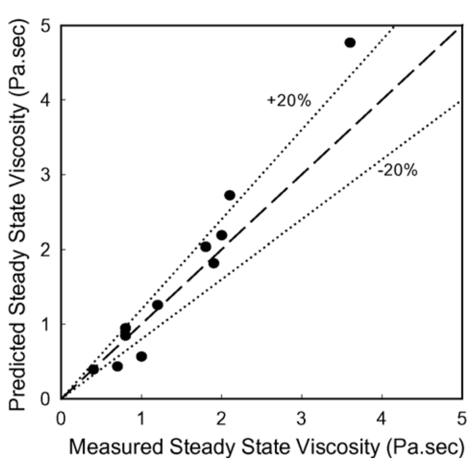

Fig. 4. Measured and predicted steady state viscosities.

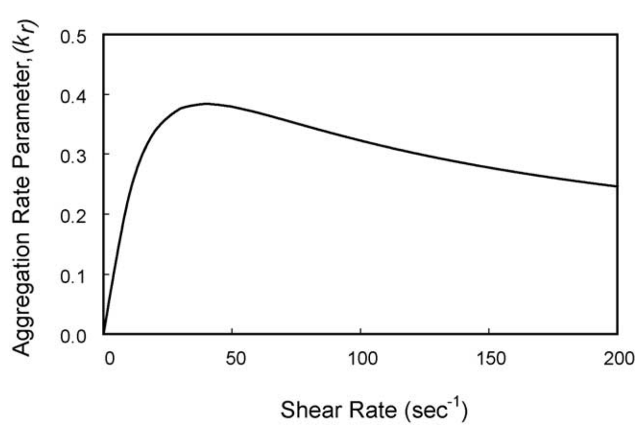

Fig. 5. Aggregation rate parameter (k_r) as a function of shear rate.

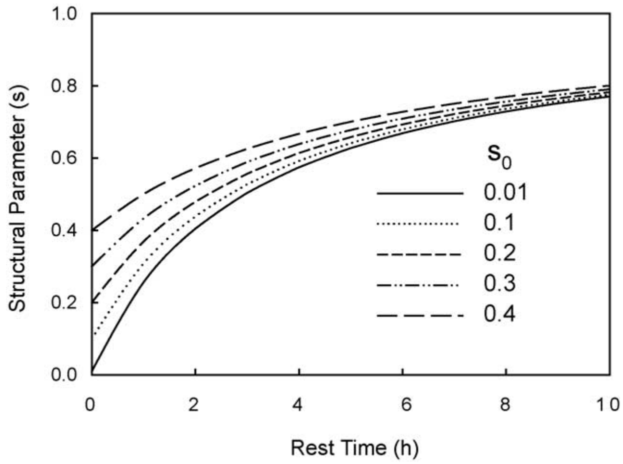

Fig. 6. Evolution of structure at rest under different initial states of structure s_0.

4. Concluding remarks

The kinetic equation for structural parameter or aggregation index, which scales shear stress both in steady state and dynamic state, plays a central role in the model formulation. Even though introduction of a structural parameter in quantification of the thixotropic phenomenon is not new [21], the right choice of the specific breakage and agglomeration rate constants are application specific and crucial to the success of the modeling scheme. Unfortunately, their functional forms are not obvious and require considerable trial and error search. As such, any explanations proffered for the final functional forms are admittedly after the fact rather than grounded in sound physical principles governing the multiphase flows. This of course is a major shortcoming of the models of this type including the present one. One can always set up a population balance equation for suspended entities, with coupled breakage and agglomeration events, similar to what is commonly done in the analysis of cold suspensions [19,20]. The challenge lies in identifying the rate parameters, numerical computation of the set of nonlinear equations and, more importantly, conversion of the computed aggregate size spectrum into an equivalent structural parameter. It should be recognized that the somewhat large number of model parameters is merely a reflection of the physical nature of the problem, rather than a deliberate attempt to over fit the data. Even then, our model requires significantly less number of parameters and provides better overall simulation than in the approach of Liu et al. [16], the only other model known to us that attempts to track fast transients. This suggests that it is perhaps possible to attain reasonable accuracy with built-in model robustness for simulations of dynamic and steady state thixotropic regimes in SSM processing.

Acknowledgements

The authors would like to acknowledge Professor Mathai Joseph, Executive Director, Tata Research Development Centre, Pune, India, for providing necessary facilities and encouragement while carrying out this work.

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