Asociación Argentina
de Mecánica Computacional

Mecánica Computacional Vol XXVII, págs. 975-984 (artículo completo)
Alberto Cardona, Mario Storti, Carlos Zuppa. (Eds.)
San Luis, Argentina, 10-13 Noviembre 2008

COMPUTATIONAL MODEL TO CHARACTERIZE THE RHEOKINETIC RESPONSE OF THE GELLING PROCESS

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Key words: Gelling Process, Rheokinetic Model, Thixotropy, Shear Rate Histories.

Abstract. The approach toward the sol-gel transition may be described by a basic structural parameter that evolves to the percolation value under static conditions. In this framework, two asymptotic responses are well identified for the gelling process of macromolecular solutions. One involves the initial sol viscosity that may be associated with the equilibrium viscosity value when the structural parameter is null (the microstructure is fully broken). The other is the percolation zero shear rate viscosity and corresponds to the maximum value of the structural parameter. Under flow, thixotropic theories allow one to convert directly experimental data obtained as shear stress versus time for a given shear rate into the time evolution of the structural parameter. Consequently rheometric experimental data available places the search for a kinetic model of the structural parameter. Here, an expression for this model is investigated computationally, which involves both the rates of structure breakdown and buildup, where the sizes of floccules are governed by the value of the shear rate. The rate equation thus obtained may be then applied, in principle, to any arbitrary rate of deformation history. Numerical results of the rheokinetic model proposed in this work fit well experimental rheometric data obtained in shear flow for the sol evolution of gelatin solutions.

1 INTRODUCTION

The gelling process through chemical or physical crosslinking mechanisms involves a transition from an initial sol state (associated typically with the solvent-macromolecular solute pair) to a gel (the percolation condition), where the apparent rheometric viscosity function at near zero shear rate increases to very high values before fracture. Between these two states, the material evolution may be sensed rheometrically as a thixotropic fluid response, in which the microstructure is destroyed mechanically (breakdown process) and simultaneously formed kinetically (build up process) at relatively higher rates than those of conventional thixotropic materials formed by concentrate pastes and suspensions. In this sense, it is possible to establish that all shear thinning materials are thixotropic, because a finite time is required to produce the microstructural arrangements that are necessary to respond mechanically as shear thinning (Barnes, 1997, 1999).

From the continuum phenomenological point of view, one observes that thixotropy is mainly associated with the structure breakdown and buildup of materials tested through a deformation history imposed, for instance, in a rheometric cell. Therefore, under flow, it is expected an equilibrium structure formation at long times that depends on the appropriate measure of the rate of deformation process. This measure is typically the shear rate in most studies carried out and reported in the literature (see, for instance, the reviews of Bauer and Collins, 1967, Mewis, 1979, and Barnes, 1997). Although thixotropy may be found in a wide spectrum of material types (lubricating greases, drilling mud, foodstuffs, filled polymers, electrorheological fluids, flour-water dough, maturing macromolecular solutions, gels, etc.) at present it is quite evident that a common structural characteristic of these materials is responsible for the thixotropic response under deformation: the state of segregation of the particulate phase suspended in a fluids must change for each value of a given measure of the rate of deformation.

In general it is found two different types of responses in thixotropic fluids by starting from the full structured state. Thus one finds an initial elastic deformation prior to yielding followed by a viscous response (or eventually a viscoelastic response) during the start-up of a constant shear flow. Further, in this process, the material may change from an “elastically dominated phase” to a “viscous dominated phase” passing thus through a plastic flow quite gradually, as described by Mujumdar et al. (2002). It is also possible to find some materials where avalanche and shear localization or banding are predominant phenomena; thus the material presents both sharp solid like and shearing fluid like zones (Coussot et al., 2002a-b; Varnik et al., 2003; Roussel et al., 2004; Huang et al., 2005). Therefore the predictive expectations from a tensorial constitutive model of thixotropic materials may meet several limitations due to the complexity of the present state-of-the-art of this subject (Beris et al., 2008). This situation places the actual research framework into studying mainly simple 1-D mechanical histories like, for instance, sequences of shear rates (steps up and down), shear rate loops (also designated thixotropic loops) and others tests expressed through specific designed time functions of shear rates, which may help to visualize micro-scale mechanisms associated with the breaking (also designated rejuvenation) and forming (or aging) structural rate processes. Most of the constitutive equations for thixotropy that applies to arbitrary shear rate flows has been presented and tabulated by Mujumdar et al. (2002), where they are classified into two groups: (a) phenomenological models and (b) structural kinetic models. This last one may also be secondarily classified as direct and indirect models. At present, the indirect structural kinetic model has gained more attention in the literature, perhaps due to its apparent simplicity. This model is applied to the gelling process, and it is the subject of the present work.

From the above framework, it is interesting to indicate here that the rheokinetics of maturing gelatin solutions (aqueous solvent with dissolved macromolecules that reverts to the tropocollagenic structure in a disordered state) is a relevant example of gelling fluid prone to be studied as a thixotropic material in shear flow (see, for instance, Huang and Sorensen, 1996; de Carvalho and Djabourov, 1997) in order to get relevant information concerning the microstructure evolution, mainly in the following aspects: (a) the rate of structure formation is relatively fast and competes with the breaking process in relatively small time intervals, placing thus emphasis in the thixotropic response more than in the asymptotic and conventional pseudoplastic behavior manifested for a rapid structure reconstruction (Barnes, 1997), (b) the thixotropic response may be detected following the inverse process of the classical studies in thixotropy; thus, from the fully unstructured fluid toward the fully structured material.

In this context of analysis, inferences on the kinetic nature of structure formation is also possible mainly by following the work of Baravian et al. (1996), where a structural parameter is evaluated from viscosity measurement (the procedure is described below). Within this framework, we present here a computational model to characterize the rheokinetic response of the gelling process in shear flow of maturing gelatin solutions, based on the indirect structural kinetic model approach proposed by Baravian et al. (1996) and also on the recent analyses of thixotropic phenomena carried out by Mujumdar et al. (2002), Moller et al. (2006) and Dullaert and Mewis (2006, 2005).

Throughout this work the sol-gel transition may be described by a basic structural parameter Γ that evolves to the percolation value Γ_c under static conditions (when no flow is imposed) and hence, it is convenient to define the normalized structural parameter $\lambda = \Gamma / \Gamma_c$ for the gelling process. Therefore, one recognizes two asymptotic responses of the gelation process of macromolecular solutions. One involves the initial sol viscosity that may be associated with the equilibrium viscosity value η_∞ when the normalized structural parameter λ is null (the microstructure is fully broken). The other is the percolation zero shear rate viscosity η_o at $\dot{\gamma} \to 0$ and corresponds to $\lambda = 1$, with $\eta_o \to \infty$ (Winter and Chambon, 1986). These definitions allow one to convert directly experimental data obtained as shear stress versus time t for a given rate of deformation history into the evolution of the structural parameter $\lambda(t)$ as described below. Consequently the experimental data available through $\lambda(t)$ places the search for a kinetic expression $\dot{\lambda}(t) = g(\lambda, \dot{\gamma})$ of the normalized structural parameter, where $\dot{\gamma}(t)$ is the shear rate function, describing the shear rate history (typically a sequence of shear rate steps). The rate equation thus obtained may be then applied, in principle, to any arbitrary rate of deformation history. Here we investigate computationally an expression for $g(\lambda, \dot{\gamma})$, involving both the rates of structure breakdown and buildup, where the size of floccules are governed by the shear rate value (see also de Carvalho and Djabourov 1997).

2 MODELLING THE GELLING PROCESS FROM THIXOTROPY

2.1 On the structural parameter

Within the framework of thixotropy, the knowledge of the structural kinetic equation $\dot{\lambda} = g(\lambda, \dot{\gamma})$ is relevant because it allows one to predict the shear stress from an arbitrary mechanical history. Nevertheless, the determination of the function $g(\lambda, \dot{\gamma})$ through basic rheometric data is not a simple task. From the analysis of the literature and taking several basic studies for different thixotropic systems (Moller et al., 2006), we propose here a quite general equation described as follows,

$$\dot{\lambda} = Y(\dot{\gamma})(1-\lambda)^{q(\dot{\gamma})}\lambda^{c} - X(\dot{\gamma})\lambda \qquad (1)$$

where $X(\dot{\gamma})$ is the breakdown function satisfying $X(0) \to 0$. Also, $Y(\dot{\gamma})$ is usually found to be a kinetic constant, here designated k_2, and $q(\dot{\gamma}) > 0$ (constrained to $q(0) \geq 1$) is associated with the kinetic order of the build up process, which is proportional to the distance from the actual structural state λ to the percolation state $\lambda = 1$, where one expects to find an infinitely high asymptotic apparent viscosity $\eta = \tau/\dot{\gamma}$ at null shear rate, defined as the ratio between shear stress τ and shear rate $\dot{\gamma}$. Also it is frequently assumed that the breakdown process is proportional to the amount of structure formed at present time. In Eq. (1), c is a constant close to one, although in some gelling material $c = 0$ is required because the initial increase of the normalized structural parameter is rapid. One concludes that in shear flow, λ evolves through two basic mechanisms, one involves the growing of microstructure, which is mainly concerned with attractive forces and the participation of the associated Brownian force, and the other considers the breakdown of microstructure by mechanical forces (here in particular that caused by shear rate). Most of the structural kinetic equations proposed in the literature may be derived from Eq. (1) by selecting appropriate expressions for $X(\dot{\gamma})$, $Y(\dot{\gamma})$ and $q(\dot{\gamma})$. For the particular case $\dot{\gamma} \to 0$, with $q(0) = 1$ and $c = 0$, the normalized structural parameter satisfies,

$$\lambda = 1 - \exp(-k_2 t), \qquad (2)$$

which is able to describe the approach toward the sol-gel transition as the maturation time increases.

It is then clear that $\dot{\gamma} \to 0$ is the strict condition to approach the transition sol-gel, and hence one infers that for $\dot{\gamma} \neq 0$ the two right hand terms of Eq. (1) survives, thus not allowing the material to reach the percolation point ($\lambda \to 1$). Here one expects to find a suspending phase composed by growing floccules of the macromolecules dissolved in the solvent. This phase has an equilibrium state value of the structural parameter λ_e described by the condition $g(\lambda, \dot{\gamma}) = 0$. Consequently from Eq. (1) and in particular for $q(\dot{\gamma}) = 1$ and c=0, it is found,

$$\lambda_e = \frac{Y}{Y + X} \qquad (3)$$

where, λ_e is a decreasing function of shear rate. Once more from a different point of view Eq. (3) demonstrates that the percolation point is achieved only for $\dot{\gamma} \to 0$.

Since $q(\dot{\gamma})$ is an increasing function of shear rate in general, the value λ_e shall be determined numerically because the functions assumed above to obtain analytic expressions are usually too simple for practical applications, although they are qualitatively correct.

An analytic solution of Eq. (1), for $Y(\dot{\gamma}) = k_2$, $X(\dot{\gamma}) = k_1\dot{\gamma}^p$, $q(\dot{\gamma}) = 1$ and $c = 0$, may be readily obtained,

$$\lambda = \lambda_e\{1 - \exp[-(k_2 + k_1\dot{\gamma}^p)t]\} \qquad (4)$$

This equation shows simply that $\lambda = \lambda_e$ and $\lambda = 0$ for $t \to \infty$ and $t \to 0$, respectively, as one would expect physically following the concepts mentioned above. More generally, due to nonlinear terms, one needs a numerical solution of the full structural kinetic equation (Eq. (1)) for applications of this theory to gelling fluids.

2.2 On the constitutive model for shear stress

Within the context of the indirect structural kinetic modelling of thixotropy for gelling solutions, the relation between shear stress and shear rate and the normalized structural parameter has been formulated through different expressions in the literature, which are not necessarily equivalent. Thus, one may start by considering that the apparent viscosity function for a given constant temperature is a function of the full set of mechanical variables for a quite generalized thixotropic fluid,

$$\eta = \eta(\dot{\gamma}(t), \gamma(t',t), \lambda(t,\dot{\gamma}), p_i) \tag{5}$$

where $\dot{\gamma}(t)$ is the shear rate history, $\gamma(t',t)$ is the shear deformation between preset time *t* and any a generic time *t*′, $\lambda(t,\dot{\gamma})$ is the normalized structural parameter evolution for the applying shear rate history and p_i (*i*= *1…n*) is a set of *n* physical parameters. In this context of the analysis it is usually proposed,

$$\tau = \tau_y \lambda + K\dot{\gamma}^n (1-\lambda)) \tag{6}$$

where τ_y is the classical yield stress. Thus by introducing the structural parameter into the Bingham-Herschel-Bulkley equation type one is able to conciliate thixotropy with yielding fluids (Moller, et al., 2006). Further, Mujumdar et al. (2002) introduced a smooth transition from solid-like to fluid-like by expressing,

$$\tau = G\gamma_e \lambda + K\dot{\gamma}^n (1-\lambda)) \tag{7}$$

with the constraint $\gamma_e(t,t) < \gamma_c \lambda(t,\dot{\gamma})^c$, otherwise only the pure fluid response survives. It is clear that in this equation $G\gamma_e$ is the elastic response mainly for high values of the structural parameter, which for classical thixotropic fluids is unity at the initial time. It should be observed that this situation is the opposite to that of the gelling process, which starts from the null structural parameter.

An interesting particular case of Eq. (5) is to consider the following expression,

$$\tau = \eta(\lambda(t,\dot{\gamma}), p_i)\dot{\gamma} \tag{8}$$

Within this model, one finds the relation proposed by Baravian et al. (1996) indicating that the normalized structural parameter is related to the apparent viscosity function through the following expression,

$$\lambda = (1-\sqrt{\frac{\eta_\infty}{\eta}})/K \tag{9}$$

where,

$$K = (1-\sqrt{\frac{\eta_\infty}{\eta_o}}) \tag{10}$$

For gelling solutions at a shear rate asymptotically null ($\dot{\gamma} \to 0$) the condition $\lambda = 1$ is achieved and hence $\eta_o \to \infty$ at the percolation point. Also, at the initial time, the sol viscosity

η_s is that corresponding to the equilibrium viscosity value η_∞ when $\lambda = 0$ (the microstructure is fully broken and no maturation has been effective yet). Thus, from Eqs. (9) and (10) the normalized structural parameter is,

$$\lambda = (1 - \sqrt{\frac{\eta_s}{\eta}}), \qquad K = 1 \tag{11}$$

Consequently the only physical parameter used here is the viscosity of the macromolecular solution, $p_i = \eta_s$. Far from the elastic response of the maturing solution, and at shear stress above the yield point, one can assume that the material is evolving in the rheometric cell as being mainly an inelastic thixotropic fluid, where the fluid like response covers the whole flow domain (slip and shearing banding are excluded; see, for instance, Moller et al., 2006, and Baudez and Coussot, 2004). For the inelastic thixotropic fluid, the above theory applies and one readily gets,

$$\eta(\lambda(t, \dot{\gamma}), p_i) = \eta_s / (1 - \lambda(\dot{\gamma}, t))^2 \tag{12}$$

Other constitutive models for the indirect structural kinetic equation may be found in Mujumdar et al. (2002).

2.3 On the numerical solution of the model proposed

The model proposed here for the shear stress response of gelling macromolecular solution is composed of Eqs. (1), (8) and (12) having Eqs. (2) and (3) as the asymptotic responses for zero and high values of shear rates, respectively, strictly valid for $q = 1$ and c=0. Conversely, experimental information concerning the structural parameter is obtained through Eq. (11) when data of the apparent viscosity from the rheometric cell are available. Consequently the numerical prediction of λ through Eq (1) must fit experimental data provided by Eq. (11). The numerical code generated for this purpose has the following steps: (1) Expressions for $X(\dot{\gamma})$, $Y(\dot{\gamma})$ and $q(\dot{\gamma})$ are selected by following the trend of preliminary results and studies (see following section). (2) Then Eq. (1) is written in finite differences and the simple Euler type subroutine is introduced to seek solutions $\lambda(t, \dot{\gamma})$ for sudden inceptions of different constant shear rates. Also the Runge-Kutta algorithm of fourth order is introduced to crosscheck invariance of numerical results in relation to time step sizes (of the order of 10^{-4} s) with a quite exigent convergence criterion (relative error between methods lower than 10^{-4}). (3) Numerical results obtained for λ are compared with experimental values reported at the same shear rate step through Eq. (11). This procedure allows one to fix and evaluate physical parameters and constants of the selected functions. The fitting process follows several simple rules. For instance, $Y(\dot{\gamma}) = k_2$ is estimated from the slope of the curve λ as a function of time for t=0 as indicated by Eq. (1) with $\lambda(0) = 0$. Further, $X(\dot{\gamma})$, $Y(\dot{\gamma})$ and $q(\dot{\gamma})$ controls the asymptotic value λ_e observed in the experimental data, as indicated qualitatively by the analytic version of λ (Eq. (3)) for c=0 and q=1. It is then clear that increasing the shear rate, $q(\dot{\gamma})$ increases and λ_e decreases toward a lower equilibrium value with a smaller equilibrated cluster size on the average (see also below). (4) From steps (1) to (3) the structural kinetic equation (Eq. (1)) is fully determined (function $g(\lambda, \dot{\gamma})$ is known now); hence the model is able, in principle, to predict the apparent viscosity function for any shear rate history $\dot{\gamma}(t)$ by using the same algorithms described above with the functions and parameters already evaluated in steps (1) to (3). In particular, below we present numerical studies carried out for different sequences of three increasing and decreasing steps of shear rates, to study the effect on the model of discontinuities in the shear rate evolution, which on the basis of these results requires reformulation of initial conditions after each shear rate jumps. Also numerical predictions are compared with experimental data reported by de Carvalho and Djabourov (1997) and discussed in relation to Huang and Sorensen (1996) results involving gelling gelatin solutions.

3 ANALYSIS AND DISCUSSION OF RESULTS

Figure 1 (a and b) shows that the rheokinetic model proposed here fits well experimental data of the structural parameter for a sequence of three decreasing (a) and increasing (b) steps of shear rates. Here we used experimental data from our laboratory of the apparent viscosity function (see Section 2.2) concerning the maturation of gelatin solutions with 6.66 % in protein (Bloom 266 g; the gelatin was obtained from bovine hide). Tests were carried out at 26 ºC. In this figure one finds a good agreement between model and experimental data. Nevertheless, after each sudden shear rate change, it is necessary to re-initialize the structural parameter λ to follows the correct track of the maturation evolution. This last result has two relevant conclusions. One of them indicates that, for our gelatin solutions, reversibility is not satisfied because the re-initialization of λ cannot be imposed from the known family of curves at different shear rates (from 76 to 418 s^{-1} in this case) used to define the parameters and functions of the model (see caption of Figure 1).

For more dilute gelatin solutions of around 3% (gelatin source was bone) Huang and Sorensen (1996) showed that the reversibility condition was approximately satisfied. The other conclusion is that, the structural kinetic equation (Eq. (1)) can handle appropriately continuous mechanical histories only.

Further, experimental data of the apparent viscosity function concerning the maturation of gelatine solutions at different constant shear rates reported by de Carvalho and Djabourov (1997) were fitted well, thus validating the model proposed here (results to be published). These authors used gelatin solutions 6.5 % in protein (Bloom 256 g; the gelatine was obtained from bones with photographic grade) and tests were carried out at 26 ºC.

In addition, by considering the quenching of the gelling process, it is worth to observe that for a given value of the normalized structural parameter, the projection of the apparent viscosity function (Eq. (12)) into a macroscopic fluid model, like for instance the Bingham fluid, may be expressed as follows:

$$\eta_s / (1-\lambda(\dot{\gamma},t))^2 = \tau_y(\lambda) / \dot{\gamma}(t) + \eta_s \tag{13}$$

Figure 2 depicts numerical results obtained from Eq. (13) for the gelatin solution described in the caption of Figure 1. Thus, for a constant shear rate, the yield stress $\tau_y(\lambda)$ becomes higher as the gelling time increases, due to the growth of microstructure. Further, $\tau_y(\lambda)$ is higher at any fixed value of gelling time when the constant gelling shear rate is increased, indicating that a smaller average diameter of floccules is generated at the higher shear rates. Thus a more effective structural packing is obtained. It is clear that these results are valid when a suspension of clusters is formed at relatively high values of shear rates, far from the network formation approaching the percolation point.

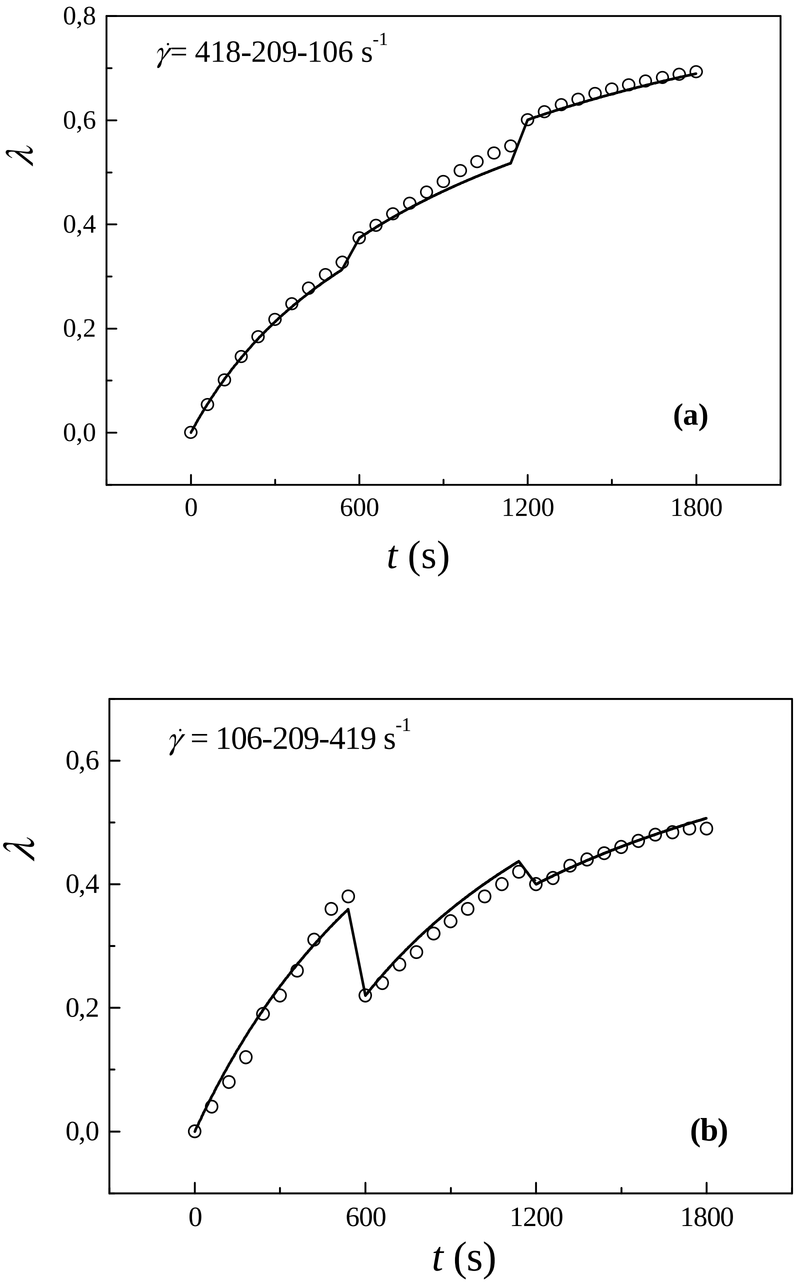

Figure 1: Structural parameter λ as a function of maturation time t for a sequence of shear rate steps, down (a) and up (b). Symbols are experimental data as indicated in the text. Full lines are the rheokinetic model predictions with re-initialization of the structural parameter λ after each shear rate jump and for $X(\dot{\gamma}) = k_1 \dot{\gamma}^p$, $q(\dot{\gamma}) = (1.788 + 0.0145\,\dot{\gamma})^{0.5}$, $Y(\dot{\gamma}) = k_2 = 10^{-3}$ s^{-1}, $k_1 = 10^{-9}$ s^{-1+p}, $p = 1.3$, $c = 0$.

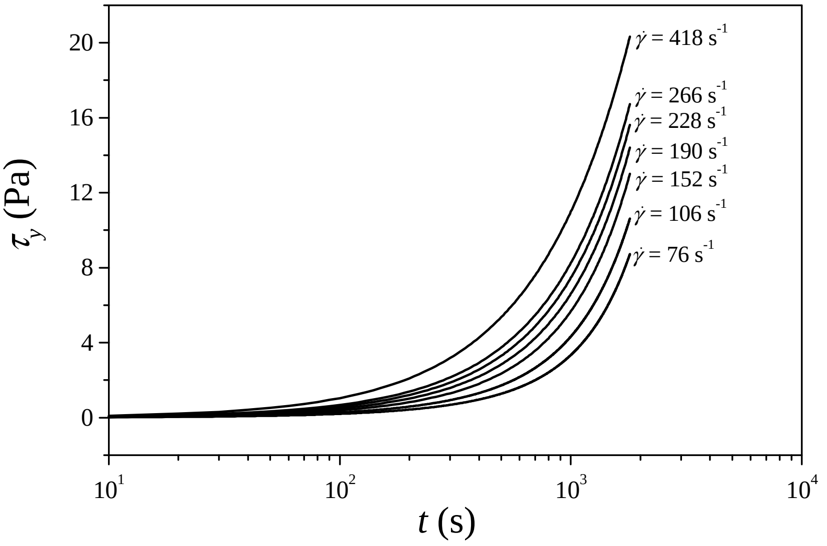

Figure 2: Yield stress as a function of gelling time for constant shear rates. Full lines are the numerical predictions with Eq. (13). The structural parameter λ is obtained from Eq. (1) with $X(\dot{\gamma}) = k_1 \dot{\gamma}^p$, $q(\dot{\gamma}) = (1.788 + 0.0145\,\dot{\gamma})^{0.5}$, $Y(\dot{\gamma}) = k_2 = 10^{-3}$ s^{-1}, $k_1 = 10^{-9}$ s^{-1+p}, $p = 1.3$, $c = 0$.

4 CONCLUSIONS

Numerical results of the rheokinetic model proposed here fit well experimental rheomeric data obtained in shear flow for the sol evolution of gelatin solutions. Different steps of shear rates are required for a consistent evaluation of parameters and functions included in the structural kinetic equation. Other shear rate functions, like for instance, sequences of step shear rates, up and down, describe the complexity of thixotropic phenomena associated with the gelling of gelatin solutions. Predictions in general indicate the progresses and limitations of modeling the rheokinetic gelling phenomenon, requiring more accurate rheological constitutive models at present.

Acknowledgments

Authors wish to thank the financial aid received from Universidad Nacional del Litoral, Santa Fe, Argentina (CAI+D 2006) and CONICET (PIP 5728).

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