Aging in a colloidal glass in creep flow: Time-stress superposition

Yogesh M. Joshi[*] and G. Ranjith K. Reddy

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
(Received 16 August 2007; revised manuscript received 2 January 2008; published 4 February 2008)

We study the aging behavior of aqueous laponite suspension, a model soft glassy material, in creep. We observe that the viscoelastic behavior is time dependent and is strongly influenced by the deformation field; the effect is known to arise due to aging and rejuvenation. We show that irrespective of the strength of the deformation field (shear stress) and age, when the imposed time scale is normalized with a dominating relaxation mode of the system, universal aging behavior is obtained, demonstrating time-stress superposition, a phenomenon that may be generic in a variety of soft materials.

Glasses are out-of-equilibrium materials and cover only a part of the phase space available to them. In molecular glasses a rapid decrease in temperature leads to an ergodicity breaking while in colloidal glasses insufficient mobility due to crowding of arrested entities leads to ergodicity breaking [1]. Common in both glasses is the aging phenomenon that lowers the potential energy of the system with time [2]. In soft (colloidal) glasses aging is achieved by the activated dynamics of the individual arrested entities, thereby lowering the energy [3]. Understanding the dynamics of such "out-of-equilibrium" materials—for example, pastes [4], gels [5], concentrated suspensions [6–9], and emulsions [10,11] and other soft materials [12,13]—is important from both industrial and academic points of view. A prominent characteristic feature common in these materials is extremely slow relaxation behavior with dominant mode scaling with the age of the system. Clearly the properties of these materials strongly depend on the deformation history, which leads to significant obstacles in analyzing and predicting the behavior of these materials. Application of a deformation field weakens the dependences of the dominant mode on age, the phenomenon generally addressed as rejuvenation [4]. In this paper we exploit this behavior. Since the rheological behavior is intrinsically dependent on the characteristic time scale of the system, the weakening dependence of the same on age at large stresses suggests a possibility of predicting rheological responses at large stresses by carrying out short-time tests at small stresses, thereby leading to a "time-stress" superposition.

Most of the soft glassy systems rejuvenate under flow field, so that aging under flow is very slow compared to that under "no-flow" conditions [14]; however in order to observe the influence of flow, its time scale needs to be smaller than the dominating time scale of the material [15]. Thus, the strength of the flow field changes the extent of rejuvenation, which may affect the distribution of the relaxation time differently [6]. Very recently Wyss *et al.* [16] demonstrated strain-rate frequency superposition and suggested that structural relaxation driven by an imposed strain rate results in the same response as the equilibrium structural relaxation at

much larger time scale (lower frequency). Cloitre *et al.* [4] observed that creep curves at different ages become superimposed when plotted against t/t_w^μ, where t is the creep time, t_w is the age, and μ is a positive exponent first introduced by Struik [17] for aging amorphous polymers [also see Fielding *et al.* [18]]. They inferred that the characteristic relaxation time of the system scales as age ($\tau \sim t_w^\mu$) with μ depending on the creep stress. Derec *et al.* [8,19] carried out a similar superposition for stress relaxation experiments for a concentrated suspension of silica. Significantly, in this work, we take advantage of the weak dependence of the characteristic relaxation time on age at large stress to predict rheological behavior at large stress by carrying out short-time tests at small stresses. We observe that irrespective of the value of the creep stress (or μ), the system shows universal creep behavior by carrying out a systematic shifting procedure, thereby demonstrating time-stress superposition. Moreover, we also observe that stress plays the same role in colloidal glasses that temperature plays in molecular glasses while reversing the effect of aging.

Laponite RD, a synthetic hectorite clay, is composed of disk-shaped nanoparticles with a diameter of 25 nm and a thickness of 1 nm. Suspension of laponite in water shows a two-stage evolution of the α relaxation mode and undergoes ergodicity breaking over practical time scales [20]. Laponite RD used in the present experiments is procured from Southern Clay Products, Inc. The white powder of laponite was dried for 4 h at 120 °C before mixing with de-ionized water at pH 10 under vigorous stirring for 15 min. The couette cell of the stress-controlled rheometer, AR 1000 (inner cylinder diameter of 28 mm with a 1-mm gap) was filled up with the sample. After keeping the system idle for 3 h, oscillatory deformation with stress amplitude of 50 Pa and frequency of 0.1 Hz was applied for a short while to carry out shear melting. The sample yields under such a high stress and eventually shows a plateau of low viscosity that does not change with time. We stopped the shear melting experiment at this moment, from which the aging time (t_w) was measured. A shear melting procedure is used to achieve a uniform initial state for all samples used in the present study. Subsequently, in the aging experiments, oscillatory shear stress with an amplitude of 0.5 Pa and frequency of 0.1 Hz was employed to record the aging behavior with respect to t_w. The detailed experimental procedure is also reported elsewhere [9]. All

─────────
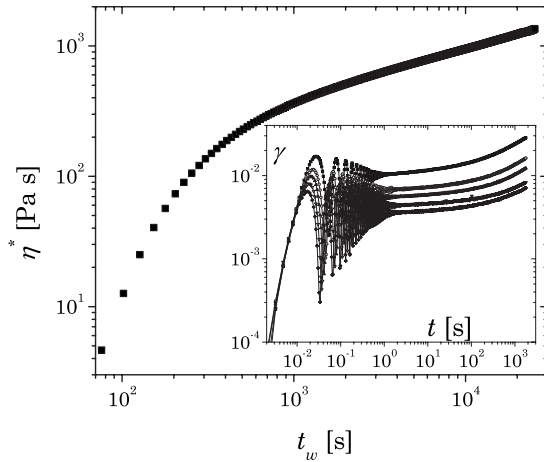*Corresponding author. FAX: 0091 512 259 0104.
joshi@iitk.ac.in

FIG. 1. Aging curve for 3.5 wt % aqueous laponite suspension. The inset shows creep curves obtained at various ages (from top to bottom: 1908 s, 5430 s, 9719 s, 18 725 s, 25 272 s) for a creep stress of 3 Pa.

FIG. 2. Normalized creep compliance plotted against t/t_w^μ for $\mu=0.45$ (creep stress=3 Pa). At this value of μ, creep curves obtained at different ages show superposition (squares. 1908 s; circles, 5430 s; up triangles, 9719 s; down triangles, 18 725 s; and diamonds, 25 272 s).

results reported in this paper relate to 3.5 wt % laponite suspension and temperature 20 °C. To avoid evaporation of water or CO_2 contamination of the sample, the free surface of the suspension was covered with a thin layer of low-viscosity silicon oil throughout the experiment. We also carried out a frequency sweep experiment on independent samples at the end of a waiting period of 3 h. We observed that the storage modulus is independent of frequency while the loss modulus showed a slight decrease with respect to frequency in the experimentally accessible frequency range. This observation is similar to that observed by Bonn *et al.* [21], and according to Fielding *et al.* [18] this ensures the system to be in the nonergodic regime.

Figure 1 shows the evolution of complex viscosity for a shear-rejuvenated laponite suspension, wherein the corresponding increase in complex viscosity is plotted against the age of the sample. We carried out aging experiments for all independent samples until the predetermined value of age (corresponding complex viscosity between 300 and 1400 Pa s) is reached. After stopping the oscillatory test each time, creep experiments were performed with various creep stresses in the range 0.5–5 Pa. As shown in the inset of Fig. 1, in the initial period up to $O(1$ s), the system shows damped oscillations in strain which are known to occur due to instrument inertia coupled with the viscoelastic character of the fluid [9].

As the sample ages, its relaxation dynamics becomes slower and slower. We have discussed above that the dominant relaxation time of the system scales as age ($\tau \sim t_w^\mu$) with μ depending on the creep stress. Thus normalization of the creep time by t_w^μ is expected to give superposition of creep curves after an appropriate vertical shifting of the creep curves is carried out. Vertical shifting is needed to accommodate the thixotropic character of the system that is responsible for a significant increase in the modulus with time shown in Fig. 1. In Fig. 2 we plot the creep curves obtained at a stress of 3 Pa with the ratio of creep compliance $J(t_w + t)$ and zero-time compliance $J(t_w)[=1/G(t_w) \approx 1/G']$ as or-
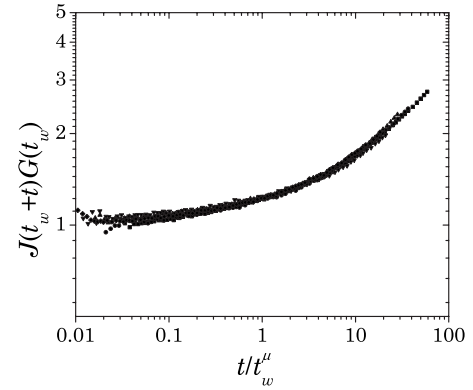
dinate and t/t_w^μ as abscissa. We have considered creep data beyond $t > 1$ s only to omit the oscillatory part. It can be seen that for $\mu=0.45$, the creep curves indeed superimpose onto each other.

In order to understand this behavior let us assume that the system is represented by a Maxwell model (an elastic spring and a dashpot in series). In principle, in order to observe damped inertial oscillations, the spring of the Maxwell model needs to be replaced by a Kelvin-Voigt element (an elastic spring and a dashpot in parallel) [9]; however, since we are omitting the inertial oscillations, consideration of a simple Maxwell model suffices for the present purpose. The strain induced by application of step stress (σ) to the Maxwell model is then given by

$$\gamma(t_w + t) = \frac{\sigma}{G} + \int_0^t \frac{\sigma}{\eta} dt. \tag{1}$$

Here G and η represent the modulus and viscosity associated with the Maxwell model. The viscosity of the Maxwell model can be represented as $\eta = G\tau$, where τ is the characteristic relaxation time of the system. Struik [17] (and more formally Feilding *et al.* [18]) suggested that τ scales as

$$\tau = A \tau_0^{1-\mu} t_w^\mu, \tag{2}$$

where A is a numerical factor, τ_0 is a microscopic time [18], and μ is a function of stress. Incorporation of Eq. (2) in Eq. (1) gives:

$$\gamma(t_w + t) = \frac{\sigma}{G} + \frac{\sigma \tau_0^{\mu-1}}{GA} \int_0^t \frac{1}{(t_w + t)^\mu} dt. \tag{3}$$

We have taken G out of integration assuming that it changes negligibly over the creep time in the limit of $t \ll t_w$. Integration in Eq. (3) can be easily solved, and after rearrangement in the limit of $t \ll t_w$, we get
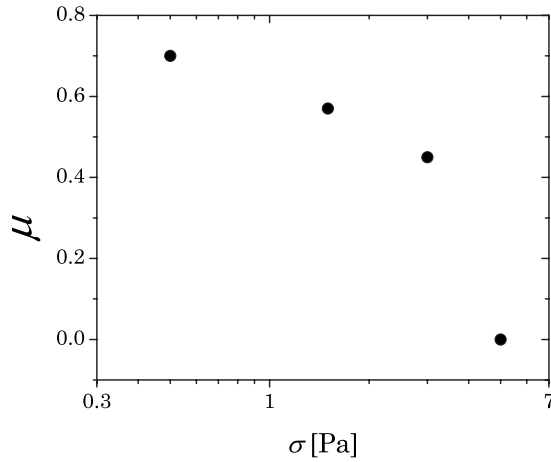
FIG. 3. Parameter μ is plotted as a function of creep stress. An increase in stress enhances the extent of rejuvenation, causing a decrease in μ.

$$J(t_w + t)G(t_w) = 1 + \frac{\tau_0^{\mu-1}}{A}\left(\frac{t}{t_w^\mu}\right). \qquad (4)$$

Equation (4) shows that after appropriately carrying out the vertical and horizontal shifting, as represented by the term on the left-hand side and the second term on the right-hand side, respectively, a unique value of μ should show superposition.

By adopting the same procedure as in Fig. 2 we obtained superposition for other creep stresses as well. Figure 3 shows the value of μ for which the master curve is obtained plotted against the creep stress. It can be seen that the larger the value of the stress, the smaller the value of μ. As stress increases, it rejuvenates the system to a greater extent, reducing the effect of aging. For a creep stress of 5 Pa, complete rejuvenation occurs (no aging) and we get $\mu=0$, showing that the yield stress of the present system is between 3 and 5 Pa. Thus, μ depends on the extent of aging and/or rejuvenation. When rejuvenation completely erases the effect of aging, $\mu \rightarrow 0$, while for simple aging, the theoretical higher limit on μ is unity [17,18]. Interestingly for polymeric glasses Struik [17] also observed a decrease in μ with increasing stress; however, now it has been accepted that mechanical rejuvenation may not be responsible for this effect [22,23]. For structural glasses μ becomes affected by temperature and strain. Struik [17] and more recently O'Connell and McKenna [24] observed that for polymer glasses, μ rapidly approaches zero as the temperature approaches T_g. Thus, for molecular glasses, an increase in temperature reverses the effect of aging; while for soft glassy systems, application of stress reverses the effect of aging.

We observed that when the creep time is normalized by t_w^μ and compliance is normalized by $G(t_w)$, creep curves become superimposed for a particular value of μ, which is a function of stress. In this study we employ four creep stresses leading to four sets of superimposed creep curves each having a unique value of μ as shown in Fig. 3. Each of this set of superimposed creep curves can then be shifted horizontally by multiplying by a factor of $a(\mu)$ to obtain a universal mas-
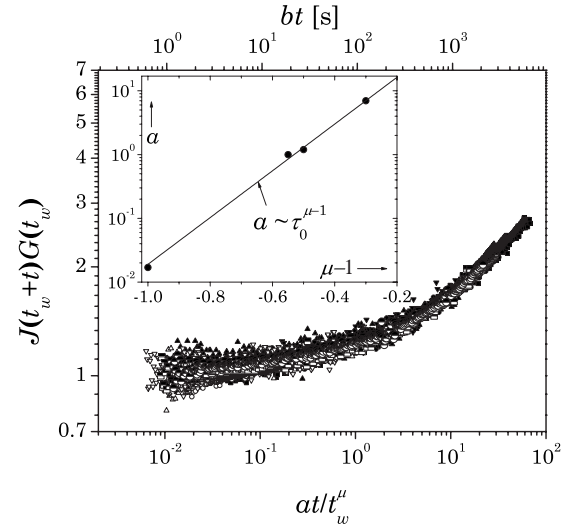

FIG. 4. Universal master curve for different ages and creep stresses. The parameter a is a shift factor for horizontal shifting, and the inset shows that its dependence on $\mu-1$ follows $a \sim \tau_0^{\mu-1}$. The shift factor b is given by $b=\tau_0^{\mu-\mu_0}t_{w0}^{\mu_0}/t_w^\mu$ (see text for discussion).

ter curve. In Fig. 4, 17 different creep curves at different stresses and ages (different values of μ) are shown to become superimposed to form a universal master curve. We have shifted all sets of creep curves onto a set of creep curves with $\mu=0.45$ (creep stress 3 Pa) by carrying out a horizontal shifting by varying parameter $a(\mu)$. The minor scatter in the universal master curve is due to decaying inertial oscillations that are observed beyond the creep time 1 s as shown in the inset of Fig. 1. Equation (2) suggests that $a(\mu)$ should have a logarithmic dependence on $\mu-1$ given by $a \sim \tau_0^{\mu-1}$. The inset of Fig. 4 shows a semilogarithmic plot of a vs $\mu-1$. It can be seen that a straight line representing $a \sim \tau_0^{\mu-1}$ indeed fits the data very well. The same plot can be represented as a time-stress (or time-μ) superposition with the top abscissa corresponding to the time axis. Such a superposition represents all creep curves with different values of μ (different creep stress) and different ages shifted on a creep curve with $\mu=0.45$ and $t_w=25\,272$ s. The shift factor b can be represented by $b=\tau(\mu_0,t_{w0})/\tau(\mu,t_w)=\tau_0^{\mu-\mu_0}t_{w0}^{\mu_0}/t_w^\mu$, where t_{w0} and μ_0 are the values pertaining to the reference creep curve (in present case $\mu_0=0.45$ and $t_{w0}=25\,272$ s).

A fit to estimated values of a with respect to $\mu-1$, as shown in the inset of Fig. 4, leads to an independent estimation of the product $A\tau_0$ to be equal to around 53 s. This is the characteristic time scale of the system in the limit of $\mu \rightarrow 0$. In order to validate the same quantitatively, the shear viscosity and modulus of the samples wherein a creep stress of 5 Pa ($\mu=0$) was applied was used to estimate the characteristic time scale ($\tau \approx \eta/G$). We observed that the relaxation time computed from the shear viscosity and modulus comes out to be in the range 60–80 s for various samples and is very close to a value of 53 s obtained from the inset of Fig. 4. This observation clearly validates the present protocol quantitatively.

Cloitre *et al.* [4] showed that creep curves at different ages but same creep stress can be shifted to form a master curve. In the present paper we show that creep curves at different stresses and creep times can also be superimposed to form a universal master curve. Furthermore, the shift factor required for time superposition shown here is derived from the expression for the dominating relaxation time [Eq. (2)] proposed by Fielding *et al.* [18]. We believe that the time-stress superposition shown in Fig. 4 is a significant result which can be attributed to the sole dependence of the rheological behavior on the dominating relaxation time which is altered by stress and age. A deformation field or stress retards the structural evolution (or aging) by influencing the activated dynamics. Consequently aging that occurs for a shorter period of time at lower stresses is the same as what occurs for a longer period of time at larger stresses. Therefore one can predict the latter behavior from the short-time test at low stress as shown in Fig. 4.

In conclusion, we have investigated the aging and rejuvenation of soft solids of aqueous suspension of laponite using creep experiments. We observe that the characteristic relaxation time shows a power-law dependence on age. The corresponding power-law index characterizes the extent of rejuvenation such that it decreases when higher stress rejuvenates the system. Significantly, this study shows that when the creep time is normalized with the dominating relaxation mode, which is dependent on age and creep stress, a universal master curve demonstrating time-stress superposition is obtained. We explicitly show that stress plays the same role in soft glassy materials as temperature plays in structural glasses while reversing the extent of aging. We believe that the various features of aging in soft materials discussed in the present paper are generic and can be applied to a variety of soft glassy materials.

[1] E. Donth, *The Glass Transition* (Springer, Berlin, 2001).

[2] D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, England, 2003).

[3] P. Sollich, F. Lequeux, P. Hebraud, and M. E. Cates, Phys. Rev. Lett. **78**, 2020 (1997).

[4] M. Cloitre, R. Borrega, and L. Leibler, Phys. Rev. Lett. **85**, 4819 (2000).

[5] B. Ruzicka, L. Zulian, and G. Ruocco, Phys. Rev. Lett. **93**, 258301 (2004).

[6] V. Viasnoff and F. Lequeux, Phys. Rev. Lett. **89**, 065701 (2002).

[7] M. A. Treece and J. P. Oberhauser, Macromolecules **40**, 571 (2007).

[8] C. Derec, G. Ducouret, A. Ajdari, and F. Lequeux, Phys. Rev. E **67**, 061403 (2003).

[9] Y. M. Joshi, G. R. K. Reddy, A. L. Kulkarni *et al.*, Proc. R. Soc. London, Ser. A **464**, 469 (2008).

[10] P. Hebraud, F. Lequeux, J. P. Munch, and D. J. Pine, Phys. Rev. Lett. **78**, 4657 (1997).

[11] T. G. Mason, J. Bibette, and D. A. Weitz, Phys. Rev. Lett. **75**, 2051 (1995).

[12] L. Cipelletti and L. Ramos, J. Phys.: Condens. Matter **17**, R253 (2005).

[13] P. Bursac, G. Lenormand, B. Fabry *et al.*, Nat. Mater. **4**, 557 (2005).

[14] B. Abou, D. Bonn, and J. Meunier, J. Rheol. **47**, 979 (2003).

[15] R. Di Leonardo, F. Ianni, and G. Ruocco, Phys. Rev. E **71**, 011505 (2005).

[16] H. M. Wyss, K. Miyazaki, J. Mattsson, Z. Hu, D. R. Reichman, and D. A. Weitz, Phys. Rev. Lett. **98**, 238303 (2007).

[17] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Houston, 1978).

[18] S. M. Fielding, P. Sollich, and M. E. Cates, J. Rheol. **44**, 323 (2000).

[19] C. Derec, A. Ajdari, G. Ducouret, and F. Lequeux, C. R. Acad. Sci., Ser. IV Phys. Astrophys. **1**, 1115 (2000).

[20] Y. M. Joshi, J. Chem. Phys. **127**, 081102 (2007).

[21] D. Bonn, P. Coussot, H. T. Huynh *et al.*, Europhys. Lett. **59**, 786 (2002).

[22] L. C. E. Struik, Polymer **38**, 4053 (1997).

[23] G. B. McKenna, J. Phys.: Condens. Matter **15**, S737 (2003).

[24] P. A. O'Connell and G. B. McKenna, Polym. Eng. Sci. **37**, 1485 (1997).