# Thixotropy and Physical Aging in Acrylic Emulsion Paint

**Bharat Baldewa, Yogesh M. Joshi**
*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India*

**In this article we study thixotropic and time-dependent rheological behavior of commercial acrylic emulsion paint using a framework of soft glassy rheology. We observe that acrylic emulsion paint, which shows thixotropic rheological behavior, demonstrates various characteristic features of a soft glassy materials such as weak but certain increase in elastic modulus as a function of aging time, maximum in viscous modulus as a function of strain at the onset of yielding, and slow increase in elastic modulus as a function of frequency. Stress relaxation measurements, subsequent to step strain, carried out at different aging times demonstrate slowing down of the relaxation dynamics. This behavior is similar to that observed in polymeric glasses and other soft glassy materials undergoing aging dynamics. Relaxation modulus when plotted against appropriately rescaled time yields a superposition irrespective of the aging time. The rescaled time also known as effective time, which adjusts the material clock by accounting for increasing relaxation time, enables estimation of the rate of change of relaxation time with the aging time. We conclude by relating thixotropy in an emulsion paint sample to an interplay between physical aging and shear melting in the same. POLYM. ENG. SCI., 51:2084–2091, 2011. © 2011 Society of Plastics Engineers**

## INTRODUCTION

It is a usual observation that an emulsion paint kept for a long duration under quiescent conditions in a container is highly viscous. Painters stir it manually, which gradually lowers the viscosity as a function of time. However, if stirring is stopped, viscosity of the same gradually increases with time. Other than paints, many soft materials of immense commercial importance such as toothpastes, concentrated emulsions and suspensions, colloidal gels, industrial slurries, pharmaceutical and cosmetic creams and variety of soft food items such as jam, jelly, mayonnaise, etc., demonstrate time-dependent evolution of viscoelastic properties that are strongly affected by a deformation field [1–15]. In the rheology literature this behavior is termed as thixotropy [16, 17], and is normally associated with build-up of a structure in these complex fluids under quiescent conditions and break-up of the same under a deformation field. Over last 15 years, there has been a renewed interest in these soft thixotropic materials, as the time-dependent phenomena observed in the same is akin to aging dynamics showed by molecular (including polymeric) glasses [4, 18, 19]. In addition, extension of theoretical frameworks known for molecular and spin glasses to aforementioned soft materials have provided much valuable insight into the understanding of their thixotropic behavior. These materials have been termed as "Soft Glassy Materials" [20, 21], and their spectroscopic, rheological, and theoretical study is considered to provide deeper understanding into the ever perplexing glassy dynamics.

Glasses are out of thermodynamic equilibrium [22–24] due to restricted mobility associated with constituent molecules of the same. It is well known that for temperatures less than glass transition temperature, isothermal annealing of amorphous polymeric materials accompany structural evolution so as to enhance their density slowly as a function of time elapsed since thermal quench [25–28]. Struik was the first to term this phenomenon as physical aging [26, 29, 30]. Aging in glassy materials continues until it reaches the thermodynamic equilibrium state, if it exists, associated with the material at that temperature and pressure. Aging in glassy materials is known to slow their relaxation time as a function of time elapsed since thermal quench. In the absence of any dominating time scale in the glassy materials, relaxation time ($\tau$) of the same is usually observed to be scaling linearly as a function of time elapsed since thermal quench ($t_w$): $\tau \propto t_w^\mu$ with $\mu \approx 1$. In a seminal contribution, Struik proposed a procedure to estimate $\mu$ using an effective time theory [31, 32], which accounts for change in relaxation time to adjust a material clock [26]. This procedure requires carrying out step stress or step strain rheological experiments at different aging times ($t_w$). Appropriate rescaling of time axis leads to a master curve of all the creep or stress relaxation data. The Master curve is also known as time–aging time superposition and a dependence of shift factor on aging time yields a value of $\mu$ [26, 33, 34]. It should

be noted that time–aging time superposition works only if all the relaxation modes age in a similar fashion so that aging time affects only an average value of relaxation times keeping a shape of the spectrum intact [19, 26].

Similar to molecular glasses, many high viscosity soft materials as mentioned earlier are also thermodynamically out of equilibrium due to physical jamming of constituent elements (particles, drops, bubbles, etc.) [4, 35]. In a jammed state, the elements associated with soft glassy materials can be considered to be arrested in physical cages formed by the surrounding elements. This scenario can be represented by considering the caged elements trapped in the energy wells [18, 21]. Under such conditions, a thermal motion of an arrested element is not sufficient to break a cage or jump out of an energy well. Under quiescent conditions, these elements are considered to undergo microscopic motions of structural rearrangements that lower their energy as a function of time elapsed since structural arrest. This phenomenon is typically termed as physical aging in soft glassy materials and is similar to that observed in molecular glasses. However, unlike molecular glasses, where specific volume (or entropy) reduction accompanies aging; which analogous thermodynamic property undergoes aging in soft glassy materials is not clear [19]. Nonetheless, similar to molecular glasses, in the absence of any externally imposed time scale or nonphysical structural evolution, relaxation time of soft glassy materials has been postulated to scale linearly with respect to age of the material. Application of deformation field enhances potential energy of the elements trapped in their respective energy wells. This reduces the energy barrier for them to jump out of the wells [20, 21, 36]. In a soft material, where various elements are trapped in wells having a distribution of energy barriers, the deformation field of a given strength lets the elements trapped in shallower wells to escape, whereas elements trapped in deeper wells continue to age. This induces partial shear melting or rejuvenation of the material, which weakens the dependence of relaxation time on aging time [37, 38]. Similar to observation of time–aging time superposition for molecular glasses, similar superposition is also observed for soft glassy materials [8, 37, 39–42]. Recognizing profound effect of stress field and temperature field on aging in soft glassy materials, time–aging time superposition has recently been extended to include both these variables to demonstrate time–aging time–stress [43, 44] and time–aging time–temperature superposition [45].

In this study, we investigate physical aging behavior of commercial acrylic emulsion paint and also demonstrate its correspondence to the thixotropy. It should be noted that, the term "physical aging" used in this study represents aging akin to glasses and should not be confused with "aging" of emulsions with regard to their stability wherein total number of droplets per unit volume go on decreasing due to coagulation of the same [46]. There are no studies in the literature that investigate physical aging

TABLE 1. Details of emulsion paint.

| | |
|---|---|
| Manufacturer | Kansai Nerolac Paints Limited, Mumbai |
| Brand | Excel Anti Peel Emulsion® |
| Type | Water-based acrylic emulsion |
| Usage | Exterior wall coating |
| Color | White |
| Solid Content | 48% ± 0.03% w/w[a] |
| Application method | Brush, roller |

[a] Solid content was estimated by measuring mass of paint before and after placing the same in an oven at 120°C for 8 h.

behavior of emulsion paints, though there are several reports that observe soft glassy dynamics in concentrated emulsions [47–60], which are also known to show thixotropic behavior [46, 61].

## MATERIAL AND EXPERIMENTAL PROCEDURE

In this study, we have used commercial acrylic emulsion paint manufactured by Kansai Nerolac® (Mumbai). Other details of the paint are described in Table 1.

The rheological measurements were carried out on Anton Paar MCR 501 rheometer in a couette geometry (bob diameter 5 mm with gap 0.2 mm). In quiescent state, emulsion paint has a consistency of paste and is very viscous. A new paint sample was loaded in the couette cell at the beginning of each experiment. To remove any history associated with its condition in the container and that of loading, each sample was pre-sheared (shear melted) under oscillatory flow field with $2 \times 10^5$% strain and 0.1 Hz frequency. Shear melting was continued for 300 s. Aging time of the sample was measured after stopping the shear melting experiment. Preshear or shear melting is necessary to ensure that all the samples have same state before aging. Subsequent to shear melting, viscoelastic evolution of the sample was explored by applying small amplitude oscillatory shear with 0.5% strain amplitude and 0.1 Hz frequency. Aging was continued over the predetermined durations in the range of 600–9600 s before applying various deformation fields. To avoid drying or evaporation of water from a sample, free surface was covered with a thin layer of low viscosity Silicone oil. All the experiments mentioned in this study were carried out at 25°C. A detailed procedure of various experiments performed in this study is schematically represented in Fig. 1.

## RESULTS AND DISCUSSION

Concentrated emulsion paints are thixotropic in nature. To study this behavior, we carried out strain rate sweep experiment on an emulsion paint sample having 9600 s of age (experiments were started 9600 s after stopping the preshear, as described in Fig. 1). In a forward strain rate sweep experiment we increased strain rate as a function of time, whereas in a backward experiment we decreased strain rate in a similar fashion as shown in an inset of
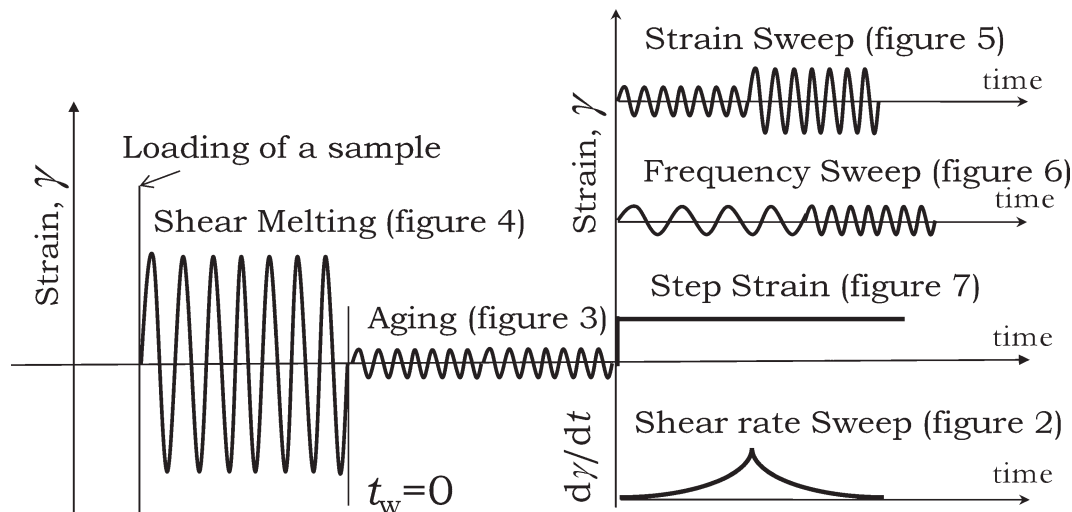
FIG. 1. Schematic of experimental procedure. After loading, sample was shear melted by applying large amplitude oscillatory perturbations. End of shear melting marked the beginning of an aging process, in which we applied small amplitude shear to probe the evolution of elastic and viscous moduli. Aging was carried out for a predetermined duration, and subsequently the samples were subjected to various flow fields as described in the schematic.

Fig. 2. Stress induced in the sample as a function of time in response to applied strain rate is also plotted in the inset. It should be noted that strain rate sweep experiment does not guarantee a steady state. In Fig. 2, we have plotted stress as a function of strain rate in a forward and backward experiment. Overall stress induced in the material is greater in a forward path compared to that in a backward path. This behavior is usually explained in terms of breakdown of structure in a forward path. Since build-up is a slow process, stress induced in a sample with decreased viscosity due to break-up falls below the stress in a forward path. We will revisit this phenomenon from a point of view of a soft glassy rheology later in this section.

We will now investigate acrylic emulsion paint from a point of view of soft glassy behavior. In Fig. 3, we have plotted evolution of elastic ($G'$) and viscous ($G''$) moduli for a shear melted paint samples as a function of aging time ($t_w$). It can be seen that elastic modulus shows a weak but certain increase with respect to aging time ($G' \propto t_w^{0.023}$), whereas viscous modulus remains almost constant. Overall, elastic modulus is significantly greater than viscous modulus suggesting a solid (glassy) like nature of the same. Even though elastic modulus shows only a weak change with aging time, relaxation time of the system shows significant increase with aging time as
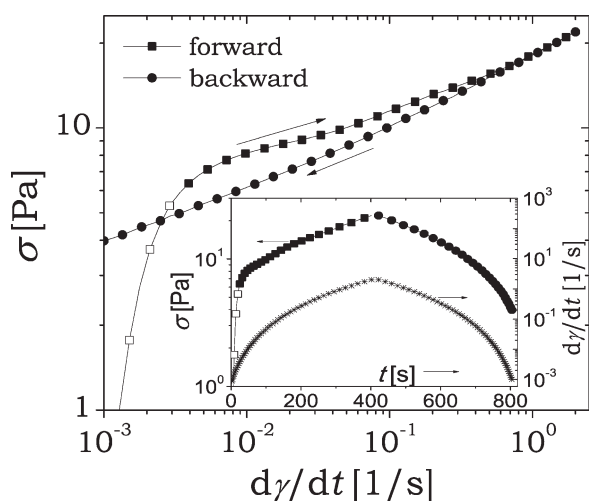
FIG. 2. Strain rate sweep experiment to investigate thixotropic behavior of an emulsion paint sample having 9600 s of age. Strain rate was first increased and then decreased as a function of time as shown in an inset, which also shows shear stress response to applied strain rate. Main plot shows stress as a function of strain rate in a forward and backward experiment. Points showed by open squares in a forward experiment are associated with stress overshoot and are therefore needed to be excluded.
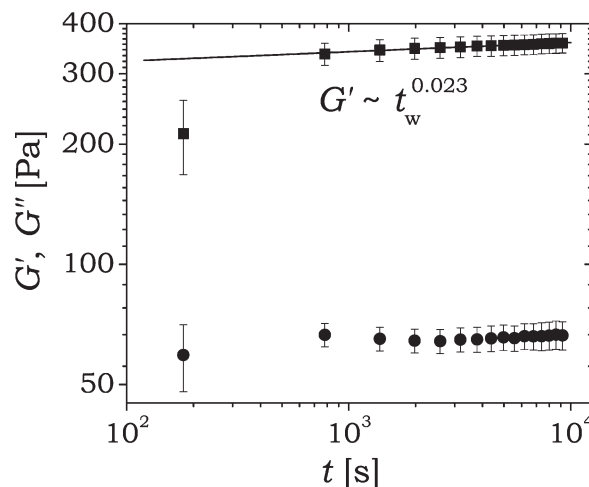
FIG. 3. Evolution of elastic (squares) and viscous (circles) moduli as a function of aging time.
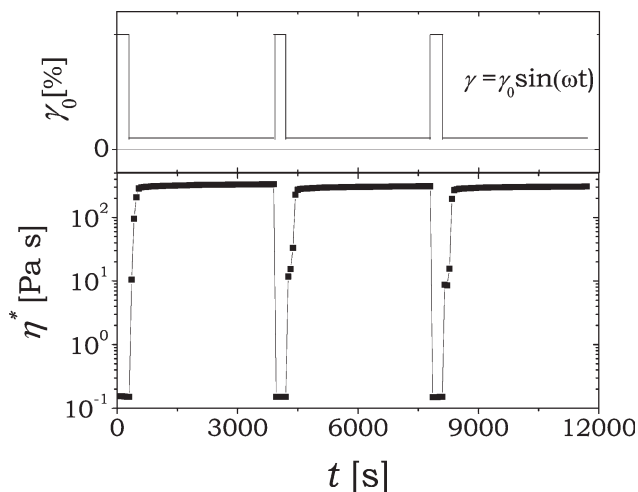
FIG. 4. Subsequent shear melting and aging experiments to study reversibility of aging process. Top part represents strain magnitude of the oscillations. We carried out three repeated experiments with shear melting for 5 min at strain magnitude of $2 \times 10^5\%$ and 0.1 Hz frequency followed by aging for 1 h at 0.5% strain and 0.1 Hz frequency. Bottom part represents behavior of complex viscosity in the shear melting and aging regimes.

discussed later. This behavior is typically known as physical aging and is completely reversible in nature upon pre-shear or shear melting. To demonstrate reversibility in aging dynamics, we carried out shear melting and aging experiments subsequent to each other as shown in Fig. 4. Top part of the figure represents strain magnitude of the oscillations. We carried out shear melting for 5 min at strain magnitude of $2 \times 10^5\%$ and 0.1 Hz frequency, whereas subsequent aging was performed for 1 h at 0.5% strain and 0.1 Hz frequency. We repeated this sequence three times. Bottom part of Fig. 4 represents behavior of complex viscosity in the shear melting and aging regimes. It can be seen that complex viscosity shows almost identical evolution as a function aging time in all the three experiments. In these experiments, shear melting resets
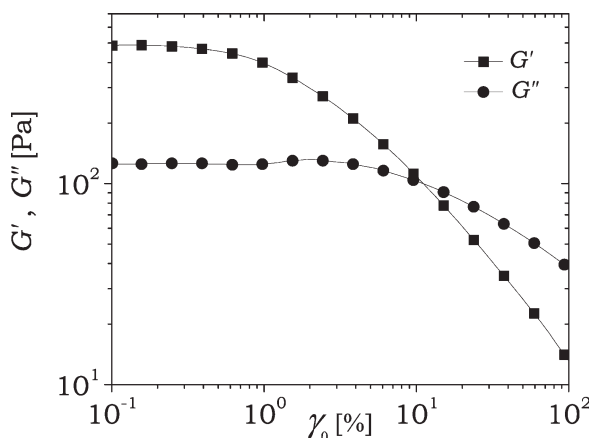


FIG. 5. Elastic and viscous moduli are plotted as a function of magnitude of oscillatory strain having 1 Hz of frequency for a sample having 9600 s of age.
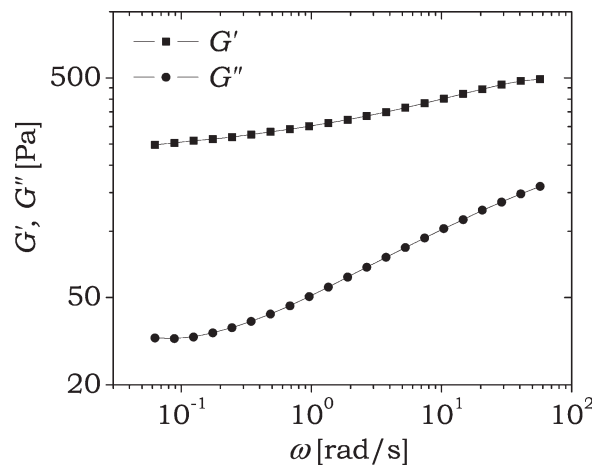


FIG. 6. Elastic and viscous moduli are plotted as a function of angular frequency for strain magnitude of 0.5% for a sample having 9600 s of age.

the material clock and subsequent physical aging starts afresh demonstrating reversible nature of physical aging. Reversibility of physical aging upon shear melting is a characteristic signature of soft glassy materials.

Furthermore, to study the effect of strain amplitude on the material behavior, we carried out strain sweep experiment on a sample having 9600 s of age at frequency 1 Hz. In a strain sweep experiment, we ensured that the total duration of an experiment is significantly smaller than the age of a sample. This protocol guarantees that the aging over a duration of experiment is not significant so as to affect the results, and the experiment indeed represents characteristic behavior at the mentioned age. In Fig. 5, we have plotted $G'$ and $G''$ as a function of strain amplitude $\gamma_0$. It can be seen that for strains below 1%, system is in a linear regime where both the moduli show a constant value. At higher strains elastic modulus decreases, which is accompanied by a small increase in viscous modulus before decreasing. Observation of a maximum in viscous modulus at higher strains, though much smaller in magnitude compared to other soft glassy materials, is considered as a characteristic feature of glassy behavior and suggests enhancement in dissipation while system undergoes yielding. In Fig. 6, we have plotted elastic and viscous moduli as a function of angular frequency for a sample having 9600 s of age. It can be seen that elastic modulus, which is significantly greater than viscous modulus, weakly increases with frequency. Such weak increase in $G'$ as a function of frequency is also a typical glassy character. Viscous modulus, on the other hand, shows stronger increase with frequency than elastic modulus (we are unable to explore very low frequency response due to restriction: experimental time $\ll$ age). Similar increase in $G''$ at higher frequencies has also been reported by Mason and coworkers [50] for a concentrated emulsion in glassy regime. Overall, various linear visco-elastic experiments on emulsion paint system strongly suggest that this system indeed behaves like a soft glassy material.

Subsequent to carrying out aging for a predetermined time ($t_w$), we applied step strain to the sample as shown in Fig. 1. In Fig. 7, we have plotted stress relaxation as a function of time following a step strain of 2% at various aging times. It can be seen that stress relaxes slowly in the initial part of the relaxation. In addition, stress relaxation is faster for the experiments carried out at smaller aging times. Particularly, for a sample having 9600 s of age, stress relaxation is extremely slow over the time explored in this experiment. This behavior suggests that system demonstrates progressively slowing down of the relaxation dynamics (increase in relaxation time), which is also a typical characteristic feature of a glassy behavior. In general, the behaviors observed from all the Figs. 3–7 demonstrate various features, which suggest that the time-dependent phenomena observed in acrylic emulsion paint is indeed a physical aging.

For the systems that are under thermodynamic equilibrium, linear viscoelastic response is represented by Boltzmann superposition principle. For such systems, the response function (in the present case, the stress relaxation modulus) depends only on the difference between the present time ($t$) and the time at which deformation was applied ($t_w$) [in the present case, the step strain]. Stress induced in the material is then given by [62]:

$$\sigma_{12} = \int_{-\infty}^{t} G(t - t_w) \frac{d\gamma}{dt_w} dt_w. \tag{1}$$

Here, $G(t - t_w)$ is relaxation modulus, which is given by:

$$G(t - t_w) = \sum_n G_n \exp\left(-\frac{t - t_w}{\tau_n}\right), \tag{2}$$

where relaxation times $\tau_n$, ($n=1, 2, \ldots$) represent distribution of relaxation times while $G_n$ represent modulus scales associated with $\tau_n$. However, in case of soft glassy systems, the physical behavior of the material depends also on time elapsed since mechanical perturbation. Therefore, the response function for such systems depends not just on the difference between the present time ($t$) and the time at which deformation was applied ($t_w$), but also depends independently on $t_w$ [21, 63]:

$$\sigma_{12} = \int_{-\infty}^{t} G(t - t_w, t_w) \frac{d\gamma}{dt_w} dt_w. \tag{3}$$

Under such circumstances, it is customary to replace the real time scale by an effective time scale ($\xi$) given by [21, 31, 32, 42]:

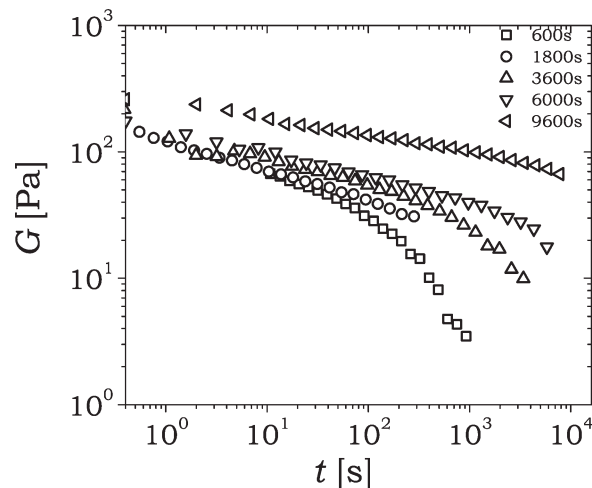$$\xi_n(t) = \tau_0 \int_{0}^{t} \frac{dt'}{\tau_n(t')}, \tag{4}$$



FIG. 7. Stress relaxation modulus subsequent to step strain plotted as a function of time for experiments carried out at various aging times.

where $\tau_0$ is microscopic relaxation time, whereas $\tau_n$ is age-dependent relaxation time. In a modified Boltzmann superposition principle, difference between the real times: $t - t_w$ is replaced by difference between the effective times $\xi_n(t) - \xi_n(t_w)$. The modified relaxation modulus is then given by [21]:

$$G(t - t_w, t_w) = \sum_i g_n\{\xi_n(t) - \xi_n(t_w)\}. \tag{5}$$

For a system whose relaxation mode shows power law dependence on aging time:

$$\tau_n(t') = \tau_0^{1-\mu_n} t'^{\mu_n}, \tag{6}$$

difference in effective times is given by:

$$\xi_n(t) - \xi_n(t_w) = \tau_0 \int_{t_w}^{t} \frac{dt'}{\tau_0^{1-\mu_n} t'^{\mu_n}} = \tau_0^{\mu_n}\left\{\frac{\left(t^{1-\mu_n} - t_w^{1-\mu_n}\right)}{1 - \mu_n}\right\}. \tag{7}$$

However, when all the relaxation modes age in a similar fashion, only a single power law constant $\mu$ determines the aging behavior ($\tau_n(t') = \tau_0^{1-\mu} t'^{\mu}$). Consequently, aging affects only an average value of relaxation times keeping a shape of the spectrum unaffected. Under such conditions, if relaxation modulus is plotted against difference in effective time, various curves irrespective of their age are expected to show a superposition for a unique value of power law constant $\mu$ [19, 26].

To test behavior of emulsion paint in comparison with effective time approach we plotted vertically shifted relaxation modulus shown in Fig. 7 as a function of $(t^{1-\mu} - t_w^{1-\mu})/(1-\mu)$ in Fig. 8. It can be seen that various stress relaxation curves superpose for $\mu = 2.13 \pm 0.06$. The curve belonging to 9600 s of age, however, shows
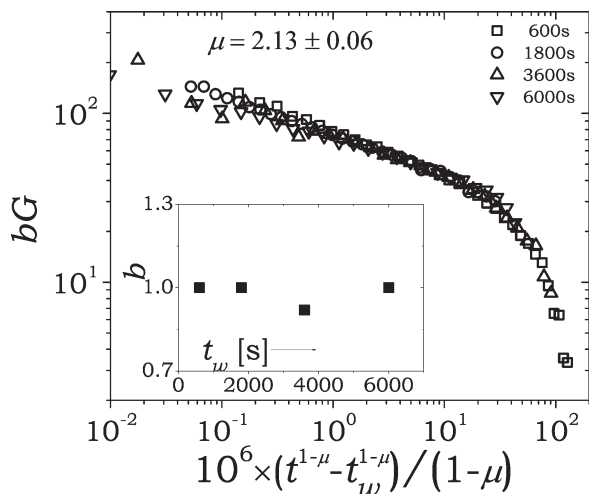
FIG. 8. Time–aging time superposition for the stress relaxation data are shown in Fig. 7. Inset shows vertical shift factor plotted as a function of aging time.

significant deviation from superposition (not shown in figure) because of its very slow relaxation behavior. The possible reasons for deviation could be: variation in aging dynamics for different modes of relaxation time (different values of $\mu$ for lower and higher modes) for this highest age sample and/or uneven rejuvenation of these modes in a step strain experiment at this age. According to *Eq. 6*, power law coefficient $\mu$ represents logarithmic rate of change of relaxation time as a function of waiting time: $\mu = d \ln \tau / d \ln t_w$ and, therefore, suggests that relaxation time evolves as a function of aging time according to: $\tau \propto t_w^{2.13}$. Power law index stronger than linear represents hyper-aging behavior. Although it is not common to see hyper-aging in polymeric materials, many groups have observed hyper aging behavior for soft glassy materials [3, 13, 64]. Importantly, the time–aging time superposition shown in Fig. 8 enables prediction of long time rheological behavior from short time tests in this class of materials. It should be noted that the time aging time superposition shown in Fig. 8 is different from that proposed by Struik as it is not constrained by the Struik protocol wherein only part of the stress relaxation data is used in superposition to ensure that aging does not occur during the experiment. This is a major advantage of the proposed methodology, which uses effective time approach in which the effect of aging during an experiment is incorporated [42].

Finally, it is necessary to understand physical origin of time dependent and/or soft glassy rheological behavior in concentrated emulsions in general and acrylic emulsion paints in particular. In an emulsion, dispersed phase (in case of acrylic emulsion paint, dispersed phase contains acrylic polymer) forms droplets in continuous phase (water). The droplets are stabilized by surfactant molecules. The droplets of the dispersed phase usually have size distribution (unless efforts are taken to have mono-dispersed droplets). In an emulsion paint, size of dis-

persed droplet is in the range of 0.1–10 $\mu m$ [65]. In case of a dilute emulsion, where various drops do not interact (touch) with each other, the preferred shape of a drop is spherical as it minimizes surface area for a given volume and hence is the lowest energy state. However, concentrations above certain critical volume fraction, value of which depends on the size distribution [66], droplets get compressed and acquire a polyhedron type of shape to accommodate dispersed phase in a given volume [54]. This causes caging of droplets by surrounding droplets. These compressed (non-spherical) droplets possess high energy (high surface area than minimum per unit volume) compared to that associated with a spherical shape. In an aging process, various droplets undergo local dynamics of shape rearrangement and try to progressively lower the surface area as a function of time. This phenomenon sets in time dependency in a material wherein relaxation time increases with time. In an aged emulsion, application of deformation field recompresses the drops and progressively reverses the effect caused by aging [50]. Under the application of strong deformation field, system forgets the evolution that it has undergone completely, and starts aging afresh after cessation of shear melting. Since compression of drop requires deformation of the dispersed phase, viscosity and elasticity of the dispersed phase also plays an important role in determining the aging characteristics and viscosity of a concentrated emulsion.

Apart from erasing the physical aging effects, deformation field also causes decrease in viscosity of emulsions [28]. In Fig. 9, we have plotted apparent viscosity ($\sigma/\dot{\gamma}$) as a function of shear rate for a data shown in Fig. 2. It can be seen that shear rate causes significant decrease in apparent viscosity. However, in a direction of shear rate increase, observation of greater viscosity compared to that in the reverse direction is due to aging effects. In a forward path deformation field erases physical aging causing shear melting or rejuvenation of the emulsion paint. Since
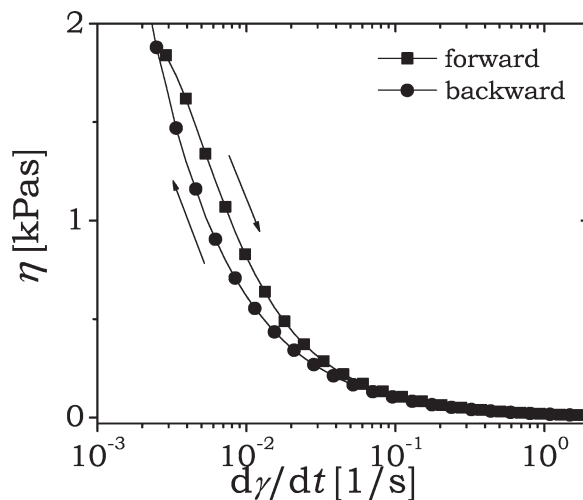


FIG. 9. Apparent viscosity as a function of shear rate for data shown in Fig. 2.

the paint sample does not age back to the same extent during the backward course of the experiment, lesser stress gets induced in the material yielding lower viscosity as observed in Figs. 2 and 9. Interestingly, in an apparent contradiction to present observation, Malkin and coworkers [66] observed that for a highly concentrated water in oil emulsion (91%), application of shear rate sweep (up to 100/s) in a forward and backward direction shows a rheopectic (anti thixotropic) behavior. In a rheopectic response increase in viscosity is observed in a backward course of strain rate sweep experiment. Such behavior is indeed possible if the deformation caused by applied shear rate is not sufficient to rejuvenate or shear melt such highly concentrated system to completely erase the aging dynamics. Similar observation of increase in viscosity and elasticity of soft glassy materials undergoing deformation have been reported in the literature [38, 67] and can originate from aging of those elements which are trapped in deep energy wells and have not been rejuvenated by the applied deformation field [38]. Therefore, this behavior suggests that both thixotropic as well as rheopectic responses are possible in this class of time-dependent materials depending upon strength of applied deformation field.

## CONCLUSIONS

In this article, we study thixotropic and physical aging behavior of commercial acrylic emulsion paint. We observe that acrylic emulsion paint, which shows a typical thixotropic behavior, indeed behaves as a model soft glassy material that undergoes slow structural reorganization as a function of time. Such reorganization, also known as physical aging, leads to enhancement of characteristic relaxation time with respect to time. In addition, the aging dynamics shown by emulsion paint is completely reversible in nature. Application of deformation field reverses the structural reorganization thereby reducing the relaxation time as well as its dependence on time. This system also shows typical additional characteristic features of glassy behavior such as: maximum in viscous modulus as a function of strain at an onset of yielding suggesting dissipation and slow increase in elastic modulus as a function of frequency. Investigation of stress relaxation followed by step strain, carried out as a function of time elapsed since shear melting (aging time), shows faster relaxation for experiments performed at smaller aging times. Overall stress relaxation curves obtained at different aging times superpose after replacing time by an effective time that adjusts the material clock by accounting for the change in relaxation dynamics. Such superposition leads to an estimation of rate of change of relaxation time on aging time. We conclude by drawing analogy between conventional thixotropic behavior and aging and shear melting in soft glassy rheological behavior. Overall, this study provides a new insight into understanding of rheological and otherwise physical behavior of emulsion paints from a point of view of glassy dynamics.

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