Ageing and yield behaviour in model soft colloidal glasses

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We use multi-arm star polymers as model soft colloids with tuneable interactions and explore their behaviour in the glassy state. In particular, we perform a systematic rheological study with a well-defined protocol and address aspects of ageing and shear melting of star glasses. Ageing proceeds in two distinct steps: a fast step of $O(10^3 \text{s})$ and a slow step of $O(10^4 \text{s})$. We focus on creep and recovery tests, which reveal a rich, albeit complex response. Although the waiting time, the time between pre-shear (rejuvenation) of the glassy sample and measurement, affects the material’s response, it does not play the same role as in other soft glasses. For stresses below the yield value, the creep curve is divided into three regimes with increasing time: viscoplastic, intermediate steady flow (associated with the first ageing step) and long-time evolving elastic solid. This behaviour reflects the interplay between ageing and shear rejuvenation. The yield behaviour, as investigated with the stress-dependent recoverable strain, indicates a highly nonlinear elastic response intermediate between a low-stress Hookean solid and a high-stress viscoelastic liquid, and exemplifies the distinct characteristics of this class of hairy colloids. It appears that a phenomenological classification of different colloidal glasses based on yielding performance may be possible.

Keywords: soft colloids; creep rheology; ageing; yielding

1. Introduction

Soft colloidal suspensions have received a great deal of attention lately owing to their importance in widespread applications and recent developments in their theoretical description, synthetic chemistry (obtaining model systems) and physical experimentation (Cates & Evans 2000; Likos 2001; Witten 2004). Typically, they are characterized in reference to much-studied hard-sphere...
suspensions (Pusey & van Megen 1986; Pusey 1991). Here, we are interested in the dense state, where colloids can be trapped to a metastable kinetically frustrated glassy state (Pusey & van Megen 1986; Pusey 1991, 2008; Sciortino & Tartaglia 2005). The viscoelastic properties around the glass transition have been investigated recently for both hard spheres and soft spheres (Mason & Weitz 1995; Cloitre et al. 2003; Crassous et al. 2005; Helgeson et al. 2007; Konmakis et al. 2008; Le Grand & Petekidis 2008; Carrier & Petekidis 2009). Mode coupling theory (MCT) provides a powerful theoretical framework for a variety of colloidal glasses (Cates 2003; Fuchs & Cates 2003; Holmes et al. 2005; Kobelev & Schweizer 2005a, b). Recent experimental work with model colloidal systems explored analogies between hard- and soft-sphere suspensions (Vlassopoulos 2004; Crassous et al. 2005; Gopalakrishnan et al. 2005; Le Grand & Petekidis 2008). Both soft- and hard-sphere suspensions show evidence of caging associated with restricted thermal motion owing to the presence of neighbouring particles, which eventually leads to kinetic arrest at the glass transition (Frenkel 1946; Pusey & van Megen 1987; Cohen & de Schepper 1991; Pusey 1991; van Megen & Underwood 1994). A cartoon representation of caging is illustrated in figure 1 for colloidal glasses made of hard-sphere particles or star-like particles. In the latter case, some interpenetrability owing to the internal structure of these particles (Likos 2001; Vlassopoulos 2004) is possible and marks the difference (inner dynamics) from hard spheres.

The dynamics and rheology of soft colloidal glasses are of particular interest, as they can form the basis for understanding the behaviour of a wide range of systems such as micelles (Buitenhuis & Förster 1997; Watanabe 1997), grafted particles (Derec et al. 2003), soft pastes (Cloitre et al. 2000; Eckert & Bartschbibib20; Meeker et al. 2004), foams (Höhler & Cohen-Addad 2005) and emulsions (Mason et al. 1996). Recently, the onset of yielding, i.e. the critical stress (or strain) value beyond which the colloidal glass loses its macroscopic cohesiveness and flows, has been the subject of intense studies (Petekidis et al. 2002, 2003, 2004; Fuchs & Cates 2003; Höhler & Cohen-Addad 2005; Kobelev & Schweizer 2005a; Möller et al. 2006). The nature of the interactions appears to affect the yielding behaviour (mechanism and magnitude of yielding) as observed with large-amplitude oscillatory shear measurements (Petekidis et al. 2003; Helgeson et al. 2007; Pham et al. 2008). Creep recovery has proved to be a powerful tool for the unambiguous determination of the yield stress and yield strain in hard-sphere colloidal glasses (Petekidis et al. 2004; Pham et al. 2008). Comparison of the experimental yield values of arrested systems with theoretical predictions using MCT of activated hopping MCT appears promising (Fuchs & Cates 2003; Kobelev & Schweizer

Figure 1. Cartoon representation of cages illustrating the topological constraints in the glassy state of concentrated colloidal suspensions. The black neighbouring particles cause the macroscopic arrest of (a) the grey hard spheres and (b) the stars.
Soft colloid ageing and yielding

2005a,b). This methodology has also been applied to study the yielding of glasses from soft colloids consisting of polystyrene latex coated with a thermosensitive poly-N-isopropyl acrylamide (PNIPAM) network (Le Grand & Petekidis 2008).

Ageing is an inherent feature of glassy dynamics (Pham et al. 2004; Cipelletti & Ramos 2005). The trap model first proposed by Bouchaud (1992) introduced some key ideas to describe the possible processes that cause ageing. It was later developed into the soft glassy rheology (SGR) model by Sollich et al. (Sollich et al. 1997; Sollich 1998, 2006). In this model, ageing was accounted for by mesoscopic material elements exploring the free energy landscape and being trapped in progressively deeper traps (Fielding et al. 2000). This process resulted in an enhanced storage modulus over time. On the other hand, mechanical yielding was an activated process caused by a combination of thermal energy and shearing. Recently, Purnomo et al. (2006, 2008) performed a systematic investigation of ageing and glassy dynamics in suspensions of thermosensitive PNIPAM-based particles and demonstrated the ability of the SGR model to capture the main features and differences from hard-sphere glasses.

Ageing phenomena were addressed for a wide range of soft materials, including hard spheres (Cipelletti & Ramos 2005; Martinez et al. 2008), colloid–polymer mixtures (Pham et al. 2004), pastes (Cloitre et al. 2000, 2003), multi-lamellar vesicles (Ramos & Cipelletti 2005), clays (Joshi & Reddy 2008) and nanocomposites (Letwimolnun et al. 2007; Treece & Oberhauser 2007). One of the challenges that emerged from these studies is the identification of universal features and differences among systems in order to develop an appropriate description of the associated phenomena, at least phenomenologically.

In this work, we examine the ageing and yielding of multi-arm star polymers used as model soft colloidal glasses. We explore aspects of their time-dependent rheology and shear melting to identify universal, as well as distinct, features of this system. We compare our results to the literature and other colloidal glasses, especially hard spheres.

When suspended in good solvents, star polymers serve as model soft colloids owing to their monodispersity and well-defined repulsive interactions (Roovers et al. 1993; Likos 2001; Vlassopoulos 2004). Their interactions can be fine-tuned by varying the size and/or number of the star arms, or the suspending medium, concentration and temperature (Likos et al. 1998; Likos 2001). At high volume fractions, these colloidal systems form soft glasses (see also the cage picture in figure 1). Earlier work has demonstrated glass formation (Kapnistos et al. 2000; Helgeson et al. 2007), and linked ageing behaviour to the development of banded structures under steady shear (Rogers et al. 2008). A systematic study of ageing has not been performed thus far. Recently, microgel pastes, which are also established as model colloidal particles with tuneable interactions (based on the suspending environment) (Cloitre 2009), were studied extensively with respect to ageing. The waiting time (i.e. the time elapsing between pre-shear homogenization of the glass and rheological probing) was shown to serve as the scaling parameter (with a certain power law) for collapsing all creep data onto a master curve (Cloitre et al. 2000). Several common features with hard spheres were identified, especially in relation to the scaling of the flow curve and yield stress (Cloitre et al. 2003). In the same spirit, the ageing of a glassy laponite suspension was analysed very recently (Joshi & Reddy 2008), and universal behaviour and validity of time–stress superposition were proposed.
The paper is structured as follows. In §2, a short description of the materials and methods used is given; in §3, experimental results showing the time-dependent rheology of stars are shown. The yielding of these systems as determined by creep recovery is also shown. Comparison of our results to those obtained from hard spheres is carried out, and the unique features of the star solutions are identified. Finally, in §4, we draw the key conclusions.

2. Experimental part

(a) Materials

We used a star polybutadiene-1,4 with nominally \( f = 128 \) arms and arm molar mass \( M_a = 80,000 \text{g mol}^{-1} \), coded as 12880 (the actual values are \( f = 122 \) and \( M_a = 72,100 \text{g mol}^{-1} \)) synthesized by Roovers et al. (1993). It was dissolved in nearly athermal solvent squalene (boiling point 285°C at atmospheric pressure), where its hydrodynamic radius is \( R_h \approx 53 \text{nm} \), as measured by dynamic light scattering. Solutions were prepared by adding the required amount of star to the solvent under gentle prolonged stirring (for the highest concentration, a volatile cosolvent, tetrahydrofuran, was used to facilitate dissolution). An antioxidant (4-methyl-2,6-ditert-butylphenol) was also added at about 0.1 wt% in order to reduce the risk of degradation. Two concentrations were studied, namely 47 and 70 mg ml\(^{-1}\), which correspond to \( 2c^* \) and \( 3c^* \), respectively, with \( c^* \) being the hydrodynamic overlapping concentration.

(b) Methods

Ageing was studied by stress- and strain-controlled rheometry. A TA (formerly Rheometric Scientific) DSR-200 and an Anton-Paar MCR 501 stress-controlled rheometers were used, along with a TA ARES 100FRTN1 strain-controlled unit. Most measurements reported in this work are creep and recovery tests, but we also performed small-amplitude oscillatory shear (dynamic frequency sweeps) and large-amplitude oscillatory shear (dynamic strain sweeps) measurements. All experiments were carried out at 20°C. Temperature control was achieved via a Peltier system or a recirculating water–ethylene glycol mixture. Cone-and-plate geometries were used (diameters 25–40 mm and angles 0.04–0.2 rad), with fixtures made of titanium or invar (nickel–steel alloy). We note that, whereas wall slip may occur during large-amplitude oscillatory shear or nonlinear creep measurements (Russel & Grant 2000; Dullaert & Mewis 2005), with this particular star system, no such issues were encountered (Helgeson et al. 2007). A well-defined pre-shear protocol was used in order to account for the ageing: the samples were first rejuvenated by applying an imposed stress (for creep experiments) or strain above the yield values (\( \sigma_y \) and \( \gamma_y \), respectively). Their viscoelastic properties were then measured after a certain elapsed time. The latter time, which varied from zero to several thousands of seconds, is called the waiting time, \( t_w \). At the end of the measurement (time \( t_r \)), the stress was released and the recovery to quasi-equilibrium was probed. A schematic of the protocol used in creep experiments is depicted in figure 2.
3. Results and discussion

(a) Time evolution of linear viscoelasticity

First, we pre-sheared the samples with large strain amplitude ($\gamma_0 = 100\%$) oscillatory (1 rad s$^{-1}$) shear deformation for 30 s. Subsequently, after a waiting time $t_w = 0$, we performed a long dynamic time sweep experiment where we recorded the evolution of the storage ($G'$) and loss ($G''$) moduli during small-amplitude oscillatory shear deformation (in the linear viscoelastic regime), with $\gamma_0 = 0.05\%$ and angular frequency $\omega = 1$ rad s$^{-1}$. Typical results are depicted in figure 3a for the 47 mg ml$^{-1}$ star solution. One can clearly observe a complex, two-step ageing process, associated with an increase in $G'$ and a decrease in $G''$. As seen in this figure, the first step occurs very rapidly (almost instantly) and leads to a first state of the material (apparent moduli plateau), whereas the second step occurs at much longer times (of the order of $10^4$ s), leading to the second slow state. Such behaviour has not been observed before. It is attributed to the caging of the stars allowing for faster internal cage processes (arms disengagement) and slower cage rearrangement involving the overall star movement (Kapnistos et al. 1999; Helgeson et al. 2007).

We also performed a different kind of ageing experiments in order to assess the frequency dependence. More specifically, we preformed ‘dynamic ageing sweeps’, where dynamic frequency sweeps were performed sequentially on the ageing sample (while maintaining a fixed strain amplitude and frequency range of 100–0.1 rad s$^{-1}$), and dynamic time sweeps were performed between consecutive frequency sweeps. Dynamic ageing sweeps, showing the two-step ageing process for a 70 mg ml$^{-1}$ star solution, are plotted in figure 3a, whereas figure 3b depicts the dynamic frequency sweep data. One can clearly see the evolution of the moduli becoming more pronounced at lower frequencies, and thus the overall change of the linear viscoelastic spectrum with ageing. On the other hand, the sample ages during the course of a frequency sweep measurement. This has consequences on the data as they become age dependent. Hence, we use these results only as supporting qualitative information for the ageing (change of frequency-dependent moduli at different times), although we note that similar studies recently attempted to quantify such results with PNIPAM suspensions (Purnomo et al. 2006).

The increase in $G'$ and the decrease in $G''$ at long times are consistent with an ageing process, for example, the progressive caging of particles in deeper traps as per the SGR model (Fielding et al. 2000; Sollich 2006). However, this model
Figure 3. Ageing studies of glassy stars following a rejuvenation protocol as described in the text. (a) Time variations of storage and loss moduli of the 47 and 70 mg ml$^{-1}$ (the gaps in the latter data correspond to the time when dynamic frequency sweep measurements were performed) star solutions in squalene. The solutions were subjected to an oscillatory strain of amplitude $\gamma_0 = 0.05\%$ and frequency $\omega = 1$ rad s$^{-1}$. (b) The loss $G''$ (filled points) and the storage $G'$ moduli (unfilled points) versus frequency at 70 mg ml$^{-1}$ concentration. Different curves reflect measurements initiated at different times (indicated in the inset) from the end of the rejuvenation ($t_w = 0$). The arrows indicate the time evolution of the curves.
Figure 4. Dynamic strain sweep test to characterize yielding. Data are shown for a 47 mg ml$^{-1}$ star solution at 1 rad s$^{-1}$. The yield point is determined from the change of slope between the low-strain and high-strain regions of the strain–stress curve. The values of the slopes $\mu$ and $\nu$ are $-1.31$ and $-0.63$, respectively. The vertical arrows indicate the end of the linear regime (strain $\gamma_c$), the onset of (viscoplastic) yielding (strain $\gamma_y$) and complete fluidization, that is, liquid-like response (strain $\gamma_f$) as discussed in the text.

(or any other known to us) does not predict the two time regimes governing the ageing of this system, as already discussed (Bandyopadhyay et al. 2006; Sollich 2006; Zondervan et al. 2008). With reference to figure 3a, we note, in the second slow regime, that the moduli evolve gradually through the longest times measured (up to $3 \times 10^4$ s), indicating that the star samples continue to age. It is interesting to note that a similar two-step evolution (albeit more complex owing to nonlinear response) was also observed in stress transients at given shear rates (Beris et al. 2008; Rogers et al. 2008).

(b) Characterization of shear melting

A common way of characterizing complex fluids is the dynamic strain sweep test (Hyun et al. 2002, 2003). This not only indicates the limits of linear viscoelastic response (strain-independent moduli), but also identifies the solid-to-fluid transition, say in a colloidal glass. Therefore, the yield stress and strain can be determined. This methodology has been used to investigate complex yielding in a variety of glassy colloids, colloid–polymer mixtures and stars (Petekidis et al. 2003; Helgeson et al. 2007; Pham et al. 2008). Here, we report a few indicative studies as a means of characterization of the star glass (e.g. figure 4 for a 47 mg ml$^{-1}$ star solution in squalene). We pre-sheared the sample using the above-mentioned protocol with a waiting time in the range of 500 s, which corresponds to the first ageing step as per figure 3a. Then, we varied the strain amplitude at constant frequency (1 rad s$^{-1}$) and observed the different regimes of
the glassy suspension: at low strains, \( G' > G'' \) and both moduli are independent of strain, and hence the stress–strain relationship is linear (Cloitre 2009). The end of the linear regime is marked by the critical strain \( \gamma_c \) in figure 4. Upon entering the nonlinear regime (\( \gamma_0 > \gamma_c \) in figure 4), \( G'' \) increases progressively with increasing \( \gamma_0 \) and goes through a maximum, whereas simultaneously \( G' \) decreases. The peak in \( G'' \) coincides with the transition from solid-like to liquid-like response at the specific frequency. One can determine the onset of yielding at this peak (Helgeson et al. 2007), but for this particular situation (\( \omega = 1 \text{ rad s}^{-1} \)) this is the onset of complete fluidization with respective stress and strain values as \( \sigma_f = 25 \text{ Pa} \) and \( \gamma_f = 9\% \). In the fully fluidized regime, \( G'' \) and \( G' \) achieve a fixed \( \gamma_0 \) dependence. In fact, the ratio of the slopes of \( G'' \) and \( G' \) (identified as \( \nu \) and \( \mu \), respectively, in figure 4) is 2, although the slopes appear to be concentration dependent (Helgeson et al. 2007). These features are predicted almost quantitatively by the SGR model (Sollich 1998) and other phenomenological or MCT-based approaches (Derec et al. 2003; Miyazaki et al. 2006; Carrier & Petekidis 2009). Note, however, that deeper into the glassy state (higher star concentration or different age times), the yielding response may be more complicated (Helgeson et al. 2007). Figure 4 also depicts the corresponding total stress as a function of strain. The change of slope in the stress–strain curve marks the viscoplastic yield point (Pham et al. 2008) associated with the rapid decrease in \( G' \) with strain and a power-law stress–strain relationship. Note that the transition from linear to power-law relationship is not always as clear as indicated by the sharp change of slope in figure 4. For example, in microgels, this transition is gradual and occurs over a range of strain amplitudes (Cloitre 2009). For the particular example of figure 4, the characteristic yield values are \( \sigma_y = 10 \text{ Pa} \) and \( \gamma_y = 4\% \).

(c) Analysis of yielding using creep and recovery data

An alternative, robust way to determine the yield stress consists of performing creep measurements at different stresses (2–50 Pa), with the same duration (\( t = 200 \text{ s} \)) and rejuvenation protocol. The latter involved pre-shearing of the sample at 100 Pa for 50 s and \( t_w = 0 \). Figure 5a depicts typical results for the 70 mg ml\(^{-1}\) star sample in the form of time-dependent accumulated strain during creep, whereas the respective time-dependent shear rate is shown in figure 5b. One can observe that, throughout the duration of the creep test, the material keeps on creeping for \( \sigma < 10 \text{ Pa} \), whereas it achieves a steady state under larger stresses. From these figures, the yield stress corresponding to constant shear rate appears to be in the range 20–30 Pa.

Creep recovery tests can serve as another unambiguous measure of yielding and eventual flow of a solid-like suspension (Rehbinder 1954; Zosel 1982; Ketz et al. 1988; van der Aerschot 1989; Chen & Zukoski 1990; Uhlherr et al. 2005; Tiu et al. 2006). Actually, this was demonstrated recently in a systematic study of glassy hard-sphere suspensions, where the recovered strain upon cessation of flow exhibited a linear dependence on applied stress in the subyield region and was independent of stress in the post-yield region (Petekidis et al. 2004). This behaviour was rationalized by invoking the cage picture: in the low-stress elastic regime, the slope of the strain–stress curve is the inverse storage (plateau) modulus of the glass, whereas the constant strain in the high-stress fluid regime is the maximal elasticity of the entropic cage before it breaks and the glass melts under...
Figure 5. (a) The time dependence of the strain, $\gamma(t)$ (%), in linear representation, achieved during a creep experiment of a star 70 mg ml$^{-1}$ solution, for several stresses. (b) Respective double logarithmic plot of shear rate against time. (c) Time dependence of the recovered strain $\gamma_r$ (%) after the applied stress is removed, for the same stresses, in linear representation.
Figure 6. Two characteristic instantaneous recovered strains as functions of stresses. The squares show the measurements at $2c^*$ concentration (47 mg ml$^{-1}$), where, at each creep test, the pre-shear stress was 100 Pa and the waiting time was equal to 200 s. The yield stress is about 10 Pa and the yield strain is about 6.5%. The elastic modulus in the linear low-stress regime is $G' = 266$ Pa. The triangles show the measurements at $3c^*$ concentration (70 mg ml$^{-1}$), where, at each creep test, the pre-shear stress was 200 Pa and the waiting time was equal to 200 s. The yield stress is about 40 Pa and the yield strain is 12%, whereas $G' = 341$ Pa. The arrows indicate the characteristic stresses ($\sigma_c$, $\sigma_y$ and $\sigma_f$) (discussed in the text) for the 70 mg ml$^{-1}$ case.

Shear. Thus, the crossover point determines the yield stress and yield strain of the suspension. Figure 6 shows, with dashed lines, a typical yielding behaviour for a hard-sphere suspension at a volume fraction of 0.62 (Petekidis et al. 2004). In the same figure, we present instantaneous recovered strain data as a function of the applied stress for the two star systems studied (note that the results are essentially identical if instead of the instantaneous recovered strain at $t = 30$ s, we plot the long-time recovered strain at $t = 2000$ s).

Let us discuss these results in more detail. At low stresses, the recovered strain ($\gamma_r$) evolves linearly with stress. This is the elastic Hookean regime where $\delta\gamma_r/\delta\sigma \cong 1/G'$. Values for $G'$ calculated in this manner stand in excellent agreement with the linear viscoelastic data of figure 3. Then, in contrast to glassy hard spheres, where a strain plateau is reached (maximum elasticity of the cage), star solutions exhibit a pronounced nonlinear regime, which characterizes the transition of these soft colloidal glasses from the ideal elastic to the fluid state. We attribute this to the softness of the stars and in particular to their interpenetrability and deformability upon stress, which results in an intermediate regime of viscoplastic solid that eventually becomes a viscoelastic fluid by breaking into pieces via disengagement of the stars (which corresponds to their maximum stretching). Note that such complex creep recovery curves have been reported for other...
systems with soft interactions or attractions such as grafted particles (Le Grand & Petekidis 2008) or attractive colloidal glasses (Pham et al. 2008). This appears to be a useful method to distinguish hard-sphere glasses from other colloidal glasses. Taking as an example the 70 mg ml\(^{-1}\) star solution, one can identify three regimes in stress: at low stresses there is a linear elastic regime that extends up to a stress value of \(\sigma_c\), signifying the onset of a nonlinear response (note that the \(\sigma_c\) and \(\gamma_c\) values of the 47 mg ml\(^{-1}\) star are very similar to those determined from the dynamic strain sweeps of figure 4). The nonlinear regime extends up to the recovered strain plateau, which is also identified by \(\sigma_f\), signalling the Newtonian flow of the glass. The crossover of the initial linear elastic and the terminal flow regions (shown in figure 6 with the extrapolated lines) marks the yielding of the star glass (\(\sigma_y\)). At this point, the material exhibits a transition from viscoplastic to viscoelastic.

Interestingly, the nonlinearity in transition region (convex nonlinear curve) indicates an increasing apparent modulus (ratio \(\sigma/\gamma\)), and this is attributed to enhanced interpenetration of the stars via outer blobs (Seghrouchni et al. 1998; Helgeson et al. 2007). On the other hand, for non-interpenetrating but deformable soft particles, such as PNIPAM-coated latex particles studied recently, the concave curve suggests a reduced apparent modulus, possibly owing to overall particle deformation (Le Grand & Petekidis 2008). Even more complex is the response of attractive glasses because of the particle bonding induced by the added polymer (Pham et al. 2008). It is tempting to consider this nonlinear regime as a phenomenological classification of different types of colloidal glasses based on deformability and corona penetration. Note, however, that the present study does not attempt to contribute to the discussion of different types of yield stresses (Bonnecaze & Brady 1992), although the present analysis (onset of incomplete recovery) appears close to the static yielding.

One may also note that the nonlinear transition region is much more pronounced for the 70 mg ml\(^{-1}\) stars solution compared with the 47 mg ml\(^{-1}\) one. The former is a more elastic glass, and the disengagement and cage escape processes require more mechanical energy. Not unexpectedly, there is a connection between the creep recovery and strain sweep data. If we consider the 47 mg ml\(^{-1}\) star glass, the yield stress is hardly distinguished from that of the onset of complete fluidization (about 10 Pa), whereas the corresponding strain is 6.5\%, which is in good agreement with the viscoplastic \(\gamma_y\) value from the strain sweep test (figure 4).

\[(d)\] Long-time creep without waiting time

Focusing on ageing, we performed creep measurements of very long duration (\(2 \times 10^4\) s) at different stresses below the yield value. The protocol used consisted of pre-shearing the sample at 100 Pa for 30 s and \(t_w = 0\). Figure 7 depicts typical results for the 47 mg ml\(^{-1}\) star sample. One can note some fluctuations in the creep response at early times. This ringing phenomenon is due to the inertia of the system and can be accounted for (Coussot et al. 2006), as shown in the upper inset of figure 7a. The pre-yield glassy sample creeps for a long time. In the region between 100 and 1000 s, it appears that a constant creep slope has been reached, represented by a constant shear rate (figure 3b), signifying an intermediate flow regime. This is more pronounced for the higher applied stress. However, at times
Figure 7. Creep behaviour for a 47 mg ml\(^{-1}\) star solution at different applied stresses \(\sigma < \sigma_y\) (from top to bottom: 7, 6, 5, 4, 3 and 2 Pa). Graphs (a) and (b) show the variations of the strain and shear rates with time, respectively. Inset of figure 7a: a detail of the early-time ringing behaviour for \(\sigma = 4\) Pa (see text). Symbols are data and the solid line is the prediction from which the plateau modulus \(G'\) is extracted (Coussot \textit{et al.} 2006).
Figure 8. Onset of long-time apparent strain plateau $\gamma_{\text{onset}}$ (squares) and respective time $t_{\text{onset}}$ (triangles) during creep as a function of applied stress for two star concentrations: 47 mg ml$^{-1}$ (filled symbols) and 70 mg ml$^{-1}$ (unfilled symbols). Lines are drawn to guide the eye.

exceeding 5000 s, the slope is dramatically reduced and one can claim that an apparent plateau in strain is reached (figure 7a), or equivalently a drastic drop in the corresponding shear rate (figure 7b), indicating that the material becomes a glassy solid. This apparent plateau regime is reached after creeping for a long time and accumulation of strain of the order of 1000%. This situation reflects the interplay of ageing with shear rejuvenation, which relates to thixotropy (Mewis & Wagner 2009). Here, such interplay nearly results in a standstill of the sample under stress. However, it is important to note that, even in this long-time region, the material is not in equilibrium and properties evolve with time, i.e. the material ages. The onset of the long-time apparent strain plateau regime is marked by a characteristic time ($t_{\text{onset}}$) and strain ($\gamma_{\text{onset}}$), which was crudely estimated by the intersection of the lines through the long-time apparent strain plateau and the long-time creep (up to 5000 s in figure 7a). Their dependence on applied stress ($\sigma < \sigma_y$) is depicted in figure 8. Concerning $t_{\text{onset}}$, for a given stress, this time is clearly longer for the higher concentration star, a result that we attribute to the fact that densification leads to longer caging times, as well as to the internal modes (stronger interpenetration) that allow for longer creep before the solid-like state is reached. This could be related to the arm engagement of the stars. On the other hand, the increase in $\gamma_{\text{onset}}$ with stress reflects the similar behaviour of the first (short-time) apparent strain plateau (proportional to the applied stress). Note that the higher values of $\gamma_{\text{onset}}$ for the higher concentration star clearly reflect the higher accumulated strain, in harmony with the longer $t_{\text{onset}}$ results.

(e) Effects of waiting time on creep response

Since an important measure of ageing is the waiting time, we used the above pre-shear protocol and varied the waiting time while keeping the applied stress constant at a subyield value (for the 47 mg ml$^{-1}$ star presented here,
Figure 9. Effect of waiting time on creep properties for a 47 mg ml$^{-1}$ star solution at $\sigma = 8$ Pa$<\sigma_y$. (a) Creep strain as a function of the actual measurement time $t - t_w$, for different $t_w$ values (top to bottom: 1, 10, 100, 1000 and 2000 s). Inset: respective data for $t_w = 2 \times 10^4$ s. The horizontal arrow indicates the extent of the first ageing state in figure 3a. (b) The same data plotting apparent shear rate versus time.

we used 8 Pa). This experimental procedure allows us to account for the effects of $t_w$ and provide a framework for comparing stars against other soft colloidal glasses that were subjected to the same analysis. The results are compiled in figure 9a,b. By simple inspection, one can clearly distinguish three time regimes in the creep curves.
In the early time regime, extending up to $t \approx 100$ s, there is a clear effect of $t_w$ on creep, and the material exhibits viscoplastic behaviour with continuous creeping. The intermediate regime is characterized by a steady-flow behaviour (constant shear rate in figure 9b) and, eventually, an elastic regime, at very large values of strain, governs the material’s behaviour at long times and becomes more pronounced as the waiting time increases. The intermediate fluid-like behaviour scales with $t - t_w$ (Erwin et al. submitted), but the overall creep curve does not, and does not follow the scaling of Struijk (1978) that was shown to work for polymer glasses and also for microgel pastes (Cloitre et al. 2000). Note, however, that application of a small stress to stars may induce local topological rearrangements (partly accommodated by the fluctuating arms ends), whereas in microgels, it induces deformations that accumulate. By comparing figures 9 and 3, one can observe that this intermediate flow regime corresponds to the first (faster) of the two ageing states in this particular star concentration (extending to about 2500 s). This is indeed a regime where, after the end of shear rejuvenation, the stars are caged and interpenetrated, but cages are weak and can break thermally rather fast, giving rise to fluid behaviour as seen in figure 9 (Helgeson et al. 2007; Erwin et al. submitted); in such a cage, the detectable relaxation time rather than the waiting time is the relevant scaling parameter. At longer times, the cages rearrange and form a strong solid (figure 7) that ages in a similar fashion to colloidal hard spheres or microgels (figure 9). In such a situation, the stars are considered to be trapped in the deeper traps of the caged glass (Bouchaud 1992). We speculate that the elasticity of the stars (which could be deformed in their cages in the first ageing state) may play a role in the transition to the strong solid state. At this point, a comparison with hard spheres is useful. Although a complete set of creep measurements at different waiting times is not currently available, preliminary long creeps below the yield stress after a similar shear rejuvenation protocol in hard-sphere glasses reveal a gradually solidifying system (with diverging effective viscosity), in agreement with the present findings in multi-arm star glasses (N. Koumakis, A. Le Grand & G. Petekidis 2009, unpublished data). It thus appears that the interplay of shear with sample ageing might be generic in soft glasses (Møller et al. 2006). However, particular aspects of the system response, such as two-step ageing and the associated intermediate flow regime independent of waiting time (figure 9), might be unique features of star-like colloids.

Note that, recently, similar regimes were observed in commercial yield stress fluids and, in particular, the transition from the early to the intermediate regime was discussed (Caton & Baravian 2008). It was marked by a local minimum in shear rate versus time (which can be also seen in figure 9b) and the corresponding ‘transition time’ was found to be a universal function of the applied stress.

Figure 10 depicts the effect of $t_w$ on the long-time onset of apparent strain plateau $\gamma_{\text{onset}}$ and the respective $t_{\text{onset}}$ (or end of shear-rate plateau of the intermediate fluid region) for the two star samples investigated. One can note that, at long waiting times (above 500 s), the apparent modulus ($\delta \sigma/\delta \gamma_c$) increases. Moreover, for $t_w > 10^3$ s (corresponding to the transition from the first to the second slow ageing state), $t_w$-dependence of $\gamma_{\text{onset}}$ and $t_{\text{onset}}$ is observed. This appears to be consistent with the overall different behaviour of the two ageing states.

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Figure 10. Onset of long-time apparent strain plateau $\gamma_{\text{onset}}$ (squares) and respective time $t_{\text{onset}}$ (triangles) as a function of $t_w$ for two star samples: 47 mg ml$^{-1}$ (filled symbols) and 70 mg ml$^{-1}$ (unfilled symbols).

Figure 11. Effects of the creep measurement time protocol on the stress-dependent recovered strain behaviour for the two star solutions in squalene: 47 mg ml$^{-1}$ (squares) and 70 mg ml$^{-1}$ (triangles). Unfilled symbols refer to $t = 200$ s and filled symbols to $t = 2 \times 10^4$ s.

The ageing results presented here strongly suggest that a complete understanding of the time-dependent glassy dynamics of soft colloids is not yet reached. In fact, a universal picture is not emerging. The different behaviour between stars and microgels (Cloitre et al. 2000) with respect to $t_w$ scaling...
is indeed intriguing and is attributed to the different ways of packing in the dense state (star interpenetrability provides an additional mechanism that is absent in the microgels, as well as in hard spheres). Note that recent work on micellar block copolymer suspensions with vastly reduced interpenetrability (owing to internal structure of the corona) suggests that Struik’s scaling works, albeit with a different scaling exponent compared with microgels (Merlet-Lacroix 2008).

In closing, we wish to address the effect of time on the stress-dependent instantaneously recovered strain. In figure 6, the yield behaviour was studied by reporting the recovered strain after creeping for 200 s. Figure 11 depicts respective data obtained after creeping for $2 \times 10^4$ s. Whereas data are only available in the low-stress linear region, it is clear, at least for the 47 mg ml$^{-1}$ solution, that the obtained $\gamma_t$ is decreased in the latter case and the extracted plateau modulus increased, consistent with the ageing of the sample. The available data for the 70 mg ml$^{-1}$ solution do not exhibit any creeping time effects.

4. Conclusions

Colloidal star glasses age over long times in a way that is different from that of hard spheres or other soft colloidal particles, especially with respect to the scaling of viscoelastic properties with waiting time. Ageing proceeds in two distinct steps, a fast step that extends for up to about a few thousands of seconds and a slow step that extends for tens of thousands of seconds. For stresses below the yield value, three creeping regimes are observed with increasing time: viscoplastic, intermediate steady flow (that is linked to the faster ageing step) and long-time evolving elastic solid. The long creep behaviour reflects an interplay between ageing and shear. The yielding of these soft glasses is also distinct and characterized by a nonlinear (viscoplastic to viscoelastic) region between the linear elastic and the terminal Newtonian, as the applied stress increases. Although not yet properly quantified, arm interpenetration and the associated internal cage dynamics of the stars appear to be the key for rationalizing the observed differences.

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