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Yielding in Surfactant Suspension Pastes: Effect of Surfactant Type

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Abstract In this work, we study the rheological properties and the yielding behavior of cleaning pastes containing surfactant and abrasive particles, for three different types of surfactants, namely linear alkyl benzene sulfonate (LAS), alpha olefin sulfonate (AOS) and sodium lauryl ether sulfonate (SLES). All the pastes were observed to have soft solid-like consistency with their elastic modulus significantly greater than the viscous modulus. With around 36 volume percent of particulate matter, the high stiffness of the pastes suggests that particles form a space spanning network. Interestingly, when subjected to oscillatory shear deformation with increasing strain amplitude, the elastic modulus undergoes a decrease in two steps thereby showing a two-step yielding behavior. It is observed that the first yield stress does not show frequency dependence, and for LAS-containing paste was the largest followed by AOS- and SLES-containing pastes, respectively. The second yield stress, on the other hand, for all the three pastes is observed to increase with frequency. Careful assessment of the experimental data suggests that the first yielding event is due to rupture of the network which leads to formation of particulate aggregates. The second yielding event is attributed to breakage of aggregates. In both yielding phenomena, surfactants play an important role. Since, the phase behavior of surfactant in water determines the inter-particle interaction and network density, the nature of surfactant has a pivotal influence on both the yielding phenomena in surfactant suspension pastes used for cleaning purposes.

Introduction

Many commercial products with soft solid like consistency such as toothpastes, soaps, pharmaceutical and cosmetic creams, paints, shaving foams, etc., are composed of multicomponent colloidal mixtures with complex inter-particle interactions [1, 2]. Typically such products contain mixtures of surfactants and solid particulate matter including clays, salts, polymers, etc., in aqueous or organic media. While some of the constituents contribute towards efficacy associated with an intended application, the others are added to render a material stability against phase separation, sedimentation, creaming, and/or adverse thixotropic effects. One of the most common rheological behaviors associated with this class of materials is the presence of a yield stress, wherein a material does not flow (or undergoes extremely slow flow) below a critical stress [3, 4]. The presence of a yield stress in a material is useful for many applications, where the flow is not intended at small stresses (or under its own weight), and for ease of transportation and packaging. Interestingly it has been observed lately that many materials demonstrate multiple yielding transitions, which has been attributed to presence of hierarchy of micro-structures over different length-scales or time scales [5–12]. Such multiple yielding events

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indeed affect the processing and the conditions associated with the intended applications. Therefore there is a demand for better understanding of the same with respect to nature of the constituents of a material.

Soft materials show a yield stress if the constituents, particularly the particulate matter, experience restricted mobility due to physical or energetic cages [2–4]. Consequently, stresses smaller than a critical stress cannot induce flow in a material. On the other hand, above a critical stress a cage or the arrested structure breaks down to facilitate flow. Experimentally yield stress can be measured by using variety of techniques, which include application of increasing and decreasing ramp of linear or oscillatory shear stress, squeeze flow, and various non-viscometric methods employed industrially [13]. Out of these, oscillatory measurement techniques are usually preferred as they provide a better control over strain inducement in a material and lead to clear demarcation between linear and non-linear (yielded) viscoelastic regime. Typically in an oscillatory experiment, in the limit of small stresses or strains, the elastic modulus (G') and viscous modulus (G'') remain constant such that $G' > G''$. At a critical stress, which we represent as a yield stress, G' decays over a very narrow range of stress and G'', on the other hand, shows a maximum before decreasing. The maximum in G'' depends on frequency, which independently controls the deformation timescale applied to a material [14].

Many materials with a soft solid-like consistency exhibit a two-step decay in G' when subjected to an oscillatory stress sweep. This behavior has been termed two-step yielding [5–12]. While the first yielding (or decay in G') indeed indicates transition from no/slow flow to moderate flow, the second yielding event represents breakdown of a 'certain' structure over a narrow range of stresses. The second yielding event therefore can be considered as a moderate flow to strong flow transition. The two-step yielding has been observed for a variety of systems including carbopol microgel with attractive interactions [6], suspensions with anisotropic particles [7], suspension of polymeric particles with hard sphere as well as attractive interactions [8, 11], magnetorheological systems [9], bi-disperse particulate suspension [10], hard sphere colloidal glasses [12], etc. The various rheological characteristics associated with the observed experimental behavior of these systems have been recently reviewed [5]. A common origin of all the two-step yielding behaviors appears to be the presence of structure over two distinctly different length-scales or the presence of two dominant well-separated structural timescales that cause decay in G' in multiple steps. Similar to the observation of multiple yielding events as a function of magnitude of strain, multiple yielding as a function of time under application of constant

stress magnitude have also been observed [15, 16]. Very recently Gibaud *et al.* [16] reported multiple yielding process in the colloidal gels of carbon black, wherein it undergoes enhancement in fluidity in multiple steps over time when subjected to constant amplitude oscillatory stress. The authors analyze the behavior using ultrasonic imaging technique.

Recently our group studied the yielding behavior of surfactant suspension paste containing around 36 vol% particulate matter including abrasive particles of calcite and clay [5]. The paste contained mixture of two anionic surfactants namely linear alkyl benzene sulfonate (LAS) and sodium lauryl ether sulfonate (SLES). Even though the total concentration of surfactant mixture (LAS 12 % and SLES 2 %) was only 14 wt%, when normalized with respect to water, the concentration becomes 56 wt% for LAS and 9 wt% for SLES. In addition to the surfactants and water, the paste had ~ 6 wt% of sodium carbonate. While the phase diagram for this surfactant mixture is not available in the presence of sodium carbonate, consideration of the LAS phase diagram suggests that the isotropic phase coexists with the lamellar phase but is dominated by the latter. The paste had a soft, solid-like consistency with $G' > G''$ in a linear regime irrespective of the frequency. Even though the concentration of particulate matter was only 36 volume %, the soft solid-like consistency suggests abrasive and clay particles formed a space spanning attractive gel network [2, 5]. When subjected to oscillatory flow, with increasing strain or stress amplitude, the paste showed G' to decay in two-steps. It was postulated that the first yielding event was related to a breakage in the attractive network that led to the formation of disconnected clusters flowing in the shear melted continuous media. With an increase in magnitude of strain or stress, these clusters broke causing the second yielding event. Interestingly the stress and strain associated with the first yielding event were observed to be independent of frequency; however yield strain associated with the second yielding event decreased with frequency.

The two-step yielding is expected to be very sensitive to the inter-particle interactions, which influence not only the strength and the extendability of the network before the breakage but also the nature of the aggregates formed after the breakage. It has been observed that presence of micellar surfactant aggregates enhances the attractive interactions among the particles via depletion interaction [17–19]. Consequently, the nature and phase behavior of a surfactant is very crucial in determining interparticle interactions and hence the stiffness of a paste for a fixed concentration of particulate matter. A surfactant reduces oil–water interfacial tension, thereby aiding faster removal of greasy stains. Furthermore, it helps in generating foam, a common visual

cue for efficacy. Owing to its amphiphilic nature, it also binds various constituents of the paste. Moreover depending on phase behavior, surfactant forms different microstructures that help to suspend the abrasive/insoluble particles forming a stable paste. Anionic surfactants are commonly used in cleaning products [20]. However the microstructure in such mixed systems is extremely difficult to analyze. In this work, we study the effect of three different kinds of surfactant LAS, SLES and alpha olefin sulfonate (AOS) at a fixed concentration. These surfactants show different phase behaviors or microstructures in aqueous media. We study the yielding behavior of resultant formulations and analyze the same with respect to the nature of the surfactant.

Experimental

Materials and Sample Preparation

The paste samples used in this work comprise surfactants, abrasive particles (calcite), sodium carbonate, alumino-silicate (Sigma Aldrich, LR), kaolin clay (Dhirajlal and Co, India) and deionized water. Three types of surfactants have been used in this work, namely linear alkyl benzene sulfonate (LAS, Rhodia Surfactants), sodium lauryl ether sulfate (SLES, Galaxy Surfactants, India) and alpha olefin sulfonate (AOS, Godrej Surfactants, India). In a formulation, the abrasive particles enhance the cleaning process by acting as a scrubber. All the other ingredients help either as structurants or as rheology modifiers. LAS acid, which is an acidic precursor, was neutralized by NaOH and resultant Na-LAS is used as the surfactant. Although LAS has been termed to have a linear alkyl chain, industrial samples tend to have batch to batch variation with a typical 10 % variation in alkyl chain configuration [21]. The other two surfactants: SLES and AOS, which are commercially available in a neutralized form, were used as purchased. The calcite (specific gravity of 2.7 and Mohs hardness of 3 [22]) used in this work has a particle size in the range 0.6–1905 μm. The volume weighted mean diameter of calcite, which is defined as $D_{4,3} = \sum_i n_i d_i^4 / \sum_i n_i d_i^3$ (n_i is the number of particles having diameter d_i) is 87 μm. The surface of these particles was observed to be rough with sharp edges [5].

In this work, three types of samples have been prepared with identical content except the type of surfactant. The samples were prepared in accordance with the existing protocol present in the literature [5, 23–26], wherein surfactant was initially mixed with water for 5 min at 50 rpm using an overhead stirrer. Subsequently calcite, kaolin clay, sodium carbonate and alumino-silicate were added to the same and

stirred for further 5 min. The temperature of 25 °C was maintained during the mixing. The resultant paste was then stored in an airtight container. The samples were labeled as LAS, SLES and AOS depending upon surfactant used to prepare the respective samples. The typical formulation contains (all concentrations in weight %) 9 % surfactant, 45 % calcite, 8 % kaolin clay and 7 % other ingredients (sodium carbonate and aluminosilicate) and remaining water. In the case of LAS surfactant, equimolar NaOH is added to LAS acid to form 9 wt% of Na-LAS. The volume fraction of solid particles in an each system is ∼36 %. It should be noted that in our previous work we used 14 % surfactant (12 % LAS + 2 % SLES) [5]. In the present work, we study the effect of surfactant type.

The rheological experiments were conducted using an Anton Paar MCR 501 rheometer with a Couette shear cell (cup diameter 10.818 mm with gap of 0.407 mm). Before starting the experiments, the shear cell was filled with the paste sample ensuring no entrapment of air bubbles. After loading, in order to erase any shear history, a sample was subjected to shear melting for 10 min by applying oscillatory strain of 10,000 % at a frequency of 0.628 rad/s. Subsequent to shear melting the following experiments were carried out. In a time sweep experiment (also called aging experiments) a sample was probed using a small amplitude oscillatory strain ($\gamma = 0.1$ %, $\omega = 0.628$ rad/s), wherein evolution of elastic (G′) and viscous (G″) moduli were recorded as a function of time. In an oscillatory strain sweep experiment, a sample was subjected to oscillatory strain with increasing magnitude at a fixed frequency. The oscillatory strain sweep experiments were also conducted at different, but fixed, frequencies. In a frequency sweep experiments, a sample was subjected to oscillatory strain having fixed magnitude in a linear range ($\gamma = 0.1$ %) with varying frequency. In the oscillatory experiments, G′ and G″ were obtained by averaging the stress response over six cycles. It should be noted that over the entire range of explored strains the third harmonic of stress was observed to be less than 20 % smaller than the first harmonic. Consequently the material behavior can be represented in terms of G′ and G″ as has been routinely done in the literature [27, 28]. Oscillatory strain sweep experiments were also conducted on a similar cleaning formulation with a lower abrasive content, in serrated and smooth walled Couette geometry. The results were found to be identical to each other within experimental uncertainty, suggesting absence of wall slip in the present measurements. In all the experiments, the free surface of a sample was covered with a thin layer of low viscosity silicon oil to prevent drying. All the experiments were conducted at 25 °C.

Results and Discussion

All the three samples prepared as mentioned in the previous section were extremely viscous with a paste-like consistency. Under such conditions it has been usually observed that the samples are not in thermodynamic equilibrium, and due to thermal energy associated with the constituents, their structure evolves as a function of time. Such structural evolution usually leads to change in G′ and G″ as a function of time [2]. In Fig. 1, we plot time dependent evolution in G′ and G″ for all the three samples. It can be seen that LAS sample shows the highest values of moduli, followed by AOS and SLES samples. For all the three samples, both the moduli increase very sharply over the initial 120 s (first 12 cycles leading to 2 points), beyond which it significantly slows down. Interestingly G′ and G″ of LAS and AOS samples show a slow but noticeable increase with time suggesting presence of physical aging in these samples. For SLES sample, on the other hand, G′ and G″ practically remains constant indicating absence of measurable physical aging in the same.

We also analyze frequency dependence of G′ and G″ of the three samples as described in Fig. 2. For LAS sample G′ shows a very weak increase with an increase in frequency while G″ shows a minimum. For AOS and SLES samples G′ shows a prominent increase with frequency. For SLES sample, G″ can be seen to be showing a minimum at low frequency of 1 rad/s, while for the AOS sample G″ can be seen to be increasing with frequency. For the AOS sample, it could be possible that the minimum in G″ is below the experimentally explored frequency window. An
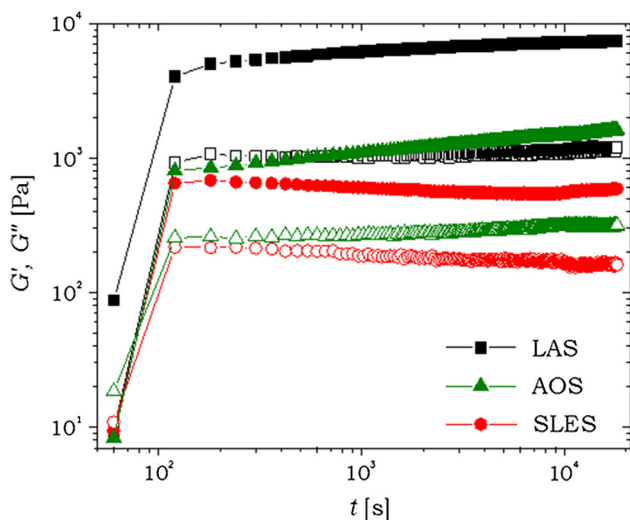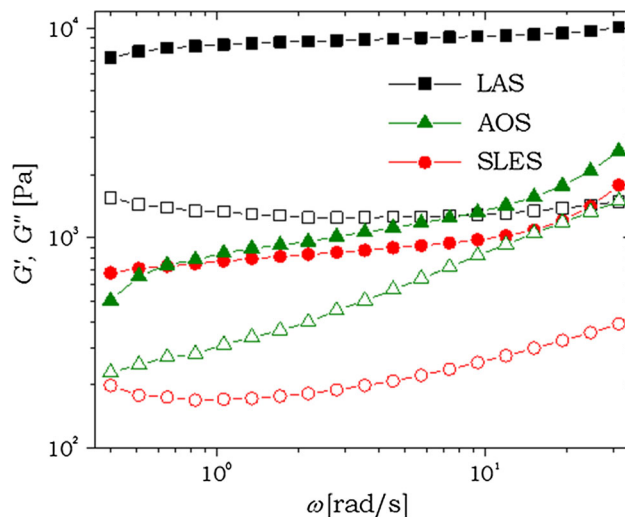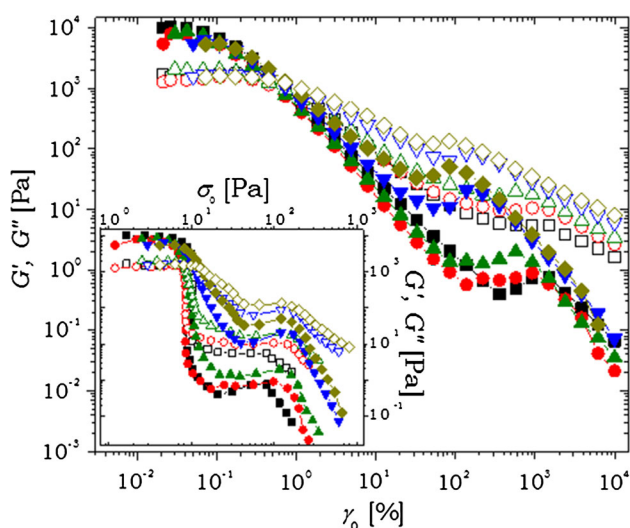

Fig. 2 Storage modulus (G′, *filled symbols*) and loss modulus (G″, *empty symbols*) are plotted as a function of frequency for $\gamma_0 = 0.1$ %. The curves are for LAS (*squares*), AOS (*up triangles*) and SLES (*circles*) containing paste systems. For all the three systems the storage modulus is higher than loss modulus, thus indicating solid like behavior for the experimental frequency window

increase in G′ with an increase in frequency indicates pastes having AOS and SLES possess structures with fast timescales, essentially implying dominance of structures with small length-scales [29]. Presence of a minimum in G″ has been observed for variety of soft glassy or pasty materials. In many systems the inverse of frequency associated with the minimum is related to the magnitude of the short timescale present in the system [30].

In Figs. 3, 4 and 5 we plot results of strain sweep experiments wherein strain amplitude is varied from a low (linear regime) to a very high value for different values of frequency, respectively for pastes containing LAS, AOS and SLES. It can be seen that in all the figures G′ and G″ are constant with G′ > G″ in the limit of small strains (linear response regime). With an increase in strain both the moduli start decreasing with G′ decreasing with a steeper slope than G″ causing G′ to cross over G″. Such a decrease in both the moduli has been termed as a yielding event. In the insets of Figs. 3, 4 and 5, the same data of a main figure have been plotted as a function of stress amplitude for the respective pastes. At a point of yielding, G′ can be seen to be undergoing a sharp decay and the corresponding stress is termed the yield stress. The yielding behavior can also be seen to be affected by frequency. In the linear response regime, unlike the paste containing LAS, G′ and G″ of the pastes containing AOS and SLES show prominent dependence on frequency, which is in accordance with that plotted in Fig. 2. On the other hand, for all three systems, the decay in both the moduli can be seen to be getting progressively sharper with decrease in

Fig. 1 Evolution of storage modulus (G′, *filled symbols*) and loss modulus (G″, *empty symbols*) is plotted as a function of time at $\omega = 0.628$ rad/s and $\gamma_0 = 0.1$ %. The curves are for LAS (*squares*), AOS (*up triangles*) and SLES (*circles*) containing paste systems
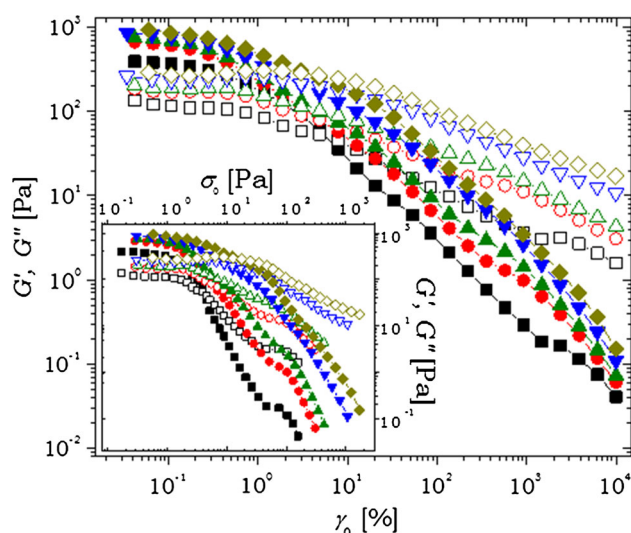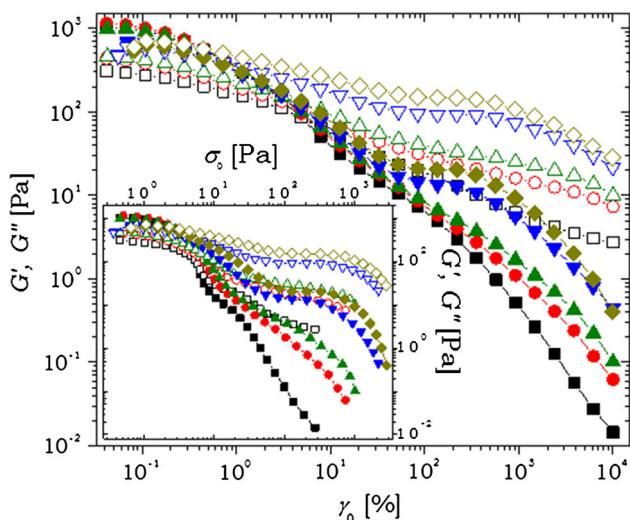
Fig. 3 Behavior of G′ (*filled symbols*) and G″ (*empty symbols*) plotted as a function of magnitude of oscillatory strain for LAS-containing paste at different frequencies $\omega = 6.28$ rad/s (*diamonds*), 3.14 rad/s (*down triangles*), 0.628 rad/s (*up triangles*), 0.314 rad/s (*circles*), 0.0628 rad/s (*squares*). *Inset* shows G′ and G″ plotted as a function of magnitude of stress

Fig. 5 Behavior of G′ (*filled symbols*) and G″ (*empty symbols*) plotted as a function of magnitude of oscillatory strain for SLES-containing paste at different frequencies $\omega = 6.28$ rad/s (*diamonds*), 3.14 rad/s (*down triangles*), 0.628 rad/s (*up triangles*), 0.314 rad/s (*circles*), 0.0628 rad/s (*squares*). *Inset* shows G′ and G″ plotted as a function of magnitude of stress


Fig. 4 Behavior of G′ (*filled symbols*) and G″ (*empty symbols*) plotted as a function of magnitude of oscillatory strain for AOS-containing paste at different frequencies $\omega = 6.28$ rad/s (*diamonds*), 3.14 rad/s (*down triangles*), 0.628 rad/s (*up triangles*), 0.314 rad/s (*circles*), 0.0628 rad/s (*squares*). *Inset* shows G′ and G″ plotted as a function of magnitude of stress

frequency. This behavior is more obvious in the insets wherein G′ and G″ are plotted as a function of stress amplitude.

With further increases in strain amplitude, G′ associated with some systems show a plateau over a certain range of frequencies before decreasing again. This second decrease in G′ has been termed the second yielding event,

which shows a transition from a moderate flow to a strong flow. While the characteristic features of the first yielding event are not observed to be affected by the nature of surfactant type, Figs. 3, 4 and 5 show that the overall rheological behavior subsequent to the first yielding, including the second yielding event, does depend on the type of surfactant present in the paste. It can be seen in Fig. 3 that in an LAS paste both G′ and G′ show a plateau after the initial decay. However the plateau occurs at higher level of modulus with increasing frequency. For a paste with AOS, the width of a plateau subsequent to the first decay in G′ and G″ goes on increasing with the increase in frequency as shown in Fig. 4. For a paste containing SLES, while G′ continues to decrease with the increase in strain (or stress), G″ shows a weak peak at the onset of yielding before decreasing as shown in Fig. 5. While at low frequencies both the moduli show an indication of a presence of a plateau, the width of the same goes on decreasing with frequency so that at high values of explored frequencies the plateau vanishes completely. Interestingly this behavior is opposite of what is observed for paste containing AOS. Presence of plateau whose width goes on decreasing with increasing frequency is more apparent in the inset of Fig. 5, where G′ and G″ have been plotted as a function of magnitude of oscillatory stress. However, similar to that observed for LAS-containing paste, the plateau—wherever apparent—is observed at a higher value of modulus for both SLES as well as AOS-containing pastes.
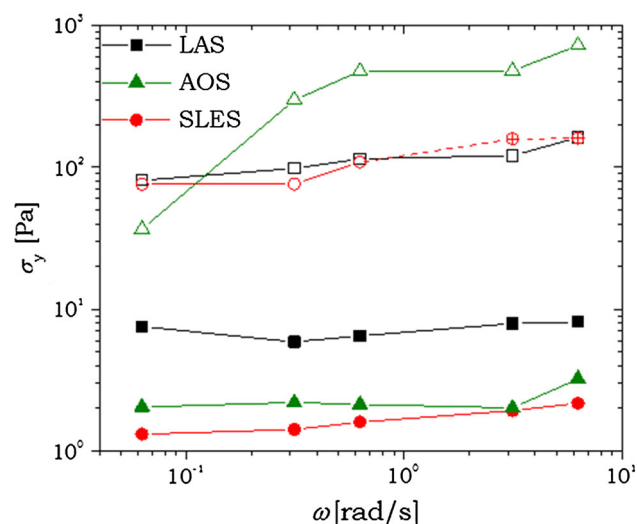
Fig. 6 Yield stresses associated with the two yielding events for LAS (*squares*), AOS (*up triangles*), and SLES (*circles*) containing pastes are plotted as a function of frequency. The *filled symbols* represent the first yield stress (σ_{y1}) while the *empty symbols* represent the second yield stress (σ_{y2}). For SLES-containing paste owing to lack of clear second yielding transition at two high frequencies, stress associated with a shoulder in G′ is shown by *circle with plus sign*
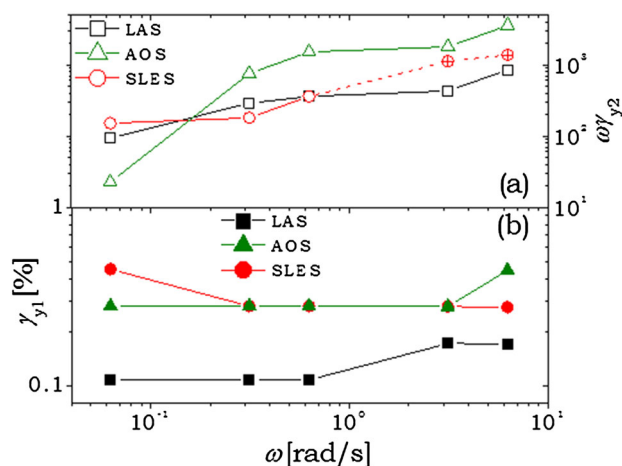
Fig. 7 a Product of frequency and second yield strain ($\omega\gamma_{y2}$) and **b** First yield strain (γ_{y1}) are plotted as a function of frequency for LAS (*squares*) AOS (*up triangles*), and SLES (*circles*) containing pastes. The $\omega\gamma_{y2}$ for SLES-containing paste at higher two frequencies is shown by *circles with plus sign*, as mentioned in the caption of Fig. 6

In order to more clearly distinguish the effect of surfactant type on the yielding behavior, the stresses and strains associated with both the yielding events are analyzed as a function of frequency. The first yield stress $\left(\sigma_{y1}\right)$ and strain $\left(\gamma_{y1}\right)$, plotted respectively in Figs. 6 and 7b, can be seen to be the weak functions of frequency for all the three surfactant paste systems. Furthermore, similar to that observed for a magnitude of G′, σ_{y1} is the highest for the

paste containing LAS followed by AOS and SLES. On the other hand, while γ_{y1} is practically identical for AOS- and SLES-containing pastes, the same for LAS-containing paste is lower in magnitude. The second yield stress (σ_{y2}) shows almost identical values for LAS- and SLES-containing pastes and can be seen to be weakly increasing with frequency. For SLES-containing paste a clear second yielding transition was observed only for the lowest three explored frequencies. For the two higher frequencies, while we do not observe a clear yielding transition when G′ is plotted against γ_0, a noticeable shoulder can be seen in a G′ verses σ_0 plot. We represent the stress and strain at which the shoulder appears as a circle with a plus sign in it. Overall, σ_{y2} of LAS- and SLES-containing paste can be seen to show nearly the same values. On the other hand AOS-containing paste can be seen to have significant enhancement in σ_{y2} with increase in frequency. It should be noted that second yielding event is a moderate flow to strong flow transition. Consequently, rather than plotting γ_{y2}, we plot $\omega\gamma_{y2}$ as a function of ω in Fig. 7a. It can be seen that $\omega\gamma_{y2}$ increases with ω for all the three paste systems.

As mentioned before, with 36 vol% particulate matter, the soft solid-like consistency of the pastes stems primarily from the space spanning particulate network. In our previous work, the two-step yielding was attributed to breakage of network followed by that of particulate aggregates [5]. Consequently the yielding behavior of all the suspension pastes expected to be sensitive to interactions among the abrasive and bentonite clay particles. The inter-particle interactions are primarily determined by charges on the particles and/or depletion interaction. The latter can originate from the structure that surfactant forms in aqueous media. If we exclude other ingredients and simply estimate the concentration of surfactant in water, it comes out to be about 33 wt%. The phase diagram of LAS in water suggests that at this concentration, LAS is observed to be in co-existing isotropic and lamellar biphasic region [31], while the phase diagram of SLES suggests that, for the mentioned concentration, it is in co-existing isotropic and hexagonal biphasic region (unpublished results). On the other hand AOS is observed to be in isotropic phase at 33 wt% concentration (unpublished results). Existence of surfactants in different phases may be one of the reasons for different rheological behaviors shown by the systems. In non-absorbing polymer particulate system the strength of depletion interaction among the particles is known to depend upon the coil size of polymer molecule in a liquid media [1]. Extending the same logic to surfactant particulate mixtures, the length-scales of the structures that surfactant form in aqueous media may determine the depletion interactions among the particles. Since relative extent of

respective structures and their length-scales are different for each surfactant system, the strength and nature of a network structure in corresponding pastes is expected to be different.

Figures 1 and 2 clearly indicate that the elastic modulus of paste containing LAS is more than that of paste containing AOS followed by paste containing SLES. The elastic modulus is also represented as energy density: $G' \sim E/b^3$ [2, 32], where E is the average energy associated with the inter-particle interactions and b is the characteristic length-scale of a network (average length of the network strands between the junctions). Higher G' therefore suggests stronger interparticle bonds (higher value of E) and/or denser network (smaller values of b) in a paste. Since the conventional yield stress, which is σ_{y1} in the present case, is known to be proportional to elastic modulus: $\sigma_{y1} \sim G'$, it is not surprising that σ_{y1} for LAS-containing paste is the largest followed by AOS and SLES respectively containing pastes similar to that observed for G'. Interestingly γ_{y1} for LAS-containing paste is observed to be lower than that of AOS- and SLES-containing pastes suggesting the former to be more brittle than the latter two. Since a denser network of particles is expected to make a material more brittle, for LAS-containing paste not just interparticle interaction appears to be stronger but also the network also seems to be denser. On the other hand, for AOS- and SLES-containing pastes γ_{y1} is observed to be nearly the same, suggesting interparticle interactions in the former to be stronger than the latter, but the network density may not be very different.

Interestingly the strain associated with the first yielding event is also observed to be nearly independent of frequency, which suggests primarily the amplitude of strain influences the first yielding process. As proposed by Sollich and coworkers [33] energy associated with inter-particle interaction E gets reduced under an application of strain γ as: $E - \frac{1}{2}k\gamma^2$, where k is the spring constant. Since life time of an energetic interaction is related to this reduced energy through an Arrhenius relationship: $\tau = \tau_0 \exp\left[\left(E - \frac{1}{2}k\gamma^2\right)/k_B T\right]$ mobility of constituting elements increase with increase in strain but is not directly influenced by the frequency of oscillations [34]. Consequently with an increase in strain amplitude, irrespective of the applied frequency, enhanced mobility facilitates yielding at nearly constant strain amplitude. Furthermore, since $\sigma_{y1} \sim G'\gamma_{y1}$, the stress associated with the first yielding event can also be seen to be nearly independent of frequency.

Subsequent to the first yielding, both G' and G'' decrease but the slope of decrease becomes weaker with an increase in frequency such that both the moduli show higher values with an increase in frequency. It should be noted that a

rupture of network during the first yielding event does not obliterate all the interparticle bonds, but only the weaker ones, which leads to formation of aggregates composed of unbroken part of the network [35]. Upon yielding, these aggregates that may have varying sizes, flow along with the continuous media. The abrasive particles used in the present work have rough surfaces [5]. Consequently, higher stresses are required to overcome friction when the aggregates brush past each other in a flowing continuous media. An increase in frequency at any given magnitude of strain increases the rate at which the paste becomes deformed. It is therefore not surprising that subsequent to the first yielding greater stresses generated at higher deformation rates cause enhancement in G' and G'' with an increase in frequency.

The second yielding event has been attributed to breakage of the aggregates [6, 35]. The pastes containing LAS and SLES show a weak but noticeable increase in σ_{y2} as a function of frequency. The second yield stress σ_{y2} of AOS-containing paste, on the other hand, demonstrates significant increase with frequency. Similar to σ_{y2}, $\omega\gamma_{y2}$ also shows noticeable enhancement for paste containing LAS and SLES while much stronger increase is observed for AOS-containing paste with an increase in frequency. As mentioned before, the net volume fraction of the particulate matter in the pastes is around 36 %, which leads to a greater volume fraction associated with the aggregates. It is known that in the concentrated suspensions, higher values of shear rates lead to the formation of clusters due to hydrodynamic effects [3]. Therefore at higher frequencies due to an increase in the 'deformation rate scale' various agglomerates coming together due to hydrodynamic effects to form larger aggregates cannot be ruled out. Since greater values of stress are required to break these bigger clusters, both σ_{y2} and $\omega\gamma_{y2}$ show enhancement as a function of frequency.

Figures 3, 4 and 5 show a plateau subsequent to the first yielding event. For LAS-containing paste, the width of the plateau does not change much with changes in frequency. The width of the plateau, however, respectively decreases and increases with frequency for SLES- and AOS-containing pastes. For SLES-containing paste the plateau is practically unnoticeable in a G' verses γ_0 plot, and is apparent only in G' verses σ_0 for lower frequencies. For higher frequencies, only a shoulder is observed that gives a hint of a second yielding step. While it is difficult to comment on how a specific surfactant microstructure leads to the observed rheological behavior, a more gradual decay in G' without a very strong yielding step suggests the aggregates are being broken over a broad range of stress magnitudes. While the specific effects of microstructure on inter-particle depletion interactions are difficult to

comprehend, the results clearly suggest that the surfactant plays a very crucial role in determining yielding behavior of the studied surfactant suspension pastes.

Yielding is a vital phenomenon in pastes containing abrasive particles used for cleaning purposes. A paste remains in a semi-solid form in the container and yields only under a large enough stress under application of a scrubber. However, this yielding does not break the network to obtain an elementary particle level thereby maintaining high viscosity that does not cause dripping of the fluidized paste from the scrubber. An optimum design of a paste therefore should be such that the difference in stresses associated with the two yielding events is large enough to facilitate required take up on the scrubber without letting it drip. The present work clearly shows that for an otherwise identical system, use of different kinds of surfactants allows variation of the elastic modulus of a paste over a broad range but also the difference between the two yielding events allow significant flexibility.

Conclusions

In this work we have studied the rheological behavior of the formulations containing clay, abrasive particles and three different types of surfactants, namely LAS, AOS and SLES among various other ingredients. The total volume fraction of the particulate matter in the pastes is estimated to be around 36 %. All the pastes show soft, solid-like consistency with $G' > G''$ over all the explored frequencies. This observation suggests that the particles form a space spanning network surrounded by a surfactant-water mixture as a continuous media. Overall the LAS-containing paste is observed to have larger moduli followed by AOS- and SLES-containing pastes. For all the pastes, G' remains constant in a limit of small strains (linear response regime), but undergo decay in two-steps with increases in strain, which has been termed as the two-step yielding phenomena. Interestingly similar to the modulus, the yield stress associated with the first yielding event is observed to be the largest for LAS-containing paste followed by AOS- and SLES-containing pastes. The first yield strain on the other hand, is observed to be smallest for LAS-containing paste while comparable for the other two, suggesting that the former is more brittle than the latter two. Since the modulus can be represented as an energy density, the behavior of elastic modulus and yield strain suggest that the inter-particle interactions are stronger and the network is denser in LAS-containing paste. Both the yield stresses and the strains associated with the first yielding event are observed to be very weakly dependent on frequency, indicating the first

yielding to be a strain controlled phenomenon caused by rupture of the network and is independent of the rate of strain. Subsequent to the first yielding, aggregates of unbroken components of the prior network flow in a continuous media so that G' decays below G'', and shows a plateau or a shoulder before decreasing again. The yield stress and characteristic strain rate at the second yielding event, which is attributed to breakage of particulate aggregates, are observed to increase with frequency. Such enhancement suggests possibility of growth of aggregate size due to hydrodynamic effects before getting broken. Importantly both the yielding events that represent, respectively the network rupture followed by aggregate breakage are very sensitive to inter-particle interactions. Since, different surfactants show varying phase behaviors or microstructures in water, which influence the inter-particle interactions, the two-step yielding behavior is observed to be sensitive to the surfactant used in a paste. Consequently variation of the rheological behavior of a paste over a broad range by using different types of surfactants render greater flexibility to the manufacturer in preparing pastes with desired properties.

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