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Structure and rheology of composite soft solids: Particles in lamellar phases

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We study the structure and rheology of new classes of composite soft solid materials, formed by incorporation of hard particles into the ''onion texture'' of a lyotropic lamellar phase. The onion texture is obtained by prolonged steady shearing of a lamellar sample. Depending on the size of the particles (compared to the onions), their volume fraction, and the stage during the preparation process at which the particles are added, we find three structurally distinct classes of composite. These are ''stuffed onions,'' in which the particles are sequestered at the center of the onions; ''decorated onions,'' in which, as well as replacing the onion core, the particles decorate the polyhedral lattice of edges between the onions; and onion/particle ''alloys.'' The latter are formed when the particles are added late in the shearing procedure, in which case the (preexisting) onions remain intact and the particles reside entirely in the interstitial regions between them. (At high enough particle densities these regions occupy a significant volume fraction, and the onions revert from a polyhedral to a spherical shape.) Although structurally distinct, these three materials all have remarkably similar rheological properties (at least in the range of volume fractions of dopant particles studied here, $\lesssim 4\%$), which, to within experimental error, do not differ from those of the pure onion system without particles. All of these structures are metastable but have lifetimes long compared to the case where particles are added to a lamellar phase in which the onion texture is not present. [S1063-651X(99)12103-2]

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I. INTRODUCTION

In thermal equilibrium, bilayers made of surfactant molecules (swollen by oil or water) can adopt a variety of spatial arrangements, ranging from a simple stacking of the bilayers (the lamellar phase L_α) to a random bicontinuous arrangement (the sponge phase L_3). Changes in the properties of these phases, and transitions between them, can be brought about by varying thermodynamic parameters such as temperature and ionic strength [1].

Changes in the arrangement of bilayers can also be brought about by shearing. In particular, Roux and coworkers [2,3] have shown that prolonged steady shear in a Couette cell causes a dynamic transition from the L_α phase to one of monodisperse multilamellar vesicles, called ''onions,'' the size of which is controlled by the shear rate, $\dot{\gamma}$. The detailed mechanism of onion formation remains unclear at present. Although the onions appear spherical when the system is expanded by addition of a solvent, it is inferred from scattering and freeze fracture studies that, in the dense state, they form a polyhedral structure resembling a foam [4]. This structure contains regions of quite high curvature (at the onion cores, along the edges and vertices where the onions meet, and also at certain planes internal to the onion) which are thought to contribute strongly to the elastic response of the bulk material under shear [5]. In these regions one expects a radius of curvature of the order of the penetration depth, $\Lambda=(K/\overline{B})^{1/2}$, with K and $\overline{B}$, respectively, the curvature and compression moduli (at constant chemical potential) of the lyotropic smectic phase. In practice, Λ is usually several times the bilayer separation. The strongly curved regions between the onions form a network which resembles the network of Plateau borders in a (rather dry) foam.

The equilibrium phase behavior of mixtures of lyotropic bilayers (of uniform powder texture, not onions) and *small* spherical particles has been investigated [6]. A low concentration of magnetic or nonmagnetic solid particles with a size $\lesssim 20\%$ of the bilayer spacing can be incorporated into the lamellar phase. It is much harder to disperse particles larger than the membrane spacing: in equilibrium such particles tend to be expelled because they would induce a large curvature energy cost for the surrounding bilayers.

In this work, we investigate the behavior of mixtures of relatively large spherical particles and lyotropic bilayers under shear. We find that the particles modify but do not prevent the formation of onions, and that the resulting composite materials are very stable: the particles are not expelled over a long period (months). The presence of particles leads to interesting structural modifications of the onion texture, giving rise to a range of new composite soft solid materials. Rather surprisingly, however, the rheological properties of these, as far as they can be probed by small-amplitude oscillatory shear measurements, are very similar to one another and to the corresponding onion phase without particles.

Our work has various motivations. One of these is to use the particles to track the formation history of the onions and thereby shed light on the mechanism of their formation. This aspect will be developed in a separate paper [7]. In the present work, we are interested in establishing the range of composite structures, and the resulting rheological properties, that can be obtained by adding hard colloidal particles at various stages during the shear preparation. Since the relationship between structure and rheology in composite soft solids is itself unclear, it is valuable to have a range of similar, but distinct, well-characterized composites of this type to examine. The composites we describe may have various applications. An obvious one is as stable pastes which could form delivery systems for abrasives or other cleaning agents: as mentioned already, the particles remain stably suspended

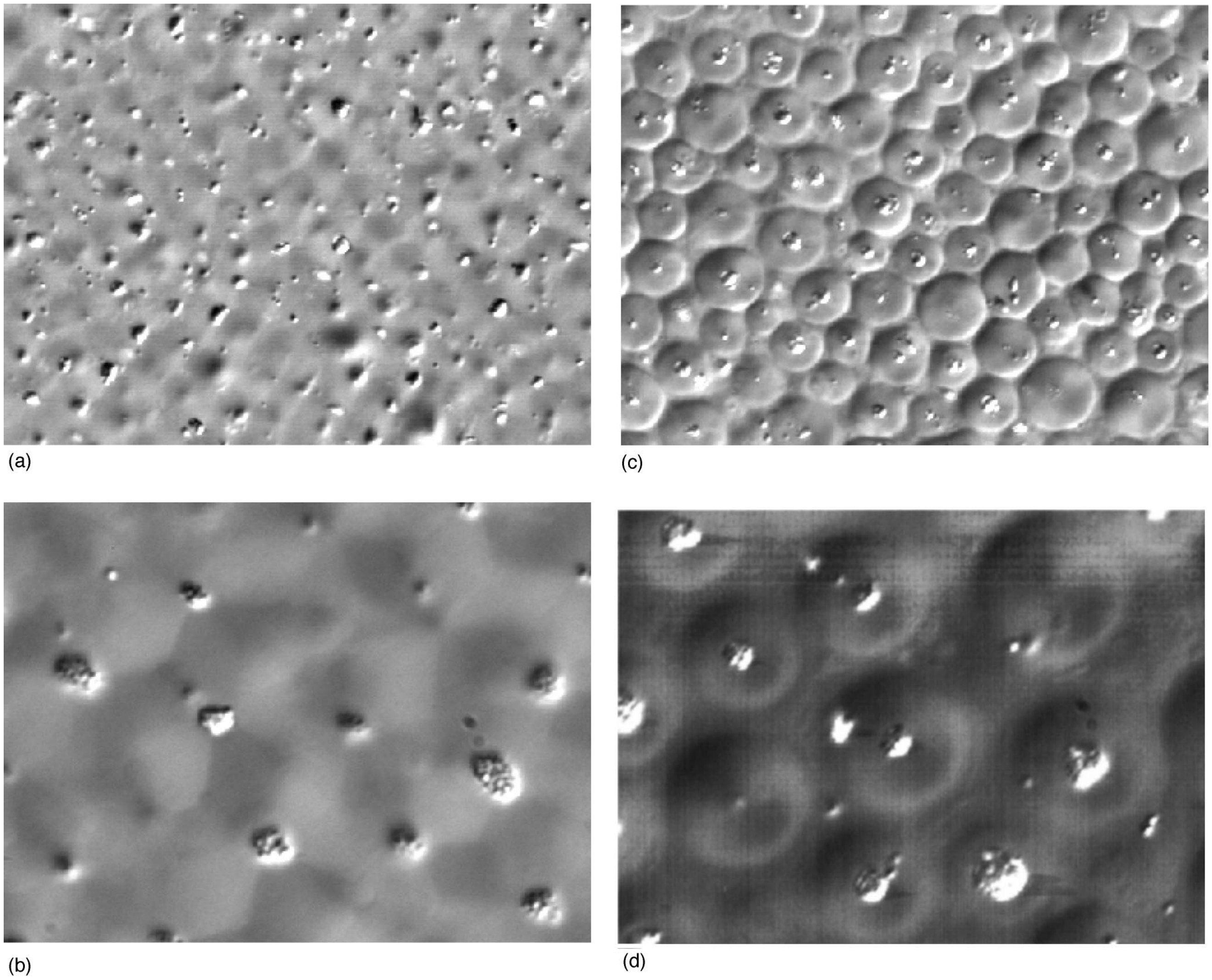

FIG. 1. DIC optical micrographs of AOT membranes, $\phi_m = 0.20$, sheared for 5 h at $\dot{\gamma} = 2\ \mathrm{s}^{-1}$, giving onions with diameter $D \approx 8\ \mu\mathrm{m}$; with 0.4-$\mu$m-diam polystyrene particles at volume fraction $\phi_p = 0.4\%$ w/w. (a) ×40 objective. (b) Same as (a) but ×100 objective. (c) The sample in (a) diluted by brine, ×40. (d) Same as (c) but ×100. Width = 72 μm, (a) and (c), and 30 μm, (b) and (d).

for much longer than they would be if added to a nontextured lamellar phase. To check the robustness of our results to the type of particulate used, we have performed a few runs with an industrial particulate (zeolite powder) rather than the well characterized polystyrene latices used for our main study. As indicated below, there seems to be no fundamental difference between the behavior in these two cases. Another possible application to optical materials is discussed in Sec. V.

The rest of this paper is organized as follows. In Sec. II we give the experimental details and in Secs. III–V we describe the preparation protocols leading, respectively, to three classes of composites we have discovered: ''stuffed,'' ''decorated,'' and ''alloyed'' onions. In each of these sections the resulting structure and rheological properties are described. In Sec. VI we offer a brief conclusion and suggestions for further work.

In a previous paper we reported preliminary results for one of these three classes (''stuffed'' onions) in two different systems [sodium dodecyl sulphate, dodecane, pentanol, and water; AOT and brine] [9]. In what follows, however, we consider mainly the AOT/brine system.

II. EXPERIMENTAL SYSTEMS AND PROCEDURES

A. Materials

The lamellar phase studied is pseudobinary and consists of AOT bilayers separated by brine (15 g/l of NaCl) [10]. Surfactant was supplied by Sigma (at least 99%) and used without further purification. The bilayer concentration was $\phi_m = 0.20$, with bilayer thickness $\delta = 2.3$ nm and bilayer spacing $d = \delta/\phi_m = 9.8$ nm. We used as solid particles polystyrene spheres with ionizable acrylic acid on the surface (diameter 0.4 μm, polydispersity $\approx 20\%$) dispersed in distilled water, dispersion stability being confirmed by optical microscopy; smaller (0.2 μm) particles of a styrene butadiene copolymer were also used. (Both kinds of particles were supplied by Rhône-Poulenc.) Note that at the salt concentration used in preparing the AOT bilayers, any electrostatic repulsion between our polystyrene particles is completely screened; these are probably close to being a hard-sphere system. Selected experiments were repeated with powdered zeolites replacing the colloidal spheres.

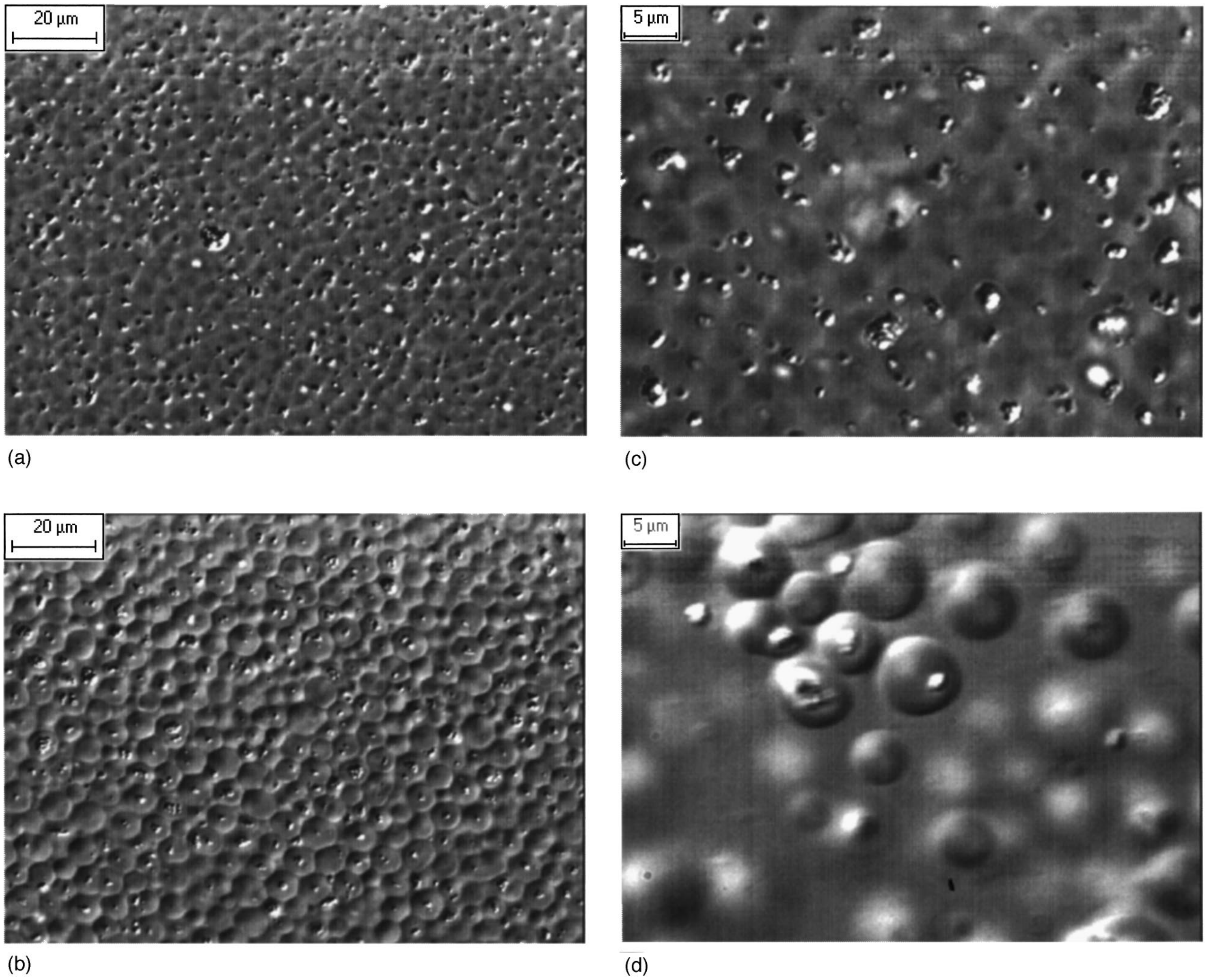

FIG. 2. DIC optical micrographs of AOT membranes, $\phi_m = 0.20$, sheared for 6 h at $\dot{\gamma} = 1.5 \ \mathrm{s}^{-1}$, giving onions with diameter $D \approx 9 \ \mu\mathrm{m}$; with zeolite particles, mean diameter $\sim 1 \ \mu\mathrm{m}$, $\phi_p = 0.3\%$ w/w. (a) ×40 objective. (b) The sample in (a) diluted by brine, ×40. (c) Same as (a) but ×100. (d) Same as (b) but ×100.

B. Sample preparation

Two separate protocols for sample preparation were used. In the first, a pure L_α phase and a stable particle dispersion (up to a few percent volume fraction of particles in the solvent) were mixed using a vortex mixer; the air bubbles introduced in the process were subsequently removed by brief centrifuging. At this point, samples looked homogeneous but turbid, the latter due to the large refractive index mismatch between the added particles and the solvent. Optical microscopy (phase contrast and polarizing) confirmed that individual particles were randomly dispersed in a texture characteristic of a lamellar phase [1]. Shearing experiments were then performed by loading freshly mixed samples into a cone-and-plate cell (6 cm diam, angle 2°) of a Carrimed CSL^{2}100 rheometer. The sample temperature was controlled at $21 \pm 0.1\,^\circ\mathrm{C}$. Evaporation of the solvent was reduced by a solvent trap on the top of the cell. Bilayer/particle mixtures were then subjected to prolonged ($\gtrsim 3$ h) shear at a constant shear rate, $\dot{\gamma}$, until a steady state was reached (as established by monitoring the time-dependent shear stress). In some cases the stress curves continued to evolve over very long times (hours) and in these the shearing was terminated before a true steady state was reached. However, subsequent observations showed the system to be made up of complete onions in such cases, even though the structure was still evolving in time.

This first protocol was found to lead to stuffed and/or decorated onion structures, dependent primarily on the size of the particles (Secs. III and IV). The second protocol was similar to the first, with one very important difference. Here the lamellar phase was first sheared without particles. Once the main transient response was over, the shear cell was carefully opened and the suspension of solid particles added. The cell was then reassembled and the sample sheared again (at the same shear rate) until a steady state (or close to one) was recovered once more. This protocol led to alloyed structures (Sec. V).

C. Structural and rheological characterization

To study the structure of the resulting composites, samples removed from the shear cell were examined in an Olympus BX50 microscope using either the bright-field mode between cross polars or differential interference contrast (DIC or Nomarsky) optics. The latter produces a

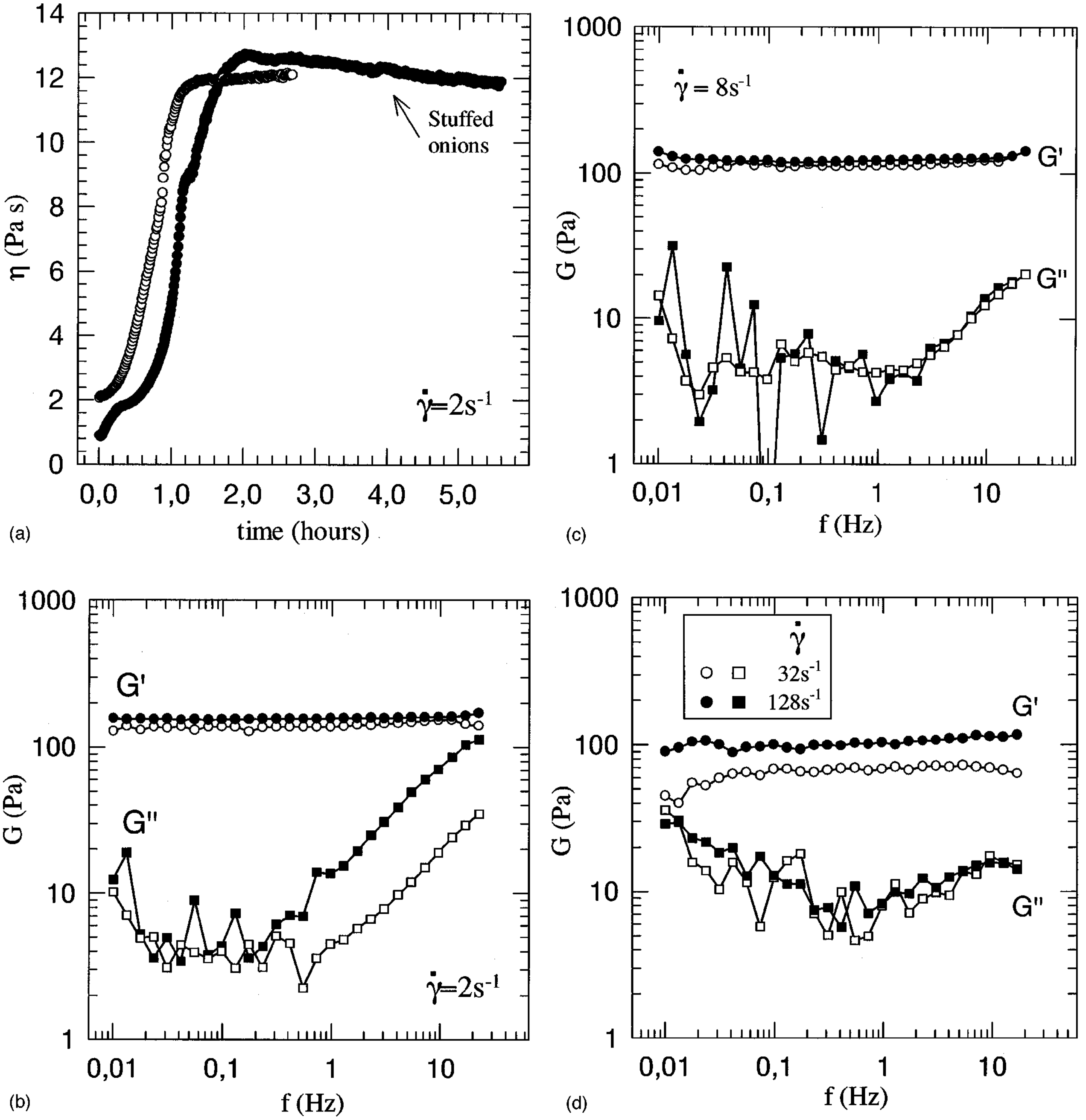

FIG. 3. Comparison of the rheology of the bare and stuffed onions. (a) Flow experiment: transient viscosity $\eta(t)$ under constant shear rate $\dot{\gamma}=2\ \mathrm{s}^{-1}$ for a sample with no particles (bare onions) and a sample with 0.4 % w/w of polystyrene particles. (b)–(d) Viscoelastic measurements for onion samples with particles added and without particles for several shear rates of preparation: (b) $\dot{\gamma}=2\ \mathrm{s}^{-1}$, (c) $\dot{\gamma}=8\ \mathrm{s}^{-1}$, (d) $\dot{\gamma}=32\ \mathrm{s}^{-1}$, and $\dot{\gamma}=128\ \mathrm{s}^{-1}$. Open and closed symbols in (b) and (c) refer to samples without and with particles added, respectively. All data in (d) refer to samples with added particles. For all runs, the applied controlled shear stress was $\sigma_{\mathrm{osc}}=0.04$ Pa, which gave an almost frequency-indepedent strain amplitude of 0.08 %.

''shaded'' appearance of a spherical phase object whose center lies in the focal plane [11]; it also gives complex but easily identified patterns from birefringent objects, such as multilamellar vesicles [3].

As mentioned above, the viscosity of the material (shear stress divided by strain rate) was monitored throughout the formation process in all cases. Subsequent to formation, the steady shear was switched off and a further rheological characterization made by small-amplitude measurement of the viscoelastic spectrum $G^{*}(\omega)$. The applied stresses used were small ($\lesssim 0.06$ Pa) resulting in strains of about 0.08%. Although for metastable system such as the ones we study it is impossible to be completely sure that this represents a linear viscoelastic measurement [12], it nonetheless gives a reproducible characterization of the material over the whole frequency range studied ($0.01-10$ Hz) so long as the stress is actually specified. This contrasts somewhat with previous work by Panizza *et al.* [5], who found that the very low frequency ($0.01-0.1$ Hz) data were less reproducible.

Alongside the linear viscoelastic spectra, one can also measure the creep and/or yield stress behavior of the onion/particle composites [5]. However, these results are somewhat

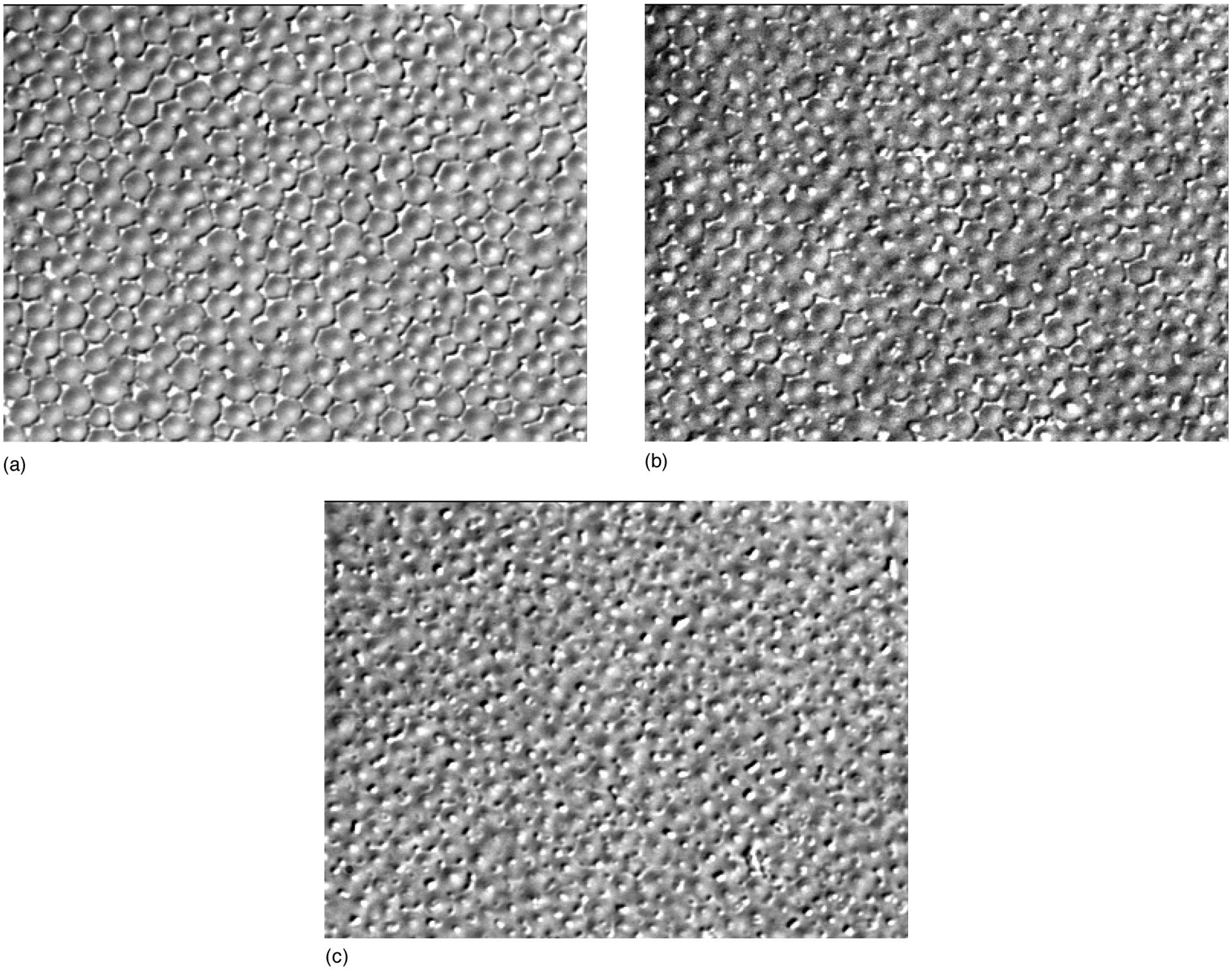

FIG. 4. DIC optical micrographs of AOT membranes, $\phi_m = 0.20$, containing 0.20-μm-diam latex spheres at concentration $\phi_p = 1.0\%$ w/w. The sample is sheared for 3 h at $\dot{\gamma} = 2\ \mathrm{s}^{-1}$, giving onions of diameter $D \approx 8\ \mu$m. ×40 objective. (a) View of the sample next to the upper microscope slide ($z = 0$). Particles are seen as ''ridges'' along the edges of polyhedral onions and as rounded clumps in onion cores. (b) Same as (a) but deeper in the bulk ($z = 2\ \mu$m). Again, particles are seen along edges and in the cores. (c) Same as (a) but with $z = 4\ \mu$m. Very few decorated edges are seen. Width of all frames $= 150\ \mu$m.

irreproducible even for simple onion phases without particles. Therefore, it would require a very extended study to detect statistically significant differences between the creep behavior of pure onions and the composites studied here; for this reason, creep measurements are not reported.

III. STUFFED ONIONS

As described previously, the initial stage of the sample preparation involves mixing the lamellar phase with a suspension of polystyrene lattices in a vortex mixer. We found that, if left undisturbed after this process, samples would always demix into particle-rich and bilayer-rich phases over hours or days (the time scale depending on the viscosity of the L_α phase). The pure lamellar phase is stabilized by the Helfrich undulation mechanism [10], and the particles used are many times the size of the pure lamellar spacing, so that almost complete demixing is expected on thermodynamic grounds. Our results demonstrate that the rearrangement kinetics of an ordinary lamellar phase are too rapid to allow particles to remain suspended for long in a metastable state.

However, for particle volume fractions in the range $0 < \phi_p \lesssim 1\%$, long-lived metastable dispersions can be formed by prolonged shearing. This occurs within the region of onion formation in the ''orientation diagram'' as previously reported in the $(\dot{\gamma}, \phi_m)$ plane [3]. For these small volume fractions of solid particles, there is no significant shift in the boundaries of this region. The resultant onions, however, now incorporate particles, the vast majority of which are sequestered, in roughly spherical clumps, at the onion centers. This can be seen most clearly if a small amount of brine is added to the system. This allows the densely packed, polyhedral onions to separate slightly and relax to a spherical shape. (Interesting but different phenomena are observed if pure water is used as the swelling agent: in this case the onions expand strongly and the particle clumps start to separate and to undergo vigorous Brownian motion. This has been described previously [9].)

A sample of stuffed onions is shown in Fig. 1. Here the

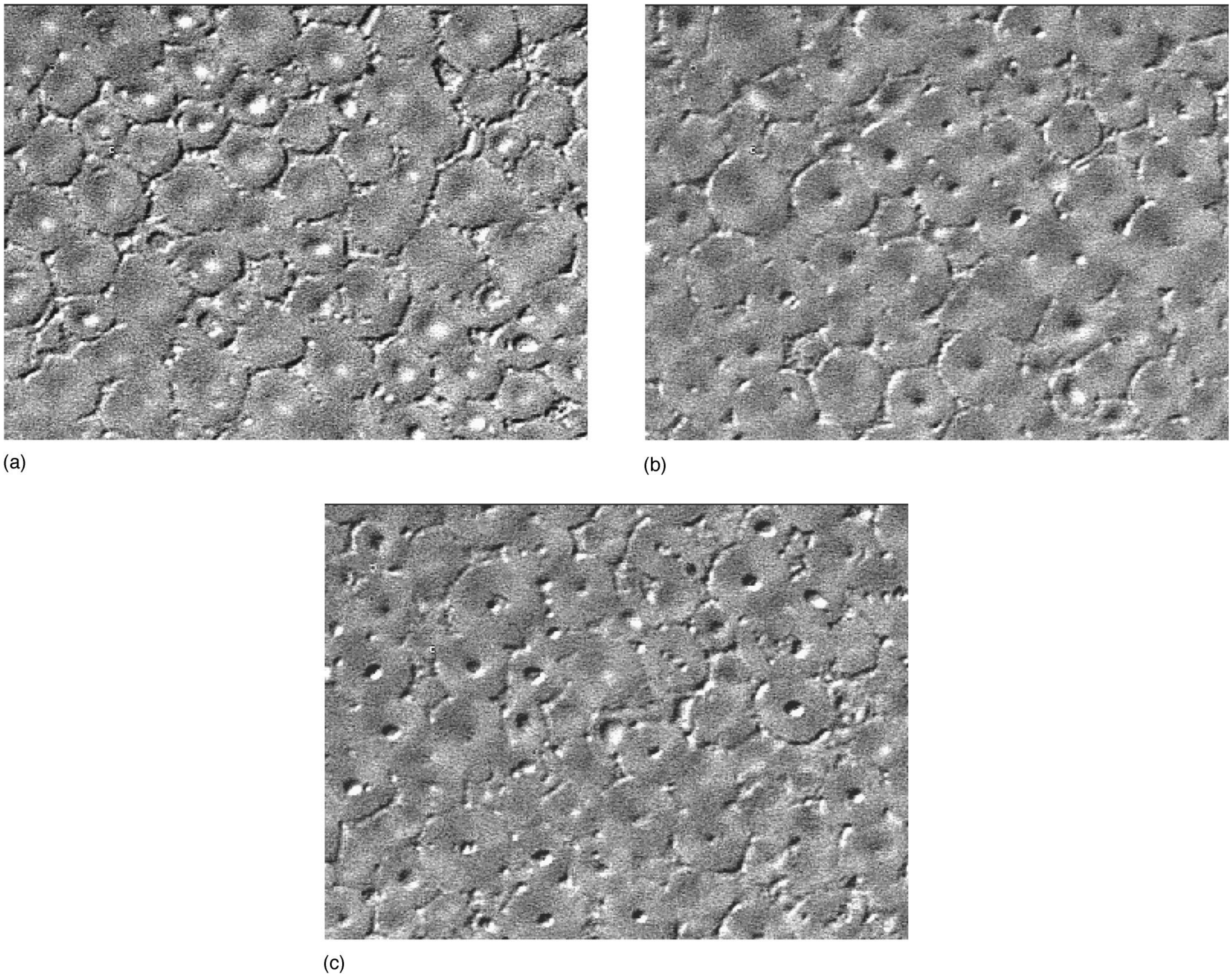

FIG. 5. Further example of decorated onions, $\phi_p = 0.5\%$ w/w, prepared with $\dot{\gamma} = 2\ \mathrm{s}^{-1}$ for 3 h. Views of the sample at different heights: (a) $z = 5\ \mu$m, (b) $z = 7\ \mu$m, and (c) $z = 9\ \mu$m, measured downward from the top surface. Width of all frames $= 45\ \mu$m.

mean onion diameter is roughly $D = 8\ \mu$m. At the given particle concentration ϕ_p (less than 1%) and diameter $a = 0.4\ \mu$m, one expects a mean number of particles per onion of around $n \sim \phi_p(D/a)^3 \simeq 10$ if most of the particles are incorporated into onion cores. This is not far from the observations. Attempts to incorporate higher volume fractions of these particles were unsuccessful. Instead of larger numbers of particles sequestering into onion cores, we found large (tens of microns) aggregates of unsequestered particles dispersed among stuffed onions each still only having a small number of particles in its core. It is not clear what effects determine the apparent limit to the size of the core region that can be replaced by particles, although we expect that the onion formation kinetics will be important [7].

It seems to be relatively easy to form stuffed onions in the AOT system, regardless of the particle type used, so long as the particles are (a) introduced at low enough volume fraction and (b) small compared to the mean onion size itself. Figure 2 shows a similar experiment in which a 0.3% w/w aqueous suspension of zeolite (MAP 24A, kindly supplied by Unilever PLC, mean particle size $\sim 1\ \mu$m) was used instead of polystyrene lattices. Although the resulting texture is less uniform than with quasimonodisperse lattices, it is basically very similar, with most of the zeolite sequestered in clumps at or near the cores of the onions. As described elsewhere, the same phenomenon has also been seen in a nonaqueous (SDS) system with particles of diameter $\sim 1\ \mu$m [9].

Given that the particles represent a small volume fraction and are sequestered at the onion cores, it is perhaps not surprising that the stuffed onion composite is very similar in its rheological behavior to a particle-free onion phase with the same mean onion size (Fig. 3). It is less obvious, but also true, that within experimental error the presence of the particles leads to only a small shift in the mean onion size at a given shear rate of formation. However, some small rheological differences are detectable. One of these is the somewhat more erratic and irreproducible behavior of the loss modulus G'' at low frequencies in the particle-laden system, Figs. 3(b)–3(d). This may be consistent with the idea that the loss modulus at low frequencies, like the creep behavior [5], is sensitive to grain boundaries or other organizational features in the system at a scale rather larger than the onion size itself. These depend on the entire processing history of the sample, which is not exactly the same when particles are

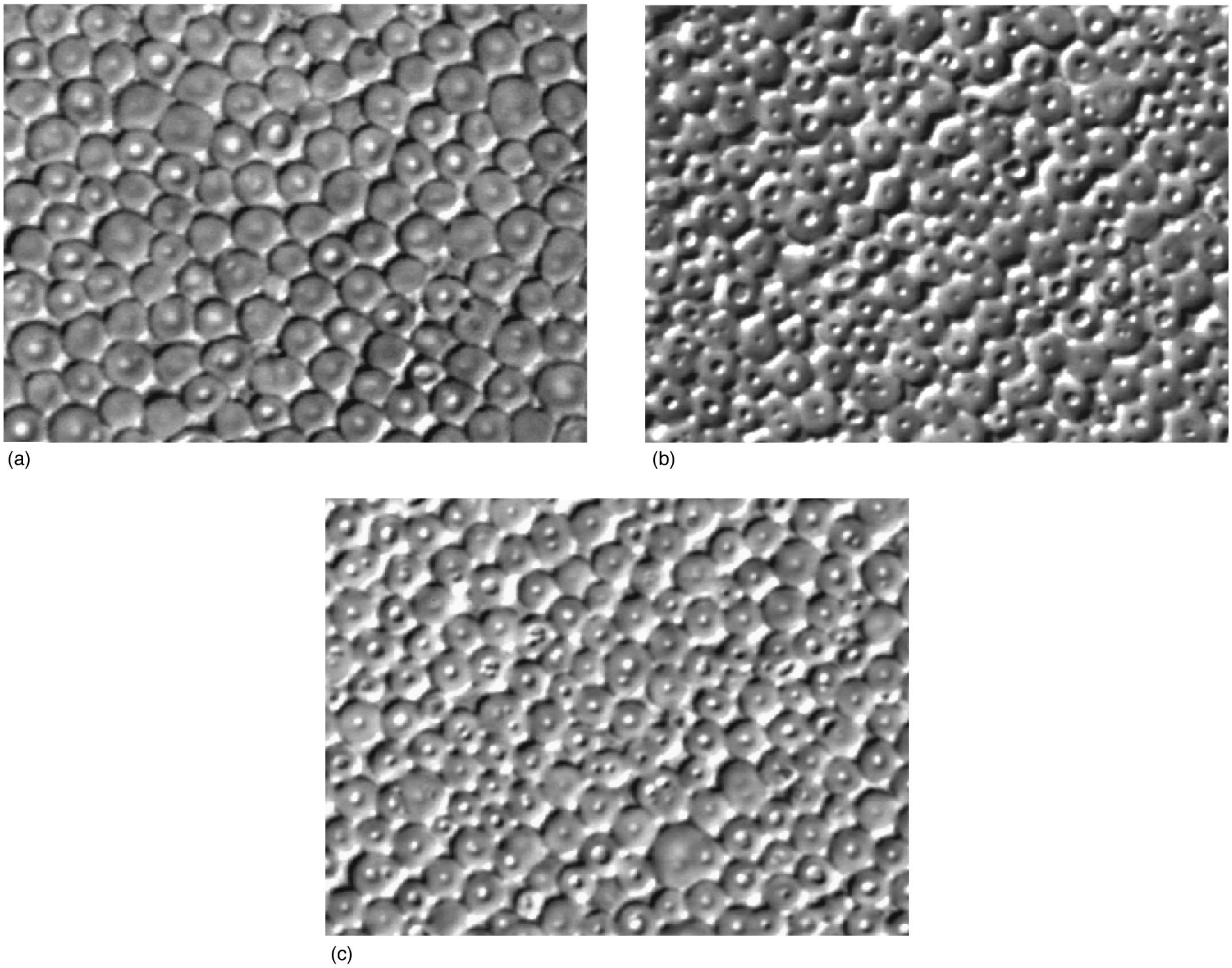

FIG. 6. An example of decorated onions with a larger concentration of solid particles, $\phi_p = 4.0\%$ w/w. The shear rate of preparation was $\dot{\gamma} = 1.5\ \mathrm{s}^{-1}$, giving onions of diameter $D \approx 9\ \mu\mathrm{m}$. Three views of the sample at different heights: (a) right next to the upper microslide $(z=0)$, (b) $z=3\ \mu\mathrm{m}$, and (c) $z=9\ \mu\mathrm{m}$. Width of all frames $=100\ \mu\mathrm{m}$.

present. Indeed, the buildup of viscosity, as the onions are formed, is somewhat delayed [Fig. 3(a)]. Moreover, a small overshoot is seen in the viscosity as a function of time which was not present for the pure onion texture: this is not understood. [A significant overshoot is also visible in Fig. 9(a) below.]

More generally, one finds that for a given shear protocol (fixed strain rate) the processing history (as measured by the buildup of stress) is *significantly less reproducible* when particles are present, showing much larger variation between runs with the same nominal preparation. Thus, for example, we have no explanation for the significantly enhanced loss modulus at high frequencies visible in Fig. 3(b), for which there is no counterpart in Figs. 3(c) and 3(d). The appearance of a power-law region at high frequencies in Fig. 3(a) somewhat resembles the results for foams [13], although again this is less evident in Figs. 3(c) and 3(d); it is not explained by the model of Ref. [5]. An apparently decreasing trend in the storage modulus with increasing $\dot{\gamma}$ in Figs. 3(b)–3(d) is spoiled by the data for $\dot{\gamma} = 32\ \mathrm{s}^{-1}$; such a trend would again contradict Ref. [5] but may not be significant in view of the scatter. More detailed data along these lines will be presented elsewhere [7].

IV. DECORATED ONIONS

If the same protocol as described in the preceding section is used, but with *smaller* particles, then clumps of particles are still observed at the cores of the onions, but now particles are also found ‘‘decorating’’ the exterior of the onions. Figure 4 shows the result of such a preparation, using particles of diameter 0.20 μm at volume fraction $\phi_p = 1.0\%$ w/w. A sequence of images is shown, moving down from the top surface of the sample (a)–(c). This reveals that the decorating particles remain mainly along the *edges* separating the close-packed polyhedra that make up the onion texture, and at the vertices where these edges meet, but *not* at the flat faces. The particle volume fraction in this sample is low enough that the decorating particles cause very little perturbation to the onion packing itself — they in effect provide labels for the polyhedral edges.

In detail, at the upper surface of the sample, Fig. 4(a),

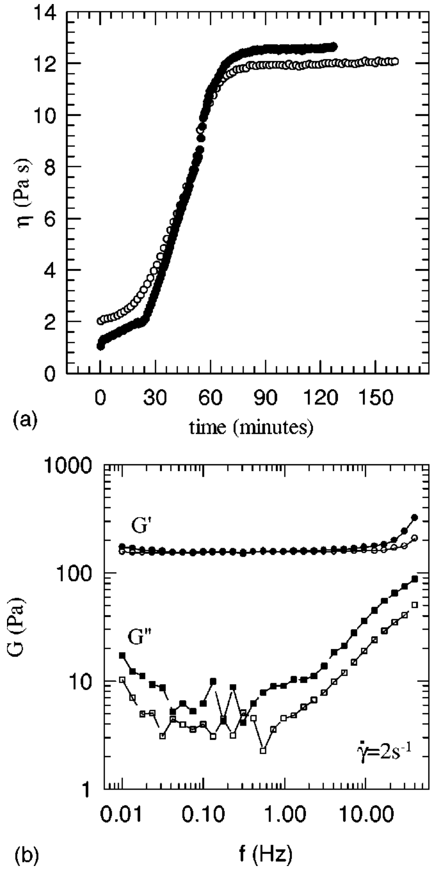

FIG. 7. Rheology of the decorated onions (filled symbols) compared to the bare onions (open symbols). (a) Flow experiment. Transient viscosity $\eta(t)$ under constant shear rate $\dot{\gamma}=2\ \mathrm{s}^{-1}$ for a sample with no particles (bare onions) and a sample with 1.0 % w/w of polystyrene particles. (b) Viscoelastic measurements. Storage and loss moduli for bare onions (open symbols) and decorated onions (1.0 % w/w; filled symbols). The applied oscillatory shear stress was $\sigma_{\mathrm{osc}}=0.05$ Pa and the measured strain amplitude was of order of 0.09%.

there are many edges parallel to the plane of view. These decrease as one moves deeper within the bulk, Fig. 4(b). At a depth z of approximately half the onion diameter ($D/2 \approx 4\ \mu\mathrm{m}$), most of the particles appear localized in bright dots (these may include edges perpendicular to the plane of view, as well as the cores of the onions). This sequence can be understood if there is a rather well-ordered layer of onions in proximity to the top surface. Well within the bulk of the sample one observes a more homogeneous distribution of edge orientations. Nevertheless, the bulk polyhedral packing has a reasonable degree of short-range order. In those regions where the layers of onions are horizontally oriented, images similar to those observed near the top glass surface can sometimes be seen. Figure 5 represents such a sequence which, relative to the top surface, is displaced vertically downward by about $D/2$ compared to the one in Fig. 4.

These observations are consistent with the idea that the particles migrate towards regions of high bilayer curvature in the system. These regions include the cores of the onions but also the edges and interstices — notably they do not include the flat faces of the polyhedra, which are locally indistinguishable from any other region of uniform lamellar organization. The partitioning of particles between the cores and edges of the onions seems to be determined by the detailed kinetics of onion formation from the lamellar phase as shear proceeds, and varies somewhat from one run to another [7].

By looking closely at the decorated onion edges and scanning vertically (as in Fig. 4), it should be possible to reconstruct the geometry of individual polyhedra in the undiluted onion packing, thus allowing detailed structural characterization in a manner impossible for undecorated onions of this size. While we have not obtained quantitative information using our micrographs, the results shown in Figs. 4 and 5 nevertheless provide the first direct *in situ* confirmation that the undiluted onion packing consists of a three-dimensional ‘‘foam’’ of polyhedral droplets.

Another vertical scanning sequence is shown in Fig. 6 for a sample with a much larger concentration of particles ($\phi_p = 4.0\%$ w/w). Here the particle concentration is high enough to perturb significantly the onion texture, not only at the cores but at the edges between onions. The relaxation of local curvature by sequestering the particles at the edges is very apparent in these pictures: the onions appear distinctly rounder than before. The distinction between particle-filled edges and flat contact faces between onions is less obvious (the faces are reduced in size) but still detectable.

Since it is apparent that the onion borders are decorated to a thickness of more than one 0.2 μm particle, it is unclear why 0.4 μm particles do not decorate the onions in the same way: the energetic consequences should be very similar in the two cases. (This might not be true if decoration were limited to a *monolayer* of particles, which is not what we observe.) Again, the detailed kinetics of onion formation may be an important deciding factor.

In Fig. 7 we show the rheological data for a decorated onion sample, compared to that of the particle-free onion phase. As with the stuffed onion case, the two samples are extremely similar, which is more surprising in this case because the particles are not entirely enclosed within the onions, but form a spanning network of dense colloidal material.

V. ONION/PARTICLE ALLOYS

We now turn to our second experimental protocol for sample preparation. As stated previously, this involves the addition of a suspension of polystyrene latices to a preformed onion sample, by carefully opening the shear cell, adding the particles, and then shearing again for a second prolonged period. As in the previous experiments, the shear rates used in the preparation (typically $\dot{\gamma}=2\ \mathrm{s}^{-1}$) mean that the onions are an order of magnitude larger in diameter than the individual latex particles.

With this protocol, the resulting composite soft solid is one in which *all* the solid particles are dispersed in the interstitial space between the onions; there are none observed within the onions themselves, Fig. 8. This sheds light on the evolution of the onion structure under shear: it appears that onions, once formed, do not have the kind of dynamic breakdown and reassembly kinetics that would allow the newly added latex particles to be incorporated into the cores, even

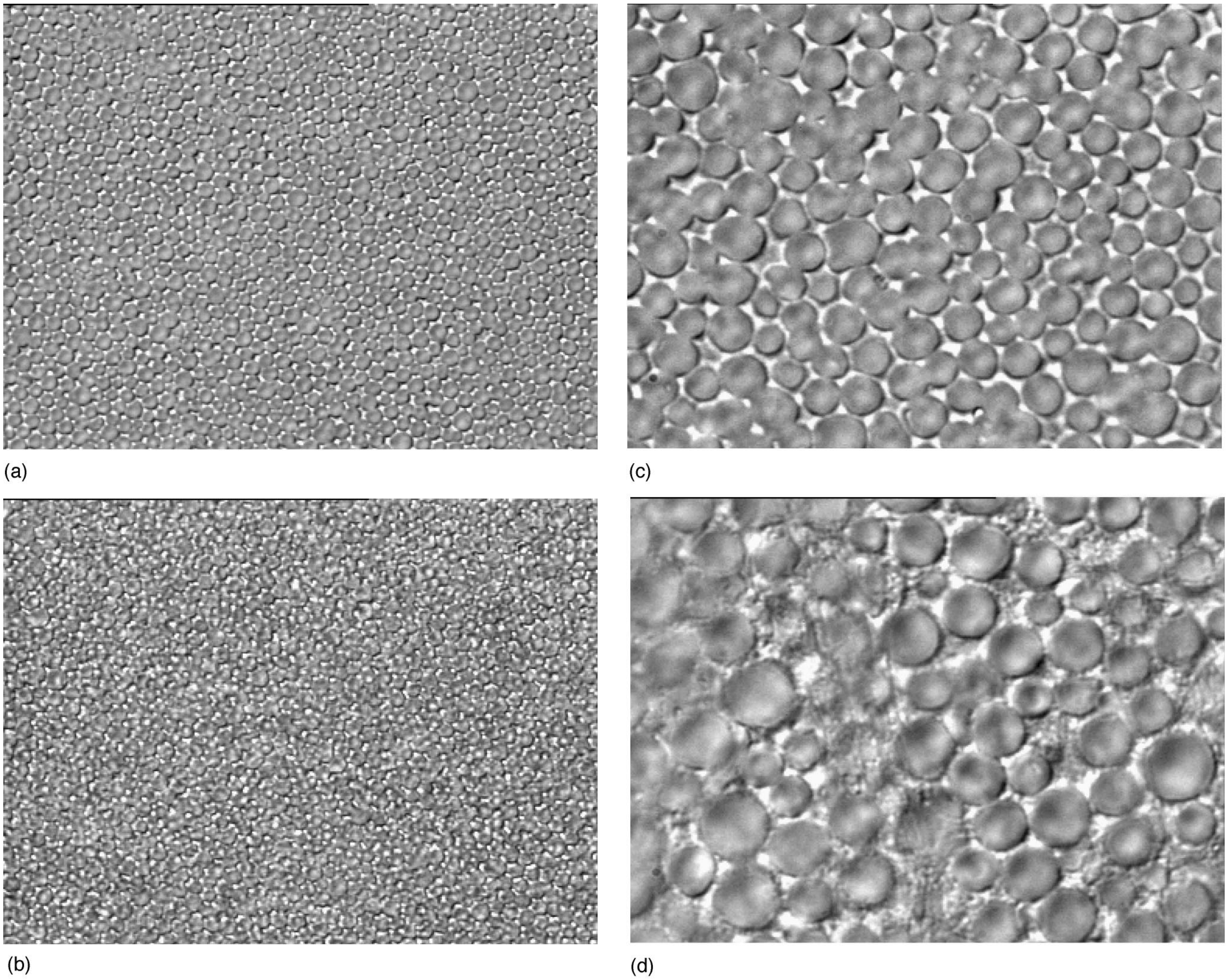

FIG. 8. DIC optical micrographs of AOT membranes, $\phi_m = 0.20$, and 0.2-μm-diam latex particles, $\phi_p = 1.2\%$ w/w. For this sample, the onions (with no added solid particles) were first formed by shearing ($\dot{\gamma} = 2\ \mathrm{s}^{-1}$ for 1 h), shear was then stopped, the particles were added, and the sample was finally sheared again (at the same shear rate) for 30 min. Typical onion diameter is $D \approx 8\ \mu$m. (a) Low magnification (×40 objective) view of the sample next to the upper microscope slide surface. (b) View in the bulk of the sample in (a). (c) High magnification (×100 oil immersion objective) view of the sample in (a). (d) Same as (c) but slightly diluted with brine. Width $= 120\ \mu$m in (a),(b) and 80 μm in (c),(d).

though by doing so they could substantially relax the curvature energy there.

In Fig. 9 we show rheological data on an onion-particle alloy system at $\phi_p = 1.2\%$ w/w. In the time evolution of the viscosity one observes a drop after the addition of the particles but the system soon recovers on further shearing (although the viscosity does not quite regain its previous level). Remarkably, once again, the linear viscoelastic spectrum then measured (by stopping the flow and applying a low-level oscillatory shear) is barely distinguishable from the same scan applied to a particle-free onion sample (as measured before the particles were added).

We note that some of the ''alloyed'' materials have a bicontinuous topology: there is a network of densely packed latex particles in which onions remain embedded and in contact with each other. For refractive index purposes the structure resembles an open-cell foam. Were more particles to be added, one might cause the onions to cease to touch, and thereby achieve a continuous medium of high refractive index in which low refractive index particles are embedded. This combination may be of interest for localization of light [8], although one would ideally require a shorter length scale, and also a more ordered structure, than those presented below. Since we have made no attempt at optimization of these features, this avenue may deserve further investigation.

VI. CONCLUSIONS

We have described three distinct new types of composite soft solid formed by dispersion of solid particles in the onion texture, itself obtained by shearing a lyotropic lamellar phase. We focused on the case where the particles are much smaller (by one order of magnitude) than the onions themselves. The particles are, however, much larger than the interbilayer spacing. The composites formed, while still presumably metastable, have lifetimes that are orders of

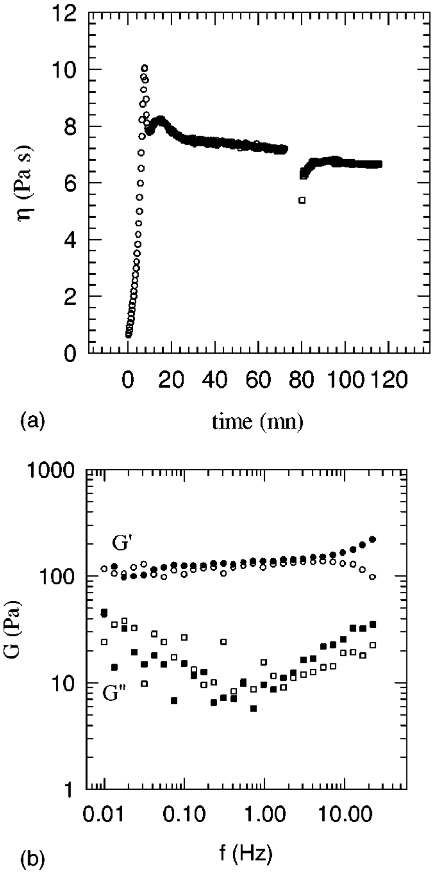

FIG. 9. Rheology of the alloy system. (a) Transient viscosity $\eta(t)$ under constant shear rate $\dot{\gamma}=2\ \mathrm{s}^{-1}$. The first part of the curve (up to $t=70$ min) corresponds to the bare system without latex particles. At $t=70$ min, shear was stopped and the solid particles ($\phi_p=1.2\%$ w/w) were then added. This mixture was then shear again (from time $t=80$ min) until steady state was achieved. (b) Viscoelastic spectra for bare onions (open symbols) and the alloy (filled symbols). The measurement for the bare onions was made just after shear has been stopped (i.e., at $t=70$ min). The applied controlled shear stress was $\sigma_{\rm osc}=0.06$ Pa and the measured strain amplitude was of order of 0.08%.

magnitude longer than if particles were dispersed in an unsheared lamellar phase.

In general, the particles reside at regions of high bilayer curvature as expected on energetic grounds. When larger particles (0.4 μm in this work) are added before shearing begins, they are incorporated almost entirely at the onion cores (‘‘stuffed onions’’). If the particles are sufficiently small (0.2 μm in this work), some of them also decorate the interstices and edges of the polyhedral onion packing (‘‘decorated onions’’). This allows the packing itself to be visualized in real space (and, by scanning vertically, in three dimensions) confirming the structural analogy between dense onion assemblies and foams. Indeed, the decorated regions are analagous to the Plateau borders of a foam (close to the dry limit). If instead the particles are added after the onions have already been created by shearing, they reside exclusively in these ‘‘Plateau border’’ regions; it seems that they cannot penetrate the cores of preexisting onions.

In the absence of particles, the onion assembly is characterized by large preexisting strain energies (from compression of onions, which would otherwise be spherical, into a polyhedral packing). It is small changes to these energies which are responsible for the elastic behavior of the material [5]. Although it is natural for any isotropically textured lamellar phase to show a finite modulus, the actual magnitude of these preexisting strain energies depends on the details of the geometry. For example, the modulus of a perfect array of polyhedral onion domains of size R is predicted to scale as $G_{\rm perf}\sim\sqrt{K\bar{B}}/R$ (so long as the array has a symmetry axis along the shear gradient direction). This is dominated by contributions from regions of high curvature (internal facets) which arise from the competing requirements of filling space while minimizing curvature. Even at the small volume fractions that we used, the added particles (by replacing the onion cores and/or swelling the interstitial regions) can significantly alleviate the frustration in the packing, as judged by microscopy pictures in which the onions appear much more spherical (see, e.g., Figs. 6 and 8).

On this basis one would expect significant shifts (probably downward) in the elastic moduli of the medium. It is therefore quite puzzling that, even for decorated and alloyed onions, such shifts are not observed. Instead, for particle volume fractions up to about 1%, all three types of composite have viscoelastic spectra that are, within experimental error, barely different from the onion phase without particles. This may suggest that the arguments behind existing estimates for the elasticity of onion packings [5] need closer examination. Alternatively, the reduction of the modulus by the mechanism described above could be compensated for by the presence (in the decorated and alloyed cases) of a percolating network of rigid particles which could serve to stiffen the composite.

Depending on the particular protocol used, and the size of the particles, we have incorporated up to ≈4% w/w of particles into the onion phase. Higher particle volume fractions increasingly led to irreproducible results, and often gave samples showing large aggregates of undispersed particles. The reasons for this are unclear.

In future structural studies it would be interesting to decrease greatly the onion-to-particle size ratio so that the two are comparable in size. This has already been done [9] for a 5:1 size ratio (in a nonaqueous system). Stuffed onions were observed, but beyond a certain particle volume fraction (roughly one particle per onion) the excess particles did not decorate the interstices but instead formed large clumps (a form of phase separation). Proceeding further in the same direction, for example to a 1:1 size ratio, might give very interesting structures in the case of alloys.

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