Rheological Aging and Rejuvenation in Microgel Pastes

Michel Cloitre,* Régis Borrega,[†] and Ludwik Leibler
Laboratoire CNRS-ATOFINA, 95, rue Danton, 92303 Levallois-Perret, France

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We have studied experimentally the rheological behavior of concentrated suspensions of soft deformable microgels below the yield point. We have found history-dependent effects which are interpreted in terms of aging and rejuvenation phenomena, analogous to those existing in glassy systems. The stress amplitude controls the long-time memory and determines the slow evolution of the suspensions.

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Controlling the flow properties of soft concentrated dispersions such as emulsions, foams, and colloidal pastes is a key to success in many applications. Yet, several peculiar features of the rheology of these materials remain poorly understood. For example, at low stresses, they behave like weak elastic solids, whereas they flow like viscous liquids above the so-called yield stress. A day-to-day illustration of this interesting behavior is toothpaste which spreads out only when the tube is pressed strongly. The very existence and significance of a well-defined yield point is still a subject of vivid controversy. On one hand, it is technically difficult to perform reproducible measurements near the yield threshold [1]. On the other hand, the properties of soft concentrated dispersions seem to vary in time and to depend strongly on sample preparation and measurement history [2]. However, whether this is just a nuisance or, more interestingly, a manifestation of the very nature of the physics of these systems is an open and important problem.

In this context, a recent analogy between the rheology of soft materials and the dynamics of glasses is particularly appealing [3]. It has been argued that structural disorder in concentrated dispersions creates energy barriers that cannot be overcome by thermal motion alone. When a stress is applied, the energy landscape is modified and a different metastable state can be reached. There is no intrinsic relaxation time, albeit the very long one after which thermal equilibrium is attained: the system evolves constantly. Consequently, soft concentrated dispersions should exhibit aging phenomena analogous to those found in structural glasses [4–8] and spin glasses [9–12]: the response to a mechanical perturbation should depend on the time elapsed after preparation [13]. However, the connection between aging and rheology has not been established experimentally so far.

In this Letter, we present new experimental results which show that history-dependent phenomena in paste rheology exhibit all the characteristic features of aging. The pastes are made of soft colloidal microgel particles. Their mechanical behavior is dominated by the existence of a yield stress. When a stress exceeding the yield stress is applied, the shear rate reaches a constant value independent of the mechanical history: the pastes flow like liquids. When the applied stress is removed, macroscopic flow stops and a slow logarithmiclike strain recovery takes place. The rheological properties of pastes after flow cessation are probed by applying stresses smaller than the yield stress. The strain responses depend on the time t_W elapsed after flow cessation and, remarkably, they can be rescaled onto universal functions when the experimental time is scaled by t_W^{μ}, μ being an exponent smaller than 1. This is the main characteristic feature of aging. However, there is a major difference between aging in classical glassy systems and in pastes. In glasses, a metastable state is reached when the system is brought below the glass transition temperature, and rejuvenation happens when the temperature is increased. In pastes, rejuvenation is achieved by applying a large stress and metastability appears upon flow cessation. Both the preparation and the measurements are done mechanically. Consequently, the strain response of pastes and the scaling properties crucially depend on the amplitude of the applied stress. A spectacular evidence of metastability and slow dynamics in pastes is that the long-time response may be in the opposite direction to the applied stress.

The pastes studied here are made of polyelectrolyte microgels. Microgels consist of cross-linked acrylate chains bearing methacrylic acid units. When the acidic units are ionized, microgels swell. In dilute aqueous suspensions, they are spherical and have a radius of about 200 nm. The typical polymer concentration inside a swollen microgel is of the order of 0.01 g/g. The rheology of dilute microgel suspensions is very similar to that of hard colloidal particles [14]. The viscosity diverges at the overlap concentration, i.e., for a polymer concentration of about 0.01 g/g, where microgels begin to be closely packed. In contrast to hard colloids, it is possible to concentrate microgel suspensions much further because the individual particles are deformable and able to deswell. Concentrated suspensions behave like pastes. They exhibit exceptional physicochemical stability, and they are free from physical sources of aging such as coalescence or coarsening, which are often encountered in concentrated soft materials [15]. In pastes, microgel particles adapt their volume and shape to steric constraints by developing flat facets at contact. The number and orientation of the facets vary from one particle to another depending on the local neighborhood. This makes the internal structure of pastes intrinsically disordered and metastable.

The rheology of pastes has been studied by stress-controlled rheometry. The rheometer is a commercially available apparatus Haake RS150 working in a cone and plate geometry (angle: 2°; diameter: 35 mm). At low stress amplitudes, because of small imperfections, the actual torque applied to the material is slightly different from the nominal torque. We have measured the discrepancy and found that it varies between $-0.02\ \mu\mathrm{N}\cdot\mathrm{m}$ and $0.25\ \mu\mathrm{N}\cdot\mathrm{m}$ depending on the angular position of the cone. These values are negligible compared to the torques applied in this study which are larger than $10\ \mu\mathrm{N}\cdot\mathrm{m}$. Strains are measured with an accuracy of 3×10^{-5}. The surfaces of the cone and of the plate are slightly roughened by sandblasting to avoid wall slip. The paste is isolated from the ambient atmosphere by a closed vessel which controls water evaporation. All measurements on a given sample are perfectly reproducible on a time scale of about 10 hours.

Rheological measurements below the yield stress are not reproducible unless the initial preparation and the stress history are perfectly controlled. Accordingly, we devised the following experimental procedure: (i) a stress σ_p larger than the yield stress σ_y is applied during a time interval $t_P = 60$ s; (ii) at $t = 0$, the stress is set to zero and the pastes are allowed to rest under zero stress for a time t_W; (iii) at $t = t_W$, a step stress σ_m lower than the yield stress σ_y is applied to probe the mechanical properties of the pastes. This procedure was used in all the experiments reported below. During step (i), the pastes are fluidized and flow like viscous suspensions. This step is designed to erase all internal stresses coming from the loading of the rheometer and to prepare the pastes in a reproducible state. After flow cessation, they become solids. During step (ii), the strain recovers slowly. In Fig. 1, we have plotted data measured for various experimental conditions. The strain origin and the time origin are taken at the end of preparation. We observe that the strain recovery after flow cessation does not depend on the magnitude of σ_P provided that it exceeds the yield stress σ_y. We have also checked that the duration of step (i) plays no role provided that stationary flow conditions are achieved. When the direction of the preshear in step (i) is reversed, the direction of the strain recovery in step (ii) is also reversed but the amplitude and the time variation are exactly the same. This demonstrates that the strain recovery which follows flow cessation is associated with the relaxation of elastic deformations stored during flow. The recovery cannot be characterized by an intrinsic relaxation time like in viscoelastic materials. Instead, it is well represented by a logarithmic variation over at least five decades in time. Logarithmic relaxations have already been reported in systems as different as spin glasses [10], granular materials [16], and nematic elastomers [17]. In our experiments, the fact that strain recovery persists up to the longest times experimentally accessible indicates that mechanical equilibrium is not reached during the waiting time t_W and that, in step (iii), we probe an out-of-equilibrium material. Nevertheless, by studying the response to the probe stress σ_m when the stress amplitude and the waiting time are varied, we are able to obtain valuable information about the rheological properties and their time evolution.

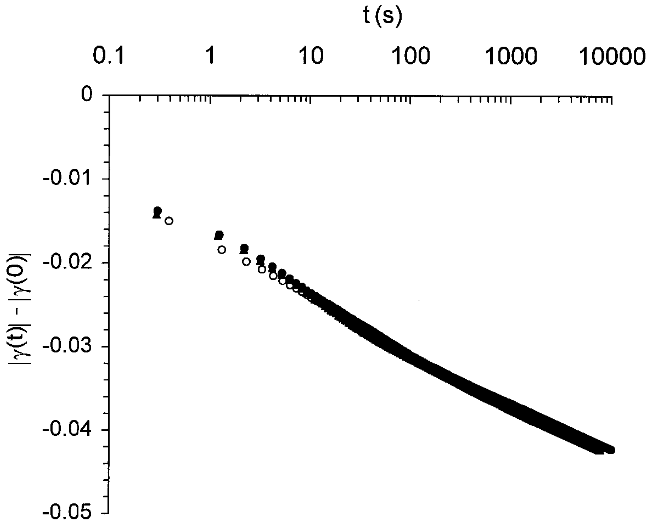

FIG. 1. Strain recovery following flow cessation for different conditions of preparation; ▲: $\sigma_P = 60$ Pa; ●: $\sigma_P = 180$ Pa; ○: $\sigma_P = -180$ Pa (the flow direction is reversed). σ_P is applied for 60 s.

Let us first consider that the amplitude of the stress σ_m is small. Figure 2 shows typical responses measured for different values of the waiting time t_W when $\sigma_m = 1$ Pa. The strain origin and the time origin are taken at the end of the waiting time. At $t = t_W$, the strain jumps instantaneously to a value which is found to be proportional to

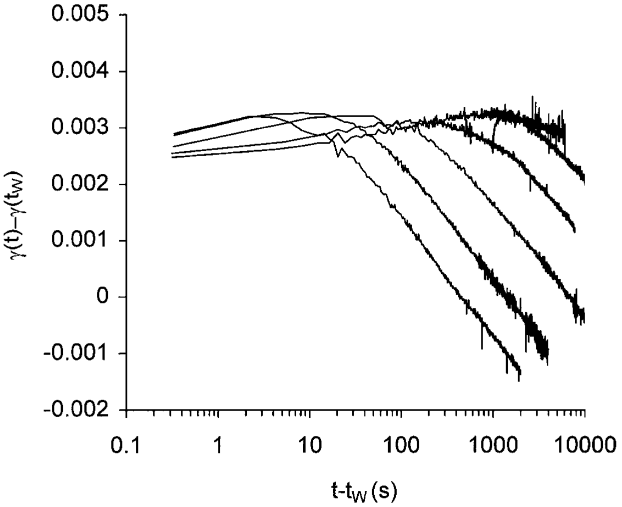

FIG. 2. Strain responses measured at different waiting times when the probe stress σ_m is smaller than σ_C ($\sigma_m = 1$ Pa, $\sigma_C = 4$ Pa). From left to right: $t_W = 10$ s, $t_W = 30$ s, $t_W = 100$ s, $t_W = 300$ s, $t_W = 1000$ s, $t_W = 2000$ s.

σ_m. This is the typical behavior of an elastic material. However, two important features make the strain response different from that of a simple elastic solid. First, we observe that the initial response depends on the waiting time. It is the largest for the smallest waiting time, indicating that the elastic modulus increases with time after flow cessation. This shows that the structure of the pastes evolves during the waiting time. Second, after remaining practically constant, the strain starts to recover even though the paste is still under load. Remarkably, the time where this occurs is of the order of the waiting time. This long-time response always proceeds on the opposite direction to the flow created during preparation. It reflects the underlying continued recovery following the preparation step.

Figure 3 shows that the response also depends on the waiting time when the probe stress σ_m is higher. The short-time response is still that of an elastic material, the response being the largest for the smallest waiting time. At long time, the paste creeps, the time variation of the strain being well described by a logarithmic variation. Creep begins later and is slower when the waiting time is larger. In practice, we have found that the long-time response changes from strain recovery to plastic creep when the probe stress σ_m exceeds some particular value σ_C which, for the particular concentration studied here is equal to 4 Pa. Interestingly, σ_C is of the order of the stress above which the response becomes nonlinear [18]. The value of σ_C depends on the microscopic structure of microgels through several parameters such as the cross-link density and the ionic strength.

In Fig. 4, to account for the unusual dependence of the mechanical behavior on the waiting time t_W, we plot the variations of the responses measured at low stress amplitudes as a function of $(t - t_W)/t_W$. Remarkably, this operation suffices to collapse all the curves almost perfectly. There is a slight t_W dependence for short waiting times but the curves become hardly distinguishable in the limit of large waiting times. This universal behavior is the characteristic feature of aging phenomena [4,7,9–11].

This simple scaling does not work when the probe stress σ_m is higher than σ_C, the discrepancy being the largest near the yield stress where the suspension begins to flow. This suggests that plastic flow is responsible for large internal rearrangements which partially rejuvenate the pastes and erase aging. In Fig. 5, we account for this deviation from full aging by plotting the strain as a function of the variable $(t - t_W)/t_W^{\mu}$, μ being a positive exponent smaller than 1. This scaling variable was originally proposed in the context of polymeric glasses [7]. Clearly, the creep curves measured at different ages collapse perfectly onto a single master curve. The same analysis holds at different values of the probe stress σ_m apart from the fact that μ depends on σ_m. The inset of Fig. 5 shows that μ decreases from $\mu = 1$ when $\sigma_m < \sigma_C$ (full aging) to $\mu = 0$ when $\sigma_m \geq \sigma_y$ (no aging). The new result here is that exponent μ can be used to quantify the partial rejuvenation due to a finite disturbing stress and the deviation from full aging.

Our results suggest the following microscopic picture of the dynamics of soft colloidal pastes. When subjected to stresses exceeding the yield stress, microgel pastes are fluidized. Thin water films lubricate the contacts between microgels which move and exchange positions very rapidly. This mechanism is supported by detailed studies where microscopic parameters like polymer concentration, cross-link density, and ionic strength have been varied [18]. When the external stress is removed, macroscopic flow stops and microgels get trapped in a metastable spatial arrangement corresponding to that existing in the fluidized paste. The evolution of the paste involves the reorientation, contraction, or expansion of the facets existing between microgels in a random way imposed by the disordered nature of the packing and the thermal fluctuations.

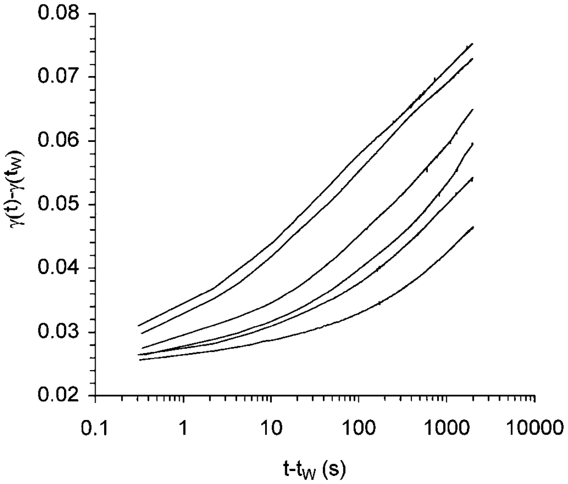

FIG. 3. Creep curves measured at different waiting times when the probe stress σ_m is larger than σ_C ($\sigma_C = 4$ Pa, $\sigma_m = 10$ Pa, $\sigma_y = 20$ Pa). From top to bottom: $t_W = 15$ s, $t_W = 30$ s, $t_W = 300$ s, $t_W = 1000$ s, $t_W = 2000$ s, $t_W = 10\,000$ s.

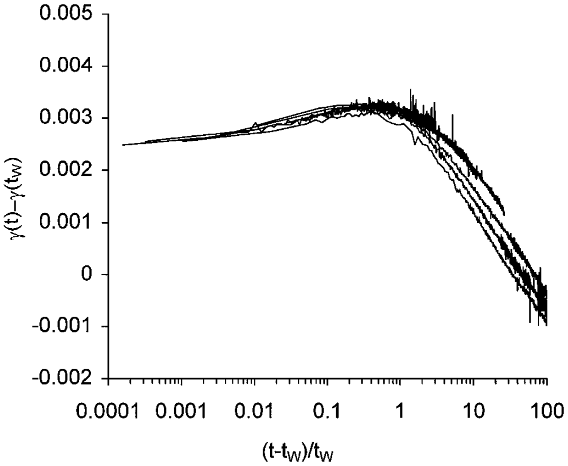

FIG. 4. Same curves as in Fig. 2 plotted as a function of $(t - t_W)/t_W$.

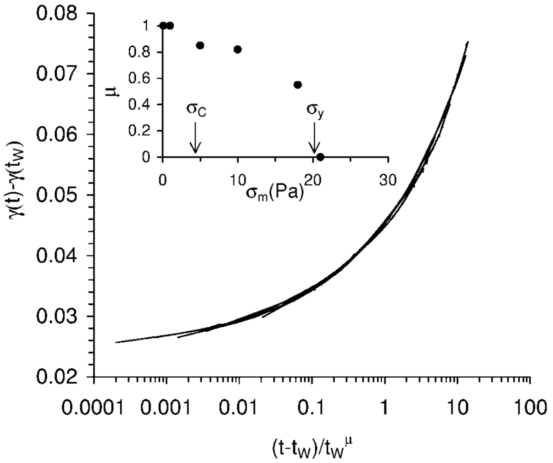

FIG. 5. Same curves as in Fig. 3 plotted as a function of $(t - t_W)/t_W^\mu$ ($\mu = 0.80$). The inset gives the values of μ obtained for different σ_m.

A change of the local topology between two contacting microgels induces long range perturbations between second, third, and even further neighbors. Moreover, local topological changes, although favorable, may be incompatible with more global constraints. Therefore, strain relaxation is closely associated with collective rearrangements and frustration. These two generic properties may be responsible for the logarithmic strain recovery which is observed upon flow cessation. During aging, different spatial configurations of microgels with a broad distribution of relaxation times coexist in the paste. At time t_W, only those configurations with relaxation times smaller than t_W have relaxed, others have not but will eventually relax later on. When a very small stress σ_m is applied at time t_W to probe the system, it does not create large topological rearrangements but it induces small deformations which add to the strains which did not have time to relax during t_W. The short-time response is that of a viscoelastic solid with many relaxation times. The paste continues to evolve and, at times comparable to t_W, the response becomes dominated by the relaxation of the strains which have not relaxed during aging. In contrast, when the stress σ_m is larger than σ_C, large rearrangements become possible and the pastes creep. The response is then a combination of aging and of partial rejuvenation.

In conclusion, time-dependent phenomena in paste rheology exhibit all the main features of aging in glassy systems. Rheological aging is closely associated with frustration and cooperative relaxation of steric constraints between interlocked neighboring particles. In that respect, we think that this is a general behavior which should be found in many other systems once the proper protocol to deal with far-from-equilibrium systems is recognized and implemented.

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*Corresponding author.
Email address: michel.cloitre@levl.elf-atochem.fr

†Present address: Spontex, Recherche et Développement, 74, rue de Saint-Just-des-Marais, 60026 Beauvais Cedex, France.

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