

Abrupt Transition from Viscoelastic Solidlike to Liquidlike Behavior in Jammed Materials

J. C. Baudez¹ and P. Coussot^{2,*}

¹*Cemagref, Domaine des Palaquins, Montoldre, France*

²*LMSGC (UMR113 LCPC-ENPC-CNRS), Institut Navier, Marne la Vallée, France*

(Received 4 July 2003; published 14 September 2004)

Using a new rheometrical technique, which makes it possible to determine both the velocity field in steady state and the strain field in the very first instants of the flow, we show that, beyond a critical deformation, typical pasty materials (a foam and a polymeric gel) turn abruptly from a viscoelastic solidlike behavior to a steady liquidlike behavior at a shear rate larger than a critical value.

DOI: 10.1103/PhysRevLett.93.128302

PACS numbers: 83.80.Hj, 64.70.Dv, 83.60.La, 83.85.Fg

Concentrated emulsions, suspensions, foams, granular materials, or polymeric gels are of common use in civil engineering, food, cosmetic, and pharmaceutical industries. Each of these materials appears capable of flowing only when a sufficiently large stress has been applied to it, a characteristic feature associated with their “jammed” structure. Since these materials might constitute a new state of matter [1] reminiscent of the glassy state, they are actively studied in physics [2].

In general the dual rheological behavior of jammed systems has been coped with by considering independent constitutive equations applied either to the solidlike or liquidlike regime. Until now, in the liquidlike regime, they were assumed to follow a simple yielding behavior, i.e., such that the shear rate increases continuously from zero with the difference between the applied stress and the yield stress. However, it has been shown recently that these materials are incapable of flowing steadily at a rate smaller than a critical, finite value [3]. This behavior, which appears to be quite general for pasty materials, was confirmed by direct observations of the velocity field under flow [4]. The resulting discontinuity in the shear rate is reminiscent of that found recently for various wormlike micellar systems [5] also leading to shear banding but, with the usual jammed systems, the general result is a coexistence of solidlike and liquidlike regions. In parallel, the solidlike regime has been studied with the help of dynamic tests, and some characteristic features have been found for model systems (e.g., see [2]), but our knowledge of the processes occurring at the solid-liquid transition in such materials remains relatively poor. For suspensions it is generally assumed that the initial continuous network of interactions progressively turns to smaller aggregates (flocs) with shear intensity and time, which, respectively, induces shear thinning and thixotropy [6], but such considerations mostly follow from interpretations of (macroscopic) rheological data.

Here we focus on this problem by studying the deformation and velocity profiles within typical pasty materials starting to flow. We used a new (rheometrical) technique described in detail elsewhere [7], and which relies on the reconstruction of the tangential deformation

or velocity profiles in time within a wide-gap Couette geometry from a series of tests under qualitatively similar stress histories but with smaller, absolute, torque values. Unlike standard magnetic resonance imaging (MRI), particle imaging velocimetry, or light scattering techniques, this approach makes it possible to observe the deformation profiles within the material during the very first instants of flow. We thus show that beyond a critical deformation, the behavior of pasty materials turns abruptly from a viscoelastic solidlike regime to a steady liquidlike regime with a shear rate larger than a critical value. One consequence is that the apparent viscoelastic behavior of the material is partly governed by the spatial evolution of the solid-liquid distribution in the gap.

The materials used were a commercial, polymeric, hair gel (“May gel-normal,” made by *Yplon S.A.*, Belgium) basically made of water and Carbopol and extremely stable under various conditions, and a foam (“regular,” *Gillette*, France) which significantly ages in time. These materials have an apparent yield stress [2,8] and are often used as model yield stress fluids. In order to determine the internal flow characteristics we used a *Bohlin C-VOR200* rheometer equipped with a coaxial cylinder geometry (inner diameter: 24.5 mm; outer diameter: 100 mm; length: 35 mm) and carried out systematic creep tests under different torque levels. For each of these elementary tests we started from the material in the same state obtained after a preshear at a high velocity followed by a rest period. In a Couette geometry, in the absence of inertia and edge effects, it may be demonstrated [9] that $\gamma = -r\partial\varphi/\partial r$ (and equivalently $\dot{\gamma} = -r\partial\omega/\partial r$), and $\tau = M/2\pi hr^2$, in which M is the torque applied to the inner cylinder, γ is the deformation, $\dot{\gamma}$ is the shear rate, φ is the rotation angle, ω is the rotation velocity, and τ is the shear stress, within the material. The velocity profile in time for the highest torque level may then be “reconstructed” from such a set of tests. Indeed, since the shape of the shear stress distribution does not vary with the distance, the local rotation velocity at some finite distance within the material for a given applied torque is identical to the rotation velocity of the inner cylinder for a sufficiently smaller torque applied. This result is in fact

strictly valid, and thus the technique is rigorous and does not rely on any assumption concerning the material behavior, if the ratio of the outer to the inner cylinder diameter is infinite [7], or if there is an unsheared region within the gap, a situation which should occur with yield stress fluids under some conditions. Otherwise this approach provides only an approximation of the effective deformation or velocity profile. This technique has been validated from MRI data [7] for a steady-state flow of the gel. Note also that this technique is valid as long as no perturbing effects such as wall slip, fracture, or material heterogeneities develop in the gap, but some of these effects may be detected from the aspect of the apparent velocity profiles [7].

During a creep test under a given torque, in the first instants of the flow (first flow regime), the obtained profiles of rotation angles (φ) within the material remain slightly inclined and parallel (Fig. 1). Afterwards (second flow regime) there is a much larger deformation of the fluid starting near the inner cylinder and apparently progressing towards the outer cylinder as time goes on. The rotation angle associated with the corresponding mobile interface between this widely deformed region and the rest of the fluid remains roughly constant: about 0.2 rad for the gel and 0.15 for the foam. The transition between the two flow regimes is thus associated with a critical rotation angle (φ_c). Note that the last profiles for the foam appear uneven, an effect which might be due either to aging during our series of tests or to some fluctuating slippage which we could observe along the inner cylinder near the free surface. Finally both fluids appear to stop flowing after about 0.1 s of flow beyond a critical distance (r_c), corresponding to the asymptotic position of the interface between the two regions described above. This distance may be associated with a critical stress ($\tau_c = M/2\pi hr_c^2$), which is used to scale any stress value in this Letter. The torque values are scaled with the help of the

critical torque for which τ_c is reached along the inner cylinder: $M_c = 2\pi hr_1^2 \tau_c$.

Since the first flow regime concerns the very beginning of the motion it is natural to assume that it mainly corresponds to an elastic regime, i.e., such that $\tau = G\gamma$, where G is the elastic modulus of the material. Dynamic tests tend to confirm this hypothesis: up to a critical torque amplitude ($M/M_c \approx 1$) leading to a rotation angle approximately equal to φ_c along the inner cylinder, the flow regime appears to be mainly elastic; i.e., the phase shift is very small and the apparent deformation (rotation angle) is proportional to the torque amplitude (cf. Fig. 3). For a purely elastic material it follows from integration of the above equations that, starting from rest [$\gamma(t=0) = 0$], the expected deformation profile is

$$\varphi(r) = \frac{M}{4\pi hGr^2} = \frac{\gamma}{2}. \quad (1)$$

The profiles in the first regime (cf. Fig. 1) effectively appear perfectly parallel to an equation of the type (1). Now the apparent critical angle at the transition between the two regimes finds a direct correspondence with a critical strain γ_c of the material. A simple elastic behavior below a critical deformation associated to yielding was already suggested for describing the behavior of some pasty fluids [10]. However, we do not obtain a single deformation profile independent of time as predicted by (1) but different parallel profiles at a mean level increasing with time. This finds a simple explanation: in this regime the material is not a pure elastic body but a viscoelastic solid which, under a given stress τ , needs some time before reaching its asymptotic deformation. For example, for a material following a simple Kelvin-Voigt model, i.e., such that $\tau = G\gamma + \mu\dot{\gamma}$, we have $\varphi(r) = (M/4\pi hGr^2)[1 - \exp(-Gt/\mu)]$, i.e., successive similar profiles at increasing levels in time. Using this model we can compute the time needed to reach

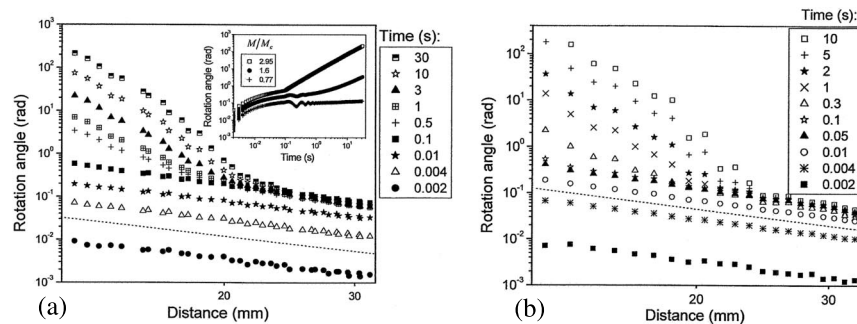


FIG. 1. Creep test with (a) the gel ($M/M_c = 2.95$) and (b) the foam ($M/M_c = 3.55$): profiles of rotation angles within the gap at different times after the initial instant as reconstructed from systematic creep tests under smaller torques. The dashed line corresponds to the pure elastic behavior given by Eq. (1). The inset shows typical creep curves under different dimensionless torque values. Preparation: the materials were presheared at 20 rad/s (gel) or 50 rad/s (foam) during 30 s (gel) or 15 s (foam) and then left at rest for 20 s (gel) or 10 s (foam).

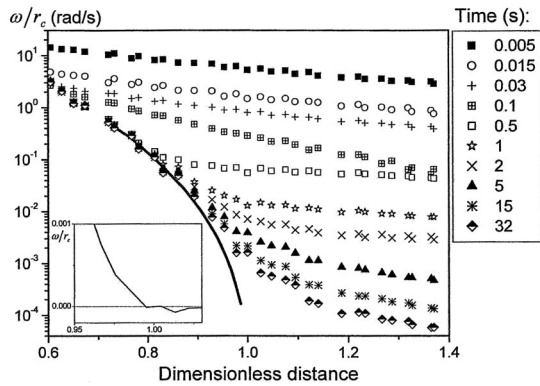


FIG. 2. Rotation velocity profiles at different times in the gap of the Couette system during the creep test of Fig. 1. The data are presented in terms of the ratio ω/r_c as a function of the dimensionless distance r/r_c ($r_c = 21.55$ mm for the gel). In such a representation a master curve for the velocity profiles under different boundary conditions may be obtained in steady state, which makes it possible to plot the steady-state MRI data of Ref. [6] corresponding to another rotation velocity in the same diagram (dark line). The inset corresponds to MRI data at a smaller (linear) scale.

$\gamma_c : t_c(\tau) = -(\mu/G)\ln(1 - G\gamma_c/\tau)$, which takes very small values for large stresses and very large values for stresses close to $\tau_c = G\gamma_c$. This result is in qualitative agreement with our data (cf. Fig. 1) which show a rapid transition from the first to the second regime close to the inner cylinder where the stress is large and a much slower transition farther in the fluid. In summary these materials are viscoelastic solids below a critical deformation which can be overcome only if the applied stress is larger than the critical stress.

Let us now look at the velocity profiles in time during a creep test (Fig. 2). In the analyses below we focus on the data obtained with the gel, keeping in mind that those with the foam give qualitatively, though more noisy, similar results. As expected, in the viscoelastic region (sufficiently far from the inner cylinder) the velocity profiles remain approximately parallel, but the mean velocity level decreases in time because the deformation saturates. In the meantime a part of the profile close to the inner cylinder remains stuck to a fixed curve while the rest of the profile goes on decreasing. The inner part of the curve appears to exactly correspond to the steady-state velocity profile for the gel as determined by independent MRI tests (cf. Fig. 2) [7]. Thus, as soon as it leaves its initial viscoelastic regime, the fluid starts to flow and almost immediately reaches its steady-state flow conditions, which *a priori* corresponds to its liquidlike behavior. Also note that the steady velocity profile as determined by MRI and the reconstruction technique over longer times of flow exhibit a slope rupture at a certain distance within the gap (see the inset of Fig. 2) [7], which corresponds to a discontinuity in shear rate and

is typical of various pasty materials [3,4]. Thus our data show that the material abruptly turns from a viscoelastic solid to a liquid flowing at a rate larger than a finite, critical value ($\dot{\gamma}_c$). This effect in fact appears from macroscopic data in creep tests: the rotation angle vs time curves exhibit a slope rupture at the transition between the two regimes (see the inset of Fig. 1). Note that for the foam a few seconds are necessary for reaching the steady state in the liquid regime, which suggests that some thixotropy effects may also play a role in this regime.

Some oscillations of the elastic part (see the inset of Fig. 1) occurred between 0.1 and 0.6 s. They are likely due to an effect of elastic relaxation in the solidlike region, which occurs when the solid network suddenly breaks close to the inner cylinder at the critical deformation, i.e., when the material near the inner cylinder becomes liquid. The oscillations might result from the coupling of this elastic relaxation with inertia.

Finally the complete constitutive equation of the fluid initially at rest (after some restructuration) as deduced from our observations is as follows: *viscoelastic solid* as long as $\gamma < \gamma_c$, with $\gamma = f(\tau, t)$, where $f(\tau, t)$ remains finite when $\tau < \tau_c$ and its maximum value in that case is $\gamma_c = f(\tau_c, \infty)$; *liquid* when $\gamma > \gamma_c$, with $\dot{\gamma} = g(\tau)$, where g is an increasing function such that $g(\tau_c) = \dot{\gamma}_c \neq 0$.

It is worth noting that this model also predicts a discontinuity of the shear rate vs time curve at the solid-liquid transition, since in general $g(\tau) \neq \partial f(\tau, t)/\partial t$ when $\gamma = \dot{\gamma}_c$.

The agreement of this model with results from dynamics tests can be further tested using again the reconstruction technique. Indeed the spatial distribution of phase shift angles at a given time during torque oscillations may be found from a set of rotation velocities of the inner cylinder under torque oscillations at smaller amplitudes but under the same frequency, starting from the same initial state [7]. Thus we could obtain the distribution of

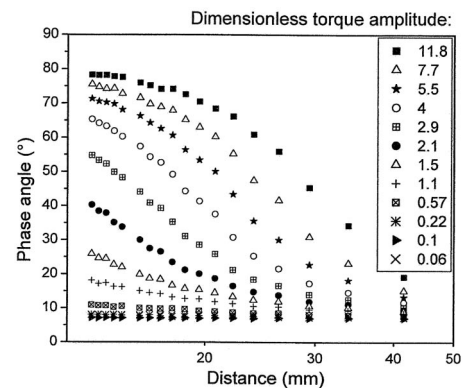


FIG. 3. Reconstructed profiles of the phase shift within the gap during ramps of oscillations (frequency: 2 Hz) under increasing torque amplitudes with the gel. The ramp duration is 75 s and the torque is increased logarithmically.

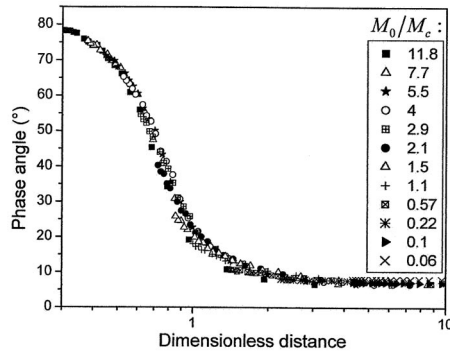


FIG. 4. Phase shift profiles as a function of the dimensionless distance for different torque amplitudes during a ramp of oscillations under a given frequency (2 Hz) for the gel (data of Fig. 3).

phase shift in the gap as a function of time during a ramp of torque amplitudes (Fig. 3). For small torque amplitude the phase shift is small, and the material remains mostly elastic; for larger torque amplitudes the material starts to liquefy in a region close to the inner cylinder: the phase shift tends to $\pi/2$. The thickness of this region then increases with the torque amplitude. Let us now assume that in our tests stationary oscillations were reached at each torque amplitude. According to the above model, this implies that a region close to the inner cylinder (up to $\tau = \tau_c$) has liquefied while the outer region is still solid. The rotation angle at a given point in the fluid results from the motion of these two regions, which is $\varphi(r, t) = \int_0^t [\int_{r_c}^r (\dot{\gamma}/x) dx] dt + \int_0^t (\gamma/x) dx$. For a given torque amplitude M_0 we have $\tau = M_0(\sin\omega t)/2\pi hx^2 = \tau_c(\sin\omega t)/y^2$ in which we used $y = x/r_c$, where $r_c = \sqrt{M_0/2\pi h\tau_c}$ is the location of the interface between the liquid and solid regions. We can further transform the above equation using our model and a change of variable ($y = x/r_c$) so as to get $\varphi(r, t) = \int_0^t (\int_1^X [g(\tau_c \sin\omega t / y^2)/y] dy) dt + \int_0^t [f(\tau_c \sin\omega t / y^2)/y] dy$. It follows that the phase shift at any distance within the gap, which is a function of the two terms of this equation, depends only on $X = r/r_c$, and not on the torque amplitude. Thus different dynamic tests under different torque amplitudes should provide similar data in terms of phase shift if plotted as a function of X . The validity of this superposition principle effectively appears from our data (cf. Fig. 4), but one must keep in mind that the assumption of stationary oscillations basically conditions this result.

Our results show that in simple shear these typical pasty materials exhibit two possible states: they are either viscoelastic solids or liquids. The transition between these two states is abrupt: the material almost instantaneously becomes a liquid which steadily flows at a shear rate larger than a critical value. When there is apparently no (or weak) time dependence of the liquid behavior, the

apparent, progressive transition from an elastic solid to a liquid as the imposed stress, deformation, or frequency increases in various types of rheometrical tests does not directly result from the solid-liquid transition of the material at a given point but from the spatial propagation of the interface between the solid and liquid phases. In particular, under dynamic tests the transition from the solid to the liquid regime cannot be associated with the crossover of the elastic and viscous moduli or to a specific value of the phase shift: the liquid region progressively invades the gap as the frequency, stress, or strain amplitudes increase. Thus the apparent viscoelasticity of various systems (foams, emulsions, polymer gels, etc.) in their liquid regime might result only from both the elasticity of the solidlike region and the displacement of the solid-liquid interface. Since various pasty materials were recently shown to exhibit similar trends (viscosity bifurcation and shear localization) it is likely that the present detailed description of the solid-liquid transition features in a polymeric gel and in a foam are general.

*Electronic address: coussot@lcp.fr

- [1] A.J. Liu and S.R. Nagel, *Nature (London)* **396**, 21 (1998).
- [2] A. J. Liu and S. R. Nagel, *Jamming and Rheology* (Taylor and Francis, New York, 2001).
- [3] P. Coussot, Q. D. Nguyen, H. T. Huynh, and D. Bonn, *Phys. Rev. Lett.* **88**, 175501 (2002).
- [4] F. Pignon, A. Magnin, and J. M. Piau, *J. Rheol.* **40**, 573 (1996); J. S. Raynaud *et al.*, *J. Rheol.* **46**, 709 (2002); P. Coussot *et al.*, *Phys. Rev. Lett.* **88**, 218301 (2002).
- [5] E. Cappelare, R. Cressely, and J. P. Decruppe, *Colloids Surf., A* **104**, 353 (1995); M. M. Britton and P. T. Callaghan, *Phys. Rev. Lett.* **78**, 4930 (1997); J. B. Salmon, A. Colin, S. Manneville, and F. Molino, *Phys. Rev. Lett.* **90**, 228303 (2003).
- [6] A. S. Michaels and J. C. Bolger, *Ind. Eng. Chem. Fundam.* **1**, 153 (1962); C. Tsenoglou, *Rheol. Acta* **28**, 311 (1989); P. Coussot, A. I. Leonov, and J. M. Piau, *J. Non-Newtonian Fluid Mech.* **46**, 179 (1993).
- [7] J. C. Baudez, S. Rodts, X. Chateau, and P. Coussot, *J. Rheol.* **48**, 69 (2004).
- [8] A. Magnin and J. M. Piau, *J. Non-Newtonian Fluid Mech.* **36**, 85 (1990).
- [9] B. D. Coleman, H. Markowitz, and W. Noll, *Viscometric Flows of Non-Newtonian Fluids* (Springer-Verlag, Berlin, 1966).
- [10] D. Doraiswamy, A. N. Mujumdar, I. L. Tsao, A. N. Beris, S. C. Danforth, and A. B. Metzner, *J. Rheol.* **34**, 647 (1991); R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999); P. Hébraud and F. Lequeux, *Phys. Rev. Lett.* **81**, 2934 (1998); A. Mujumdar, A. N. Beris, and A. B. Metzner, *J. Non-Newtonian Fluid Mech.* **102**, 157 (2002).