Colloid Polym Sci 278:777–782 (2000)

SHORT COMMUNICATION

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Stress-induced compaction of concentrated dispersions of gel particles

Received: 5 October 1999
In revised form: 21 December 1999
Accepted: 21 January 2000

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Abstract When submitted to successive shear stress steps, the elastic shear modulus of a concentrated dispersion of soft gel particles shows an exponential increase from 50 to 110 Pa. A slow relaxation time ($\tau_r \simeq 500$ s) attributed to the mobility of the gel particles within their free volume is obtained. The amplitude of the relaxation time distribution decreases with the number of shear stress sequences, indicating a progressive decrease in the free volume available per particle. The results are explained by an increase in the packing density as grains rearrange under the external constraint. A rate constant is determined from the evolution of the dispersion's elastic modulus ($K \simeq 4 \times 10^{-4}\,s^{-1}$). The rate of compaction shows a logarithmic decrease when the initial particle's packing fraction is increased.

Key words Granular material · Microgel · Packing fraction · Compactivity · Compaction

Introduction

Suspensions of soft particles in a liquid carrier occur in everyday life. Examples of such systems are clays, paints, slurries, and food emulsions. A striking property of those systems is that when the volume fraction of the dispersed phase attains a critical value, the suspension acquires the mechanical properties of a solid. The theoretical and experimental aspects of this phenomenon have been widely investigated on monodisperse suspensions of spherical particles [1–7]. The storage modulus of a concentrated dispersion of particles is linked to the particle's number of nearest neighbours, i.e. the radial distribution function, $g(r)$, integrated over the particle's centre–centre separation and the interaction potential between particles [5–7]. However, for irregular particles or composite materials, the elasticity is mainly controlled by structural features, such as the packing of the particles [8, 9]. For instance, the elasticity of emulsion–polymer gel composites is shown to be of entropic origin, controlled by the cluster packing rather than the osmotic pressure setting the intensity of the colloidal force [8]. Edwards and coworkers [9–12] developed a parameter called compactivity to describe the packing of a granular system. It is characteristic of the number of possible ways the grains can be arranged into a volume ΔV such that the disorder is ΔS. The two limits of the compactivity are 0 and ∞, corresponding to the maximum close packing and to the least compact arrangement of the grains, respectively. Upon vibrations, the density of granular materials evolves from a low-density initial state to a higher-density final steady state following a slow inverse logarithmic law [13–15]. This process, called granular compaction, is explained by a decrease in the compactivity of the system [16].

To our knowledge, the issue whether granular compaction can be induced by a low shear stress has not been addressed yet. In the present article, the influence of low and steady shear stress on the packing state of a concentrated dispersion of soft gel particles (termed fluid gel) is investigated. The article is organised as follows. In the first section, the gel particle critical packing fraction for which fluid gels display a viscoelastic response is determined. Then the influence of repeatedly applied steady shear stress steps on the

viscoelastic properties of the dispersion is shown. In the third section, the relaxation time distribution functions obtained from the compliance functions measured during the shear stress sequence are discussed. In the fourth section, the influence of the gel particle reduced packing fraction on the rearrangement under the external constraint is investigated. In the last part of the article, the results are discussed in terms of changes in the compactivity of the gel particle dispersion.

Materials and methods

Agar fluid gels

Agar is a polysaccharide extracted from marine red algae. When agar solution is sheared during the sol–gel transition, the ultimate structure consists of polymer-rich regions, referred to as a microgel, suspended in a polymer-depleted matrix [17–20]. These systems are called fluid gels. If the volume fraction of the gel particle is above a critical volume fraction, the dispersion behaves like "weak gels", displaying a dominant elastic component with slight frequency dependence [7, 20]. The large deformation behaviour is plasticlike, as the linear viscoelasticity region is limited to strains lower than 1% [20].

The agar fluid gels were made up as 3% polymer weight using commercial agar (agar Luxara-1253 from Arthur Branwell & Co). The impurities in this commercial batch are ash (6.5% w/w), acid-insoluble matter (1.5 % w/w), sulphate (990 ppm), lead, and other heavy metals (50 ppm). The polymer solutions were prepared by dispersing the polymer in cold water before boiling for 30 min with mild stirring. Then, the solutions were transferred to a stirred vessel. The shaft speed applied in the stirred vessel was 1000 rpm. All samples were prepared using Millipore bidistilled water. Transmission electron microscopy (TEM) images of typical agar microgels used in this work are visualised in Fig. 1A. The gel particles are irregularly shaped and have a size of a few microns. On the typical space scale of TEM, the internal structure of the particles is very similar to that of quiescent agarose gels [21]. Additionally, particle size analysis was done on the agar fluid gel using a Mastersizer-X from Malvern. In order to get a representative particle size distribution, the obscuration level was in the range 15–20%. The refractive index of a 3% agar gel was estimated to be 1.3367. The mean particle diameter over the volume distribution, $D[4, 3]$, was 2 μm (Fig. 1B).

Rheological characterisation

A Carrimed CSL500 rheometer fitted with a large-gap double-concentric-cylinder geometry [22] was used to investigate the viscoelastic behaviour of the samples (gap: 3 mm, sample filling height: 10 mm). Prior to further rheological characterisation, the extent of the linear viscoelastic region of the samples was determined. The frequency spectra were recorded at a fixed strain of 0.2%, a value for which the fluid gels were within the linear viscoelastic regime. To avoid wall slips, the metal walls of the Couette cylinder were roughened with sandpaper. The samples were covered with mineral oil to prevent water evaporation. All the measurements were made at 10 °C.

Determination of the gel particle volume fraction

Centrifugation of the fluid gels was carried out to determine the volume of interstitial water in the suspensions and to estimate the volume fraction of the gel particles. Centrifugation was performed in a relative centrifugal field of 12100g using a Beckman J2-MC at 10 °C. After 60 min the supernatant volume remained constant and corresponded to a volume fraction of free water between particles of $\varphi = 0.265$; therefore, the volume fraction of the gel particle in the system under investigation was $\phi = 1 - \varphi = 0.735$. The volume of free water did not depend strongly on the centrifugal field, but the time required to reach equilibrium showed a steep increase with weak centrifugal fields.

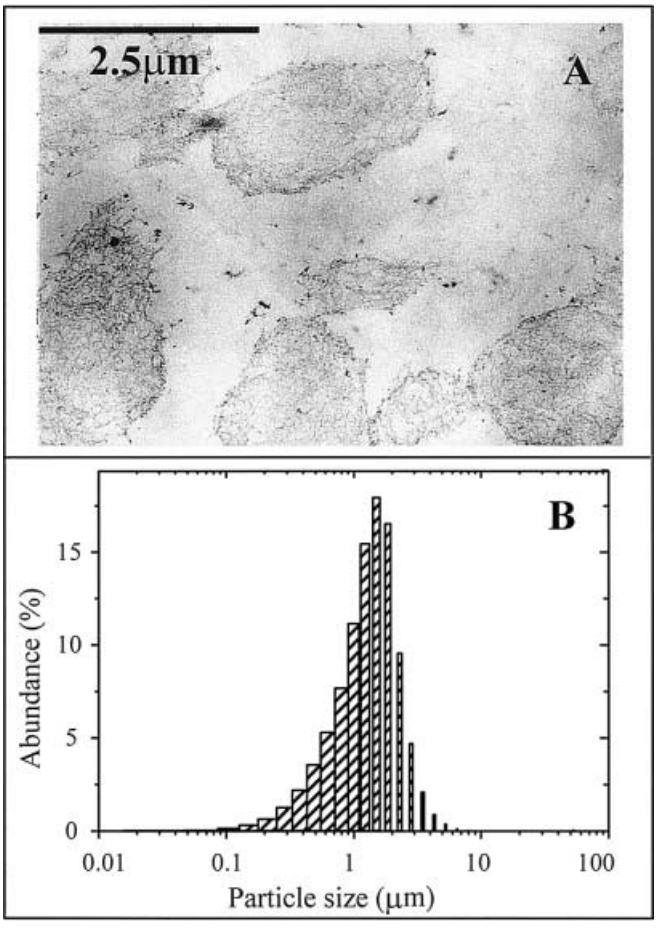

Fig. 1 **A** Internal structure of agar microgel particles observed with transmission electron microscopy (the *space bar* is 2.5 μm). **B** Gel particle size distribution for a 3% agar fluid gel processed at 1000 rpm

Results

Determination of the particle critical packing fraction

The critical particle volume fraction above which the dispersion displays linear viscoelastic behaviour was determined. A small amount of water was added to the gel particle dispersion and the viscoelastic response of the diluted sample was measured. Figure 2 depicts the evolution of the storage modulus and the loss-tangente, $\tan\delta = G''/G'$, at 1Hz as a function of the gel particle volume fraction defined as

$$\phi = 1 - (\phi_{\text{water}} + \varphi) \ , \quad (1)$$

where ϕ_{water} and φ are the volume fractions of added water and the volume fraction of interstitial water determined by centrifugation, respectively. When the volume fraction of added water reached 7.5%, the elastic response of the dispersion vanished, as indicated by the sudden increase in $\tan\delta$. Above this value, the loss modulus dominates the storage modulus and the system behaves like an ordinary suspension of soft particles suspended in a Newtonian liquid. Therefore, it can be assumed that the gel particle critical volume fraction above which the dispersion behaves like a gel is around $\phi_{\text{m}} = 0.66$. Since, loose packings of irregular particles are known to be less dense than loose packings of spheres, the value we found is higher than expected; however, polydispersity in the size of the gel particles as seen in Fig. 1 can account for denser packing [10, 11]. At this point, we use the reduced packing fraction, $\phi^* = \phi/\phi_{\text{m}}$, to describe the packing of the gel particle in the system.

Influence of stress-controlled conditioning on the viscoelastic behaviour of the system

The effect of successive creep–recovery experiments on the mechanical spectra of a fluid gel was studied. The samples were submitted to a low steady shear stress for 15 min, then the stress was released and the samples were allowed to relax for 15 min. A series of creep–recovery runs were carried out, and between each creep–recovery step, the viscoelastic response of the fluid gels was measured. This allowed the storage modulus to be monitored as a function of the time a steady shear stress was applied.

The effect induced by the shear stress steps on a fluid gel whose reduced packing fraction is $\phi^* = 1.11$ is reported in Fig. 3. An increase in the storage and loss modulus with time was observed. After numerous shear stress steps, the storage modulus reached an asymptotic value. The evolution of the storage modulus during conditioning can be fitted with a simple exponential law defined as

$$G(t) = G_0 \exp(-Kt) + G_\infty[1 - \exp(-Kt)] \ , \quad (2)$$

where G_0 and G_∞ are the initial value ($t = 0$) and the asymptotic value ($t \to \infty$) of the storage modulus. The rate constant, K, indicates the efficiency of the reorganisation process induced by the external constraint on the gel particle arrays. The best fit of Eq. (2) to the experimental data according to the least-squares criterion gives an estimation of G_0, G_∞ and K.

Study of the delayed compliance function, $J_{\text{d}}(t)$

The compliance function was recorded from 1 s to 15 min of creep times. The delayed compliance can be extracted from the creep experiment by removing the elastic compliance and the pure viscous contribution [23] as shown in Eq. (3).

$$J(t) = J_0 + J_{\text{d}}(t) + \frac{t}{\eta_\infty} \quad (3)$$

The elastic compliance, J_0, is the earliest response of the sample once submitted to the stress, and we chose

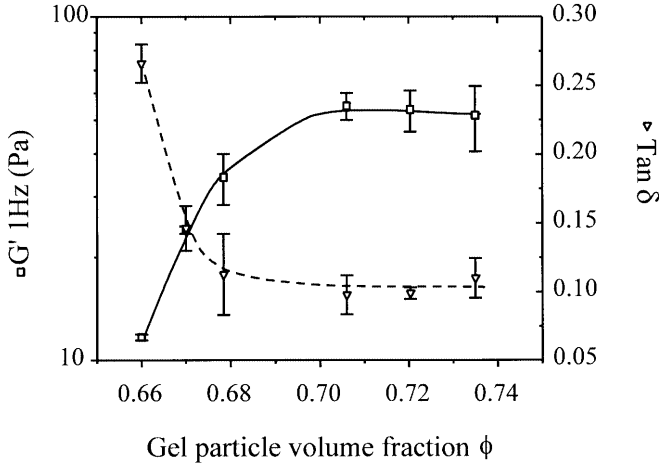

Fig. 2 Evolution of the storage modulus, G', and the loss-tangente, $\tan\delta$, at 1Hz for microgel dispersions as a function of the particle volume fraction

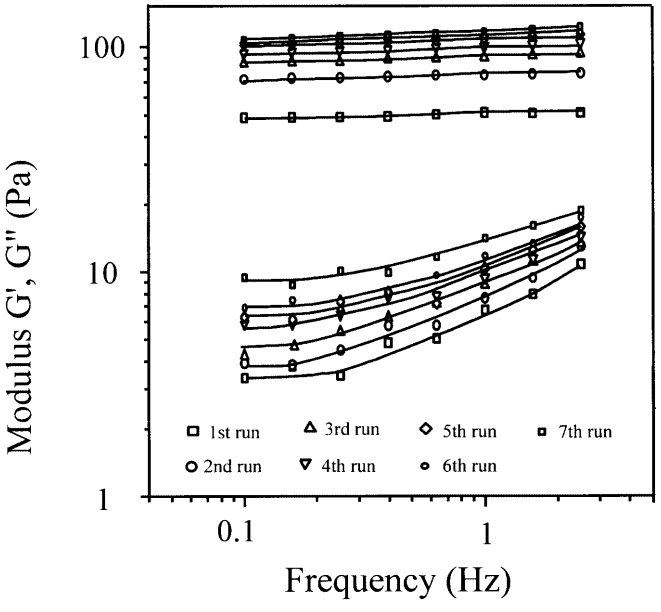

Fig. 3 Evolution of the viscoelastic spectra of microgel dispersions as a function of the number of creep runs applied. The applied shear stress is 3 Pa, the particle reduced packing fraction is $\phi^* = 1.11$

the value at 1 s as the best estimation possible for it. The term t/η_∞, which represents the plastic deformation of the sample, was approximated by the slope of the compliance just before cessation of the stress. The delayed compliance, $J_d(t)$, represents the recoverable response of a succession of elementary springs and dashpot units. If we assume an inhomogeneity of particle size or shape, $J_d(t)$ must be explained in term of characteristic time distribution functions, $L(\tau)$ as shown in Eq. (4).

$$J_d(t) = \int_{-\infty}^{+\infty} L(\tau)(1 - e^{-t/\tau}) d\ln\tau \quad (4)$$

To extract $L(\tau)$ from Eq. (4), an inverse Laplace transform resolution is needed. For doing this, the Schwarzl–Staverman method was used [24]. It gives a good approximation to $L(\tau)$ as

$$L(\tau) = \left(\frac{dJ_d(t)}{d\ln t} - \frac{d^2J_d(t)}{d\ln t^2}\right)_{t=2\tau} . \quad (5)$$

Practically, it was sufficient to fit $J_d(t)$ as a function of the logarithm of the time with a fifth degree polynomial function in order to determine both first- and second-order derivatives. The results are shown in Fig. 4, where a series of $L(\tau)$ functions is plotted as a function of the logarithm of the characteristic times. The shape of the curve shows evidence of a characteristic time peak at long times ($\tau_r \sim 500$ s), for which the amplitude decreases when the number of creep–recovery steps increases. According to the relationship between frequency and distance scale [23], the position of the peak on the time scale indicates relaxation occurring at relatively long distances in the sample, presumably due to relaxation of particles themselves.

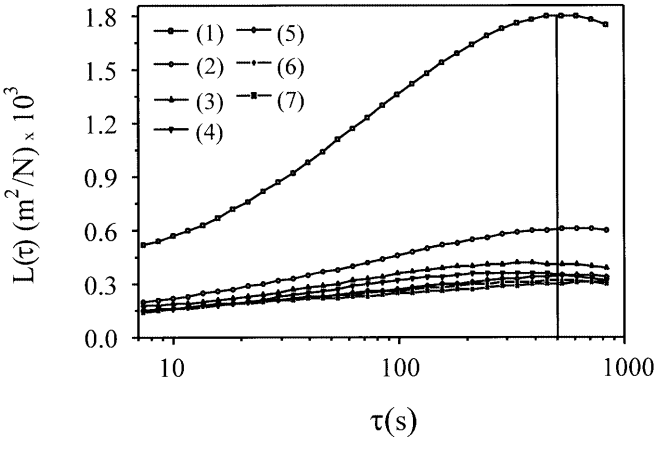

Fig. 4 Relaxation time distribution functions obtained from the compliance functions measured during conditioning. The applied shear stress is 3 Pa, the particle reduced packing fraction is $\phi^* = 1.11$

Influence of the particle packing fraction

The influence of the microgel packing fraction on the properties of the dispersion was investigated. The conditioning treatment was applied to fluid gels in which the reduced particle packing fraction ranged from $1(\phi = \phi_m)$ to 1.11. The evolution of the storage modulus at 1 Hz as a function of the time the shear stress is applied on the dispersions is reported in Fig. 5. For all the gel particle packing fractions studied, the storage modulus increased with time. The values of G_0, G_∞, and K obtained from the best fit of Eq. (2) to the evolution of the storage modulus shown in Fig. 5 are reported in Table 1. The evolution of K as a function of the reduced particle packing fraction is depicted in Fig. 6. K showed a logarithmic decrease when the initial particle's packing fraction increased.

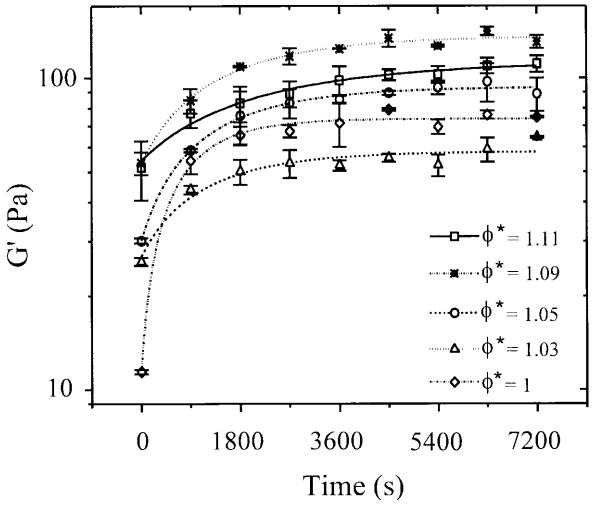

Fig. 5 Evolution of G' (1 Hz) as a function of the time the stress is applied for microgel dispersions whose reduced packing fraction varies from 1 to 1.11 The applied shear stress is 3 Pa

Table 1 Initial values, G_∞, final values, G_∞, and rate constant, K, obtained from the evolution of the storage modulus as a function of the time a shear stress of 3 Pa was applied. Various gel particle reduced packing fractions, $\phi^* = \phi/\phi_m$ were obtained by dilution of the fluid gel with water

ϕ^*	G_0 (Pa)	G_∞ (Pa)	$K \times 10^3$ (s^{-1})
1	11.4	73.9	1.17 ± 0.17
1.03	26.8	58.1	0.71 ± 0.22
1.05	30.2	93.4	0.66 ± 0.08
1.09	52.9	136.2	0.56 ± 0.09
1.11	54.3	113.3	0.38 ± 0.06

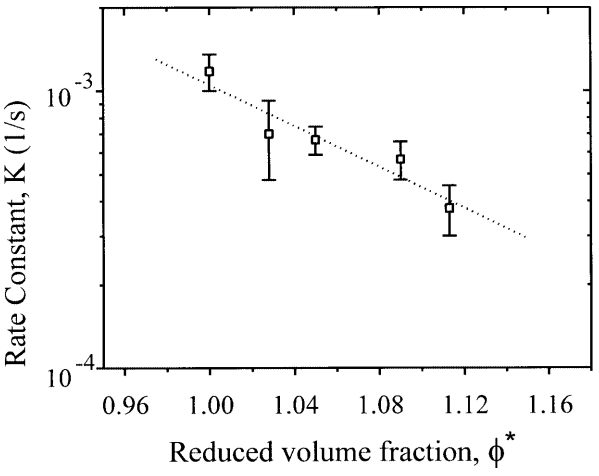

Fig. 6 Evolution of the rate of compaction of the microgel dispersion as a function of the particle reduced packing fraction

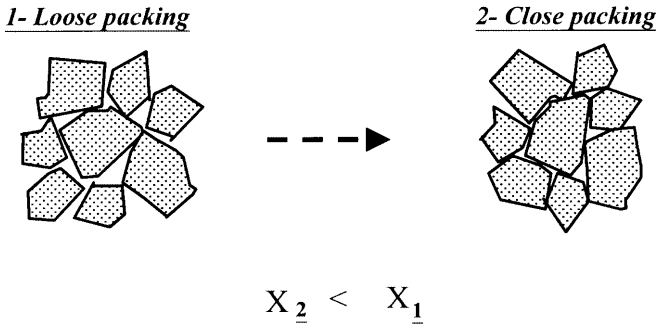

Fig. 7 Schematic representation of the effect of applied stress on the packing of a microgel dispersion, X_1 and X_2 stand for the compactivity of the suspension before and after the sample's conditioning. As the external constraint is applied the particles optimise their packing. The compactivity, X, of the system decreases; therefore, the storage modulus increase

Discussion

The storage modulus of a fluid gel depends on the reduced packing fraction of the gel particles (Fig. 2) and is therefore related to the set of particle contacts. When a fluid gel is submitted to successive shear stress steps, an increase in the storage modulus is observed. This can be explained by stress-induced changes in the compactivity of the gel particles. Under the external constraint, the gel particles rearrange themselves to maximise their packing fraction. This process leads to an increase in the connectivity of the transient network formed by the close-packed particles. As has been shown for depletion-induced gels in emulsion–polymer composites, such changes in the packing of the particles lead to an increase in the elasticity of the system. After numerous shear steps, the storage modulus tends slowly to a steady value. A similar evolution of the packing density of powder compacted by vibration has been observed and is explained by an increase in the number of entities which rearrange as the system approaches its maximum density [12–14]. As schematised in Fig. 7, the excluded volume per particle decreases during the conditioning applied to the samples. This is corroborated by the evolution of the characteristic time distribution obtained during the creep–recovery experiments.

The peak at long time observed in the $L(\tau)$ distribution represents the relaxation of the applied stress in the sample. An average relaxation time, $\tau_r \simeq 500$ s, can be attributed to particle relaxation within its free volume. The amplitude of the distribution represents the extent of the energy release due to rearrangements of the particle packing. The decrease in the peak at long time shows a decrease in the mobility of each particle within its diminished free volume. When the particle's free volume is increased by dilution the effect induced by the external constraint should be more pronounced. As a consequence, the rate of compaction has to decrease with the initial reduced packing fraction of the particle dispersion. The results reported in Figs. 5 and 6 show that this is indeed the case.

In the *configurational* statistical mechanical theory of granular materials developed by Edwards and coworkers [9–12] temperature and energy are replaced by compactivity and volume, respectively. Since the compactivity is inversely proportional to the reduced packing fraction, the evolution of the rate of compaction reported in Fig. 6 shows similarity with the Arrhenius relationship. It suggests that the slope of the logarithm of K against ϕ^* could be related to an activation volume for the particle relaxation under an external constraint. This characteristic volume should depend primarily on the shape and size polydispersity of the particles.

Conclusions

In this article we presented evidence of a stress-induced compaction of a particulate viscoelastic matrix. The increase in the shear modulus of the dispersion under an applied steady shear stress is explained by a rearrangement of the particle packing. In line with a compaction of the system, a decrease in the mobility of each particle within its free volume is observed from the analysis of the relaxation time distribution functions.

Acknowledgement The authors thankfully acknowledge N. Johnson for doing the TEM micrograph of the gel particles.

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