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Creep-recovery-creep tests to determine the yield stress of fluid gels containing gellan gum and Na⁺



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ABSTRACT

In this work, combined creep-recovery-creep tests were designed to determine the yield stress and the inception of non-linear time-dependent rheological behaviour for fluid gels containing 0.2 wt% gellan gum and 0.22 M Na⁺ as promoting cation of the gel formation. Experiments were performed from 3 Pa up to 6 Pa and samples were allowed to relax for the required equilibration time to avoid the effects of shear history. The response of these tests at the smaller stresses studied (below critical shear stress of 3.6 Pa) was controlled by non-linear viscoelasticity. Subsequently, a slight increase in shear stress above the critical shear stress by just 0.1 Pa resulted in a dramatic change in the creep flow properties. This made it possible to determine a practical yield stress and the onset of thixotropic properties. In addition, it was possible to determine the shear rate dependence of viscosity from the creep-recovery-creep tests, which illustrated the very shear thinning behaviour of these fluid gels.

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1. Introduction

Fluid gels are heterogeneous materials at the microstructure level which consist of dispersions with a structure based on the existence of gelled polymeric aggregates with similar properties to weak gels. They find applications in the food industry [1–3] and biomedicine such as oral drug delivery [4,5] or artificial lacrimal fluid [6], mainly as suspension agents [7,8] and conceivably as satiety agents [9]. From a rheological point of view, fluid gels must exhibit a rapid fall in viscosity with shear time in the shear rate range associated with industrial applications and also a rapid recovery of viscosity after cessation of shear in order to avoid a phase separation of dispersed particles. They can be considered as yield stress fluids, which are those that have a complex microstructure and need to exceed a minimum shear stress in order to flow at a significant shear rate. This minimum shear stress is known as the yield stress. These types of materials consist of structured fluids, such as foams, concentrated emulsions, colloidal gels, microgel suspensions or dense suspensions. Such materials can be divided into ideal yield stress fluids (those exhibiting Bingham or Herschel-Bulkley behaviour) and non-ideal yield stress fluids (those which also exhibit thixotropy) [10]. Furthermore, the latter are usually sensitive to thermo-mechanical history and susceptible to

ageing [11]. These rheological properties conform to their internal network structure and micro-scale heterogeneity [12]. In fact, a recently study has indicated that most of these materials consist of either colloidal glasses or colloidal gels [13]. Therefore, the rheological characterization of these materials has been traditionally difficult due to their structural complexity [14–16]. Several techniques have been used to determine the yield stress (flow curves, creep, oscillatory shear and stress ramp) [17] and the thixotropy (hysteresis loops, stepwise changes in shear rate or shear stress and start-up experiments) [18,19] of these materials. However, some of these techniques are likely to yield experimental artefacts.

In this work we determine (1) the practical yield stress value of a structured fluid exhibiting very shear thinning behaviour, which is the case of fluid gels based on low-acyl gellan gum and (2) the onset of thixotropic properties.

Gellan gum is an anionic polysaccharide that can be obtained through microbial fermentation from *Sphingomonas elodea* (ATCC 31462) [8]. In order to obtain low-acyl gellan gum fluid gels, Sworn [8] suggested that dispersion, hydration and gelation under shear must be performed, sodium being one of the cations which promote the formation of gels. Regarding the gelation step under shear, it can be achieved by two alternative procedures. On the one hand, the sample may be submitted to mechanical treatment for a given time once the threshold temperature for the inception of gelation is reached [19]. On the other hand, it can be performed by application of steady mechanical energy during the cooling step [20–22]. A recent study has demonstrated the ability of creep-recovery creep

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tests in series to determine a practical yield stress simultaneously to the onset of non-linear time-dependent rheological behaviour of a gellan gum fluid gel formulated with Ca^{2+} as gel promoting cation [21].

The objective of this study was to assess the validity of the method based on creep-recovery-creep tests to obtain both the yield stress and the inception of non-linear time-dependent rheological behaviour of fluid gels, as examples of very shear thinning materials. Namely, this work checks the suitability of the aforementioned method when applied to a low acyl-gellan gum fluid gel containing sodium as gel-promoting ion.

2. Materials and methods

2.1. Materials and fluid gel preparation

Low-acyl clarified gellan gum (Kelcogel® F™), kindly supplied by CP-Kelco (San Diego, USA), was used. Its average molecular weight was $2 \times 10^5 - 3 \times 10^5$ Da. This material will be designated as LA-gellan from now on in this paper. NaCl (purity >98%) was purchased from Panreac (Barcelona, Spain) to obtain Na^+ gel-promoting ions.

The fluid gel obtained was formulated with 0.2 wt% LA-gellan gum and 0.22 M NaCl. The concentration of NaCl was chosen to mimic the mechanical spectrum of 0.2 wt% LA-gellan fluid gel formulated with calcium chloride [22]. It is well known that Ca^{2+} concentration required to form gels is far lower than that of Na^+ [23–25]. This is also the case for gellan fluid gels, as recently demonstrated by García et al. [22]. This is attributed to the fact that Ca^{2+} promotes gelation by side binding between pairs of carboxylate groups on neighbouring helices meanwhile site binding by Na^+ is caused by electrostatic attraction of the cation to carboxylate groups of the macromolecule along with the formation of a coordination complex [26].

Deionised water was always used (electrolytic conductivity at room temperature: 2.1 $\mu\text{S}/\text{cm}$; calcium concentration: 69.1 ppb, sodium concentration: 16.6 ppb). 0.1 wt% sodium azide was used as a preservative of fluid gels.

LA-gellan fluid gel batches of 600 g were obtained by three steps (dispersion, hydration and gelation) as proposed by Sworn [8]. Powdered LA-gellan gum was added slowly to a vessel in a water-bath at 80 °C. The sample was kept at 80 °C under 700 rpm for 25 min to achieve hydration. For this purpose, an Ika-Visc MR-D1 homogeniser (Ika, Germany) and a sawtooth-type impeller were used (impeller diameter/vessel diameter: 0.85).

Afterwards, the necessary amount of NaCl was added and the solution was kept under mechanical treatment at 80 °C for a further period of 5 min. Evaporative losses were corrected for by adding appropriate amounts of deionised water. In order to achieve gelation, the solution container was placed in a thermostatic bath filled with water at 20 °C as coolant. The sample was submitted to mechanical treatment with the aforementioned Ika-Visc equipment for 1500 s in order to obtain fluid gels, which were then stored at 4.5 °C for at least 48 h before carrying out the rheological study.

2.2. Methods

Creep-recovery-creep tests on LA-gellan gum fluid gels were performed. Firstly, a constant shear stress was imposed for a shearing time of 40 s. The stress studied ranged from 3.0 Pa to 6.0 Pa. After a rest time of 40 s, the viscosity recovery was quantified by again submitting the sample to the same shear stress. These tests were carried out with an AR-2000 controlled-stress rheometer (TA Instruments), using a serrated parallel plate geometry (40 mm

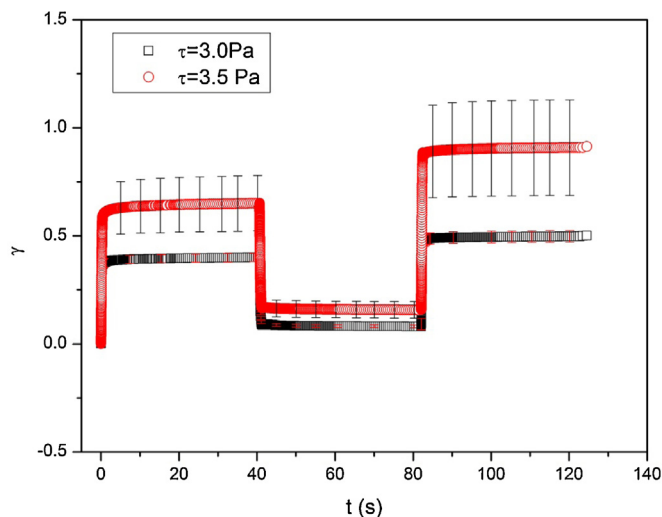


Fig. 1. Strain versus shear time derived from creep-recovery-creep tests at 3.0 Pa and 3.5 Pa for a fluid gel containing 0.2 wt% LA-gellan gum 0.22 M NaCl and 0.1 wt% sodium azide. $T = 20^\circ\text{C}$. Vertical bars indicate standard deviation data.

diameter, gap: 1 mm) to prevent wall-slip phenomena. The experiments were carried out at $20.0^\circ\text{C} \pm 0.1^\circ\text{C}$.

Equilibration time prior to rheological tests, obtained by time sweeps under oscillatory shear, was determined to be 1300 s.

To take into account the shear rate dependence of the plate radius, viscosity values and the nominal stress can be corrected according to the subsequent equations:

On the one hand, the nominal stress was calculated as follows [27]:

$$\tau_c = \frac{M}{2 \cdot \pi \cdot R^3} \left[3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right] \quad (1)$$

where, τ_c is the corrected shear stress; M is the torque applied; R is the plate radius (20 mm) and $\dot{\gamma}_R$ is shear rate at the plate rim.

On the other hand, the viscosity was corrected using Eq. (2) to account for the shear rate dependence on the distance from the plate centre as indicated by Malkin and Isayev [28].

$$\eta_{\text{corr}}(\dot{\gamma}_R) = \eta_{\text{newt}} \cdot [1 + m/4] \quad (2)$$

where, $\eta_{\text{newt}} = (2 \cdot H / (\pi \cdot R^4)) \cdot (M / \Omega)$, $m = d(\log \eta_{\text{newt}}) / d(\log \dot{\gamma}_R) = n - 1$, H is gap between plates, Ω is the angular velocity, n is the power law index and η_{newt} is the viscosity calculated at the rim of the parallel plate geometry.

All experiments were carried out at least in triplicate using freshly prepared samples and the results are reported as the mean and standard deviation of these measurements.

3. Results and discussion

The strain as a function of shear time at the nominal constant shear stresses of 3.0 and 3.5 Pa on fluid gels containing 0.2 wt% LA-gellan gum and 0.22 M NaCl are shown in Fig. 1.

In both cases, the shape of the curve obtained for the first creep test was similar to the third step. In addition, the moderate slope of the strain as a function of shear time curve suggested that the shear rate was very small (of the order of 10^{-4} s^{-1}). Although the first creep test at either 3.0 Pa or 3.5 Pa showed an apparent linear zone at the end of this test, the fact that the second creep presented slightly lower slopes than those obtained in the first one indicated that the steady-state was not achieved, as was also confirmed by analysing these results as a function of viscosity (see below). Furthermore, Muñoz et al. [29] showed LA-gellan gum fluid gels need

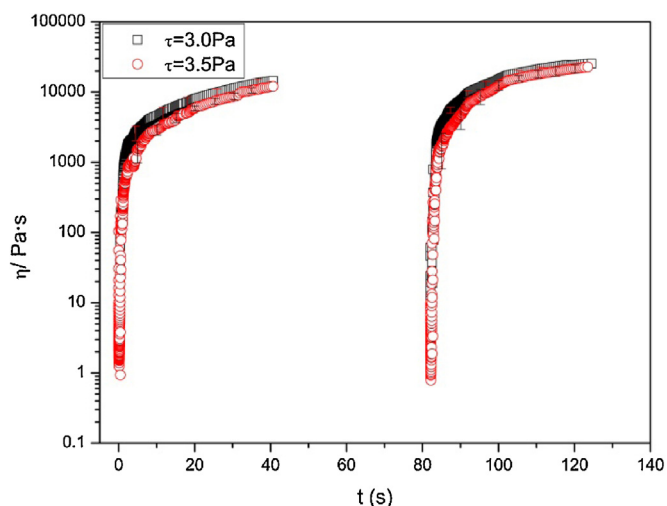


Fig. 2. Viscosity versus shear time derived from creep-recovery-creep tests at 3.0 Pa and 3.5 Pa for a fluid gel containing 0.2 wt% LA-gellan gum 0.22 M NaCl and 0.1 wt% sodium azide. $T = 20^\circ \text{C}$. Vertical bars indicate standard deviation data.

greater time to reach a steady-state, which implies that shear rate would be even lower at the steady state. Consequently, the sample elasticity control the rheological response at nominal stresses below 3.5 Pa and thus, the yield stress was higher than this shear stress. This was corroborated by the instantaneous strain recovery when the stress applied was removed. By resubmitting the sample to shear stresses smaller than or equal to 3.5 Pa in the third test, an increase in the strain analogous to that obtained in the first step occurred. This fact confirms that the sample microstructure was kept essentially undisturbed after submitting it to a creep test for 40 s at these shear stresses followed by a recovery test for another 40 s.

However, it should be noted that the error bars corresponding to standard deviation of the three replicates of the measurements carried out at 3.0 Pa were smaller than those obtained at 3.5 Pa, which indicated that the latter was closer to the yield stress value.

These results can be also analysed with respect to the time dependence of viscosity (Fig. 2). The reproducibility was excellent, although congruently with results shown in Fig. 1, the error bars were higher in the test performed at 3.5 Pa.

As can be observed in Fig. 2, viscosity increased with the time in both the first and third tests for the two shear stresses (3.0 and 3.5 Pa) studied. In addition, viscosity at the end of the third test performed at 3.5 Pa reached higher values than those of the first test which supported the fact that the steady-state response had not been achieved and that there was no confirmation of structural breakdown after the recovery test.

Fig. 3 exhibits the time dependence of strain for measurements performed in the 3.7–6.0 Pa shear stress range. As can be observed in this figure, a slight increase of 0.2 Pa in the shear stress, from 3.5 Pa to 3.7 Pa, led to a clearly different response from the previous stresses studied. In this case, strain as a function of shear time showed a practically linear evolution, presenting a clear positive slope in the first and third steps. This fact can be associated with the idea that steady state behaviour was achieved after a short time. In addition, a null recovery could be also observed. A similar response in gellan gum fluid gels containing 0.2 wt% gellan and 0.2 wt% CaCl_2 (or $1.8 \cdot 10^{-2} \text{ M}$) was observed by García et al. [21]. These authors demonstrated that yield stress of those fluid gels was achieved at 2.25 Pa. Consequently, the results exhibited a poor reproducibility when the measurement was performed at this shear stress. The inception of very shear thinning behaviour was attributed to this unstable response, which was associated with the appearance of

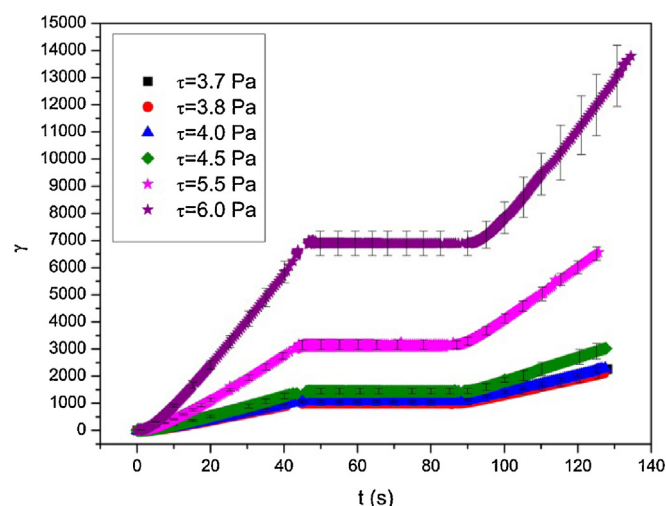


Fig. 3. Strain versus shear time derived from creep-recovery-creep tests carried out from 3.7 Pa to 6.0 Pa for a fluid gel containing 0.2 wt% LA-gellan gum, 0.22 M NaCl and 0.1 wt% sodium azide. a) strain versus shear time. b) viscosity versus shear time. $T = 20^\circ \text{C}$. Vertical bars indicate standard deviation data.

shear banding [30]. This has been attributed for a model polymer solution to the lack of concentration homogeneity induced by shear stress [31]. This phenomenon implies that a small region of the sample continues in a quiescent state, while the rest of the sample really flows as a consequence of heterogeneous microstructure. This effect may be increased by the parallel plate geometry since the shear rate rises from the centre, where it is zero, to the highest value at the rim of the plate.

Fig. 3 For this reason, it can be considered that the practical yield stress of this fluid gel, prepared with Na^+ as gel-promoting cation, may be around 3.6 Pa. It must be noted that this value is higher than the practical yield stress (2.25 Pa) of a fluid gel prepared with Ca^{2+} cation, which showed a similar mechanical spectrum to the fluid gel studied in this research [22]. In addition, it is also interesting to realise that the practical yield stress determined from creep-recovery-creep tests of the Na^+ -induced fluid gel studied in this research (3.6 Pa) was significantly higher than the value calculated for the same system from a flow curve, using the Herschel-Bulkley fitting equation (1.5 Pa) [22]. The apparent yield stress value calculated from a flow curve underestimated the actual value on account of the shear history associated to the flow curve. In other words, the lower shear stresses applied while running the flow curve brought about a progressive and increasing damage in the fluid gel microstructure, eventually resulting in a lower yielding value. This supports that the method of choice to determine the practical yield stress of a fluid gel allowed to rest for long enough as to get an equilibrium microstructure after being prepared is a creep test.

As can be observed in Fig. 3, the error bars showed that the results obtained at 3.7 and 3.8 Pa were not significantly different. The test performed at greater nominal stresses led to curves whose shapes were similar to the latter.

From 3.7 Pa, the results showed a linear increase as a function of time, typical of fluid-like response, for all nominal stresses studied. This confirms that the steady state behaviour was achieved after a short shear time when the yield stress has been overcome as indicated García et al. [21] for fluid gels prepared with Ca^{2+} . Additionally, the strain value reached at the end of the first creep experiment remained constant during the recovery step (null strain recovery), congruently with the lack of elastic response. This confirmed that fluid-like properties overwhelmingly dominated the shear flow after submitting the sample at 3.7 Pa for 40 s.

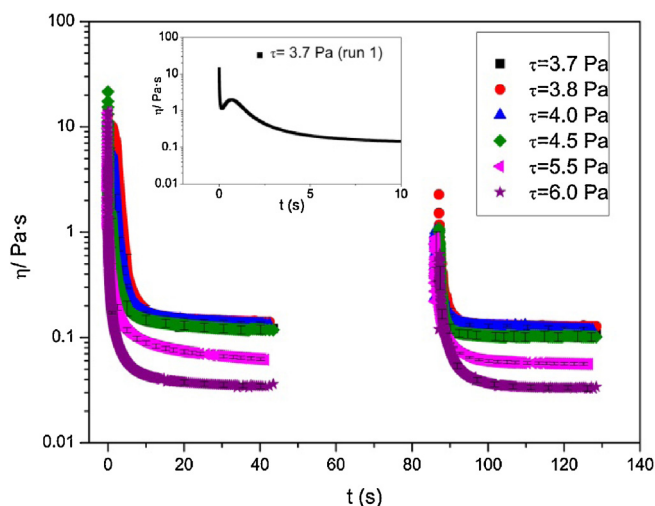


Fig. 4. Viscosity versus shear time derived from creep–recovery–creep tests carried out from 3.7 Pa to 6.0 Pa for a fluid gel containing 0.2 wt% LA-gellan gum, 0.22 M NaCl and 0.1 wt% sodium azide. $T = 20^\circ\text{C}$. Vertical bars indicate standard deviation data.

Furthermore, the steady state was achieved at shorter time in the third step, demonstrating the effect of shear history. Fig. 4 shows nominal viscosity values versus shear time. At very short time the response was rather unstable. In fact an initial jump and a fall in viscosity could be recorded, followed by a peak at 0.5 s which preceded an unsteady response (see the inset in Fig. 4) for the measurement carried out at 3.7 Pa) while approaching a steady state lower viscosity. This phenomenon is due to the coupling of equipment inertia with the elasticity of the viscoelastic sample and is commonly known as “creep ringing” [21,32,33]. Unfortunately no tendency in the peaks of initial viscosities as a function of applied stress was observed, due probably to the above-mentioned creep ringing effects. After the recovery step, a second peak was found, which was smaller than that observed in the first step, indicating a partial recovery of the viscosity after a rest time of 40 s.

In the measurements performed at higher stresses (3.8, 4.0, 4.5, 5.5 and 6.0 Pa), the shape of the curves obtained was analogous to that obtained at 3.7 Pa. Interestingly, the viscosity values obtained at 6.0 Pa as a function of shear time exhibited a peak of viscosity that was again affected by creep ringing effects. However, in the third step, these effects were much lower, indicating they may be prevented by including a pre-shear step in the experimental protocol. Steady state conditions had been practically achieved after 40 s in both the first and third step since viscosity values were rather similar to each other.

In the next section, a comparative analysis of parameters obtained from the previous test is shown (Fig. 5).

On the one hand, Fig. 5a shows viscosities at 0.5 s, which is the lowest shear time guaranteeing the lack of noise due to creep ringing, for both the first and third steps, and viscosities at 40 s, also for both steps, as a function of the nominal shear stress. On the other hand, the calculated shear rate dependence of viscosities at 0.5 s and 40 s for the two above-mentioned steps is also plotted (Fig. 5b). Viscosity results at 3.0 Pa and 3.5 Pa at 0.5 s have not been given since under these shear conditions the elastic response of this fluid gel is predominant and flow was hardly detected.

Figs. 5 a and b exhibit a decrease in viscosity of about four orders of magnitude with increasing shear stress from 3.5 to 3.7 Pa, which in Fig. 5b is reflected by a sudden increase in shear rate from $2.5 \cdot 10^{-4}$ to 1 s^{-1} . Both figures resemble the shape of standard flow curves of very shear thinning materials. It is worth highlighting that the samples were kept in a quiescent state for an equilibration time

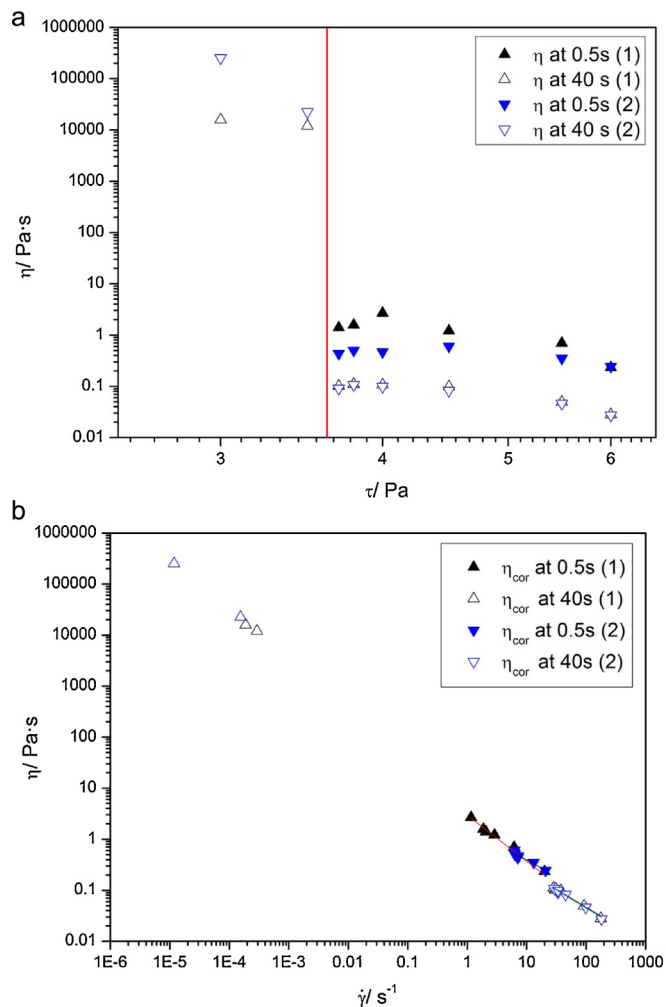


Fig. 5. Flow curve for a fluid gel containing 0.2 wt% gellan gum, 0.22 M NaCl and 0.1 wt% sodium azide. a) Viscosity as a function of shear stress. b) Viscosity as a function of shear rate. Note: all data derive from creep–recovery–creep tests. $T = 20^\circ\text{C}$. (1): data derived from the first creep test. (2): data derived from the creep test conducted after the recovery step.

before submitting them to creep tests in order to avoid the effects of shear history. Additionally, an independent measurement was carried out for each stress studied. This makes a significant difference to standard flow curves usually determined using continuous or stepped ramps of either shear rate or shear stress.

For nominal shear stress higher than 3.7 Pa, viscosities achieved at 40 s were near enough to steady state, as was supported by the results of the second creep test, which resulted in viscosity values quite similar at 40 s to those obtained in the first creep. On top of that, Fig. 4 shows that viscosity values remained constant at the longer shear times. Moorcroft and Fielding [34] reported the appearance of stable banding for different kinds of materials at lower shear stresses or rates. The variability of viscosity may be associated with the fortuitous distribution of microgel domains in the fresh sample, indicating that this phenomenon is due to the heterogeneous structure of these fluid gels as was reported by García et al. [21]. This effect seems less important at higher shear rates when completely developed shear flow is warranted as was demonstrated by rheo-optical studies [35].

The shear rate dependence of viscosity above the apparent yield stress fitted the power law (Fig. 5b) ($\eta = \eta_1 \cdot \dot{\gamma}^{n-1}$), where η_1 is the viscosity corresponding to a shear rate of 1 s^{-1} and n is the power law index) and the fitting parameters are shown in Table 1. Given

Table 1

Power law fitting parameters for the shear rate dependence of viscosities calculated at either 0.5 s or 40 s from either a first creep test (1) or a second one (2) conducted after a recovery test of 40s. “s.e.” stands for standard error of the curve fit.

	η_1 (Pa·s)	s.e. η_1 (Pa·s)	$n - 1$	s.e. ($n - 1$)	n	R^2
η_{cor} 0.5 s (1)	2.95	0.15	-0.90	0.08	0.1	0.98
η_{cor} 40 s (1)	1.17	0.30	-0.70	0.06	0.3	0.98
η_{cor} 0.5 s (2)	1.71	0.50	-0.64	0.14	0.4	0.96
η_{cor} 40 s (2)	1.14	0.21	-0.70	0.05	0.3	0.98

that, viscosity at 40 s can be considered as steady state values for shear stresses greater than or equal to 3.7 Pa, the resulting steady state shear rate dependence of viscosity is characterized by a power law index of 0.3 and η_1 is 1140 times higher than the water value at 20 °C.

Fig. 5a also showed that viscosity at 40 s was significantly lower than viscosity at 0.5 s, which illustrate the thixotropic behaviour of this fluid gel. This phenomenon is also shown in Fig. 5b since viscosity at 40 s corresponded to higher shear rates than viscosity at 0.5 s. This was due to the fact that a higher shear rate was achieved when the fluid gel was submitted to a constant shear stress equal to or higher than 3.7 Pa for 40 s instead of 0.5 s.

4. Conclusions

We have demonstrated that 3.5 Pa was the highest shear stress which yielded “creep flow” (very slow flow dominated by elastic response) during a creep-recovery-creep test carried out for a fluid gel containing 0.2 wt% gellan gum and 0.22 M Na⁺ as gel-promoting ion. This was consistent with the response of a solid-like material under creep flow. A slight increase in shear stress up to 3.7 Pa provoked a dramatic change in the rheological response of the fluid gel studied since clear fluid-like behaviour was observed. Therefore, we assigned a value of 3.6 Pa for an apparent, or better, practical yield stress. Above the practical yield stress value, a shear rate close to the steady state value was quickly reached, the elastic recovery was negligible and the viscosity versus time curve illustrated the occurrence of thixotropy with an incomplete recuperation of the initial viscosity after 40 s of recovery. The instability of the viscosity versus time curves after the first creep test at 3.7 Pa was ascribed to the proximity to the yield stress of these fluid gels. Between 4.0 and 6.0 Pa, the response became more stable, but similar to that found at 3.7 Pa. Additionally, the shear rate dependence of viscosity derived from independent creep-recovery-creep tests illustrated a very shear thinning behaviour, with a power law index of 0.3.

The results obtained support the conclusion that the presented creep-recovery-creep test is a good method to determine both the practical yield stress and the inception of non-linear time-dependent rheological behaviour of very shear thinning structured materials, such as low-acyl gellan gum fluid gels.

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