



Regular article

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

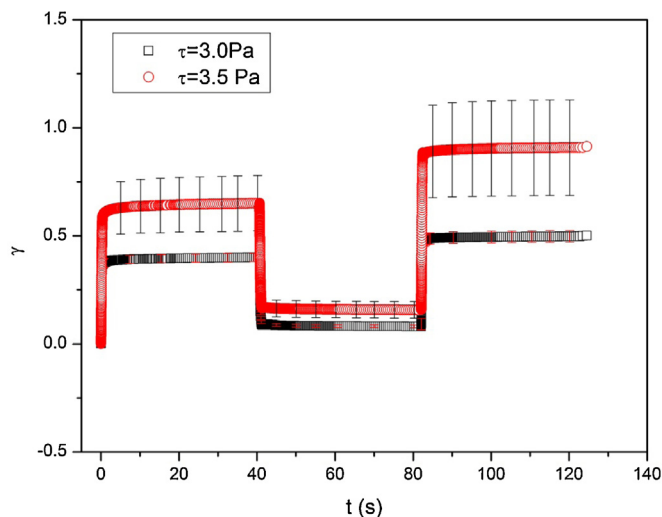


Fig. 1. Strain versus shear time derived from creep-recovery-creep tests at 3.0 Pa and 3.5 Pa for a fluid gel containing 0.2 wt% LA-gellan gum 0.22 M NaCl and 0.1 wt% sodium azide. $T = 20^\circ\text{C}$. Vertical bars indicate standard deviation data.

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

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