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Large amplitude oscillatory shear of xanthan gum solutions. Effect of sodium chloride (NaCl) concentration

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ABSTRACT

Large amplitude oscillatory shear (LAOS) results are shown to be useful to describe the mechanical behaviour of materials at large deformations, well beyond the linear viscoelastic region, which are closer to real processing conditions. We illustrate the applications of LAOS with xanthan gum aqueous dispersions at different NaCl concentrations, on account of the great technological interest in this bacterial polysaccharide. LAOS is shown to be much more sensitive than small amplitude oscillatory shear (SAOS) to the influence of NaCl concentration. This is illustrated by a complete rheological characterisation of the system by means of both full-cycle (average elastic modulus and dynamic viscosity) and local methods (strain-hardening and shear-thickening ratios). The different rheological behaviours observed were related to the microstructures of the xanthan gum molecules as a function of the NaCl content.

1. Introduction

Xanthan gum is a high molecular-weight extracellular polysaccharide produced by *Xanthomonas campestris*. The backbone of the polysaccharide chain consists of two β-D-glucose units linked through the 1st and 4th positions and the side chain consists of two mannose and one glucuronic acid. The side chain is linked to every other glucose of the backbone at the 3rd position. About half of the terminal mannose units have a pyruvic acid group linked to their 4th and 6th positions. The other mannose unit has an acetyl group at the 6th position (Sworn, 2009).

Xanthan gum is soluble in cold-water, and due to its rheological properties and thermal stability, it is commonly used as an effective stabilizer and thickener with many areas of application (Marcotte et al., 2001). Xanthan gum aqueous solutions exhibit high consistency at low gum concentrations, high viscosity at low shear rates and a marked shear-thinning nature. The rheological properties of xanthan gum solutions are closely related to its conformational state (ordered and disordered conformations) and stiffness (Renaud et al., 2005), which in turn are strongly dependent on the temperature and ionic strength of the medium (Dário et al., 2011). On the one hand xanthan gum in solutions with low ionic strength or at high temperature adopts more flexible, disordered structures. On the other hand, at high ionic strength solutions the xanthan backbone takes on an order, helical conformation (Renaud et al., 2005; Rochefort and Middleman, 1987).

Traditionally, the rheological properties of xanthan gum aqueous solutions have been determined by flow curves and small amplitude oscillatory shear (SAOS). In recent years, large amplitude oscillatory shear tests (LAOS) have received increasing attention, given that they can provide valuable information for a better understanding of complex rheological behaviours and give a deeper insight into microstructural changes (Ewoldt et al., 2010). Furthermore, another reason for the growing interest in LAOS tests is their usefulness in describing the elastic and viscous properties of complex fluids at large deformations (outside the linear viscoelastic domain), which are closer to real processing and application conditions. For instance, it has been proved recently that LAOS measurements are related to the sensory and textural properties of food, which is a topic of great interest (Melito et al., 2013).

The objective of this work was to study the influence of NaCl concentration on the rheological properties of aqueous solutions of a commercial "advanced performance" xanthan gum. This is obtained by the manufacturer by optimising the fermentation process such that it yields higher viscosities than standard xanthan gum solutions and enhanced behaviour if submitted to high pressure homogenisation. This rheological study involves flow curves, small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS). The non-linear oscillatory response was analysed using the framework proposed by Ewoldt et al. (2008) in order to obtain meaningful physical parameters.

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2. Materials and methods

2.1. Theory

In dynamic oscillatory shear tests, the strain is varied periodically, usually with a sinusoidal perturbation at a fixed frequency. Oscillatory shear tests can be divided into two regimes. One regime implies the linear viscoelastic response (small amplitude oscillatory shear, SAOS) and the other regime involves a nonlinear material response (large amplitude oscillatory shear, LAOS). As the strain amplitude is increased at a fixed frequency a progressive transition from linear to nonlinear viscoelastic rheological behaviour can occur. When the response is linear (at small strain amplitudes) the material is characterised by two components, one in phase with the strain (elastic or storage modulus $G'(\omega)$) and the other 90° out of phase (viscous or loss modulus, $G''(\omega)$).

The conditions required for the linear viscoelastic regime include: (1) stress amplitude should be linearly proportional to the imposed strain amplitude and (2) a torque response that involves only the first harmonic. The first condition implies that both moduli are independent of strain amplitude. The absence of larger harmonics in the stress response as required by the second condition ensures that the response remains sinusoidal. In this case, both storage and loss moduli are a function of the material microstructure and the oscillatory frequency (ω).

When the strain increases, the contribution of higher-order harmonics becomes significant and the stress response is not a single-harmonic sinusoid due to contribution of the other harmonics. Fig. 1 shows the evolution of normalised stress with the strain amplitude. As may be clearly observed, the sinusoidal stress is distorted when the strain increases as a consequence of the contribution of higher harmonics. A physical interpretation of the nonlinearities observed in a LAOS test is difficult since this nonlinear rheological behaviour cannot be uniquely described in terms of the linear viscoelastic moduli, G' and G''.

Different methods have been proposed to analyse LAOS; Lissajous curves (Philippoff, 1966; Tee and Dealy, 1975), Fourier transform rheology (Wilhelm et al., 1998; Wilhelm, 2002), stress decomposition (Cho et al., 2005; Ewoldt et al., 2008; Yu et al., 2009), decomposition on characteristic waveforms (Klein et al., 2007), and analysis of parameters related to Fourier transform rheology (Debbaut and Burhin, 2002; Hyun and Wilhelm, 2009).

A popular and useful tool to analyse LAOS data is the Fourier-Transform method, which uses the relative intensities of higher harmonics as a measure of nonlinearity (Kallus et al., 2001; Wilhelm et al., 1998; Wilhelm, 2002). For a sinusoidal strain input $\gamma = \gamma_0 \sin(\omega t)$, the stress response can be represented completely by Fourier series in two scale (elastic and viscous) forms (Dealy and Wissbrun, 1990):

$$\sigma(t,\omega,\gamma_0) = \gamma_0 \sum_{n=odd} \left[G'_n(\omega,\gamma_0)\sin(n\omega t) + G''_n(\omega,\gamma_0)\cos(n\omega t)\right] \quad (1)$$

$$\sigma(t,\omega,\gamma_0) = \dot{\gamma}_0 \sum_{n=odd} \left[\eta'_n(\omega,\gamma_0)\sin(n\omega t) + \eta''_n(\omega,\gamma_0)\cos(n\omega t)\right] \quad (2)$$

where γ_0 is the strain amplitude, G'_n and G''_n are the elastic and viscous moduli for the n harmonic, $\dot{\gamma}_0$ is the maximum strain rate ($1/s$), and η'_n and η''_n are the apparent viscosity in phase and out of phase with strain input for the n harmonic, respectively. Only the odd harmonics are included in this representation because the stress response is assumed to be odd symmetry with respect to the directionality of strain or strain rate, i.e., the material response is unchanged if the coordinate system is reversed (Bird et al., 1987). Even harmonic terms can be observed in transient responses, secondary flows (Atalik and Keunings, 2004), or wall slip (Graham, 1995). In the linear viscoelastic region, Eq. (1) reduces to the first harmonic $n = 1$, and the stress is a function of G'_1 and G''_1. When the strain increases, and the system undergoes a transition from the linear to nonlinear regime, higher harmonics gain ground with respect to the first. In spite of the fact that this framework is robust and allows us to detect nonlinearities and to calculate the higher harmonics, it does not result in a clear physical interpretation of the higher harmonics.

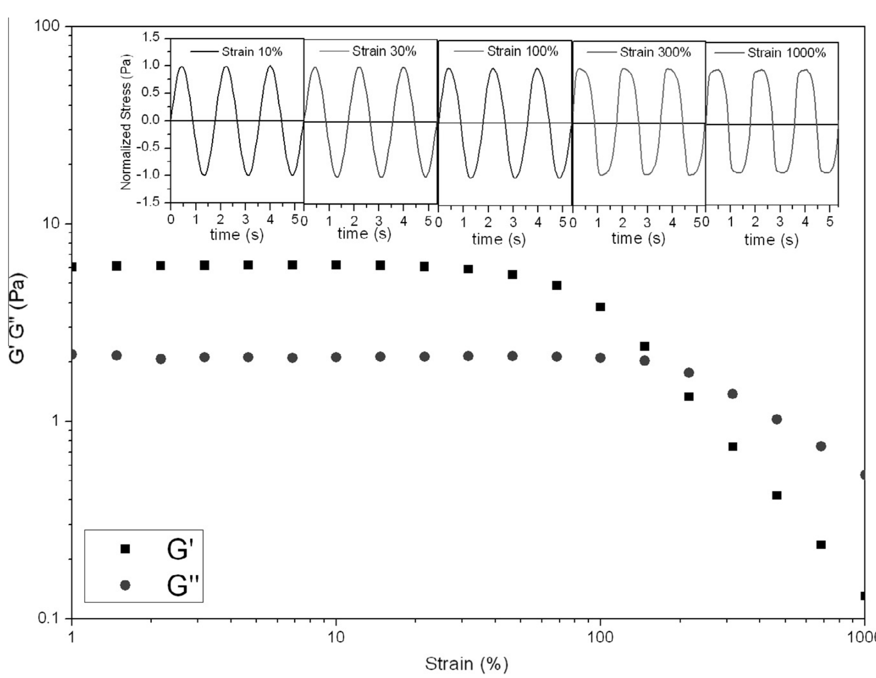

Fig. 1. Strain sweep of 0.4% (m/m) xanthan gum unsalted aqueous solution at a fixed frequency of 4 rad/s at 20 °C. In the viscoelastic linear region, the viscoleastic moduli are independent of strain, nevertheless in the non-linear region both moduli are a function of strain.