

Effect of high-pressure on the viscoelastic properties of aqueous glucomannan dispersions

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Introduction

Konjac glucomannan (KGM), a neutral polysaccharide derived from the tuber of *Amorphophallus konjac* C. Koch [1], can be used to improve the fish protein functionality lost in processing. KGM forms a time-stable gel after addition of 0.6 N KOH as alkaline coagulant [2]. Gelation occurs through the formation of a three-dimensional network by junction zones stabilized principally by hydrogen bonds and other physical interactions such as coulombic, dipole-dipole, van der Waals and hydrophobic interactions [3]. Previous papers explored the influence of thermal conditions [4, 5] and KGM concentration [6] on the rheological and structural characteristics of aqueous glucomannan dispersions (AGD). These studies provided an ample view of thermal effects on the transient properties of physical networks. Temperature acts via increases of both kinetic energy and free volume. It may therefore be useful to analyse how the pressure affects the dynamic behaviour of KGM molecules in AGD dispersions, since pressure mainly affects system volume and has a large range of applications in the food industry. Besides reducing the initial microbial load, high pressure (HP) improves the functional properties of muscle proteins [7] and induces denaturation, aggregation or gelation of myofibrillar proteins depending on the pressure level, time and temperature of the pressure treatment [8]. It could therefore offer an alternative process to induce gel formation, without heating, to obtain products resembling raw fish [9].

This work is the first step of a study whose objective is to determine the influence of high pressure on viscoelastic properties of AGD depending on pH in order to use HP treatment for making restructured seafood products. In particular, the aim of the present chapter is to explore the effect of increasing pressure on the viscoelastic characteristics of AGD dispersions

with 3% KGM and pH 9.36 (near the point of gelation), in order to choose the most suitable pressure conditions for making restructured seafood products.

Experimental Methods

Aqueous glucomannan dispersions (3%) (w/v) from konjac (glucomannan purity 100%, Guinama, Valencia, Spain) were prepared by continuous stirring for 30 min at low speed in a vacuum homogenizer (Stephan UM5, Stephan u. Söhne GmbH & Co., Hameln, Germany) at 60 °C. Then KOH (Panreac Química, S. A., Barcelona, Spain) was added to increase the pH to 9.36, mixing for 1 minute at 50 rpm to induce gel formation. Cylindrical plastic containers were then filled with this mixture and left to set, for 1 hour at 30 °C and then 4 hours at 5 °C. Once the samples had set, they were placed in a 0.2 M citrate-phosphate buffer at pH 5 for 20 hours.

Gels were then subjected to HP of 100 MPa (lot A), 200 MPa (lot B), 400 MPa (lot D) and 600 MPa (lot E), all for 10 min at 25 °C. In addition, an unpressurized lot (lot C) was made. Small amplitude oscillatory shear (SAOS) data were gathered using a Bohlin CVO controlled stress rheometer (Bohlin Instruments, Inc. Cranbury, NJ) and a RS600 Haake rheometer (Thermo Electron Corporation Karlsruhe, Germany). In both rheometers the measurements were carried out using a parallel plate (20 mm in diameter and 1 mm gap). The temperature of the lower plate was kept at 25.0±0.1 °C. Stress sweeps were obtained from 1 to 800 Pa at frequency 1 Hz. Frequency sweeps were performed over the range 0.01–10 Hz, keeping $\gamma=1\%$ constant within the linear viscoelastic (LVE) region. Transient tests were carried out under constant stress (σ) within LVE range for 600 s, followed by a further 600 s recovery time to obtain the reformation curve.

Results and Discussion

Linear viscoelastic (LVE) range

Stress sweeps were used to determine the influence of increasing HP on the limit values of the LVE range: stress (σ_{max}) and strain (γ_{max}) amplitudes and rigidity (G^*) for 3% AGD. These showed that the rigidity (G^*) of pressure-treated AGDs was significantly higher ($p<0.05$) than in the control (C) (Table 1). G^* in B was slightly higher than in the rest, indicating non-linear dependence between HP and rigidity of pressurized AGDs.

Table 1. High pressure effect on the limit parameters of the LVE range for 3% aqueous glucomannan dispersions (AGD). Stress amplitude, σ_{max} , strain amplitude, γ_{max} (%) and complex modulus, G^* . $T=25^\circ\text{C}$.

Sample	σ_{max} (Pa)	γ_{max} (%)	G^* (kPa)
C	87±9a	11.4±1.9c	0.79±0.11e
A	105±11a	10.5±0.89c	1.01±0.09f
B	194±19b	18.1±1.5d	1.08±0.08f
D	158±16b	15.3±1.9d	1.05±0.13f
E	178±18b	17.4±0.56d	1.02±0.03f

^{a-f} Different letters in the same column indicate significant differences with high pressure effect ($P<0.05$).

In the case of σ_{max} and γ_{max} , there was a particular increase of firmness and structural stability at 200 MPa (B), as evidenced by the fact that σ_{max} and γ_{max} were significantly higher than in C and A (Table 1). This indicates that ~200 MPa is a high enough pressure to improve conformational stability and molecular flexibility [10]. HP causes a reduction of the free volume in the KGM matrix, resulting in increased polymer-polymer contacts due to hydrogen bonds, van der Waals and hydrophobic interactions [3]. Moreover, it is possible that HP produces partial disruption of junction zones, reducing the number of KGM chains that act cooperatively in junctions. Thus, HP could reduce the molecular association (cross-linking level) in junction zones and so reduces the degree of order in the AGD superstructure. This contributes to a reduction of the junction thickness, consequently enhancing the conformational flexibility of pressurized AGDs, as evidenced by the fact that σ_{max} , and γ_{max} were higher in B (more noticeable), D and E than in C, (Table 1). This rheological behaviour is compatible with the increase of G^* in pressurized AGDs with respect to C (Table 1), since the chain fragments resulting from the partial breakage of junctions may reorganize. These molecular fragments detached from the principal network could also form new cross-links among themselves, increasing the overall rigidity of A, B, D and E relative to C.

Mechanical spectra

Viscoelastic moduli have been fitted to the power law (eq. 1 and 2).

$$G' = G_0' \cdot \omega^{n'} \quad (1)$$

$$G'' = G_0'' \cdot \omega^{n''} \quad (2)$$

Experimental values of G' and G'' moduli varied depending on the frequency range selected.

From 10 to 0.15 Hz, G' was somewhat higher and more frequency-dependent than G'' , indicating weak solid-like behaviour. The gel-sol transition was registered between 0.10 and 0.06 Hz (crossover interval) where $G' \approx G''$. After the transition zone, at frequencies lower than 0.06 Hz, G'' was slightly higher than G' (Figure 1), indicating loss of molecular connectivity resulting in the predominance of viscous response in AGD samples. However, there was no sign that high pressure significantly influenced these results.

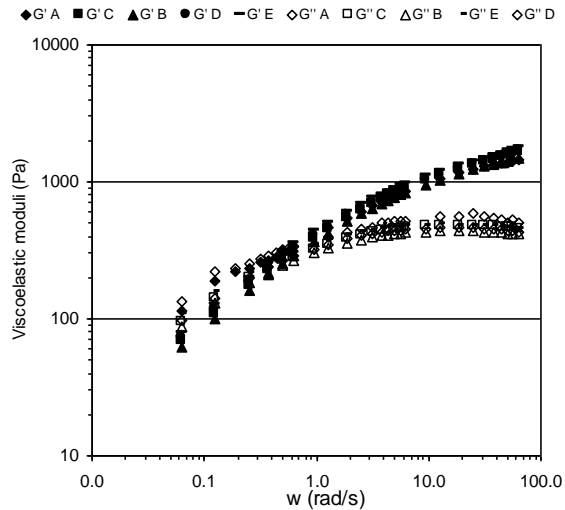


Figure 1. Influence of high pressure on Mechanical spectra of the AGDs. $T=25^\circ\text{C}$.

In the case of frequency dependence, G' showed two trends irrespective of pressure treatment: one, between 10 and ~0.15 Hz where G' presented less frequency-dependence, $n'=0.290\pm0.008$ (similar for all AGDs); and another, from the crossover to the lowest frequency, where n' significantly increased ($n'\approx0.630\pm0.011$), indicating that the AGD matrix was more time-dependent and less stable conformationally in the low frequency range, which is consistent with the sol state at low frequencies.

However, the frequency-dependence of G'' moduli was noticeably different from G' . In the high-frequency range (from 0.15 to 10 Hz), G'' values flattened, while,

in the low-frequency range (from 0.01 to 0.2 Hz) G'' decreased continuously to the lowest frequency (Figure 1) more slowly ($n'' \approx 0.430 \pm 0.020$) than G' ($n' \approx 0.630 \pm 0.011$) in the same frequency range. Thus, the viscoelastic response in the low frequency range reflects structural changes which are characteristic of the phase transition in this case from gel (high frequencies) to sol (low frequencies). Since any (cualquier) gelation process is a critical phenomena where the transition variable is the connectivity [10]. In these AGDs, the degree of connectivity was progressively reduced as the frequency decreased due to the shear stress which broke some physical links, as evidenced by $n' \gg n''$, irrespective of the HP value.

Creep and Recovery Compliances

Creep experiments are conducted by applying constant stress (σ_0), within the LVE range. The shear deformation $\gamma(t)$ is recorded with time [11], which gives the time-dependent compliance $J(t)$ on larger time scales. This is a measure of the softness of samples [12].

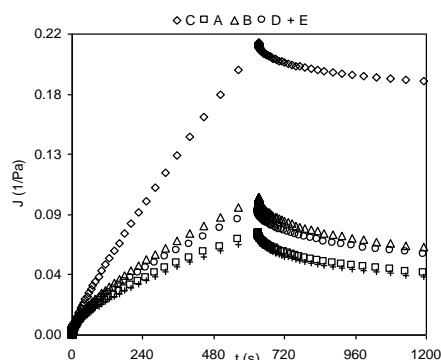


Figure 2. Influence of high pressure on creep and recovery compliances of the AGD samples. $T=25^{\circ}\text{C}$.

In the case of the control sample, $J(t)$ values were highest during both creep and recovery times. This indicates that during loading there may be a more intense and irreversible junction scission, lowering the structural resilience, as evidenced by the high $J(t)$ through the recovery time. However when HP was applied, creep-recovery $J(t)$ data significantly decreased in samples A (100 MPa) and E (600 MPa) similarly, and more effectively than in the others (Figure 2). Pressure reduces the free volume in the system, thus increasing the inter-chain attractions and probably inducing mechanical aggregation of KGM chains, which would increase the firmness of AGDs.

However, this HP-induced aggregation may be partially reversible due to the physical nature of hydrogen bonds and electrostatic interactions, since they can mechanically break and recombine [13]. This fact could explain the non-linear dependence between rigidity of AGD and the HP value, which is consistent with the transient nature of the physically cross-linked networks [2].

Conclusions

The effect of high-pressure treatment on the viscoelastic properties of 3% aqueous glucomannan dispersions varied depending on the kind of test. Mechanical spectra were practically pressure-independent, but they showed that at $\text{pH}=9.36$, there was a phase transition from gel to sol with decreasing frequency in the glucomannan dispersions. In the case of stress sweeps and creep-recovery tests, there was a considerable increase of rigidity and conformational stability in the pressurized samples, as evidenced by the fact that their complex modulus and stress and strain amplitudes were higher than in the control. Moreover, creep-recovery compliances were lower than in the control. All these viscoelastic data were mutually consistent, indicating that high pressure reinforced molecular packing of KGM chains; this caused the formation of new thin junctions, originating more flexible and stable AGDs mechanically stabilized by physical cross-linkings. Stress sweeps indicated that 200 MPa was a suitable pressure for improving the consistency and structural flexibility of glucomannan dispersions.

Acknowledgements

Thanks to the Xunta de Galicia for its financial support under the Consolidation and restructuring program of competitive research units: Strategic Research Partnerships (2009/060) and project AGL2011-24693.

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