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A. Tecante, J.L. Doublier

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> Tél.: 02 40 67 50 00 Fax: 02 40 67 50 05

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Editor

I. Emri

Center for Experimental Mechanics University of Ljubljana, Ljubljana, Slovenia

Technical Co-Editor

R. Cvelbar

Center for Experimental Mechanics University of Ljubljana, Ljubljana, Slovenia

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RHEOLOGICAL BEHAVIOR OF CROSSLINKED WAXY MAIZE STARCH-KAPPA-CARRAGEENAN MIXTURES

A. TECANTE1 and J.L. DOUBLIER

Inventaire N° 2 4 84

Institut National de la Recherche Agronomique, Rue de la Géraudière, BP 71627-44316, Nantes, France. ¹Permanent address: Depto. Alimentos y Biotecnología, FQ-"E", UNAM, México, D.F., 04510, México.

1. INTRODUCTION

The aim of this study is to get a better understanding of the rheological behavior of starch-hydrocolloid mixtures under gelling and non-gelling conditions of the latter. Crosslinked waxy maize starch (CWMS) was used because it is free of amylose and crosslinking avoids granule rupture. Hence, swelled granules are dispersed in a phase containing essentially the hydrocolloid. Application of mixtures with κ -carrageenan (κ C) in the food industry provided further motivation to this work.

2. METHODS

2.1 Materials

The CWMS sample (Clearam® CH10) was an adipate/acetate starch obtained from Roquette Frères. kC was provided by SBI (France) and was used without further treatment. Analytical grade KCl (Merck) and deionized water were used throughout.

2.2 Pasting procedure

All starch slurries were pasted in a Brabender viscograph-E at a bowl speed of 75 rpm following the thermal treatment shown in Figure 1. The apparatus was used only as a cooker and to monitor consistency changes during pasting. Dryweight concentrations were: CWMS 4%, kC 0.5%. In some slurries 20 mM KCl was added to induce kC gelation upon cooling.

2.3 Rheological measurements

Steady shear tests were carried out at 60 °C with a rotational viscometer (Rheomat 120) in a coaxial-cylinders fixture (diameters: bob = 46 mm, cup = 49 mm, height 78 mm). Two consecutive updown shear scans from 0 to 660 s⁻¹ followed by a logarithmic descent from 660 to 0.1 s⁻¹ were applied. Low amplitude (0.04) oscillatory shear was carried out at 60 °C and 25 °C in a controlled-stress rheometer (Carrimed CS50) using either the

cone/plate (diam. 6 cm, angle 4°) or grooved parallel plates (diam. 4 cm, gap 1 mm) geometries. Gap adjustment considered thermal expansion. The fixture rim was covered with paraffin oil to prevent evaporation.

2.4 <u>Solubility-swelling determination</u>

The degree of granule swelling and starch solubility were determined according to previously described procedures (Doublier 1987).

3. RESULTS AND DISCUSSION

In the following discussion A, B and C designate, respectively, CWMS, CWMS/κC and CWMS/κC/KCl. Figure 1 shows the differences in consistency. The earlier peak in C is due to κC solubilization. Swelling start-up occurred slightly earlier (~ 64 °C) in B than in A and C (~ 66 °C). All pastes displayed a rapid swelling followed by a smooth transition to an essentially constant zone during the holding period which indicates good thermal stability.

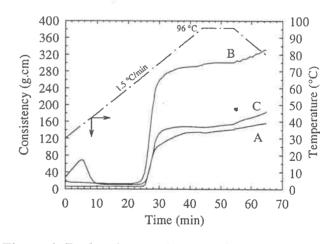


Figure 1. Brabender consistency of starch pastes.

The flow properties of hot pastes are shown in Figure 2. The first up-down scan (continuous line) reveals an anti-thixotropic behavior with C displaying the greatest hysteresis. Time-dependency essentially disappeared after

continuous shearing as shown by the second scan (dotted line) which was always superimposed to the descending curve of the first one. Shearthinning behavior is clear; nevertheless, flow curves could not be described by the power law model over all the shear rate range.

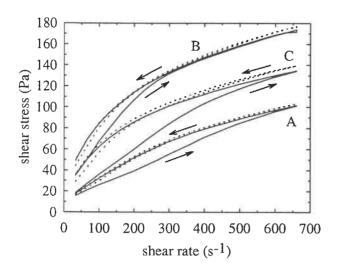


Figure 2. Flow curves of starch pastes at 60 °C.

The viscoelastic properties of hot pastes are shown in Figure 3. None of them was a self-standing gel, yet A and B exhibited apparently a solid-like behavior with G' > G'' and

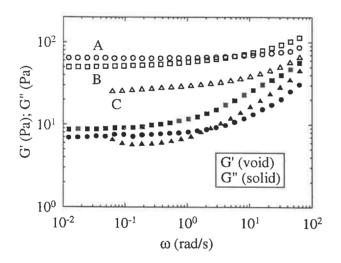


Figure 3. Dynamic moduli of pastes at 60 °C.

both independent of ω below 1 and 0.2 rad/s, respectively. In C, lower and more frequency-dependent moduli were observed. Paste A had the lowest loss angles (tan $\delta \approx 0.1$ at $\omega < 1$ rad/s), while B and C displayed higher and more frequency-dependent loss angles.

Figure 4 shows the mechanical spectra of cooled pastes. As expected, C was a self-standing gel with a typical spectrum; G'>>G" and both independent of ω . In fact, tan $\delta < 0.02$ showing an essentially elastic response. A and B exhibited a behavior similar to that at 60 °C with slightly higher moduli.

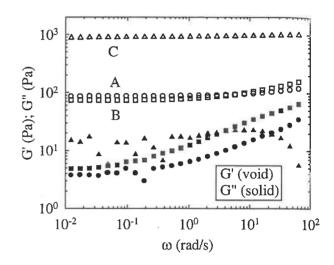


Figure 4. Dynamic moduli of systems at 25 °C.

Starch solubility was low (~ 2%) and swelling was 25.9, 27.3 and 29.3 g/g for A, C and B, respectively, which resulted in starch volume fractions very near to unity. At such value a closepacking of swelled granules can be present (Bagley and Christianson, 1982) leaving a reduced volume to the fluid phase. Therefore, our systems were highly charged and this may explain the initial antithixotropic behavior the extent of which depended on the viscosity of the fluid phase. On the other hand, at 60 °C and 25 °C (except C), the increasing dependence of moduli with frequency can be attributed to the response of the continuous phase which is to some extent overwhelmed by that of starch particles. Systems behaved as highly concentrated suspensions of starch particles in water (A at 60 °C and 25 °C) and in a macromolecular solution (B at 60 °C and 25 °C and C at 60 °C), and as a composite gel of swollen particles embedded in a macromolecular network (C at 25 °C).

4. REFERENCES

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