Solvency Effects On Biopolymer Interactions in Pectin Gels

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Abstract

Amidated low-methoxyl pectin (ALMP) gels are widely used in industry, *e.g.*, in foods and pharmaceuticals. The intrinsic and extrinsic characteristics of these systems lead to interactions directly related to gel formation (*i.e.* the development of cross-links) and microstructure. Although the presence of co-solutes (*e.g.* sugars) is not necessary for ALMP gelation, their inclusion alters interactions between the polymer chains, water, the co-solutes themselves and any added salts, which are not fully understood.

We here present the effects of cross-link development due to added Ca^{2+} ($CaCl_2$) in ALMP both in water and in the presence of high concentrations (~ 60 *wt.* %) of sugars as co-solvents. Oscillatory rheology and time-resolved Dynamic Light Scattering (DLS) techniques were used to characterise the solutions and gels.

Materials and Methods

Sample preparation

Hydrogel

Water 99.5 *wt.* %, pectin 0.5 *wt.* %, $(NaPO_3)_6$ 2 mM and $CaCl_2$ from 0 to 8 mM.

Sugar-gel

Water 99.5 *wt.* %, fructose 0.5 *wt.* %, pectin 0.5 *wt.* % $(NaPO_3)_6$ 2 mM and $CaCl_2$ from 0 to 8 mM

Tests and Techniques

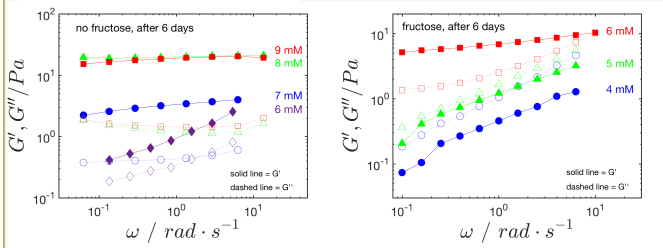
A. Ageing and [Ca^{+2}] dependence: rheology (strain and frequency sweep tests) and DLS study ($g_{2\text{-}1}$ at θ = 90° and angular dependence) for aged samples (> 6 days after preparation) at 25°C.

B. Temperature dependence: frequency sweep tests at different temperatures (from 25 to 70°C + from 70 to 25°C repeated twice) and DLS measurements (θ = 90°) from 25 to 65°C + 55/45/25°C.

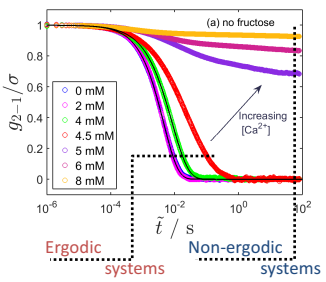
C. Water-fructose study: (i) ^{1}H NMR tests from 25 to 65°C – high field 400 MHz (chemical shift, diffusion) and low field 20 MHz (T_1 and T_2 measurement); (ii) Dielectric spectroscopy from -163 to 80°C; (iii) DSC different rates and modulated DSC.

Results and Discussion

Ageing and [Ca^{+2}] Dependence



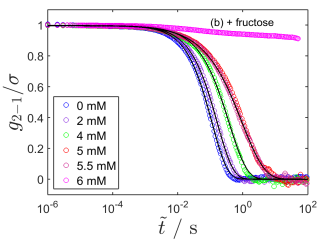
- *G'* increased with increasing the [Ca^{2+}] for both hydrogels and fructose-gels;
- Sugar-gels require less [Ca^{2+}] than hydrogels to promote crosslinks between pectin chains;
- Ageing behaviour was seen up to ≈ 6 days – for this reason, further analysis were performed on aged samples;



$$g_{2-1} = A \cdot e^{\left(\frac{-2\tilde{t}}{\tau}\right)^{\beta}}$$

Ensemble averaging[1]

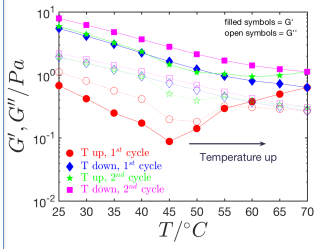
[1] Physica A., 1989, **157**, 705-741

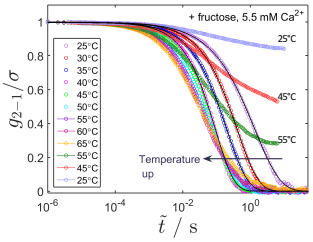


- All dynamics slowed down as a function of [Ca^{2+}] and presence of fructose;
- Characteristic time-scales slowed down by the increased viscosity;

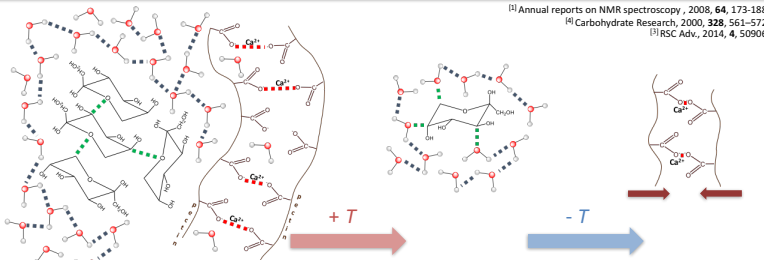
- $g_{2\text{-}1}$ hydrogel at 9 mM [Ca^{2+}] ≈ $g_{2\text{-}1}$ fructose-gel at 6 mM [Ca^{2+}]

Temperature Dependence





On heating, a non-monotonic temperature dependence of the storage modulus was observed with no melting of the gels within the temperature range (up to 70 °C). Systems with [Ca^{2+}] < 6 mM required a temperature increase to allow the formation of such non thermo-reversible gels. This suggests some mechanism of *'freeing up'* of molecules to allow more cross-links to form.



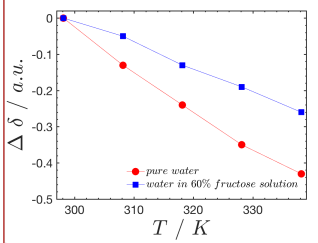
[3] Annual reports on NMR spectroscopy , 2008, **64**, 173-188
[4] Carbohydrate Research, 2000, **328**, 561–572
[3] RSC Adv., 2014, **4**, 50906

- Interactions:
  sugar-sugar > *sugar-water*[1][2][3]
- formation of sugar clusters

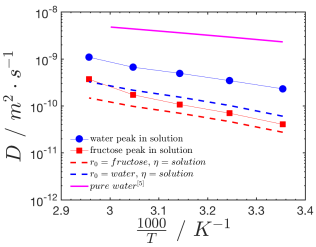
- Breakdown of sugar clusters;
- Promotion of *sugar-water* interactions;
- Reduction of free water

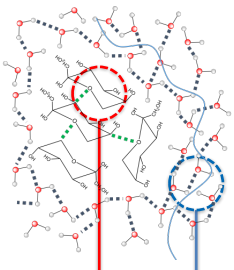
Reinforcement of cross-links between pectin chains

Water-Fructose Study



The smaller change in chemical shift of the water in 60 *wt.* % fructose suggested a more stable chemical environment than in pure water, *i.e.* possibly more stable hydrogen bonds.





For fructose:
$D_{Measured}$ (-■-) ≈ $D_{Predicted}$ (---) [*]

For water:
$D_{Measured}$ (-●-) ≠ $D_{Predicted}$ (---) [*] with a factor of 7
This effect is similar to what has been observed previously for sucrose[6]

[*] Stokes-Einstein $D = \frac{k_b T}{4\pi r_0 \eta}$ where $r_0 = \frac{1}{2}\left(\frac{M_w}{\rho N_A}\right)^{\frac{1}{3}}$

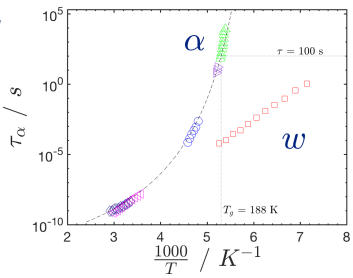
Water in 60 *wt.* % fructose is faster than Stokes-Einstein prediction

Relaxation dynamics in fructose-water solutions

This apparent anomalous D_{water} has been noted elsewhere[7] using a range of other techniques (DSC, dielectric spectroscopy, *etc.*).

Below is a summary of relaxation times (τ_α) measured in our system over 15 decades of time-scales as a function of temperature.

- Dielectric Spectroscopy
  - □ *w relaxation*
  - ○ *α relaxation*
  - ◁ *T/σ conductivity*
- DSC
  - △ *Δ rate*
  - ▷ *modulated*
- Rheology
  - ◇ *Viscosity*



The data indicate a disconnect between local and global movement motion around the glass transition temperature

[5] Phys. Chem. Chem. Phys., 2000, **2**, 4740-4742
[6] Phys. Chem. Chem. Phys., 2016, **18**, 19207-19216
[7] J. of Non-Crystalline Solids, 2005, **351**, 2858–2863