

## Networks of polysaccharides with hydrophilic and hydrophobic characteristics in the presence of co-solute

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### ABSTRACT

The present investigation deals with the changing network morphology of agarose and high methoxy pectin when mixed with polydextrose as co-solute at concentrations varying up to high level of solids. Thermomechanical analysis and micro-imaging were performed using small deformation dynamic oscillation in shear, modulated differential scanning calorimetry and environment scanning electron microscopy. Fourier transform infrared spectroscopy and wide angle X-ray diffraction were practised to examine the nature of interactions between polymer and co-solute, and the extent of amorphicity of preparations. We observed a decline in the mechanical strength of aqueous agarose preparations upon addition of high levels of polydextrose, which should be attributed to reduced enthalpic content of the coil-to-helix transition of the polysaccharide network. Glass transition phenomena were observed at subzero temperatures in condensed preparations, hence further arguing for the formation of a lightly cross-linked agarose network with changing solvent quality. High levels of co-solute induce formation of weak pectin gels at elevated temperatures (even at 95 °C), which with lowering temperature exhibit increasing strength. This results in the formation of rubbery pectin gels at ambient temperature, which upon controlled cooling to subzero temperatures convert to a clear glass earlier than the agarose counterparts.

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### 1. Introduction

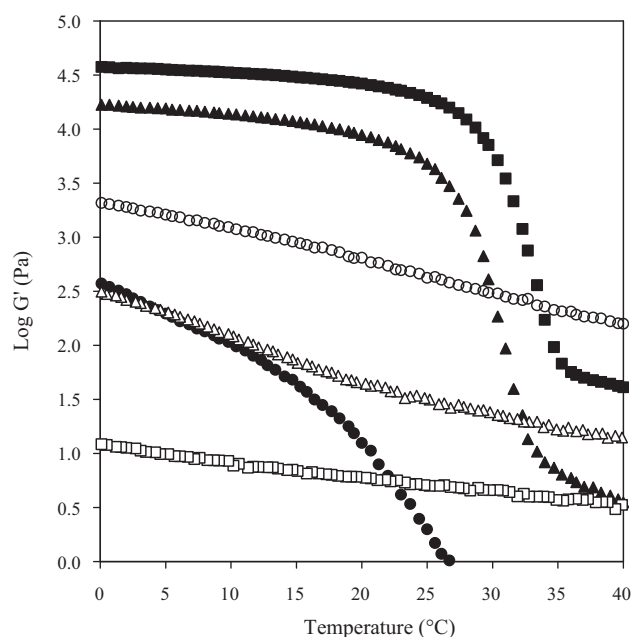
The functional property of gelling polysaccharides is an area of interest in science and technology, since they are utilised as texturisers to impart stability and viscoelastic flow in a variety of industrial applications. Scientific understanding on gelation mechanism, phase behaviour and emulsification properties of non-starch polysaccharides like agarose, alginates, carrageenans, pectins, etc. in aqueous preparations has been widely explored in the past [31]. More recently, the altered physicochemical interaction and network morphology of these polysaccharides in a changing solvent environment by the addition of sugar as the co-solute has been investigated [34].

Agarose and pectin are polysaccharides widely considered by major ingredient and product manufacturers for the development of, for example, high sugar/low polysaccharide formulations, which are central to many confectionery products. Agarose is a linear polymer of alternating (1 → 3)-β-D-galactopyranose and (1 → 4)-3,6-anhydro-α-L-galactopyranose subunits forming junction zones via the aggregation of helical chains that are further stabilised

with hydrogen bonds from the surrounding aqueous environment [1,8]. Pectin is a linear polymer of (1–4) linked α-D-galacturonate interspersed periodically with 1,2-linked rhamnosyl residues [7]. Gelation of pectin in the presence of co-solute provides viscoelastic structure, which is a combination of thermally reversible and hydrophilic interactions of the pectinic acid network at low temperatures along with the hydrophobic association of methyl ester substituents developed at high temperatures [26,27].

Changes in the physicochemical environment of the agarose and pectin networks were investigated in the presence of sugar (glucose syrup, or glucose syrup/sucrose mixtures), which was found to dramatically alter the morphology of three dimensional structures leading to the formation of gels with rubbery viscoelasticity [32]. Further, high levels of sugar (>60%, w/w) are unable to maintain a thermodynamically stable polysaccharide network with extensive aggregation, which converts into a lightly cross-linked system undergoing vitrification at subzero temperatures [20]. As an extension to the above observations, we now formulate the system with polydextrose that can serve as a bulking agent and sugar replacer in low-calorie foods. Polydextrose is a branched glucose polymer with an average degree of polymerisation of 10 or 12 glucose residues and a mixed combination of α and β linkages that prevent intermolecular association and gelation of the material. Its physiological benefits of dietary fibre, low glycemic index, and prebiotic effects

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**Fig. 1.** Cooling profiles of storage modulus ( $G'$ ) for 1.5% agarose (closed symbols) and 2% pectin (open symbols) with 0 (■, □), 50 (▲, △) and 70 (●, ○) polydextrose at a cooling rate of 1 °C/min, frequency of 1 rad/s, and strain of 0.1 and 1%, respectively.

make it a useful ingredient in novel food and nutraceutical applications [5,16].

In the present work, we undertake a systematic study of the effect of polydextrose on the thermomechanical properties of agarose and pectin gels covering a range of solids up to 80% in formulations. A series of ideas is developed to discuss changes in viscoelasticity with increasing levels of co-solute up to the condensed state. This is further aided by FTIR and X-ray studies that identify the nature of agarose/polydextrose and pectin/polydextrose interactions at the molecular level. Further, we implement a time-resolved study of the relative stability of the enthalpic/low-solid and entropic/high-solid networks of the polysaccharide/co-solute mixtures. Headway in this type of research is achieved by adapting theoretical frameworks from the “sophisticated” synthetic polymer research, which allows determination of viscoelastic functions in relation to time or temperature of observation [6]. Thus, the current investigation utilises such theoretical concepts to build molecular understanding by contrasting the structural properties of high solid agarose/polydextrose and pectin/polydextrose mixtures in terms of polysaccharide nature and co-solute concentration.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Agarose

The sample of this investigation was supplied by Sigma–Aldrich Co. (Sydney, Australia). According to the supplier, the content of water, ash and sulphate were 7, 0.25 and 0.12% respectively. It is a material of high gel strength, which achieves elastic modulus ( $G'$ ) values of  $3.75 \times 10^4$  Pa at 0 °C (aqueous preparation of 1.5% in Fig. 1).

#### 2.1.2. High methoxy pectin

The citrus peel pectin was purchased from Sigma Aldrich Co (Sydney, Australia). Polysaccharide content was 92.0% on dry weight basis of which 85.1% is galacturonate with a degree of

methyl esterification (DE) of 70.3%. Chromatographic analysis carried out by the supplier, using an ultrahydrogel linear column and eight pullulan standards, produced a number average molecular weight ( $M_n$ ) for the pectinic material of this investigation of about 154 kDa.

#### 2.1.3. Polydextrose

The material used was a product from TATE & LYLE (IL, USA). The powder was of 90% purity with 4% moisture and has passed the microbiological testing under the food grade standards. It is a readily soluble, amorphous polymer with an average degree of polymerisation of twelve glucose residues.

## 2.2. Methods

### 2.2.1. Sample preparation

The polysaccharide solutions were prepared by dissolving agarose at 1.5% (w/w) and pectin at 2% (w/w) solids in distilled water at 80 and 95 °C, respectively, by gentle stirring on a hot plate. After obtaining a clear solution, the temperature was lowered to 65 °C in the agarose solution and to 75 °C in the pectin solution for the addition of the required amount of polydextrose. The temperature of the system was maintained at 65 °C for the agarose solution and at 75 °C for the pectin solution on the hotplate until polydextrose was fully dissolved and the desired level of total solids was obtained by evaporating slowly excess water. The pH of the pectin system was then adjusted to 3.0 using 0.2 M HCl solution to create the required gelling conditions for subsequent experimentation.

### 2.2.2. Rheology

Low amplitude oscillatory measurements were performed in shear to obtain the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) which are parts of the complex shear modulus ( $G^* = G' + iG''$ ), and  $\tan \delta(G''/G')$ . The analysis was performed on AR-G2, which is a controlled strain rheometer with a magnetic thrust bearing technology (TA Instruments, New Castle, DE). Samples with total solids up to 70% (w/w) were loaded on the preheated Peltier at 60 °C using a 40 mm parallel plate, with edges covered in silicone oil from BDH (50 cS) to prevent moisture loss. According to the experimental protocol, samples were cooled to 0 °C at a scan rate of 1 °C/min followed by a 30 min isothermal run and a frequency sweep (0.1–100 rad/s) at the same temperature. These were then heated to 95 °C at 1 °C/min. An oscillatory frequency of 1 rad/s with a strain of 0.1% for agarose and 1% for pectin samples was executed throughout the experiments. Strain sweeps identified the linear viscoelastic region, which indicated that the agarose network is at least an order of magnitude more strain sensitive than the pectin counterpart.

For condensed samples with 20% moisture, a measuring geometry of diameter 10 mm was used within an extended experimental temperature range to analyse the vitrification behaviour of the network. Molten agarose samples were loaded on the preheated Peltier at 60 °C and subjected to extended cooling until –50 °C, whereas high-solid preparations of pectin were loaded at 95 °C and cooled to –60 °C at 1 °C/min. At an interval of 4 °C, frequency sweeps were performed within the range of 0.1–100 rad/s. A constant strain of 0.01% for agarose and 0.1% for the pectin counterpart was maintained, and results were modelled for estimation of the glass transition temperature at subzero temperatures.

### 2.2.3. Modulated differential scanning calorimetry

Thermal measurements were performed on MDSC Q2000 (TA instruments, New Castle, DE). The instrument used a refrigerated cooling system to achieve temperatures down to –90 °C and a nitrogen DSC cell at 50 mL/min to purge condensation. Samples were loaded in hermetic aluminium pans. Calibration of the heat flow signals using a traceable indium standard ( $\Delta H_f = 28.3$  J g<sup>–1</sup>) and the

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