Characterisation of Starch/Cellulose blends

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ABSTRACT

Gelatinisation is a major property of starch in regard to its functionality. Here we investigate the effect of chemically derivatised cellulose on the gelatinisation properties of waxy maize starch with a specific focus on the temperature of thermogelation. Two models appear to emerge which determine the extent of starch gelatinization.

INTRODUCTION

The world-wide market for industrial starches is expanding. The starch extracted every year worldwide is around 60 million tonnes of which almost 60% is used in food industry and 40% in pharmaceuticals and non-edible purposes[1, 2]. Recently, starch has been utilized as a raw material for biodegradable plastics, in agreement with the concept of sustainability and concerns over environmental and biodegradability issues[3]. Starch is a storage polysaccharide deposited in the form of insoluble granules within plant cells. The starch granule contains amorphous regions made up from amylose, an essentially linear molecule of α-(1-4) linked D-glucopyranosyl monomers, and crystalline region made up from amylopectin, a highly branched molecule containing short chains of (1-4)-α-linked D-glucopyranosyl monomers with (1-6)-α-linked branches[4, 5]. A fascinating property of starch in regard to its functionality is its rheological responses during gelatinisation process which imparts unique physico-chemical properties to the aqueous system[6,7]. Numerous studies have been published on starch gelatinisation over the past decades furthering the understanding on the mechanism of this complex phenomenon. Starch gelatinisation is defined as an order–disorder transition. In an excess of water, above the gelatinisation temperature, crystalline structures of starch molecules are disrupted[8]. This loss in organised structure is accompanied by swelling and uptake of water, changes in volume fraction of the swollen granules, and leaching of soluble components, into the aqueous phase, resulting in a complex dispersion of swollen and deformable granules in a viscous aqueous continuum (starch pastes)[9]. These events are accompanied by a dramatic increase in viscosity and the resulting complex rheological properties of these dispersions are governed by the extent of starch granule swelling and concentration[10, 11]. Many investigations have confirmed the role of hydrocolloids (e.g., guar gum, locust bean gum, xanthan gum, etc.) in enhancing or modify the gelatinisation and the rheological properties of starch pastes [12, 13]. The factors playing a key role in the rheological properties of such a composite are: the concentration, molecular structure, and molecular weight of the hydrocolloid, as well as the concentration, the volume fraction of starch and the rigidity of the swollen granules[14, 15]. In spite of this extensive literature to the best of our knowledge there are a few reports on the

effect of cellulose derivatives on starch gelatinisation[15, 16]. Cellulose derivatives used in this work are methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC), water-soluble cellulose ethers in which the hydroxyl groups at C(2,3) or C(6) are substituted with hydrophobic substituents. An important effect of this substitution is the behavior of solutions on heating since the solution will change into a gel[17, 18]. We will therefore investigate the effect of thermogelation on starch gelatinisation of starch. In order to disentangle the complex mechanism of gelation of cellulose with the gelatinisation, continuous phase viscosity was matched using guar gum, a non gelling, non-ionic polysaccharide with a β-(1-4) linked mannan (Man) backbone substituted by a single galactose (Gal) side chain through α-(1-6) linkages. The objective of this, ongoing study, is to understand a new route for physically controlling the gelatinisation and rheological properties of starch. Moreover control of these properties should enable scientists to create designed and desired microstructure.

MATERIAL AND METHODS

Commercial (WMS) of unmodified waxy maize starch (pure amylopectin; contains only trace amounts of amylose) were kindly donated by a leading starch supplier. MC and HPMC with different degree of substitution were kindly provided by Dow Chemical Co. The samples used in the starch-hydrocolloid mixtures for this study were: A4M or K4M from the Methocel range of cellulose derivatives. The letter 'A' correspond to MC while 'K' to HPMC with different level of incorporation of the two substituent's, leading to different gel formation temperature (50°C for A and 80°C for 'K') (data not shown). The letter M at the end of the abbreviation indicates the value of the viscosity in cPs for solution of 2% at room temperature, for example 4M = 4000 cP. Guar gum (GG) (Meyprodor 30, 100 and 400 ex Danisco), a non gelling

hydrocolloid with the nominal molecular weight of 1640kDa, was used in this study as a comparison.

Sample preparation

Cellulose derivatives solutions, 1.0% wt, were dissolved with the following procedure: 1/3 of the required final volume of distilled water was heated to ~ 90°C, then cellulose derivative powder was added carefully keeping the agitation of the solution by magnetic stirring. The complete solubilisation was obtained by adding the reminder water as cold water. The agitation of the solution was continued at 5°C for 30 min. Guar gum was first dispersed in distilled water using a magnetic stirrer. The dispersions were stirred at 80°C for 1h followed by continued mixing overnight on a roller mixer at 4°C before storing the samples at 4°C. Insoluble impurities were removed by centrifugation for 45 min at 4000g and 5°C. Suspension of starch was prepared before each measurement by dispersing 8 wt % of starch powder in either distilled water (control) or aqueous solution of each polysaccharide, using a magnetic stirrer.

Viscosity (RVA) profiles

The paste viscosity profiles recorded in centipoises (cP) (1 cP = 1 mPa s), for each WMS/hydrocolloid mixture, prepared as described in previous section, were investigated using the Rapid Viscous Analyzer (Newport Scientific RVA-4SA) controlled by Thermocline for Windows software (Ver. 2.2; Newport Scientific Pty Ltd. Warriewood, NSW, Australia). Dispersions were equilibrated at 50 °C for 1 min, heated at the rate of 1°Cmin⁻¹ to 95°C, held at 95°C for 2.5 mins, cooled to 50°C at a rate of 1°Cmin⁻¹ and, lastly, held at 50°C for 2 mins. A constant paddle rotational speed (160 rpm) was used throughout the entire analysis. RVA characteristics, including pasting temperature (the onset of the viscosity increase), peak viscosity,

trough (minimum paste viscosity achieved after holding at the maximum temperature); breakdown (difference between peak viscosity and trough viscosity), and final viscosity were determined from the RVA curves.

Dynamic viscoelasticity measurements (temperature sweep)

The dynamic viscoelastic functions such as shear storage modulus G' and loss modulus G'' were measured as a function of temperature using parallel plate geometry (50 mm diameter; 1 mm gap) with a control stress rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany). The sample was heated from $25^{\circ}C$ to $90^{\circ}C$ at a rate of $1^{\circ}Cmin^{-1}$. To prevent dehydration during the rheological measurements the edges of the sample were covered with a thin layer of low-viscosity mineral oil. Measurements were carried out at an angular frequency of 10 rads^{-1} and strains of 0.5% to ensure measurement were made in the viscoelastic plateau region. In order to overcome the gap change, due to the thermal expansion of the measurements systems with temperature, a true gap device was used (Physica TruGapTM). The Physica TruGapTM device does not approximate the gap size, but, directly measures real gap size during the experiment. Normal stress was kept to zero through the entire measurement.

RESULT AND DISCUSSION

Viscosity (RVA) profiles

Viscosity profile for WMS in either distilled water (control) or aqueous solution of each polysaccharide (HPMC, MC or GG) determined by the RVA are presented in Figure 1. The temperature at which the onset of the increase of viscosity occurs is the 'pasting temperature'. For waxy maize starch in water, the onset of viscosity increase is due mainly to the swelling of the granules. The pasting temperature for all the mixtures is lower than the control.
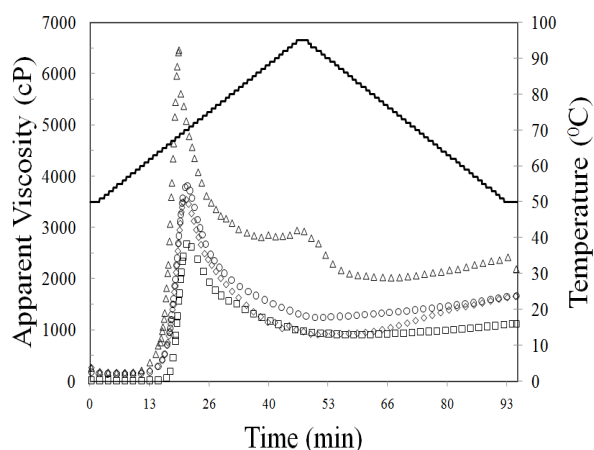

Figure 1. RVA viscosity profile for WMS (□) and in the presence MC (Δ), HPMC (◊) or GG (○).

Alloncle et al[12] described this system as starch granules embedded in a hydrocolloid solution. Hence, the viscosity of the composite would be affected by any changes in the two phases as well as the way the two phases interact with each other. Phase changes in the continuous phase on heating might explain the greatest efficacy of MC in lowering the pasting temperature among the polysaccharides tested. Phase changes in starch/MC mixture can be ascribed to the formation of a gel network in the continuous phase (MC domain), enhancing the viscosity of the continuous phase and hence the overall viscosity of the system at temperature below starch granules start to swell. Nevertheless increase in the effective concentration of starch due to the presence of gel network may promote interactions between the granules. Detection of a lower pasting temperature may arise from both of these phenomena. However, upon the addition of hydrocolloid it should be noted that the higher viscosity of the continuous phase might enable the detection of early stage of swelling of the granules, not detected when starch is dispersed in water[19]. RVA parameters, such as peak viscosity (PKV), breakdown viscosity (BDV) and final viscosity (FNV) are shown in Figure 2.
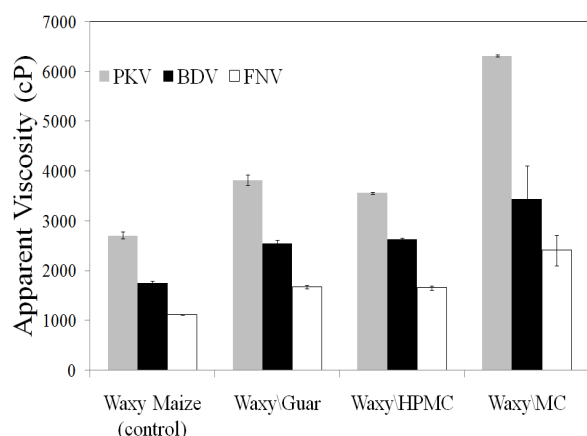
Figure 2. RVA parameters.

The peak viscosity is indicative of the water-binding capacity and extent of swelling of the starch granule. Peak viscosity for each starch/hydrocolloid system was larger than that for the control. Among the hydrocolloids tested, MC has the highest impact on peak viscosity. Norton et al[20] have shown that gelation in shear field creates gel particles, with a continuous water phase. Our system here would then be a dispersion of a MC gel particles and swellable starch granules. Such an increase in dispersed phase volume contributes to the enhanced peak viscosity upon starch gelatinisation. The larger volume occupied by the swollen granules reduces the volume of the phase accessible to the hydrocolloids. This depend on whether cellulose gelation temperature > gelatinisation temperature. If gelation temperature < gelatinisation temperature starch swells in available water after gel particles formation. The effective increase of concentration of the hydrocolloids results in the pronounced increase in the viscosity of the continuous phase. The additional swelling of the starch enhances the overall viscosity of the system. The drop in viscosity, which is called breakdown (BDV), indicates the loss of granule integrity and subsequent disruption of the granules. Christianson et al [14] attributed the higher breakdown of starch when dispersed in a hydrocolloid solution to the increase of shear force exerted on the

swollen granules due to presence hydrocolloid. Starch/MC shows the highest breakdown among the mixture studied. It should be considered that at this stage of the heating the temperature is above the critical temperature at which both cellulose (MC and HPMC) form gel network. However the gel strength for MC is greater than HPMC due to higher hydrophobicity of the substituents. We report a positive correlation between strength of gel formed by cellulose and break down of the granules; further work is needed to determine the effect of different gel network on the shear force exerted on the granules. The presence of hydrocolloids in the mixture resulted in a higher final viscosity compared to the control. At the end of the cooking process the mixture can be assumed to be made of leached amylopectin, granules ghosts and hydrocolloid. The higher final viscosity when hydrocolloid is present in the mixture may be explained as a synergistic effect on the viscosity arising from mutual exclusion between starch molecules and hydrocolloid present into the mixture based on thermodynamic incompatibility[13, 14]. The highest final viscosity observed for starch/MC mixture at $50^{o}C$ may be due to the presence of MC gel particles, because MC only reverts back to a solution at temperature around $35^{o}C$.

Dynamic viscoelasticity measurements (temperature sweep)

Large deformation occurring in RVA, although useful for viscosity measurement, may disrupt delicate networks as the one formed by the cellulose derivative, limiting the understanding of the effect of these structures on the swelling of the starch granules. Thus, in this section changes in rheology using non-destructive oscillatory measurement will be discussed. Figure 3a shows changes in G' and G" for solution of guar gum alone (open symbols) and mixed with starch (filled symbols) on heating ($1°Cmin^{-1}$) between 20°C and 95°C. The

dynamic viscoelastic function for a solution of GG showed the typical decrease in viscosity on heating, commonly observed for other polymers, with no further indication of the sharp changes that would be expected for a thermally induced network formation. Surprisingly at temperature above 80°C an increase in G' was observed. Although this seems to be an artifact, further investigations are currently being carried out for better understanding on the phenomena. The mixture of starch/GG shows a broadly similar temperature course of rheological changes below 60 °C. A further increase in temperature indicates structural changes associated with phase transition (melting) of starch granules reflected by changes in the rheological properties. In fact the onset temperature of the phase transition as measured in the micro DSC (data not shown) closely matched the temperature of the onset of both moduli increase as measured in the rheometer. This supports the idea that the initial increase of G'/G'' is due to swelling of the granules to fill the entire available volume where G'>G'', following the work of Evans et al[16] describing the "gel-like" rheology of concentrated dispersions of swollen starch granules. With further increase in temperature, both moduli increase less steeply and reach maxima at temperature close to 85°C. The subsequent decrease of G'/G'' as the temperature rises indicates a loss of mechanical strength and granule integrity at higher temperature. The temperature course of G'/G'' for a solution of HPMC alone are shown in the Figure 3b. As observed for solution of GG alone, both moduli decrease on heating. However, at temperature around 50°C a sudden increase in G' was observed. Increase in G' was observed to occur in two distinct "waves", the first concurrent with a "dip" in G'', after which increase occurs as reported by Haque et al[29] and indicative of network coarsening and rearrangement at higher temperatures.
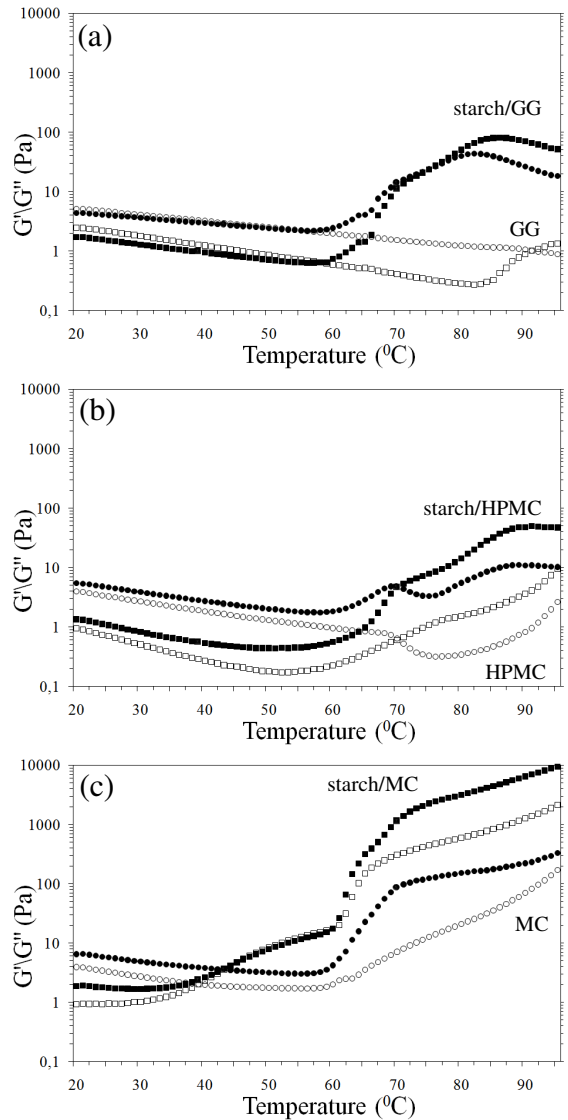

Figure 3. Temperature dependence of G' (squares) and G'' (circles) for each starch suspension (filled symbols) and solution of hydrocolloid alone (open symbols).

When starch is added the upturn in the first wave of G' increase is evident at lower temperatures. An increase of both moduli occurs at temperature close to 60°C as seen for WMS/GG mixture. However, G'/G'' reach a maxima at temperature above 85°C, and they do not show any decrease at higher temperature as seen for WMS/GG mixture. The plateau observed for both moduli in mixture containing HPMC indicates a higher efficacy of a gel network (HPMC), compared to a viscous solution (GG) in

preserving granule integrity at higher temperature. Thermogelation of MC is shown in figure 3c. The two waves of G' increase is more evident than for HPMC and occur at 32°C and 61°C, considerably lower than seen for HPMC, due to increased hydrophobicity of the methyl substituent. A comparison of MC and HPMC gelation (figure 3a and 3b) show a higher G' at comparable temperature for MC and G' is much greater than G'', indicating a more dense gel network for MC [29]. When starch is present the first "wave" of G' increase occurs at the same temperature as MC alone. The second wave of G' increase corresponds to the temperature for G' increase seen for the other starch containing mixtures. The starch contribution to the G' increase in the MC mixture is seen as a shoulder on the MC gelation curve providing a synergistic increase in composite G'. With further heating, a decrease or plateau of both moduli was not observed. Instead G'/G'' approach the same rate of moduli increase observed for MC alone. The high similarity of the moduli increase between WMS/MC mixture and MC alone indicates cellulose dominance in the composite properties. The gel structure formation at temperatures below the starch granule gelatinisation and the higher gel strength explains the greater effect of MC on the swelling and integrity of the granules among the hydrocolloids studied.

CONCLUSIONS

The present results indicate that hydrocolloids, which form a gel network structure on heating, have an impact on the rheology of composite containing starch granules. Network structure formed before starch granules start to swell, as for MC, result in a cellulose dominance in the rheology of the composite, explained as greatest efficiency of MC in affecting the swelling and integrity of the granules. Hydrocolloid providing only viscosity or weak thermo reversible gels appear to have less dominance on starch granule swelling as the composite rheological properties have a strong influence of the component starch. Further experiments are currently being carried out to gain a better understanding on the effect of the gel strength on the gelatinisation of starch.

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