Properties of Maize (Amidex®) Starch Crosslinked by Pregelatinisation with Sodium Trimetaphosphate: II. Flow Behaviours and Goniometry

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Abstract

Native maize starch (Amidex®) was cross-linked by pregelatinisation at 90 °C for 45 min and treating with sodium trimetaphosphate (STMP). The flow behaviours and goniometry of both the native and crosslinked starches were studied. These included the moisture content, swelling behaviour, effect of sodium chloride on swelling, effect of sucrose on swelling, film-forming properties, alkaline paste clarity and contact angle. The moisture content of the native starch was 8.60 while those of the cross-linked starches were 9.99, 8.49, 10.11, and 7.85 % respectively for the non crosslinked starch and starches containing 0.4, 0.8 and 1.2 g of STMP. The swelling volume and paste clarity were reduced by cross-linking and the levels of reduction were directly proportional to the degree of cross-linking. Sodium chloride and sucrose reduced the degrees of swelling of the cross-linked and non cross-linked starches. Cross-linking however, reduced the effect of sucrose on the swelling of the starch. The contact angles were generally increased with cross-linking showing that cross-linking reduced the hydrophilicity of the starch.

Keywords: Swelling behaviour, Goniometry, Maize starch, Crosslinking, Sodium trimetaphosphate.

Introduction

Starches are synthesized within the plant by the chemical interlinking of hundreds and thousands of individual glucose units to form long-chain molecules, and treatment with acid or enzymes can break the starch down to its constituent sugar molecules. They form the major food reserve materials in plants especially in the seeds and tubers, sustaining them through winter dormancy and nurturing the new plant during germination (Yong, 1984). The storage of starch in the form of granules is a convenient method since starch is an insoluble source of energy that can be gradually made available through the action of enzymes. The plant uses two different mechanisms to synthesize its starch. It may form long linear chain by the successive attachment of several hundreds of glucose units (amylose). Or when a linear chain is built up to a length of perhaps a dozen glucose units, a second mechanism may intrude to attach a glucose unit in a branching position. Glucose groups are then progressively added to each of these branches until new branch point s are started. Eventually, a large treelike polymer of several thousand glucose units is synthesized (amylopectin).

Corn starch is about the cheapest of the common starches and enjoys a huge market where cost is the prime consideration. It is similar to wheat starch in that it has a high gelatinization temperature and a high ability to gel, and also shows the phenomenon of retrogration (Glicksman, 1968). Corn starch is also the base for more specialty starches and converted starch products than any other starch. When corn starch is heated in water, the solution is cloudy, noncohesive, and upon cooling, gels or sets back to form viscous, relatively short, opaque pastes. Its pastes however have a pronounced tendency to retrograde under freeze-thaw conditions.

Structural modification of starches have been undertaken to achieve an improvement in its utility in the various segments of its application (Gessner, 1981; Albrecht *et al* 1960; Sharpe, 1981). Such modifications impart new properties, improve some of the inherent properties, or repress and modify some of their other properties.The modification involves a change in the functional properties of the starch. These functional properties can be conveniently broken down into two categories - properties of the dry starch, and properties of the processed or cooked starch. The properties of the raw starch are inherent in the type and variety of starch granule and are exhibited as differences in granule size, colour, flavour, odour, moisture content, flowability, and dispersibility in different media, among other properties. The properties of starches during and after processing, while also characteristic of the type and variety of starch, can be modified by chemical and physical treatment of the starch as well as by incorporating other ingredients that affect the inherent characteristics of the starch. Properties of starch that are important during processing are gelatinization (pasting) temperature, rate of thickening, time and temperature of maximum viscosity, and general flow properties.

Several techniques have been employed in modification of starches including heating, hydrolysis (acid or alkali), oxidisation with oxidising chemicals, addition of chemicals that will result in the introduction of new chemical groups and/or changes in the size, shape, and structure of the starch molecules, extrusion cooking and cross-linking (Glicksman, 1968; Lenaerts *et al* 1991; Herman *et al* 1989; Wurzburg, 1986). Cross-linking as a method of starch modification can be accomplished by adding multifunctional reagents capable of forming ether or ester linkages with the hydroxyl groups in the starch (Meuser *et al* 1989).

Several bifunctional reagents (cross-linkers) have been used in the past to cross-link various starches with varying degrees of successes (Salay *et al* 1990; Della Valle *et al* 1991; Chang *et al* 1992). These agents include monosodium phosphate, sodium trimetaphosphate, formaldehyde, organic dihalides, sodium tripolyphosphate, epichlorohydrin, phosphoryl chloride, adipic/acetic anhydride mixtures and succinic anhydride/vinyl acetate mixture. These cross-bonding reactions apparently take place on or near the surface of the granules, and although the degree of cross-linking is very low - approximately one cross-link per 200-1000 glucose units, the effect on the dispersion characteristics are quite pronounced.

The present study centres on the modification of a commercial product of corn starch, Amidex 3001®, through cross-linking with sodium trimetaphosphate using the method of pregelatinisation and studying of some physico-chemical properties of the products. The spectral and thermogravimetric characteristics of the cross-linked maize starch have earlier been described (Ibezim *et al*, 2006). The mechanical properties of maize starch, crosslinked by reactive processing has equally been reported (Ibezim *et al*, 2005).

Materials and Methods

Materials: The following reagents were employed in the study: ethanol (Industria Brasiliera, Brazil), sodium trimetaphosphate (Sigma, England), sodium sulphate (Merck, Darmstadt), sodium hydroxide (Vetec, Industria Brasileira, Brazil), sodium chloride (Vetec, Industria Brasileira, Brazil) and hydrochloric acid (Vetec, Industria Brasileira, Brasil). Amidex 3001® was kindly donated by Corn Pdts, Brazil.

Moisture content of native and crosslinked starches: The percent moisture content of the native starch sample was determined by the AOAC (1995) method. A 1 g quantity of the native Amidex 3001® was dried in the oven (Temp-Therma, Brazil) at 105°C for 3 h. The weight of the sample compared to the original weight was noted. The heating was continued and the weights measured at hourly intervals until constant. Three replicated determinations were taken. The moisture contents of the cross-linked starches were determined in triplicates as earlier described for the native starch.

Cross-linking by pregelatinisation: A slight modification of the method of Woo (1999) was employed. A 3% dispersion of the Amidex 3001® was pregelatinised by heating in a three-hole reflux condenser at 90°C for 45 min., with constant stirring using a Bayer stirring apparatus. Thereafter, the resulting slurry was cooled, and STMP (0.4 g), sodium sulphate (4 g) added. The pH was adjusted to 11 by addition of 0.1 M sodium hydroxide and the slurry stirred at 40°C for 3 h using a magnetic stirring set up (Corinho, Brazil). The pH was then adjusted to 6.5 using 1 M HCl. The slurry was washed with de-ionised water (4 x 300ml) to remove all traces of unreacted salts. The cross-linked starch was then precipitated with ethanol (1: 5), dried for 24 h in an oven at 60°C, and pulverised. The process was repeated for 0.8 and 1.2 g concentrations of STMP.

Swelling behaviour

General swelling properties: The method of Zimmermann *et al* (2002) with slight modification, was used. Dry hydrogels were immersed in de-ionised water and the swollen weight at equilibrium was determined for each sample. After swelling, the gels were dried at 50°C for 18 h to comprehensively remove the moisture content. Equilibrium water content (EWC) was determined according to the following expression: EWC (%) = $Ws - Wd / Ws \times 100$; Where Ws and Wd denote the weight of swollen and dry hydrogels, respectively. The method of Crosbie (1991), slightly modified by Chung *et al* (2004) was also employed to check the water absorption index of the starches. Swelling profile was also determined by the method of Gliko-Kabir *et al* (2000), for the purpose of comparison.

Effect of sodium chloride on swelling properties: The effect of 0.1 M, 0.01 M, 0.001 M solutions of NaCl in water, on the swelling behaviours of the cross-linked starches using the starch containing 0.4 g of STMP as the probe was determined, by measuring the rise in volume of a 5% dispersion of the starch in the NaCl solutions, relative to the original weight of starch, a slight modification of Gliko-Kabir *et al* (2000) technique.

Effect of sucrose on swelling properties: The effect of varying concentrations of sucrose (0 - 1.5 % w/v) on the swelling properties of the native as well as the cross-linked Amidex® using the starch cross-linked with 0.4 g of STMP as the probe was studied by measuring the swelling heights of a 5 % w/v dispersion of the starches in water over a period of 180 min. The swelling index is expressed as percentage of volume increase over the original weight of the starch.

Alkaline paste clarity: A 2 % w/v dispersion of the starch was added slowly with mild stirring into 0.95% aqueous sodium hydroxide at 25 °C. An aliquot (0.5 ml) of the alkaline paste was added to a test tube containing water (4.5 ml) at 25°C. The mixture was shaken gently by hand, and the transmittance (% *T*) at 650 nm was determined immediately using the spectrophotomer (SP-870, Turner, USA). This was replicated three times.

Film-forming properties of cross-linked starches: A 10 ml quantity of 1 % (w/v) dispersion of the starch (cross-linked or non-cross-linked) was prepared in de-ionised water and poured into a petri dish. This was stored for 18 h at a temperature of 45 °C (approximately 50 % weight loss). The resulting films formed were washed with a large volume of water and cut into discs of about 7 mm diameter, redried until no further weight loss could be observed and stored in hermetically sealed glass containers until further use. The ease of formation of films as well as the swelling behaviours of the discs were noted. The swelling behaviour was studied using the method by Gliko-Kabir *et al* (2000) by immersing a pre-weighed disc into a beaker containing 10 ml of water. The gain in weight with time was determined by blot-drying the disc and weighing.

Determination of contact angle of films: The film for the contact angle determinations was prepared by dispersing 10 % w/v of the respective starch samples in water at a temperature of 80 ^{O}C for 30 min. The dispersion was then smeared on a rectangular glass slide with a stencil at a thickness of 20 μm. The resulting smear from above was weighed and then dried in an oven at 50 ^{O}C for 15 mins. This was continued until a constant weight was obtained. The film was then stored in a desiccator at a temperature of 27 ^{O}C and humidity of 52 % for 5 days to attain equilibrium. The contact angles of a drop of water on the surface of the films were then determined using the Rame-Hart Goniometer (Rame-Hart Imaging 2001, USA). This exercise was carried out in three replicates each for the uncrosslinked starch and starch cross-linked with 0 and 1.2 g of STMP.

Results and Discussion

Crosslinking by pregelatinisation: The percentage w/w yields for the cross-linking processes were: 61.75, 75.94, 72.28 and 68.75 for the non-crosslinked starch and starches cross-linked with 0.4, 0.8 and 1.2 g of STMP respectively. The moisture contents (% humidity) of the various cross-linked starches were: 9.99, 8.49, 10.11 and 7.85 for non-crosslinked starch and the starches cross-linked with 0.4, 0.8 and 1.2 g of STMP respectively. STMP has been shown to be an effective cross-linking agent at high temperature with semidry starch and at warm temperature with hydrated starch in an aqueous slurry (Kasemsuwan and Jane, 1994). Cross-linking with STMP after gelatinisation would yield a greater cross-linking efficiency since the starch molecules would be sufficiently opened up for easier attachment of the cross-linking molecules. The pH of 11 used also favours the cross-linking reaction, as Kasemsuwan and Jane (1994) have also shown that cross-linking of starch molecules to give a distarch monophosphate is favoured by alkalinity above 10. Increasing the alkalinity in the cross-linking medium increases starch anion concentration. Kitamura *et al* (1982) have also indicated that ionization of amylose in alkali at pH ≈ 11 has been detected by changes in the polarization of fluorescein-substituted amylose, in intrinsic viscosity, and in optical rotation. The addition of sodium sulphate expectedly also favoured cross-linking. It has equally been shown by Wu and Seib (1990) that cross-linking of starch molecules especially to give distarch monophosphate is also favoured by the presence of a neutral sodium salt. Otherwise, monostarch monophosphate esters are formed. Increasing sodium ion concentration increases the uptake of alkali by starch as well as the ionic strength of the reaction medium.

According to Rutenberg and Solarek (1984) the presence of sodium sulphate in the reaction mixture, enhances cross-linking as it builds water structure and allows deeper penetration of the cross-linking agent into the granules. It can also be explained by the fact that ionic strength promotes reaction between a starch alkoxide ion and an ionic phosphoryl reactant (Wu *et* al, 1997). The degree of reactions between two negatively charged species is expected to increase with ionic strength (Hine, 1962 and Gould, 1959). Moreover, ionization of weak acids (starch hydroxyls) is also promoted by ionic strength. Finally, sodium ions increase the alkali adsorbed by starch granules (Leach, 1961), which has been attributed to the ion-exchange properties of starch (Oosten, 1990).

Overall, cross-linking increased the overall hardness of the starch granules. This was evidenced in the difficulty encountered in trying to pulverise the cross-linked starches as opposed to the non-cross-linked forms. The degree of difficulty increased with increasing concentration of the cross linking agent - sodium trimetaphosphate. The increased strength of granules is attributable to the reinforcement of the granule integrity due to the introduced cross-linking bonds.

Again the solubility behaviour of the cross-linked starches was generally different from that of the non-cross-linked ones. The non-crosslinked starch was soluble in cold and hot water while the cross-linked forms were only merely soluble in hot water. Cross-linking introduces a number of cross-linking bonds that causes a reinforcement of granule integrity thereby decreasing solubility.

Swelling properties: The general swelling properties of the starch samples as studied by the Zimmermann *et al*, Crosbie (modified by Chung *et al*), and Gliko-Kabir *et al* are presented in Figures 1 and 2 and Table 1 respectively.

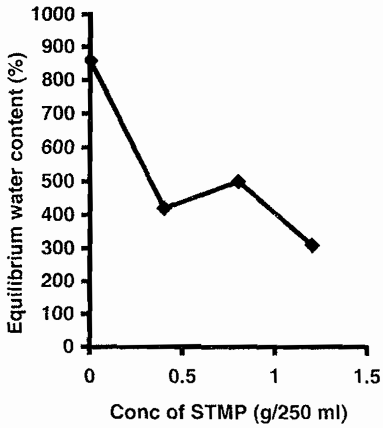

Fig. 1: Equilibrium water content of corn starches crosslinked with different concentrations of STMP

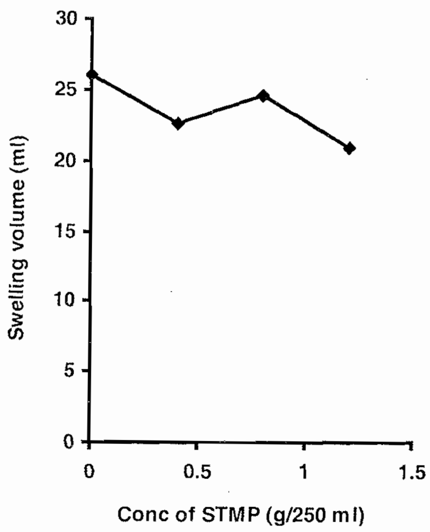

Fig. 2 - Equilibrium moisture content of corn (Amidex) starches crosslinked with different concentrations of STMP

Table 1: Swelling volumes of cross-linked Amidex® starches (Measured by Crosbie, 1991 method, modified by Chung *et al* 2004)

Sample	Swelling volume (ml/g)
Control (Non crosslinked starch	26.0
Cl-0.4	21.7
Cl-0.8	21.5
Cl-1.2	20.2

Key: Cl-04 – Starch crosslinked with 0.4 g of STMP; Cl-0.8 – Starch crosslinked with 0.8 g of STMP; Cl-1.2 – Starch crosslinked with 1.2 g of STMP

The results show that addition of STMP and sodium sulphate caused a granule structure modification that decreased the hydration capacity (Nabeshima *et al* 2001). Addition of STMP also led to an increase in the amount of phosphorous bound and this conferred a greater stability on the starch granules. Woo (1999) and Janzen (1969) had earlier attributed the decrease in swelling volume of starches treated with STMP/STPP to the formation of intermolecular bridges by the residual phosphorous. However, the water absorption reduction was more pronounced at the lower concentration of cross-linking agent i.e. at an STMP concentration of 0.4 g than at higher concentrations, in line with earlier observations by Gliko-Kabir *et al* (2000), Nabeshima and Grossman (2001) and Wurzberg (1986). This result also seems to contradict the observation by Lim and Seib (1993) that the conventional phosphorylation increased water uptake of starch derived from wheat and corn. A possible explanation of this observation is the straightening of the polymer chains due to the cross-linking reaction with a low concentration of STMP, which lead to a widening of the polymer network. Presumably, cross-linking interferes with free access of water to the starch. This in turn, causes a reduction in the swelling properties of the new polymer. However, the gradual increase in swelling observed with increasing concentration of cross-linker is caused by chain straightening, which enhances water penetration into the polymer network. This increase continues until the STMP concentration is high enough to cause the network to collapse (Gliko-Kabir *et al* 2000). As a result, a reduced swelling is observed in products containing 0.8 g and 1.2 g of STMP. A similar phenomenon was reported by Wurzberg (1986), who cross-linked corn starch and found a bell-shaped swelling dependency when native starch was included. That is, the low and high concentrations of cross-linker yielded products with lower swelling values than the swelling observed for non-treated (loosely cross-linked).

Effect of NaCl: The reaction of STMP probably caused the corn starch to lose its non-ionic nature as is evidenced by the dependency found between the extent of swelling of the cross-linked polymer and the amount of NaCl (ionic strength) in the solution (Figures 3 and 4). The figure shows that an increase in sodium chloride concentration caused a decrease in the fluid uptake of the cross-linked starch, a finding which has already been reported for other polymers (Kulick *et al* 1989; Khare *et al* 1995; Allcock *et al* 1996). The reduction in the liquid uptake is attributed to the counter-ion shield effect on charged functional groups like phosphates. The increae in the ionic strength of the solution decreases the osmotic pressure inside the charged gel and its swelling is thus reduced.

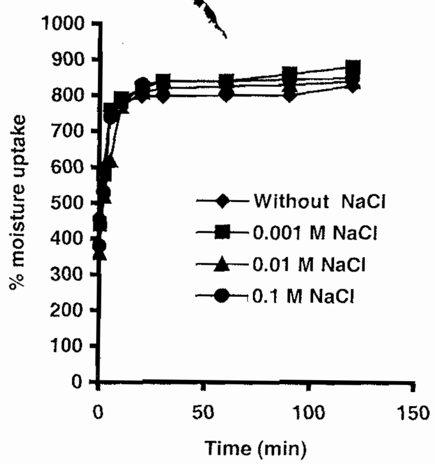

Fig. 3: Effect of NaCl on the swelling profile of non-cross linked corn starch

Effect of sucrose: The effects of sucrose on the swelling characteristics of the starches are presented in Figures 5 and 6. The presence of sucrose slowed down the degree of swelling of both the cross-linked and non cross-linked starches. Increasing the concentration of sucrose enhanced this effect.

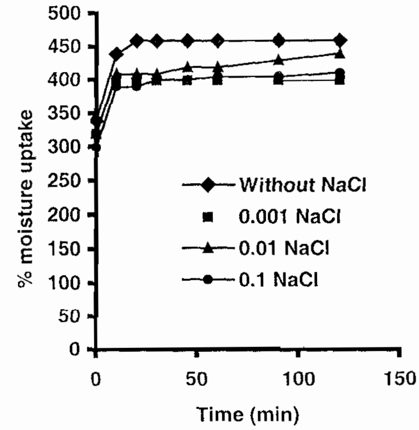

Fig. 4: Effect of NaCl on the swelling profile of corn starch cross-linked with 0.4 g of sodium trimetaphosphate

Generally, the degree of swelling was more in the non cross-linked than in the cross-linked starches. The intensity of the reduction of swelling by the added sucrose was also more with the non cross-linked than with the cross-linked starches. Sucrose has been shown to reduce the water absorbing capacity of starches thereby retarding the gelatinisation of the starch (Khare *et al* 1995). Through its superior water binding capacity, sucrose will preferentially tie up the water molecules and withold them from the starch. Increasing the concentrations of sucrose causes correspondingly greater inhibitons in the normal swelling of the starch granules, and high concentrations markedly increase the temperature at which birefringence disappears.

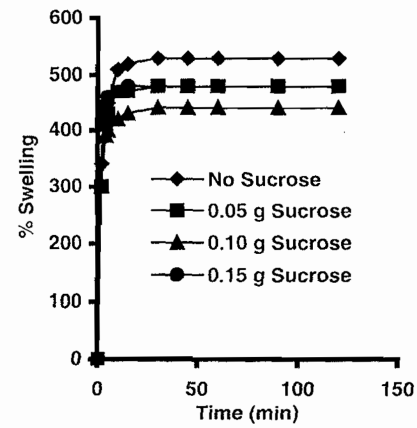

Fig. 5: Effect of sucrose on the swelling properties of non-cross linked Amidex starch

Alkaline paste clarity: Cross-linking of the Amidex starch caused a decrease in alkaline paste clarity of the starch as is evidenced from the decrease in transmittance (Fig 7). The use of change in paste clarity in the determination of the level of cross-linking of starches, is preferred to the use of increases in total phosphorous level in the starch which is confounded by endogenous phopholipids, and by the formation of phosphomonoesters (Tuschholf *et al* 1969). Differential titration of phosphodiesters and monoesters is compromised by the presence of fatty acids, phospholipids, and proteins (Robinson *et al* 1973).

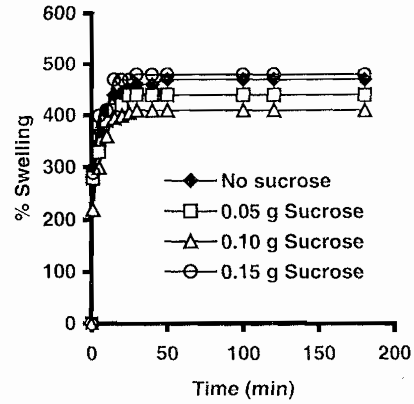

Fig. 6: Effect of sucrose on th swelling properties of Amidex starch crosslinked with 0.4 g of STMP

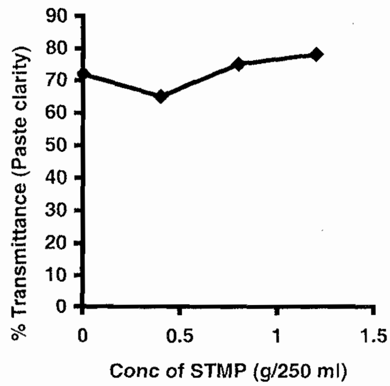

Fig 7: Alkaline paste clarity of corn starch croslinked with various concentrations of STMP

Cross-linking reduces paste clarity probably because of the increased number of cross-linking bridges formed. Since paste clarity is the result of rupture of swollen starch granules (Craig *et al* 1989) and cross-linking improves the integrity of swollen granules, it would therefore reduce clarity (Zheng *et al* 1999). The paste clarity reduced when STMP was added especially in lower amounts (i.e. at STMP concentration of 0.4). Further increases in the concentration of STMP however, resulted to an increase in paste clarity. A.similar pattern had been reported with the water profile of cross-linked starches (Craig *et al* 1989).

Film properties: The films were formed faster in the non-cross linked starch than in the cross-linked starches. The film appearances and textures were however similar. Figure 8 shows the determined contact angles of the starch samples. From the results it is obvious that cross-linking increased the conact angles of corn starch. This implies that by cross-linking, the hydrophilicity of the corn starch was decreased. Contact angles of about 30^{O} are characteristic of hydrophilic systems while those as high as 60^{O} are indicative of hydrophobic systems.

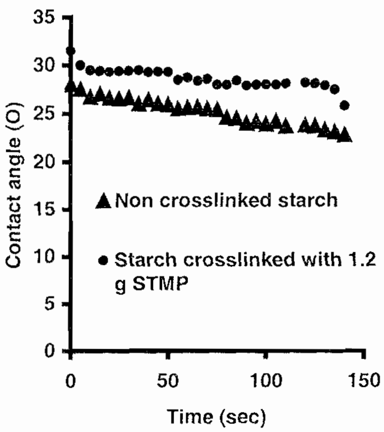

Fig. 8: Contact angles of Amidex starches as measured by a Goniometer

Conclusion: Cross-linking by the addition of phosphorous in the form of STMP showed effects on the analysed functional properties of corn (Amidex®) starch namely – moisture content, swelling characteristics, paste clarity, contact angle, solubility and filming property. The paste clarity, swelling properties and solubility were reduced while contact angle was increased. These effects had been reported as evidences of the cross-linking of starch chains by Wurzberg (1986).

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