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EFFECT OF CROSS-LINKING ON SOME PROPERTIES OF CORN STARCH

Mahmoud M. Abdrabuo[1*], T.H. Hefnawy[1], A.Y. Al-Khatib[2] and Lamiaa M. El-Maghraby[1]

1. Agric. Biochem. Dept., Fac. Agric., Zagazig Univ., Egypt

2. Agric. Chem. Dept., Fac. Agric., Mansoura Univ., Egypt

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ABSTRACT: Corn starch was chemically modified by cross-linking with Sodium tri meta phosphate (STMP)/ Sodium tripolyphosphate (STPP) (99:1 *W/W*) and the physicochemical properties of the cross-linked corn starch were vstigated as a function of the degree of cross-linking. Cross-linking decreased the solubility, swelling factor, and paste clarity of corn starch. While the viscosity significantly increased from the native starch and there was a slight increase of sediment volume. The swelling factor was highly correlated with the degree of crosslinking, the X-ray iffraction atterns did not show any significant alteration in the crystallinity of corn starch. It was by Scanning Electron Microscopy (SEM) measurement that a black zone was observed on the surface of modified starch granules as compared with native starch granules.

Key words: Corn starch, cross-linking, starch properties, IR, swelling, solubility, X-ray.

INTRODUCTION

Starch is a polymer with a very complex structure, formed by glycosidic linkages between glucose units, and presenting functional properties which make the polymer very helpful for the paper industry, textile industry, food industry and drilling oil wells **(Daiuto *et al.*, 2002).** Amylose is one of the components responsible for the grain structure, and its quantification is very important to understand starch behavior. In food industry, starch is utilised to produce various functionalities such as thickening, stabilizing, texturing, gelling, encapsulation, and shelf-life extension. It plays an important role in determining the quality and texture of many foods; controlling the acceptability and palatability of most food products. Cross-linked starch is considered one of the best types of starch used in drilling oil wells, as it is placed on the edges of the pits to prevent the soil from being grounded during drilling. Despite their advantageous properties, some starches in their native form may pose problems. For example, the tendency of its viscosity to increase rapidly and be thickened during heat treatment may cause difficulties in industrial food unit operations such as in pumps and heat exchangers. Some unmodified starches also have drawbacks such as low shear-stress and thermal resistance, thermal decomposition and high degree of retrogradation which limit their use in industrial food application **(Singh *et al.*, 2004)**. Such undesirable characteristics may be overcome by modifying the starch **(BeMiller and Lafayette, 1997)**. Modification does not alter the appearance of the starch but can improve the desired properties of the starch. The performance and properties of starch solutions can be altered through chemical modifications, by adding nonionic or charged substituents to the polysaccharides backbone such as cross-linking and hydrophobic substitution **(Rutenberg, 1980; Wu and Seib, 1990; Liu *et al.*, 1999).** The benefits from this modification are that cross-linking will reinforce the granule of starch to be more resistant towards acidic medium, heat and shearing **(Tuschoff, 1986; Wurzburg, 1986).** Cross-linking reduces the degree of subsequent whereas increases the degree of subsequent cross-linking. As hydrophobic, cationic or anionic character at relatively low

***Corresponding author: Tel.:** +201097035055
E-mail address: mahmoudabdrabuoo@yahoo.com.eg

cost **(Rutenberg and Solarek, 1984).** Therefore, the main objective of this research is to study the effect of high degree of cross-linking on corn starch through phosphorylation on physical and chemical properties such as water solubility, swelling power, pasting properties, stabilities, the sediment volume, viscosity and paste clarity.

MATERIALS AND METHODS

Materials

Corn starch, Sodium tri meta phosphate (STMP), Sodium tripolyphosphate (STPP), Sodium hydroxide (NaOH), absolute ethanol, hydrochloric acid (HCl), acetic acid, Iodine (I_2), potassium iodide(KI), All the chemicals and reagents used in this work were of analytical grade.

Starch Isolation

Starch was isolated according to **Wang and Wang (2001) and Sandhu *et al.* (2004).** Corn grains were finely ground using a hand mill. One kilogram of milled corn was mixed with 2 L of 0.1% NaOH and kept at 4 °C for 18 hr. The mixture was homogenized in an industrial blender at maximum speed (Osterizer, Wisconsin, USA) and passed first through cheesecloth to remove fibers and then through a 100-mesh sieve (150 µm) (Advantech Manufacturing, Wisconsin, USA). The suspension was let sit for 18 hr. The supernatant was discarded and the retained solids washed three times to remove NaOH. The supernatant removal process was aided by centrifugation (13,698 rpm, 15 min, 8°C; Allegra 64R Centrifuge, Beckman Coulter, California, USA). The obtained starch was placed into plastic cylindrical trays (16 × 13 × 6 cm) and dried at 40°C for 24 hr. Finally, the starch was ground in a mortar, passed through a 100-mesh sieve and stored in sealed plastic bags at 25°C until use proximate analysis of starch was conducted according to AOAC official methods **(AOAC, 2002)** to determine the ash, fat, moisture and protein content (N×6.25), respectively.

Preparation of Cross-Linked Corn Starch

Cross-linked starch was prepared according to the method of **Woo and Seib (2002).** Corn starch (50 g) was mixed with 15% (*W/W*), (based on dry weight of starch) of a mixture of STMP/STPP (99/1% *W/W*) and dissolved in 70 ml water. After the pH was adjusted to 11.0 with 0.1 N NaOH, the slurry was kept at 45°C for 3 hr., in a shaking water bath. The suspensions were neutralized to pH 6.0 with 0.1 N HCl, washed with distilled water four times, and dried at 40°C for 24 hr., in an oven. The dried samples were then ground in a mortar and sieved (100 mesh).The starch subjected to the cross-linking condition without a mixture of STMP/STPP was used as a control in each experiment.

Determination of the Degree of Cross-Linking

The degree of cross-linking of modified starches was determined from the viscosity values, according to the procedure of **Kaur *et al.* (2006)**. The peak viscosity of modified starch slurries (25% by weight) was measured from a controlled-stress rheometer equipped with a starch pasting cell. (AR1000, TA Instruments, New castle, DE, USA). A programmed heating and cooling cycle to obtain the peak viscosity was employed as follows: starch slurries were heated from 50 to 95°C at 11°C/min, and then held at 95°C for 2 min. Afterwards, the paste was cooled down to 50°C at 11°C/min and finally kept at 50°C for 2 min. The degree of cross-linking was calculated by using the equation below:

$$\text{Degree of cross} - \text{linking} = (A–B)/A\times 100.$$

Where:

A is the value of peak viscosity of the control sample (without STMP/STPP), and B is the value of peak viscosity of the cross-linked starch.

Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectrum of native starch and modified starch were acquired on a Perkin Elmer FT-IR spectrophotometer (Perkin Elmer, Inc., MA, USA) using a potassium bromide (K Br) disc prepared from powered samples mixed with dry K Br. The spectra were recorded (16 scans) in the transparent mode from 4000 to 400 Cm^{-1} **(Aurea *et al.*, 2017).**

X-Ray Diffraction

The X-ray patterns of starch were analyzed by an X-ray diffractometer (D5005, Siemens, Bruker AXS, Karlsruhe, Germany) operated with Cu-Kα radiation. The starch samples were scanned through 2θ ranging from 5 to 40° under an accelerating voltage and current of 30 kV and 30 mA conditions. Relative crystallinity **(Goni *et al.*, 1997)** was quantitatively calculated following the method of **Nara and Komiya (1983)** with MDI-Jade 6.0.

Scanning Electron Microscopy (SEM)

The size, shape, surface, crystalline structure and morphological data of native and modified starch granules were examined by Scanning Electron Microscopy (SEM) (JEOL TEM-2100) fixed to a CCD camera at an accelerating voltage of 200 kV. Each sample was prepared by suspending the sample on copper-coated carbon grids and the solvent was allowed to evaporate slowly before recording the TEM images. TEM measurements were recorded at the Central Laboratory, Electronic Microscope Unit, Faculty of Agriculture, Mansoura University, Mansoura, Egypt **(Vanier *et al.*, 2012).**

Swelling Power

Swelling power were determined by using **Leach *et al.* (1959)** method. The 0.1 g samples (native and modified starch) were heated in 10 ml distilled water in a water bath at 60°C for 30 minutes with constant mixing. The samples were centrifuged at 1600 rpm for 15 minutes. The precipitated part was weighted and calculated using equation

$$\text{Swelling power} = \frac{\text{weight of sedimental paste (g)}}{\text{weight of the sample (dry basis) (g)}} \text{ x } 100$$

Water Solubility

Water solubility were determined using **Kainuma *et al.* (1967)** method. The 0.5 g from each sample was heated in 10 ml distilled water bath at 60°C for 30 minutes without mixing. The samples were centrifuged at 1600 rpm for 10 minutes. The supernatant was separated (5 ml), dried, weighted and calculated using equation:

$$\text{Solubility (\%)} = \frac{\text{weight of the soluble starch (g)}}{\text{weight of the sample (dry basis)(g)}} \times 2 \times 100$$

Degree of Gelatinization (DG)

DG (%) was calculated by a method of **Wootton *et al.* (1971).** Wherin, 0.2g sample was dispersed in 100 ml distilled water with stirring for 5 min and centrifuged at 1500 rpm for 25 min. One milliliter supernatant was then diluted to 10 ml with distilled water and 0.l ml iodine solution was added. The method was repeated using 100 ml of 10 M potassium hydroxide instead of water and absorbance of both solutions were read at 600 nm in a Spectrophotometer (Cecil Aquarius 7400, England).

DG (%)= (Absorbance of fresh solution/ Absorbance of alkali solubilized solution) x 100

Colour Measurement

The colour of all samples was determined in a Colour Measurement Spectrophotometer (Ultrascan Vis, Hunter Colour-Lab, Virginia). **Sareepuang *et al.* (2008)**. The result was expressed as L, a, b using corresponding native rice samples as reference. The chroma value (C) of parboiled corn was calculated.

$$C = (a^2 + b^2)^{1/2}$$

L* is the intensity of lightness (0 stands for yields black)

a* is green (negative values) red (positives values)

b* is blue (negative values) and yellow (positive values).

Indicating that there was a strong relationship between L*a*b* values and the starch content.

Sediment Volume

Sediment volume of corn starch was determined with slight modification to the method of **Tessler (1978).** Starch (1g, dry basis) was weighed into beaker and 95 ml of distilled water was added. The pH of the starch slurry was then adjusted to 7.0 using 5% NaOH or 5% HCl following which the slurry was cooked in a boiling water bath for 15 min. The mixture was then stirred thoroughly and transferred to a 100

ml graduated cylinder, the volume was made up to 100 ml with distilled water. The cylinder was then sealed and kept at room temperature for 24 hr., for settlement of starch granules. The volume of the sediment consisting of starch granules was then measured for sediment volume.

Paste Clarity

The clarity (% transmittance at 650 nm) of starch paste was determined with slight modification to the method described by **Sandhu and Singh (2007)**. A 1% aqueous suspension of starch adjusted to pH 7.0 was heated in boiling water bath for 30 min with intermittent shaking. After that the suspension was cooled down to 25°C. The light transmittance was read at 650 nm against water blank

Statistical Analysis

All tests were triplicates and one-way analysis of variance followed by Duncan's test ($P \leq 0.05$ or $P \leq 0.01$) were performed using SPSS statistical software version 16.0 (SPSS Inc., Chicago, IL, USA). **Snedecor and Cochran (1989).**

RESULTS AND DISCUSSION

Proximate Composition of Isolated Starches

In general, the proximate composition found in this study is similar to that reported for other corn starches (moisture = 10%, ash content = 2%, fats=0.35%, total protein = 0.45%, starch =87.2%) (Table 1) **(Blanche and Sun, 2004; Tovar-Benítez, 2008).** Likewise, it has been reported that low fat and protein contents indicate high purity of isolated starches **(Tirado-Gallegos *et al.*, 2016).** Lipids and proteins in starch granules can increase their functionality; the protein in starch granules is associated with grain hardness, while the lipids can significantly reduce the swelling capacity of the starch paste. In the other hand, the presence of minerals in the starch has been related to the increase of clarity and viscosity of the paste. Likewise the low moisture content reduces the risk of microbial growth during storage **(Alcázar-Alay and Meireles, 2015)**.

Pasting Properties and Degree of Crosslinking

The degree of cross-linking of corn starches which were modified by different amounts of STMP/STPP (15%) was determined to be 150% (Table 2). There seemed to be a proportionally increase in the degree of cross-linking with increasing concentration of STMP/STPP. That is, compared to native starch, the structure of cross-linked starches seemed to be almost intact after heating at 95°C, resulting in the decreased paste clarity **(Morikawa and Nishinari, 2000a).** Furthermore, it has been suggested that the reduced swelling of cross-linked starches might be partly responsible for their reduced paste clarity **(Kaur *et al.*, 2006).** The swelling factor measured at 70°C decreased significantly with increasing level of the cross-linking reagent (Table 2). This result was in agreement with those finding of **Mirmoghtadaie *et al.* (2009**) who reported the reduced swelling factor of cross-linked corn starch with increasing degree of crosslinking.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of starches are presented in Fig. 1 whereas the interpretation of each peak is given in Table 3. As shown in Fig. 1, the presence of absorption band at around the starch fingerprint region (1,250 to 400 cm^{-1}) of the FTIR spectra was similar for the tested starches. The most intense peaks corresponded to carbohydrate vibrations, showing no apparent structural differences in the low range molecular order **(Pelissari *et al.*, 2012)** (Fig. 1). The peak observed at 1,640 cm^{-1} corresponded to tightly bound water molecules in the starches **(Fang *et al.*, 2004).** The region between 1,200 and 800 cm^{-1} is characteristic of the C-O and C-C stretching and C-O-C deformation modes, associated with the glycosidic bond **(Almeida *et al.*, 2010).** The spectra of starch samples showed a peak at 3,290 cm^{-1}, which corresponded to symmetric and asymmetric stretching of O–H bonds **(Pelissari *et al.*, 2012).** The peak at 2,928 cm-1 was attributed to C-H bond stretching (**Liu *et al.*, 2011**). The peaks observed between 937 and 1,156 cm^{-1} were attributed to C-O bond stretching **(Fang *et al.*, 2002).** The sharp peak at 996 cm^{-1} was related to the crystallinity of the starch **(Vicentini *et al.*, 2005)**.

Table 1. Proximate composition of isolated starches from corn

Composition	(%)
Moisture	10
Ash Content	2
Fats	0.35
Total Protein	0.45
Starch	87.2

Table 2. Pasting properties of native and cross-linked, starch samples

	Native starch	Cross-link starch
Degree of cross-linking	zero	150
Swelling power(g/g)	9.03	5.47
Water solubility	2.73	1.77
Degree of gelatinization	98.6	132.758
Colour measurement	L = 80.72 a = 0.45 b = 8.60 C= 8.6	L = 84.84 a = 1.2 b = 5.96 C = 6.08
Sediment volume	32.8	39.4
Paste clarity	30.15	0.794

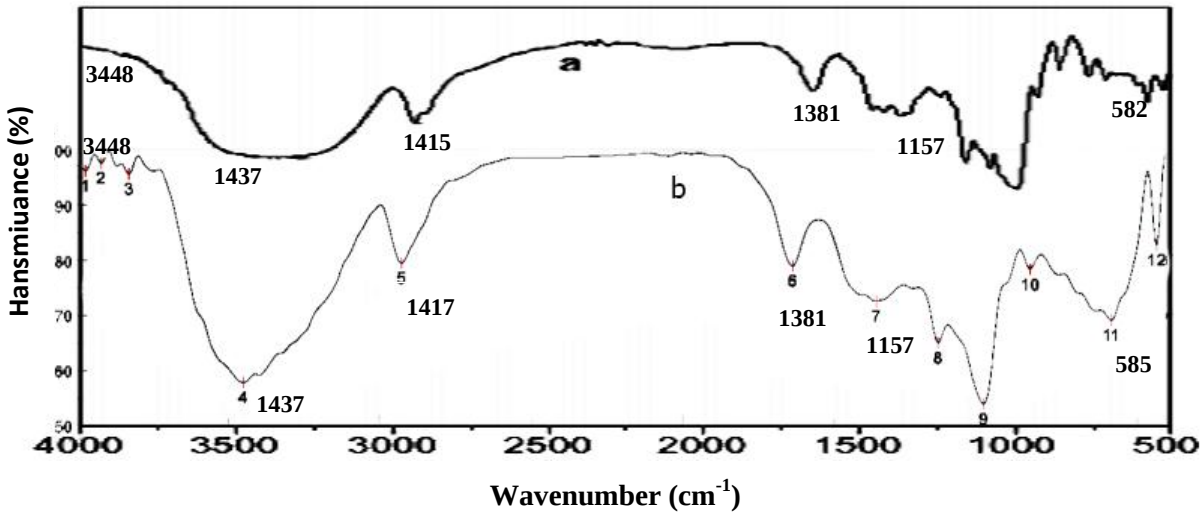

Fig. 1. IR *s*pectrum cross linking starch

a : Starch native b: Starch modified

Table 3. Band assignment of native corn starches and cross linking starch

No.	Functional groups	Wave number literature	Native starch	Cross linking starch
1	O - H stretching	3600 – 3300	3448	3448
2	C - H stretching	2931	2929	2930
3	C-O bending associated with OH group	1637	1647	1646
4	CH_2 symmetric deformation	1458	1437	1437
5	CH_2 symmetric scissoring	1415	1415	1417
6	C -H symmetric bending	1385-1375	1381	1381
7	C - O - C asymmetric stretching	1149	1157	1157

X-Ray Diffraction

X-ray diffraction patterns of the cross-linked and non-crosslinked starch are similar, with two prominent peaks at about 17° and 22°, as seen from Fig. 2. However, typical starch peaks seen at about 5° and 14° were not seen in either crosslinked or non-cross-linked film, indicating changes in crystallinity and/or the crystal structure. The control and crosslinked starch films had similar (%) crystallinity of about 17% and 14%, respectively. Cross-linked starch films also did not show any change in crystallinity (%) or peak positions, compared to native starch **(Garg and Jana, 2007).** The increase in the diffraction intensity of the cross-linked starch films but decrease in the crystallinity (%) suggests that some of the amorphous regions may be better oriented after cross-linking.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of native and chemically modified starch samples at 5000 magnification are presented in Fig. 3. Scanning electron microscopy revealed that starch granules of native and modified corn starch samples were small, and no noticeable differences were observed between the appearances of morphologies of the native and chemically modified starch granules. This indicated that the levels of cross-linking used in the present study did not cause any significant changes in the size of corn starch granules. This is consistent with the results reported by **Yeh and Yeh (1993).** Van Hung and Morita reported that starch granule size had a significant effect on morphological properties of starch granules **(Van Hung and Morita, 2005)**. Since brought about weakening of starch granules, it was easy to carry out cross-linking of corn starch, and cross-linked starch showed a lower trend of retrogradation and higher ability to resist shear compared with native starch samples.

Swelling Power and Water Solubility

The swelling power measured at 70°C decreased significantly with increasing level of the cross-linking reagent (Table 2). This result was in agreement with the finding of **Mirmoghtadaie *et al.* (2009)** who reported the reduced swelling power of cross-linked corn starch with increasing degree of crosslinking. Regression analysis exhibited that the swelling power was linearly related to the concentration of cross-linking reagent used it is well known that cross-linking strengths the bonding between starch chains, thus allowing them to resist against swelling. Therefore, the reduced swelling power would be related to the formation of inter-molecular bridges by phosphorous residual after cross-linking reaction **(Chung *et al.*, 2004).**

When the solubility of native and cross-linked corn starches was measured as a function of temperature (50-90˚C) there was an overall tendency that the solubility decreased with increasing degree of cross-linking at all temperatures tested. A similar pattern was reported by **Kaur *et al.* (2006)** for potato starches modified $POCl_3$ at different concentrations. It suggested that decreased solubility by cross-linking would be possibly due to increased density of cross-links in the starch structure which seemed to cause less disintegration of starch granules during gelatinization **(Jyothi *et al.*, 2006).**

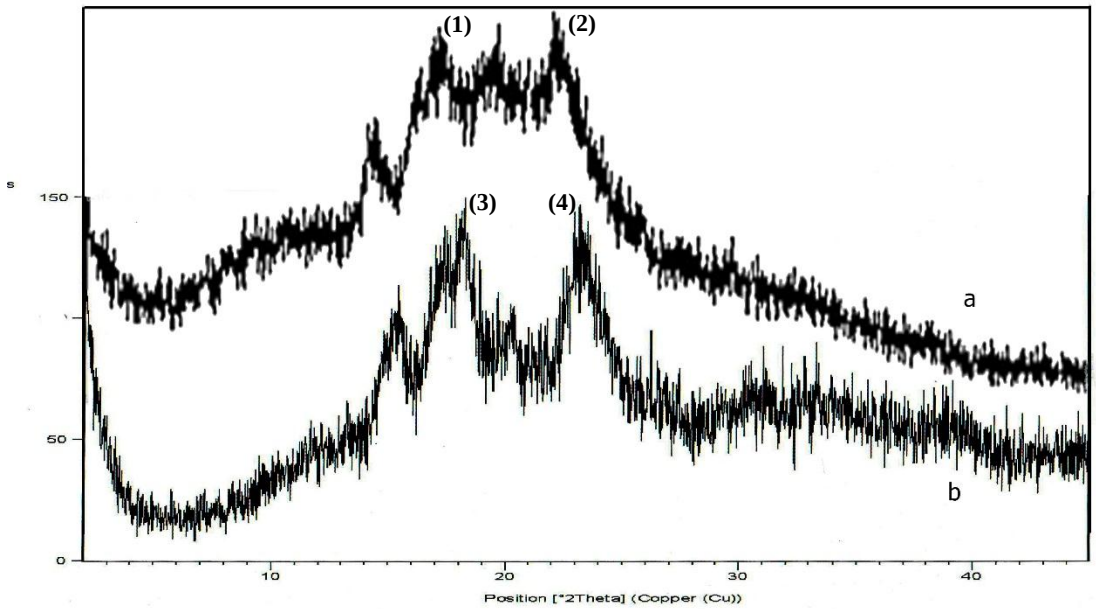

Fig. 2. X-ray cross linking starch

a : Native starch b: Modified starch

Table 4. X-ray cross linking starch

Peak number	Pos.[°2Th]	d-spacing[θ]	Height[cts]	FWHM Left[°2Th]	Rel. Int.[%]
1	13.2131	3.5421	29.24	0.5741	58.46
2	16.1251	3.068	58.21	0.4125	95.22
3	15.1313	5.85544	33.37	0.6298	52.90
4	18.2441	4.86279	63.08	0.4723	100.00

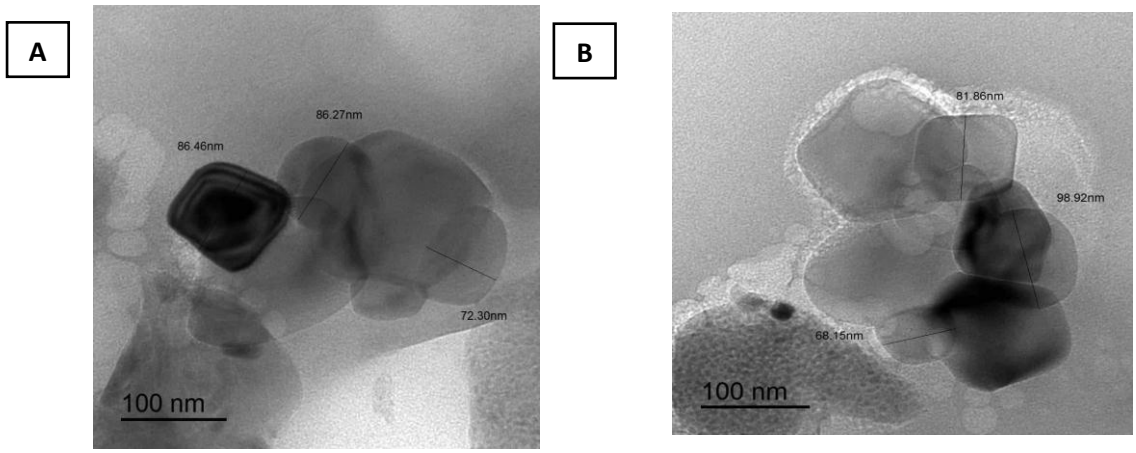

Fig. 3. Scanning electron micrographs of native and chemically modified corn starch samples (A), native; (B) cross-linked

Degree of Gelatinization

The (%) degree of gelatinization in the temperature range of 50-95^{o}C was followed by the spectrophotometric method based on the formation of amylose-iodine complex. In fact DG (%) based on measurement of absorption peak at 600 nm can be taken as the ratio of solubilized amylose sites to the total amylose sites available in cross-linking starch. Taking this point into account. The (%) degree of solubilized amylose sites to the total in the native starch was higher for cross-linking, at lower temperatures, it increased after 80^{o}C. If the amylose was the only soluble portion in starch, similar behaviors should be observed in DG (%) at 95^{o}C) indicated that mainly the amylopectin forms the soluble portion, since it only contains 1-2% amylose. Moreover no blue colour but red colouration with iodine must be considered as an indication of amylopectin in soluble portion. Using DG (%) data at 95^{o}C and taking amylose contents of starches into account, the percentage of amylose in the soluble portion has been calculated. The results obtained showed that the soluble portion of contained 24.76% amylose by weight. Cross-linking starch recorded 132.75% as DG (%) and the soluble portion of cross-linking starch nearly contained only amylose. This was also evident from the gels obtained. When cooked and formed soft gels. In contrast, high amylose gels (normal corn starch and cross-linking starch) were firm because amylose contributes gel strength and firmness and resulted in a tighter network **Aytunga *et al.* (2009)**.

Sediment Volume

The sediment volume of corn starch is 39.4 ml as presented in Table 2, corn starch is having highest sediment volume and upon modification of any starch sample there is decrease in sediment volume. The decreased values in modified starch are due to the disruption of granules resulting in decreased swelling and low volume makeup. Studies were done for cross-linked corn starch which reported reduced sedimentation volume, due to decreased interaction between starch molecules, and by inhibit swelling by cross-linking **(Raina *et al.*, 2006).**

The decreased sediment volume may also be due to large starch granules which caused decrease in bond strength upon heating.

Paste Clarity

The paste clarity at T650 of the control starch exhibited 30.15% (Table 2). However, the use of STMP/STPP cross-linking reagent led to a substantial decrease in the paste clarity. Corn starch crossedlinked with 15% STMP/STPP showed samples exhibited 0.79% paste clarity. These results were consistent with the reports by **Lim and Seib (1993)**. **Kaur *et al.* (2006)** also found that cross-linked starches showed lower pastes clarity than their counterpart native starches. The significant decrease in the paste clarity was possibly attributed to a change in the starch granular structure by cross-linking **(Morikawa and Nishinari, 2000a).** That is, compared to native starch, the structure of cross-linked starches seemed to be almost intact after heating at 95°C, resulting in the decreased paste clarity **(Morikawa and Nishinari, 2000b' Kaur *et al.*, 2006)**. Furthermore, it has been suggested that the reduced swelling of cross-linked starches might be partly responsible for their reduced paste clarity **(Reddy and Seib, 2000; Kaur *et al.*, 2006).**

Colour Measurement

As shown in Table 2, acceptable degree of whiteness was observed for corn starch with L value of 84**. Boundries *et al.* (2009)** have concluded that " L" values greater than 90 give a satisfactory whiteness for starch purity The degree of redness represented by the positive value of "a" the starch and also, the value b indicates yellow the positive "b" value is noticeably small. They pointed out that the yellowing showed a moderate decrease in the treated samples, but they remained . Almost unchanged with treatment intensity. Changes in colour values were not significant in a way that affects colour decrease in the value of 'C' was due to a decrease in the value of b when soaking to separate the components of the pill. The change in redness and yellowing is noticeably correlated, which may affect the final value of c, as well as the degree of whiteness.

Conclusion

Scanning electron micrographs of native and modified corn starch samples indicated that chemical modification of cross-linking had no significant effect on the morphological properties

of cron starch granules. At a cross-linking level of 15%, the obtained cross-linked starch compared to native starch. The low degree of cross-linking resulted in an increase in swelling power and solubility, and a decrease in paste clarity, however, a higher degree of cross-linking resulted in a decrease in swelling power and solubility, and an increase in paste clarity.

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تـأثيـر الـروابـــط العـرضيـــة علـــى بعـض خـــواص نـشـــــا الأذرة

محمود محمد عبدربه[١] – حفناوي طه حفناوي [١] – ايمن يحيي الخطيب[٢] – لمياء محمد المغربي[١]

١- قسم الكيمياء الحيوية – كلية الزراعة – جامعة الزقازيق – مصر

٢- قسم الكيمياء الزراعية – كلية الزراعة – جامعة المنصورة – مصر

تم تحوير نشا الذرة كيميائياً من خلال التفاعل مع صوديوم تراي ميتا فوسفات/صوديوم تراي بولي فوسفات (١/٩٩ وزن: وزن) وتم تقدير الخواص الفيزيائية والكيميائية لنشا الأذرة ذو الروابط العرضية أو المتقاطعة كدالة لدرجة الارتباط المتقاطع، حيث أدى الارتباط المتقاطع إلى تقليل قابلية الذوبان وعامل الانتفاخ وشفافية عجينة نشاء الذرة، بينما زادت اللزوجة بشكل ملحوظ عن النشا الأصلي وكانت زيادة حجم الرواسب زيادة طفيفة، بينما كان عامل الانتفاخ مرتبطًا بدرجة كبيرة بدرجة الروابط العرضية وعند تعريض العينة للأشعة السينية لم تظهر أي تغيير مهم في بلورة نشا الذرة. ولقد تبين من خلال قياس الميكروسكوب الالكتروني ان منطقة سوداء قد لوحظت علي سطح حبيبات النشا ذو الروابط العرضية والتي لم تحدث مع النشا لاصلي.

المحكمـون :

١- أ.د. محســن محمد سليم عسكر أستاذ التكنولوجيا الحيوية - المركز القومي للبحوث- دقي - مصر.

٢- أ.د. سيد سليمان السيد السعدني أستاذ الكيمياء الحيوية المتفرغ - كلية الزراعة - جامعة الزقازيق.