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Carbohydrate Polymers 45 (2001) 347–353

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Functional properties of pregelatinized and cross-linked cassava starch obtained by extrusion with sodium trimetaphosphate

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Received 8 December 1999; revised 2 May 2000; accepted 23 May 2000

Abstract

Cassava starch was cross-linked with sodium trimetaphosphate (STMP) on a Cerealtec single-screw extruder at different extrusion temperatures and concentrations of STMP and NaOH. The effect of variables on functional properties of the products was analysed by the response–surface methodology. The degree of substitution (DS) was influenced by NaOH and phosphorus level, and increased when their concentration increased. Extrusion temperature affected water absorption, cold viscosity and gel characteristics. The introduction of phosphate groups by cross-linking, with maximum DS of 1.5×10^{-4}, increased the gel strength, water absorption index, resistance to high temperature and shear, and decreased gel cohesiveness, starch clarity and water solubility index. The products had different DS and degree of gelatinization and thus can be applied in several kinds of foods.

Keywords: Cassava starch; Modified starch; Extrusion

1. Introduction

Cassava starch is an important food ingredient in tropical countries. It possesses a variety of interesting properties, like low gelatinization temperature, clarity and bland taste, which makes it desirable for both food and industrial applications. However, it also has negative characteristics, such as long texture (high cohesiveness), sensitivity to shear, high temperature and low pH, which makes it unsuitable for some specific uses. Furthermore, to extend its usefulness, cassava starch has often been modified, and cross-linking is the most widely used technology for this purpose (Wurzburg, 1986).

Cross-linking reinforces the hydrogen bonds in the granule with chemical bonds that act as bridges between the starch molecules. As a result, the cross-linked starches are resistant to high temperature, low pH and high shear, and improve viscosity and textural properties of the native starch (Yook, Pek & Park, 1993). Several polyfunctional chemicals can be used for cross-linking starches, sodium trimetaphosphate under alkaline conditions being one of them (Wurzburg, 1986).

The traditional starch modifications are usually carried out in an aqueous medium and require a high concentration of modifying reagent to achieve the desired degree of chemical binding. The unreacted reagents are removed usually by repeated washings with water. This operation unit generates substantial volumes of effluent water, which is difficult to recycle. Extrusion cooking can be advantageously used as an alternative process to modify starches as described by several researchers (Meuser & Gimmler, 1989; Salay & Ciacco, 1990; Della Valle, Colonna & Mercier, 1991; Chang & Lii, 1992). The major advantages of the extrusion process would be lower cost, absence of waste and a short reaction time.

The aim of the work reported here was to study the effect of some variables on production of pregelatinized and cross-linked cassava starch using the extruder as a chemical reactor and sodium trimetaphosphate as a specific reagent.

2. Materials and methods

2.1. Materials

Cassava starch (99.7% starch, 0.05% protein, 0.11% lipids, 0.12% ash, d.b.) was obtained from Corol (Rolandia-PR, Brazil) and sodium trimetaphosphate (STMP) was purchased from Sigma Chemical Co. (USA).

2.2. Preparation of cross-linked starch

Cassava starch was conditioned to 23% moisture by

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0144-8617/01/$ - see front matter
PII: S0144-8617(00)00273-3

adding water along with STMP and NaOH at levels required by the experimental design. The material was placed in sealed polyethylene bags and allowed to equilibrate for 12 h at 10°C before processing. Extrusion cooking was carried out in a Cerealtec CT L15 (São Paulo — Brazil) single screw extruder, with a barrel 420 mm in length and 19.4 mm in diameter; screw with 2:1 compression ratio and die 6 mm in diameter. Screw speed (100 rpm), feed rate (90 g min^{-1}) and feed zone temperature (60°C) were kept constant (the values of these parameters were defined in preliminary tests). The temperature of the compression zone and the die (referred as the extruder temperature) varied according to the experimental design. Samples were collected after the extruder attained a steady state, dried at 50°C in a forced-air convection oven to 8–10% moisture and ground in an Alpine mill (Augsburg, Germany) to pass a 80 mesh sieve.

2.3. Physicochemical and functional properties of modified starches

To determine the bound phosphorus content, samples of the extruded starches were washed first with an ethanol/water solution (65% v/v), and then with methanol to remove any unreacted reagent. The residual phosphorus was analyzed by Ionic Absorption Spectroscopy (ICAP Model 61E), and the degree of substitution (DS) calculated according to Rutemberg and Solarek (1984) using the following equation:

$$DS = 162P/(3100 - 124P)$$

where P is the percent phosphorus.

Water absorption index (WAI) and water solubility index (WSI) were determined by the procedure of Anderson, Conway, Pfeifer and Griffin (1969). The method of Craig, Maningat, Seib and Hoseney (1989) was used to determine the paste clarity.

The strength and cohesiveness of gels were determined using a Voland Stevens texture analyser (TA 1000 model, Voland Corp. Hawthorne, NY) as described by Takahashi, Maningat and Seib (1989). The gels were compressed, using a plunger (diam. = 12.7 mm) at a rate of 2.0 mm s^{-1}, to a distance of 10 mm using cyclic analysis. To prepare the gel, starch pastes (12% solids) were cooked, poured into tubes (49.8×41.3 mm^2) and cooled for 12 h at 10°C.

The pasting behavior of the modified starches were determined with a Brabender Viscoamylograph (C.W. Brabender Co., W. Germany) according to the procedure of AACC (1995). The viscoamylograph was operated with a 700 cmg cartridge at 75 rpm. A sample concentration of 7% (d.b.) was used.

2.4. Statistical analysis

With the aim to select better conditions for cross-linking starch by the extrusion process, the independent variables, STMP concentration, expressed as phosphorus (0.006; 0.009; 0.012%), NaOH level (0.025; 0.050; 0.075%) and extruder temperature (60, 80, 100°C), were studied. The levels of variables were defined by preliminary exploratory analysis. A factorial experimental design, consisting of 15 treatments, which included triplication of the center point (Table 1), was used (Box & Behnken, 1960). The three levels of each variable were coded as −1, 0 and 1 for statistical analysis. The dependent variables were DS, WAI, WSI, clarity, cold viscosity, gel strength and gel cohesiveness. Experimental data analysis were performed by multiple regression analysis using Statistical Analysis System

Table 1
Experimental design for extrusion experiment

Run	Coded Variables			Real Variables		
	x_1	x_2	x_3	Phosphorus (%)	NaOH (%)	Temperature[a] (°C)
1	−1	−1	0	0.006	0.025	80
2	1	−1	0	0.012	0.025	80
3	−1	1	0	0.006	0.075	80
4	1	1	0	0.012	0.075	80
5	−1	0	−1	0.006	0.050	60
6	1	0	−1	0.012	0.050	60
7	−1	0	1	0.006	0.050	100
8	1	0	1	0.012	0.050	100
9	0	−1	−1	0.009	0.025	60
10	0	1	−1	0.009	0.075	60
11	0	−1	1	0.009	0.025	100
12	0	1	1	0.009	0.075	100
13	0	0	0	0.009	0.050	80
14	0	0	0	0.009	0.050	80
15	0	0	0	0.009	0.050	80

[a] Extruder temperature.

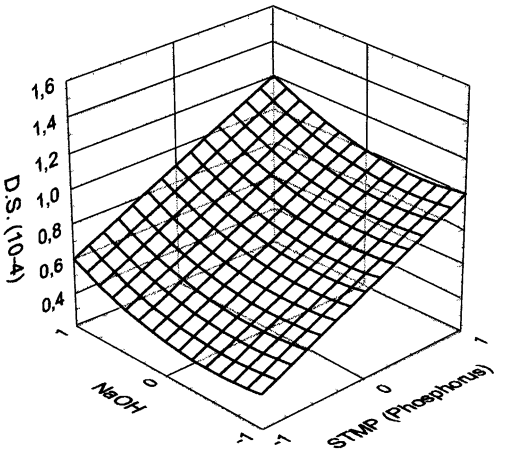

Fig. 1. Effect of NaOH and phosphorus (STMP) concentration on degree of substitution at a constant extrusion temperature of 80°C.

(SAS, 1985), and three-dimensional contour plots were generated from the fitted models using the Statistica software program (STATSOFT, Oklahoma), by imposing a constant value on one of the independent variables.

A complementary experiment was done to isolate the effect of phosphorylation from those of extrusion and NaOH. Cassava starch samples containing 0, 0.01 and 0.02% STMP were extruded at 100°C and 0.075% NaOH and the properties described earlier were determined. The significance of differences between the treatments were evaluated using the Tukey test.

3. Results and discussion

Table 2 summarizes the estimated regression coefficients for the quadratic models fitted to the experimental results and their significance together with their corresponding coefficients of determination. All the models, with the exception of those for the WSI, seemed adequate with high R^2 values (>0.89), significant F values and non-significant lack of fit. The model of WSI explained 85% of variability ($R^2 = 0.8478$), but the probability of F (>10%) indicated that the data variations were not explained adequately (Thompson, 1982). However, it could be used with caution for trend analysis. The NaOH concentration and extrusion temperature were the most important factors influencing the dependent variables.

3.1. Degree of substitution

The DS of the extruded samples was influenced by the levels of STMP and NaOH (Table 2), increasing with their increase (Fig. 1). This was expected because a higher pH catalyses starch phosphorylation (the pH of samples varied from 8.25 to 9.45). The range of DS values obtained ($0.4–1.5 \times 10^{-4}$) was similar to those observed in commercial and patented products (Lim & Seib, 1993).

3.2. Water absorption, water solubility and clarity

The statistical data presented in Table 2 showed that WAI was affected by extrusion temperature (linear and square terms), NaOH concentration and interactions between these two variables. WAI increased when the NaOH concentration and temperature increased (Fig. 2). The effect of NaOH was more pronounced when the temperature was higher. These results indicated that the combined effects of extrusion and alkaline pH caused a granule structure modification that increased the hydration capacity. As previously shown in Fig. 1, when the NaOH level increased more

Table 2
Regression equation coefficients (model — $Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_{12} + \beta_{22} X_{22} + \beta_{33} X_{32} + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \epsilon$; X_1 = STMP (as phosphorus), X_2 = NaOH, X_3 = extrusion temperature; WAI = Water absorption index; WSI = Water solubility index) for response variables (* = $P < 0.05$.;** = $P < 0.01$; *** = $P < 0.001$, respectively)

Coefficient	Response variables						
	Degree of substitution	WAI	WSI	Paste clarity	Cold viscosity	Gel strength	Gel cohesiveness
β_o	0.07	7.27	14.51	39.7	128	56.3	0.68
Linear							
β_1	0.03***	0.14	−0.53	−1.6	−6	8.4*	−0.01
β_2	0.01*	0.54***	−3.28**	−12.0***	24	17.1**	−0.05*
β_3	−0.01	1.02***	0.80	3.1	129***	−11.9**	0.04*
Quadratic							
β_{11}	0.00	−0.21	−1.81	−0.8	20	6.7	−0.06*
β_{22}	0.01	−0.04	0.94	5.2	1	−11.5*	0.01
β_{33}	0.00	0.49**	−3.03	−0.6	37	11.2*	0.01
Interaction							
$\beta_{1\,2}$	0.00	0.18	−2.18	0.0	17	3.0	0.04
β_{13}	−0.01	−0.11	0.13	1.5	−14	−8.7	0.02
β_{23}	0.01	0.24*	−0.09	−8.0*	6	−4.5	−0.03
R^2	0.9375	0.9869	0.8478	0.9448	0.9725	0.9485	0.8945

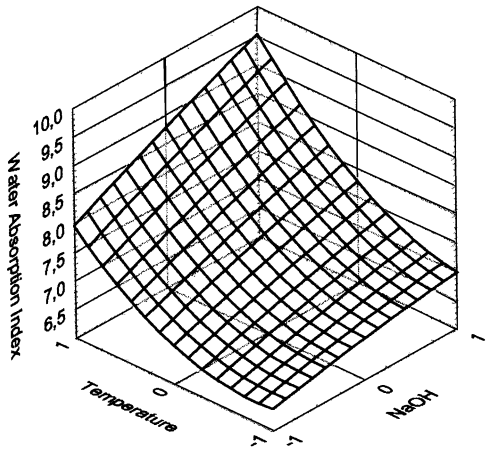

Fig. 2. Water absorption index as a function of extrusion temperature and NaOH concentration, at a constant phosphorus concentration of 0.009%.

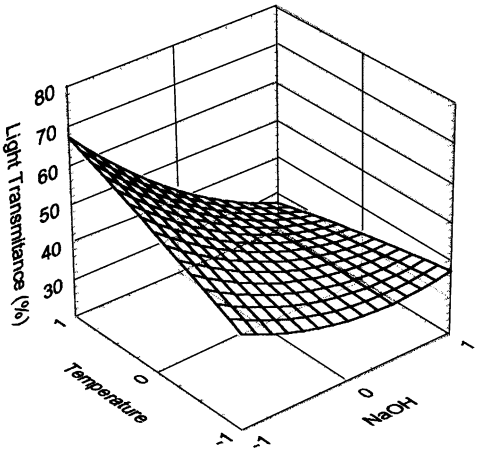

Fig. 4. Paste clarity as a function of extrusion temperature and NaOH concentration. (Phosphorus concentration 0.009%).

phosphorus was bound and this conferred a greater stability on the starch granule. Lim and Seib (1993) observed that the conventional phosphorylation increased water uptake of starch derived from wheat and corn.

The WSI was influenced only by NaOH (Table 2) and, as shown in Fig. 3, decreased when the pH increased. This occurred probably because an increase in NaOH increased the number of cross-linked bonds causing the reinforcement of granule integrity and thereby reducing solubility. Paste clarity was affected only by NaOH and by the interaction of these with temperature (Table 2). The response decreased when the NaOH level and extrusion temperature increased (Fig. 4), probably because under these conditions a higher number of cross-linking bridges were formed. Paste clarity was the result of rupture of swollen starch granules (Craig et al., 1989), and cross-linking improved the integrity of swollen granules, reducing clarity (Zheng, Han & Bhatty, 1999). On the other hand, the use of high NaOH concentration can cause dark brown coloration in the final product due to a secondary starch-browning reaction as observed by Kervinen, Suorti, Olkku and Linko (1985); Della Valle et al. (1991).

In general, the results obtained for WAI, WSI and paste clarity indicated that when the temperature and NaOH concentration increased, the cross-linking with STMP was accelerated in the same manner as in traditional processes.

3.3. Cold viscosity

Using the extruder as a reactor, it was possible to obtain a simultaneously derivatized and gelatinized starch. Cold viscosity refers to the viscosity of a starch–water suspension at room temperature. Ungelatinized starch absorbs few water molecules at room temperature, and its viscosity as measured by the Viscoamlograph has practically zero BU. The gelatinized starch, however, absorbs water rapidly to form a paste at room temperature without further heating. The viscosity of the paste depends to a large extent on the degree of gelatinization of the starch granules and the extent

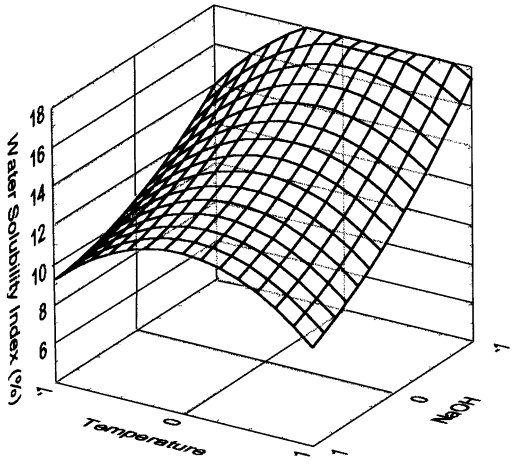

Fig. 3. Effect of extrusion temperature and NaOH concentration on water solubility index. (Phosphorus concentration 0.009%).

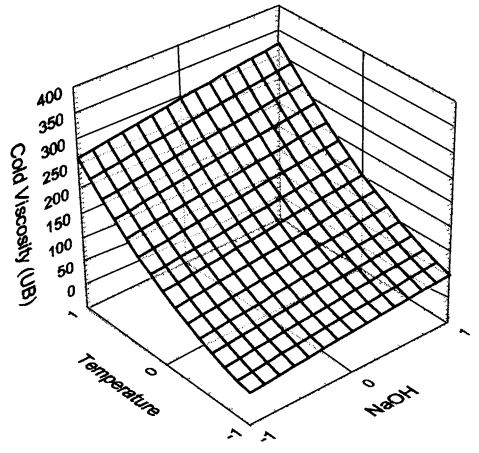

Fig. 5. Cold viscosity as a function of extrusion temperature and NaOH level (Phosphorus concentration 0.009%).

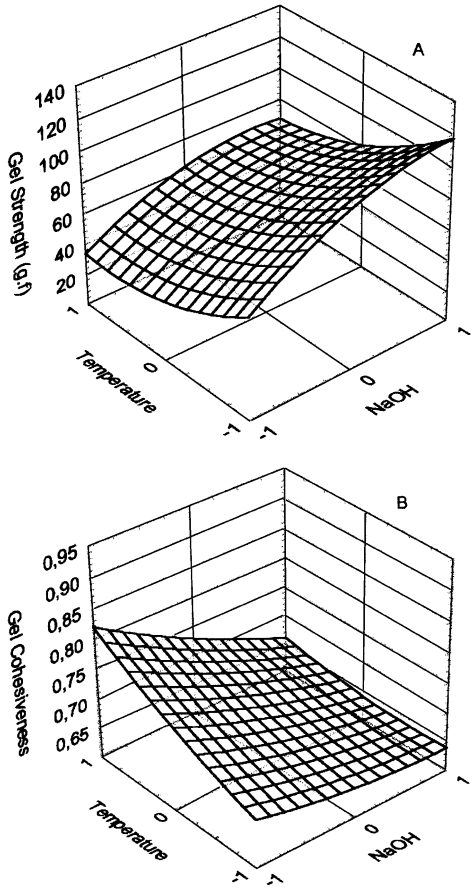

Fig. 6. Effect of extrusion temperature and NaOH concentration on: (A) gel strength; and (B) gel cohesiveness, with phosphorus concentration fixed at 0.012%.

of their molecular breakdown. The cold-paste viscosity is an important property in various food and industrial applications (El-Dash, 1981).

In this study, the cold viscosity of the processed samples was affected only by extrusion temperature (Table 2). The samples with more cross-linking (processed at high temperature) showed a higher cold viscosity (Fig. 5). Cross-linking modification maintained granule integrity in the presence of water and conditions that normally would promote rupture of hydrogen bonds responsible for the granule integrity because they have been reinforced with chemically bonded bridges (Reddy & Seib, 1999).

3.4. Gel strength and cohesiveness

Gel strength was influenced by the linear effects of the three studied variables and by the quadratic effects of NaOH concentration and temperature (Table 2). The analysis of gel characteristics showed that the gel strength increased when NaOH and phosphorous concentration increased and temperature decreased (Fig. 6A). The action of the extrusion temperature is justified because the less drastic process conditions preserve the chain structure of starch polymers, which is responsible for the gel structure. The effects of the other two variables were different from those described by Takahashi et al. (1989), who observed the reduction of gel strength for corn and wheat cross-linked starches, but agreed with the results reported by Mali (1999), which referred to distarch adipates. Discrepancies are probably attributable to the different levels of DS and native starch structures.

The quadratic effects of phosphorus (STMP) concentration and the linear effects of the other two variables were found to be important for gel cohesiveness (Table 2). An important and desirable change in gel cohesiveness of cassava starch was obtained. When cross-linking increased (at higher NaOH and phosphorus concentration) and temperature was low, the gels presented a shorter texture (lower cohesiveness) as shown in Fig. 6B.

3.5. Complementary tests

From the data showed in Table 3 it is evident that the shearing force and pressure applied during extrusion associated with the NaOH action promoted disruption of the granular structure of the starch, as demonstrated by WSI and cold viscosity of sample A.

The incorporation of P in the starch (samples B and C) showed a significant effect on the analyzed functional

Table 3
Effect of different STMP concentration (expressed as P concentration) on functional properties of extruded (extrusion performed at 100°C with 0.075% NaOH) cassava starch (means followed by the same letter within columns are not statistically different ($p > 0.001$))

Sample			Properties[a]					
	Added P (%)	DS[b] ($\times 10^{-4}$)	WAI[c]	WSI[d]	Paste clarity[e]	Cold viscosity[f]	Gel strength[g]	Gel cohesiveness[g]
A	–	0.00a	7.73b	22.50a	61.0a	180	38a	0.90a
B	0.01	2.53b	8.72a	7.50b	22.5b	280	127b	0.66b
C	0.02	5.26c	7.50b	4.65c	21.0b	125	192c	0.59c

[a] Means of three replications, except for cold viscosity (one observation).
[b] DS = Degree of substitution.
[c] WAI = Water absorption index.
[d] WSI = Water solubility index (%).
[e] % Light transmitance.
[f] BU.
[g] g.f.

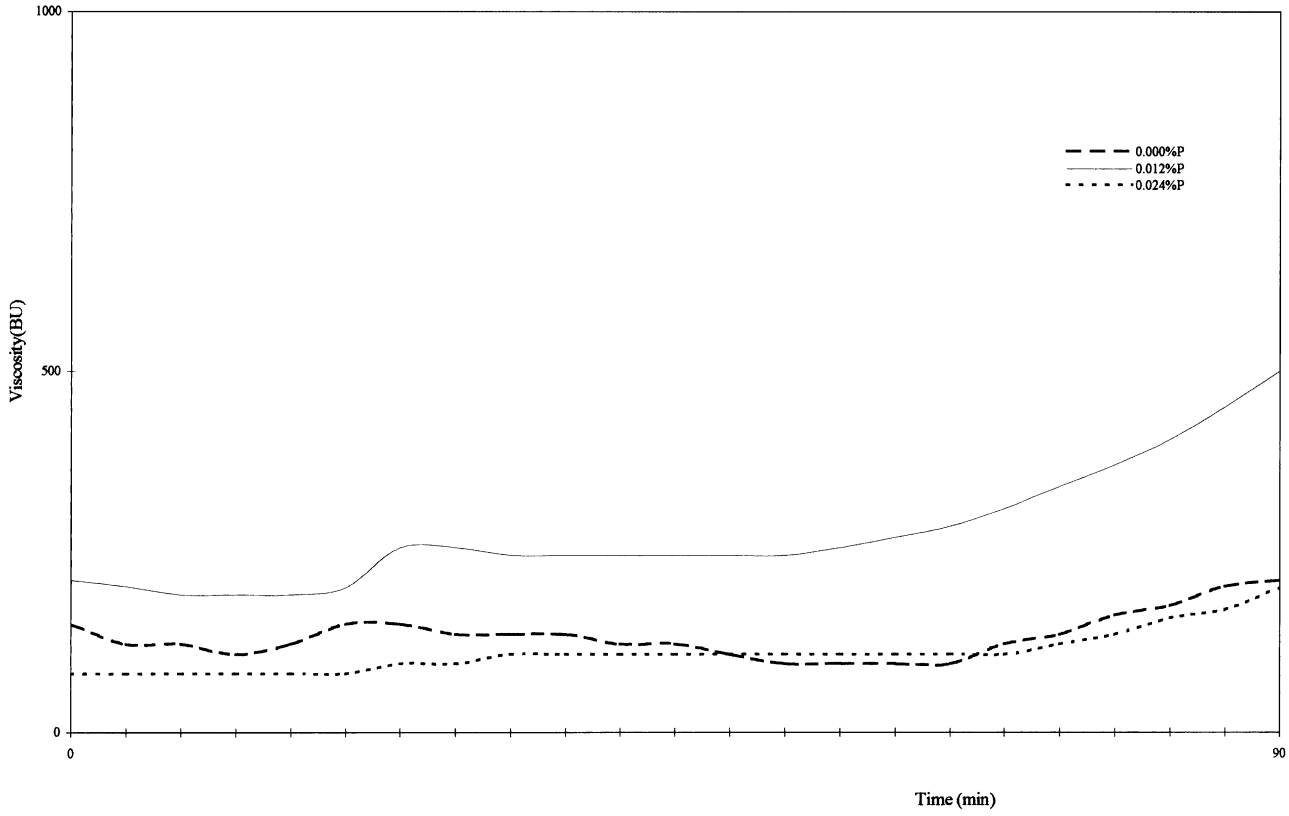

Fig. 7. Amylograms of starch samples extruded at 100°C and 0.075% NaOH, with different levels of added P.

properties. WSI, paste clarity, and gel cohesiveness were lower than in sample A and decreased with the increase of DS, while the opposite effect was observed for gel strength. WAI and cold viscosity increased when the DS was lower (sample B) but decreased with further increase of P level (sample C). These effects have been reported as evidences of the cross-linking of starch chains (Wurzburg, 1986).

The shapes of the amylograms (Fig. 7) also demonstrated the pregelatinization of starch and the occurrence of cross-linking when STMP was present. Sample B (0.01% added P) had higher initial viscosity and stability against shearing (at 95°C/20 min.) than sample A (without added P). When the level of P increased to 0.02% (sample C) the starch phosphate showed paste stability but lower paste consistency.

4. Conclusions

The results obtained from this research showed that it is possible to produce cross-linking starch using a single-screw extruder as a reactor and STMP as the reagent. This process also confirmed starch properties of pregelatinized products. Using adequate combinations of reagents (STMP and NaOH) and extrusion temperature, it was possible to obtain different DS and, consequently, different functional properties. The introduction of phosphate groups in starch during the extrusion process, with a maximum DS of 1.5×10^{-4}, caused increased gel strength, WAI, and cold viscosity, and decreased cohesiveness, WSI and starch clarity.

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