Kasetsart J. (Nat. Sci) 32 : 234 - 241 (1998)

Starch Phosphate Production by Microwave Technique

Passara Maneesriraj, Siriluk Phetkoa and Woatthichai Narkrugsa

ABSTRACT

Starch phosphate production using microwave technique was carried out with tapioca and glutinous rice starches as raw materials. Starches were mixed with phosphate reagents(sodium hexametaphosphate and sodium dihydrogen-phosphate to produce starch phosphate monoester (SPM) and starch phosphate diester (SPD) at the concentration of 10,15 and 20% (w/v in liquid phase) with the liquid/solid weight ratio 1:2. Retained moisture content(RM),bound phosphorus (BP), degree of substitution (DS) and freeze-thaw stability (FTS) of starch phosphates were analysed and examined.

The results showed that RM of SPM from tapioca and glutinous rice starch were 6.47-9.28% and 6.24-8.08%,respectively, while RM of SPD from the two starches were 5.70-9.24% and 5.35-8.08%,respectively. Starch phosphate from tapioca starch had BP (0.062-0.085% in SPM and 0.052-0.072% in SPD)lower than starch phosphate from glutinous rice starch(0.091-0.147% in SPM and 0.074-0.131% in SPD). DS of starch phosphates from tapioca starch(0.0045-0.0068 for SPM and 0.0037-0.0053 for SPD) were also lower than from glutinous rice starch (0.0053-0.0104 for SPM and 0.0047-0.0092 for SPD). FTS of SPM and SPD from glutinous rice starch were better than FTS of SPM and SPD from tapioca starch because of lower volume of seperated water after freezing and thawing. BP and DS were almost significantly positive correlated to the interaction of factors between the concentration of phosphate reagent and heating time at $P \leq 0.05$. Starch phosphate from glutinous rice starch, especially in the monoester form was more suitable to use in frozen food than tapioca starch.

Key words : starch phosphate,tapioca,glutinous rice, microwave

INTRODUCTION

Starch phosphate is one of the modified starch used in the frozen food industry (Wurzburg,1986 and Laullen,1994). It is produced by phosphorifi-cation of free hyroxyl groups of anhydroglucose units of starch molecules. They are esterfied with phosphate reagents (Kerr and Cleveland,1959,1960; Katz and and Levy,1961; Alexander, 1974; Kalber,1986;Saley and Ciacco,1990). Phosphate reagents for starch phosphate monoester are orthophosphate salts (NaH_2PO_4 , Na_2HPO_4 and $Na_5P_3O_4$) while starch phosphate diester are metaphosphate salts ($Na_3P_3O_9$ and $Na_6P_6O_{18}$) (Alexander,1974). Starch phosphate production is normally produced by using wet process (Wurzburg,1986) but it is also produced by using semi-dry process with spray drying or drum drying (Kerr and Cleveland, 1950,1960) and dry process with cooking extrusion (Kalber,1986; Salay

Department of Agricultural Industry. Faculty of Agricultural Technology. King Monkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.

and Ciacco,1990; Narkrugsa and Berghofer,1992). In 1993 Narkrugsa found that it was feasible to esterify citric acid on hydroxyl group of anhydroglucose units in the starch molecules for starch citrate production using microwave technique due to thermal energy created inside the mixture.

Therefore in this experiment, tapioca and glutinous rice starches were phosphorificated with sodium dihydrogenphosphate and sodium hexametaphosphate for studying the feasibility of starch phosphate (both monoester and diester) production by microwave technique. Their degree of substitution and freeze-thaw stability property were examined.

MATERIALS AND METHODS

Tapioca starch and glutinous rice starch with the compositions shown in the Table 1 were used as raw materials for phosphorification. Starches were mixed with sodium dihydrogenphosphate (Merk Co.Ltd.,Germany) to produce starch phosphate monoester and with sodium hexametaphosphate(Fluka Chemika Co.Ltd., Germany) at the concentration (X_1) of 10, 15 and 20% (in liquid phase) at the liquid/solid weight ratio 1:2. The mixtures were packed in PE-bag and stored at room temperature overnight for uniform moisture distribution. Then the mixtures were heated with microwave at 2450 MHz (Goldstar model 4160D, Korea) for various time (X_2) of 5,7 and 9 min for tapioca starch, and 5, 6 and 7 min for glutinous rice starch. The starch phosphates were analysed for retained moisture content(RM),bound phosphorus(BP), and examined for degree of substitution(DS) and freeze-thaw stability(FTS).

The retained moisture content of starch phosphates were analysed by the official method 925.10 of AOAC(1995). Two gram of sample was heated in hot air oven at 130°C for 1 hr. The heated sample was cool in desiccator and weighed. The weight loss was express in % of RM.

Bound phosphate was analysed using the modified method (Alexander, 1974 and Narkrugsa,1990) and expressed as the amount of bound phosphorus. The ground starch phosphate was extracted for free phosphate with 80% ethanol in Soxhlet apparatus for 8 hrs. Then ethanol was evaporated from starch phosphate at room temperature. Ten gram of dried starch phosphate was mixed with 100 ml distilled water and this mixture was adjusted to pH 2 with 6N HCl. The mixture was centrifuged at 1800 rpm for 5 min. The supernatant was discarded. The starch was washed with 100 ml of distilled water and centrifuged at 1,800 rpm for 5 min. The supernatant was discarded. The residue was quantitively transferred to 100 ml beaker and 20 ml of distilled water was added.

Table 1 Compositions of raw materials (dry basis)[1].

Raw material	Moisture content %	Crude fat %	Ash %	Phosphorus[2] %
T-starch[3]	12.17	0.85	0.25	0.004
G-starch[4]	13.27	1.27	0.23	0.014

Note : 1 Analysis using Official Method from AOAC(1995)
2 Analysis using method from Narkrugsa(1990)
3 T-starch = Tapioca starch
4 G-starch = Glutinous rice starch

Then the slurry was titrated with standard 0.1N NaOH by Autotitration (Model T80/20, TR85, Scott Gerate Comp.,Germany). The amount of titrant at pH 5(V_a) and pH 9.5 (V_b) were detected. The percentage of bound phosphate(%BP) was calculated using this following formula:

$$\%BP = (V_b - V_a) * N * 0.31/W$$

where

V_a = ml of NaOH at pH 5.0

V_b = ml of NaOH at pH 9.5

N = normality of NaOH

W = dry substance of sample (express as a decimal fraction)

Degree of substitution of starch phosphate was calculated using the following equation (Salay and Ciacco, 1990):

$$DS = \%Pd - \%Pt/12.8$$

where

%Pd = percentage of total phosphorus in the starch phosphate on a dry basis

%Pt = percentage of total phosphorus in the native starch on a dry basis

The freeze-thaw stability was examined using the modified method of Narkrugsa (1990) and Luallen (1994). Three hundred gram of 5% (w/w) starch phosphate paste in distilled water was prepared and mixed in the roter mixer (IKA-Ruhrwerk model RW20,Germany)at the speed 60 rpm for 20 min. Paste was freezed at -20°F in the freezer (Sanyo model SCF-600 2A,Japan) overnight. The frozen sample was removed from the freezer into the water baht at room temperature. Then 100 ml of sample was centrifuged at 8,000 rpm for 30 min. The volume of separated water was measured in ml and expressed as %FTS.

RESULTS AND DISCUSSION

It was feasible to produce starch phosphate monoester (SPM) and diester(SPD) by the reaction of the phosphate reagents and tapioca and glutinous rice straches during heating with microwave at 2450 MHz. The SPM retianed moisture content (RM) at 6.47-9.28% (tapioca starch phosphate monoester,T-SPM) and at 6.24-8.08% (glutinous rice starch phosphate monoester, G-SPM) while the SPD had RM at 5.70-9.24% (tapioca starch phosphate diester,T-SPD) and at 5.35-8.08% (glutinous rice starch phosphate diester,G-SPD) (Table 2 and 3). RM of the starch phosphate products were significantly negative correlated with the heating time(X_1) at $P \leq 0.05$ (Table 4 and 5).

Regarding with the amount of bound phosphorus(BP),the analytical results,Table 2 and 3, showed that T-SPM and G-SPM had BP at 0.062-0.085% and 0.091-0.147%,respectively, while T-SPD and G-SPD had BP at 0.052-0.072% and 0.037-0.0104%,respectively. It means that the phosphate reagents could react with anhydro-glucoses in the glutinous rice starch more than in the tapioca starch both in monoester and diester forms. The DS of the starch phosphates from tapioca starch were 0.0045-0.0068 for T-SPM and 0.0037-0.0053 for T-SPD, while the starch phosphates from glutinous rice starch were 0.0053-0.0104 for SPM and 0.0047-0.0092 for SPD. In Table 4 and 5, BP and DS of the products were almost significantly positive correlated with the concentration of phosphate reagents(X_2),except in the case of T-SPM, and also were significantly positive correlation with $X_1 X_2$ at $P \leq 0.05$.

The starch phosphate production models were calculated in the form of multiple regression models (shown below) and were plotted in the Figure 1 and 2. Figure 1 and 2 showed the BP of starch phosphate monoester and starch phosphate diester from tapioca and glutinous rice starches were almost non-linear correlated to the heating time and the reagent concentration during the production of starch phosphates using microwave technique.

Table 2 Retained moisture content,bound phosphorus, degree of substitution and freeze-thaw stability of starch phosphate monoester(SPM) from tapioca starch(T) and glutinous rice starch(G).

Treatment	Factors		RM	BP	DS	FTS
	Heating time X_1, min	Reagent conc. X_2, %	%	%		%
Tapioca starch						
T-SPM1	5	10	9.28	0.062	0.0045	20.76
T-SPM2	7	10	7.33	0.075	0.0056	38.00
T-SPM3	9	10	6.47	0.073	0.0054	50.90
T-SPM4	5	15	9.06	0.074	0.0055	19.00
T-SPM5	7	15	7.68	0.076	0.0056	25.70
T-SPM6	9	15	6.60	0.091	0.0068	46.90
T-SPM7	5	20	9.07	0.069	0.0051	17.20
T-SPM8	7	20	7.63	0.073	0.0054	22.40
T-SPM9	9	20	6.11	0.085	0.0063	36.60
Glutinous rice starch						
G-SPM1	5	10	8.08	0.091	0.006	0.10
G-SPM2	6	10	7.97	0.099	0.0067	1.00
G-SPM3	7	10	6.31	0.082	0.0053	10.10
G-SPM4	5	15	7.96	0.092	0.0061	1.60
G-SPM5	6	15	7.10	0.101	0.0068	9.30
G-SPM6	7	15	6.54	0.113	0.0077	24.00
G-SPM7	5	20	7.83	0.095	0.0063	12.00
G-SPM8	6	20	6.62	0.141	0.0099	24.00
G-SPM9	7	20	6.24	0.147	0.0104	26.00

Note: 1 The results in the table were means of duplicate.
2 RM =retained moisture content, BP= bound phosphorus, DS =degree of substitution, FTS =freeze-thaw stability

SPM model :

for tapioca starch

$BP,\% = 0.003375-0.001708\ X_1+0.008692\ X_2+ 0.00025\ X_1^2-0.00003\ X_2^2+0.000125\ X_1\ X_2$ $(r^2 = 0.86)$

for glutinous rice starch

$BP,\% = -0.043611+0.088917\ X_1-0.0232\ X_2- 0.010333\ X_1^2+0.000287\ X_2^2+0.00305\ X_1\ X_2$ $(r^2=0.96)$

SPD model :

for tapioca starch

$BP,\% = 0.102\ -0.008958\ X_1-0.003425\ X_2+ 0.000375\ X_1^2+0.0001\ X_2^2+0.000275\ X_1\ X_2$ $(r^2=0.96)$

for glutinous rice starch

$BP,\% = 0.238389-0.02325\ X_1-0.017\ X_2+ 0.002167\ X_1^2+0.000767\ X_2^2-0.00015\ X_1X_2$ $(r_2=0.97)$

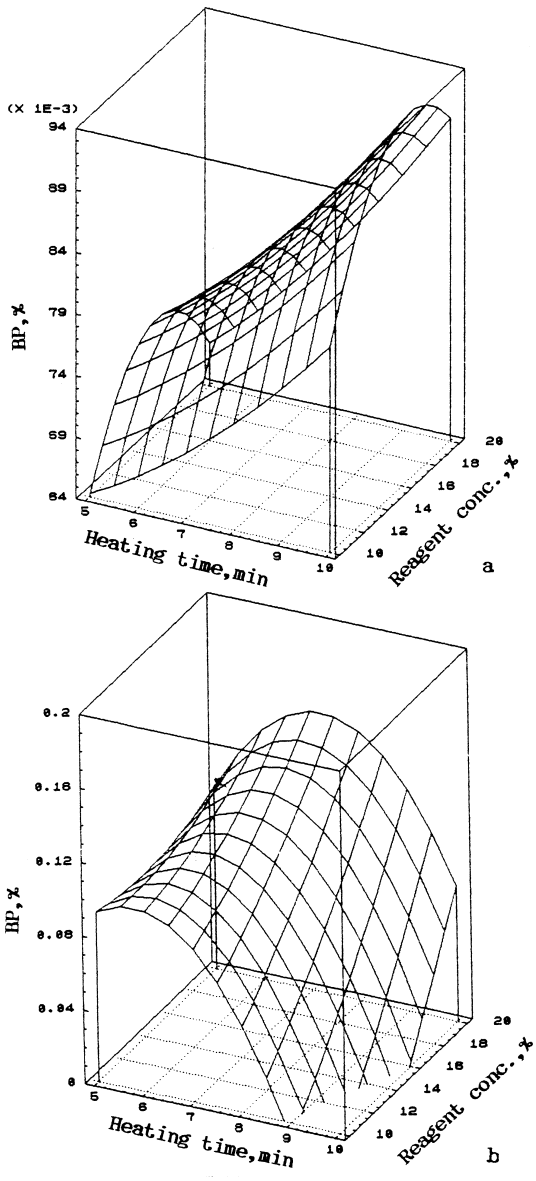

Figure 1 Response surface plot for BP of starch phosphate monoester. (a:tapioca starch, b:glutinous rice starch)

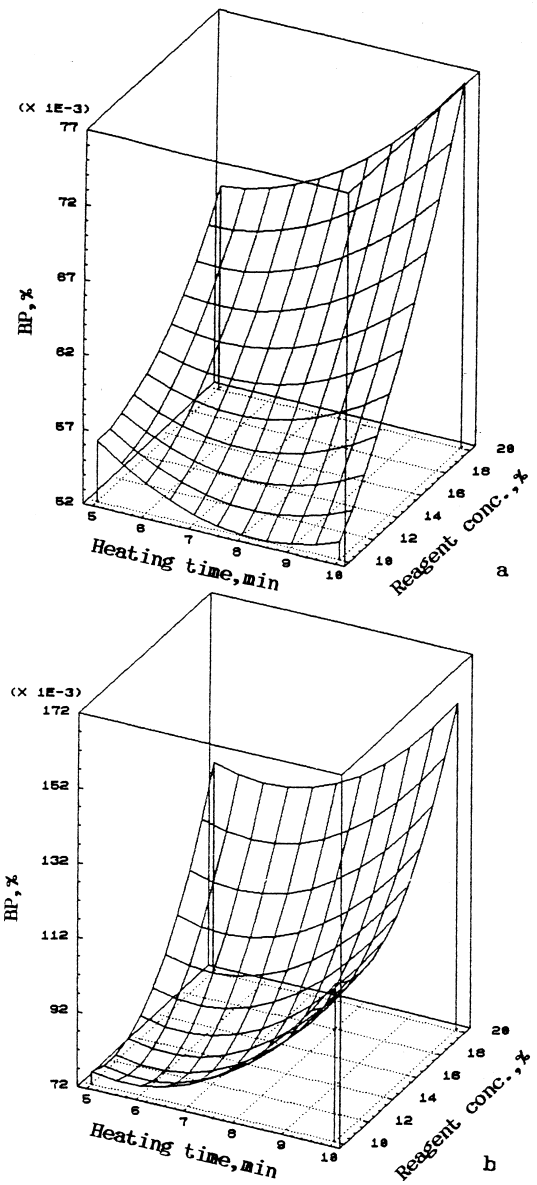

Figure 2 Response surface plot for BP of starch phosphate diester. (a:tapioca starch, b:glutinous rice starch)

Table 3 Bound phosphorus, degree of substitution and freeze-thaw stability of starch phosphate diester(SPD) from tapioca starch (T) and glutinous rice starch (G).

Treatment	Factors		RM	BP	DS	FTS
	Heating time X_1, min	Reagent conc. X_2, %	%	%		%
Tapioca starch						
T-SPD1	5	10	9.24	0.056	0.0041	18.50
T-SPD2	7	10	7.21	0.052	0.0037	43.50
T-SPD3	9	10	6.73	0.053	0.0038	15.50
T-SPD4	5	15	8.64	0.060	0.0043	32.20
T-SPD5	7	15	6.66	0.056	0.0040	38.00
T-SPD6	9	15	6.06	0.060	0.0044	40.00
T-SPD7	5	20	8.32	0.064	0.0046	47.50
T-SPD8	7	20	6.08	0.070	0.0052	43.70
T-SPD9	9	20	5.70	0.072	0.0053	50.50
Glutinous rice starch						
G-SPD1	5	10	7.13	0.076	0.0048	11.50
G-SPD2	6	10	6.70	0.074	0.0047	1.20
G-SPD3	7	10	6.01	0.078	0.0050	12.50
G-SPD4	5	15	8.08	0.079	0.0051	12.00
G-SPD5	6	15	6.66	0.087	0.0057	17.50
G-SPD6	7	15	6.44	0.081	0.0052	15.00
G-SPD7	5	20	7.02	0.131	0.0092	2.20
G-SPD8	6	20	6.55	0.120	0.0082	17.50
G-SPD9	7	20	5.35	0.130	0.0091	12.00

Note : 1 The results in the table were means of duplicate.
2 RM =retained moisture content, BP= bound phosphorus,
DS =degree of substitution, FTS =freeze-thaw stability

FTS of these starch phosphates were also examined. From the data in Table 2 and 3, FTS of SPM were 17.20-50.90% for T-SPM and 0.10-26.00% for G-SPM while FTS of SPD were 15.50-50.50% or T-SPD and 1.20-17.50% for G-SPD. The results showed that starch phosphates, monoester and diester, produced from glutinous rice starch were more useful to protect the water separation or syneresis from the frozen paste after thawing at room temperature than tapioca starch. Comparing with the same heating time and the same concentration of the phosphate reagents, most of starch phosphates produced from glutinous rice starch were more resistant to microwave heating during the reaction with the phosphate reagents than tapioca starch, eg. G-SPM1 vs T-SPM1 and G-SPD7 vs T-SPD8. Due to the degradation of the starch granules of tapioca starch, Lewandowicz *et al*. (1996) found that the brabender amylograph of tapioca starch paste after microwave irradiation gave a very low viscosity comparing to its native starch. They also found that the starch granules were destroyed after microwave irradiation at the short time. FTS was significantly positive correlated only with X_1 for T-SPM and X_2 for G-SPM and T-SPD at $P \leq 0.05$ (Table 4 and 5). The percentage of bound phosphate and DS of starch phosphates produced from both type of starch using microwave

Table 4 The correlation coefficients[1] of the process factors and its interaction to some characteristics of starch phosphate from tapioca starch.

Factors	T-SPM				T-SPD			
	RM	BP	DS	FTS	RM	BP	DS	FTS
Heating time,X_1	-0.986*	+0.753*	+0.754*	+0.887*	-0.879*	+0.086^{ns}	+0.086^{ns}	+0.091^{ns}
Reagent conc,X_2	-0.031^{ns}	+0.293^{ns}	+0.289^{ns}	-0.383^{ns}	-0.351^{ns}	+0.907*	+0.907*	+0.752*
X_1*X_2	-0.659^{ns}	+0.722*	+0.719*	+0.256^{ns}	-0.829*	+0.783*	+0.783*	+0.636^{ns}

Note : 1 The correlation coefficients were determined at $P \leq 0.05$
* means significant effect.
ns means non-significant effect.

Table 5 The correlation coefficients[1] of the process factors and its interaction to some characteristics of starch phosphate from glutinous rice starch.

Factors	T-SPM				T-SPD			
	RM	BP	DS	FTS	RM	BP	DS	FTS
Heating time,X_1	-0.888*	+0.404^{ns}	+0.404^{ns}	+0.644^{ns}	-0.847*	+0.016^{ns}	+0.016^{ns}	+0.525^{ns}
Reagent conc,X_2	-0.309^{ns}	+0.703*	+0.703*	+0.705*	-0.177^{ns}	+0.906*	+0.906*	+0.139^{ns}
X_1*X_2	-0.664^{ns}	+0.861*	+0.861*	+0.920^{ns}	-0.214^{ns}	+0.939*	+0.939*	+0.126^{ns}

Note : 1 The correlation coefficients were determined at $P \leq 0.05$
* means significant effect.
ns means non-significant effect.

heating were not linearly correlated with the freeze-thaw stability characteristic not only at high but also at small amount of bound phosphate or DS. But the suitable starch phosphates to be used in the frozen food were G-SPM1,G-SPM2,G-SPM4,G-SPD2 and G-SPD7 because of their low volume of separated water after testing.

LITERATURE CITIED

Alexander,R.J.1974. Art of manufacturing modified amylaceous materials with condensed phosphates and urea. US-Patent 3,843,377.

AOAC.1995. Official Method of Analysis,16th ed. Association of Official Analytical Chemists. Washington,DC. Chapter 32 p.32-1.

Kalber,U.1986. Untersuchung der moglichkeiten starkephosphate und kationische starken mittels kochextrusion herstellen. Diplomarbeit der Universitat Hohenheim, Germany.

Kazt,D.S. and B.M. Levy. 1961. Verfahren zur herstellung von alkalai-starkephosphaten. Deutsches-Patent 12 93 451.

Kerr,R.W. and F.R. Cleveland. 1959. Orthophosphate esters of starch. US-Patent 2,884,413.

Kerr,R.W. and F.R.Cleveland.1960. Process for preparing inorganic starch esters. US-Patent 2,961,440.

Lewandowicz,G., J.Fornal and A.Walkowski. 1996. Structural changes of tuber starches by microwave irradiation. Zywnosc Technologia Jakosc. 2 : 101-108.

Luallen,T.E.1994. The use of starches in frozen food formulation. Food Technology. 48 : 39.

Narkrugsa,W.1990. Herstellung von starke-derivaten durch heissextrusion. Dissertationarbeit der Universitat fur Bodenkultur,Wien Austria.

Narkrugsa,W. and E. Berghofer.1992. Physico-chemical properties of modified cassava flour and starch for corrugated board adhesive. Kasetsart J.(Nat. Sci.). 26 : 314-323.

Narkrugsa,W.1993. Study on the feasibility of starch citrate production by microwave technique, pp.270-280. *In* Proceeding of the 31st Kasetsart University Annual Conference February 3-6, 1993, Kasetsart University, Bangkok.

Salay,E.and C.F.Ciacco.1990. Production and properties of starch phosphates produced by the extrusion process. Starch/Starke. 42 : 15-17.

Wurzburg,O.B. 1986. Modified Starches : Properties and Uses. CRC Press,Inc. Boca Raton, Florida. 277p.

Received date : 17/09/97
Accepted date : 25/12/97