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EDITORIAL

I want to thank those associated with the Journal of Food Processing and Preservation who have so significantly contributed to its success. Authors, reviewers (see list below), publisher (especially Ms. Kathy O'Neil), and my secretary, Mary Wojciechowski, all contribute to ensuring the quality and vitality of the Journal. I also want to thank Marcus Karel, Lowell Satterlee, Romeo Toledo and Ronald Rolsted for their service on the Editorial Board. All four will once again be supporting the Journal with another three year term.

We continue to seek papers in the area of "Computer Codes and Their Applications" and "Databank". I also want to encourage authors to continue to consider the Journal of Food Processing and Preservation as a repository for their research work and selected review articles. We currently have no publication delay once papers have been accepted for publication.

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CONTENTS

PROCESSING AND EVALUATION OF CARBONATED BEVERAGE FROM JACKFRUIT WASTE (*ARTOCARPUS HETEROPHYLLUS*)

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ABSTRACT

*Edible bulbs of ripe jackfruit (*Artocarpus heterophyllus *Lam.) are consumed for their fine taste and pleasant aroma. The edible portion is about 30% by weight. About 50% of fruit, composed of rind and unfertilized floral parts, which are also rich in jackfruit flavor, are usually discarded as waste, because they are fibrous. A process for the preparation of clarified juice has been developed and involves treatment of the jackfruit waste with pectic enzyme at 0.3% concentration (v/v), incubation for 2 h at 40C and subsequent filtration, giving about 60% yield of clarified juice having 23°Brix and 0.15–0.20% acidity. Sensory evaluation of ready-to-serve (RTS) beverages (12% juice, 15°Brix sugars and 0.3% acidity) without and with carbonation at 3 levels (CO_2 gas pressures 0.775, 2.092 and 3.685 kg/cm²) by a 15-member trained panel revealed that the product was highly acceptable either without or with carbonation at 0.775 kg/cm², compared to higher levels of carbonation. It is concluded that preparation of beverage from jackfruit waste as a byproduct, besides processing of bulbs and seeds, brings about the effective utilization of jackfruit to over 80%.*

INTRODUCTION

Jackfruit (*Artocarpus heterophyllus* Lam.), a tree indigenous to India, is widely cultivated in most tropical countries (Manjunath 1948). Immature fruit is widely

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used in households as a curried vegetable (Narasimham 1990; Jacob John *et al.* 1992). Mature fruit ripens normally at 20–35C in 3 to 10 days depending on the maturity at the time of harvest (Mathur *et al.* 1952). At full maturity the fruit attains a diameter of about 25 to 30 cm (Sharma 1964). At higher altitudes, the fruit takes longer time to mature (Teaotia and Chauhan 1969).

Ripe jackfruit comprises 3 parts: (1) bulbs, (2) seeds (embedded in bulbs) and (3) the skin, rind, sheath, core and unfertilized floral parts. Fruit is valued for the tasty, well-flavored sweet bulbs, which only comprise an average of about 30% of the fruit weight. Fruits range from 5 to 50 kg with an average weight of 10 kg (Narasimham 1990). Seeds, comprising around 12% of fruit weight, are rich in starch and are roasted and eaten. The rest of the fruit, comprising rind and unfertilized floral parts, is rich in flavor but is considered inedible, being highly fibrous. The possibility of recovering pectins from this material has also been suggested (Bhatia 1953; Krishnamurthy and Giri 1949; Jain and Lal 1957; Bhatia *et al.* 1959). Oliveros *et al.* (1971) recovered from this inedible portion an essential oil, which possessed strong natural aroma of jackfruit. A procedure was given for the preparation of jackfruit squash and nectar from the blanched and blended pulp of bulbs with the addition of sugar and citric acid (Anon. 1953). In order to utilize the inedible portion of fruit more effectively, a process was developed for the preparation of a clarified juice and a ready-to-serve (RTS) beverage from it.

MATERIALS AND METHODS

Material

Fully mature, jackfruits (cv. Varikha) were harvested from three trees grown in different locations of Mysore city, based on the external visible maturity indexes such as distance between spines, number of spines per unit area, color of spines (greenish-yellow) and the number of days elapsed from fruit-set (180 days) (Narasimham 1990). Fruits were ripened to firm ripe stage in about 4 days at room temperature (22–30C, RH 50–80%) and used in this study.

Preparation of Material

Processing steps for the extraction of juice are given in the flow sheet.

Skin and spines were removed by manual peeling using a sharp knife. Peeled fruit was cut into 8 pieces by two longitudinal and one horizontal slicing, the core and bulbs (with seeds) were separated. The rest of the fruit comprising rind, sheath and unfertilized floral parts of the fruit were first shredded in a STEPHEN

Universal Machine (No. V.C.H. 25, German make) to make a coarse pulp and later passed through FRYMA Mill (Brisfelden Schweig Model No. DKE 10, German make) to produce a fine pulp with a 5% (w/w) addition of water.

RIPE JACKFRUIT
↓
PEELING AND SLICING
(removal of skin, spines, core, bulbs and seeds)
↓
SHREDDING
(of rind, sheath and unfertilized flowers)
↓
PULPING
↓
ENZYME TREATMENT
(Pectic enzyme at 0.3% concentration (v/w) for 2 h at 40C)
↓
EXTRACTION OF JUICE
(in basket press)
↓
CLARIFICATION OF JUICE
(Filtering through Buchner funnel)
↓
PREPARATION OF RTS BEVERAGE
↓
CARBONATION

Enzyme Treatments

Pectic enzyme (Pectin Ex. Ultra Sp. Ferment A.G. Ltd. Switzerland) was used to break up the pectins of the pulp and extraction of juice. Enzyme concentration, temperature and incubation were determined in preliminary experiments. For fixing the optimum concentration, the pulp was thoroughly mixed with the enzyme at concentration from 0.1 to 0.5% (v/w) with an increase in concentration by 0.1% and incubated at 30C for 2 h. Optimum duration of incubation was determined based on yield of juice, after incubating the pulp with 0.3% enzyme at 30C, for different durations from 1 to 5 h with hourly increases in duration. Similarly, the optimum temperature for incubation was determined by incubating pulp with 0.3% enzyme for 2 h at temperatures of 30, 40 and 50C. For juice yield triplicate samples of 250 g pulp was used.

TABLE 1
EFFECT OF ENZYME CONCENTRATION, ON THE YIELD OF JUICE FROM PULPED JACK FRUIT

Concn.of Pectin ex Ultra sp. Enzyme[1] % (volume/wt.basis)	yield of juice [a] (ml/100 g pulp)
0.1	7.2±0.6
0.2	37.0±0.6
0.3	53.3±0.5
0.4	53.2±0.9
0.5	56.1±0.4

a $\bar{x} \pm$ SEM of 3 replicates

[1] Duration of incubation is 2 h at 30 C temperature.

Extraction of Juice

Juice was recovered by passing pulp in a basket press. The juice obtained was filtered over Buchner funnel, using 3 mm thick pad fitted with water-suction pump. Yield of juice obtained was measured and expressed as ml/100 g pulp. The total soluble solids were determined as Brix, using a hand-refractometer (model Zeiss Opton, Germany, range 0–50°Brix) and acidity of juice was estimated by the titration method described by Ranganna (1986). Viscosity of juice was determined using a Brookfield Synchrolectric Viscometer (England) with a speed of 60 rpm using spindle No. 4 and expressed in centipoise. Clarity of the juice was determined by measuring the percent transmittance at 650 nm (Spectronic-20).

Preparation of Ready-to-Serve (RTS) Beverage With or Without Carbonation

In these studies, clarified juice was converted into RTS beverage having 12% juice, 15°Brix sugar and 0.3% acidity (as citric acid). For dilution, chilled soda or water was used to obtain a carbonated or noncarbonated RTS beverage, respectively. Three levels of carbonation was carried out at 1, 2 and 3 volumes (with CO_2 gas pressures of 0.775, 2.092 and 3.685 kg/cm^2 respectively). The level of carbonation was measured using a pressure gauge (Ranganna 1986).

TABLE 2
EFFECT OF DURATION AND TEMPERATURE OF ENZYME TREATED PULP OF JACKFRUIT WASTE ON THE YIELD AND COMPOSITION OF JUICE

Treatment	Yield (%)	T.S.S. (°Brix)	Acidity (%)	Viscosity (CPS)	Transmittance at 650 nm (%)
Duration of incubation (in h)[b]					
1 h	42	23.0	0.15	4.5	28
2 h	53	23.0	0.17	5.0	32
3 h	54	24.0	0.19	5.0	32
4 h	56	24.5	0.19	5.0	32
Control[a]	5	23.0	0.15	4.5	4
Temperature (°C)[c]					
30 (RT)	54	23	0.15	4.1	25
40	60	20	0.14	4.0	31
50	63	17	0.14	4.0	32

[a] Direct extraction of juice from pulp without enzyme treatment and incubation.

[b] Enzyme (0.3% concn) at 30 C

[c] Enzyme (0.3% concn) for 2 h duration

Sensory Evaluation

Sensory evaluation of the noncarbonated and carbonated RTS beverages was carried out by 15-member panel by 'Ranking Test.' Samples were ranked by panelists into first, second, third and fourth place of preference based on overall quality. Data were statistically evaluated by the rank sum method (Anon. 1975).

RESULTS

Increasing the concentration of enzyme from 0.1 to 0.3% showed a significant increase in the yield of juice, while further increase in concentration did not in-

TABLE 3
SENSORY EVALUATION OF NONCARBONATED AND CARBONATED JACKFRUITS RTS BEVERAGES

Treatment	CO_2 content in		Sensory score (as Rank sum)
	Volume	Gas pressure (kg/cm^2)	
Non carbonated	0	0	28^a
Carbonated	1	0.775	29^{ab}
Carbonated	2	2.092	36^b
Carbonated	3	3.685	57^c

Significance: Rank sums designated by different superscripts were significantly different ($p < 0.05$)

[a] - Significantly superior, [c] - Significantly inferior($p < 0.01$)

[b] - Significant (at $p < 0.05$) but inferior to 'a', derived by comparison of upper and lower pairs (Anon. 1975).

crease the yield of juice (Table 1). Incubation period of 2 h, and at 40C was good, as there was no increase in yield of juice either by increasing the duration or temperature (Table 2). Differences in the quality of the juice in forms of total soluble solids, acidity, viscosity and clarity of juice, are only marginal when the duration of incubation was increased from 1 h to 5 h. However, when the temperature of incubation is increased from 30 to 50C the total soluble solids showed a tendency to decrease, while the other parameters of quality, acidity, viscosity and clarity, remained unaffected (Table 2).

Sensory evaluation of the RTS beverage without and with carbonation at 3 levels (CO_2 gas pressures of 0.775, 2.092 and 3.685 kg/cm^2, respectively) by a 15-member trained panel revealed that the beverage is good without carbonation as well as with carbonation at 0.775 kg/cm^2 level; while the 2.092 kg/cm^2 level was inferior but acceptable (Table 3).

CONCLUSION

An effective utilization of jackfruit waste is possible by conversion into juice. Enzymatic solubilization of pectins and preparation of clarified carbonated or non-

carbonated RTS beverage offer good commercial prospects similar to pineapple juice. By the process developed and reported here, nearly 50% of the fruit that is going as waste could be effectively used to prepare value-added products.

ACKNOWLEDGMENTS

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A RESPONSE SURFACE METHODOLOGY APPROACH TO THE OPTIMIZATION OF THE FUNCTIONAL PROPERTIES OF UREA-MODIFIED ALKALI METAL STARCH PHOSPHATES

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ABSTRACT

Response Surface Methodology was employed to determine conditions for preparation of urea-modified alkali metal starch phosphates. Sago and tapioca starches, roasted in the presence of 0.5 g urea and 3 M phosphate at pH 3.5 and 120C, gave functional properties (viscosity, solubility and clarity) similar to a commercially modified potato starch. The R^2_a values for the models were high — 0.718, 0.819 and 0.728 for sago viscosity, solubility and clarity respectively; 0.741 and 0.904 for tapioca solubility and clarity respectively, but only 0.424 for the tapioca viscosity model. Contour plots were useful in predicting the functional properties of products made under specified conditions; only tapioca viscosity could not be easily predicted, which perhaps indicates the significance of factors other than those considered in the model. The importance of residual analysis in Response Surface Methodology is highlighted. Winsorization of outliers led to improved R^2_a values, but the predictive value of the models decreased.

INTRODUCTION

Natural starches have some deficiencies that limit their use for present-day manufacturing processes. Such deficiencies include: failure of the granules to swell and develop viscosity in cold water, uncontrolled viscosity after cooking, sen-

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TABLE 1.
DEFINITION AND LEVELS OF INDEPENDENT VARIABLES

Independent Variable	Symbol	Uncoded Levels	Coded Levels
pH	A	3.5	-1
		6.5	0
		9.5	1
		10.61	1.37
Temperature (C)	B	120	-1
		145	0
		170	1
		179.25	1.37
Urea (g)	C	0.5	-1
		3.5	0
		6.5	1
		7.61	1.37
Phosphate (M)	D	1	-1
		2	0
		3	1
		3.37	1.37

sitivity of the cooked starches to breakdown during extended cooking and lack of clarity (Wurzburg 1986). Many of the defects can be corrected by selectively modifying starch granules.

Sago starch, although abundant in South-East Asian countries, is of limited commercial value. Properties of this starch are variable, depending to some extent on the regional source. In an attempt to improve the commercial value of this starch, interrelationships between processing conditions and functional properties of modified products were investigated so as to give a product with constant properties from a variable raw material by changing the processing conditions.

This paper describes the experimental design employed and undertakes to produce a low-cost functional equivalent of commercially imported urea-modified potato (*Solanum tuberosum*) starch phosphate, using either tapioca (*Manihot esculenta*) or sago (*Metroxylon sagu*) starches, following the method of Neukom, 1958. In addition, conditions for the production of starches with wide ranging functional properties were determined. Pastes of potato, sago and tapioca starches are similar in that they are relatively clear and are highly viscous (Swinkels 1985).

Urea-starch phosphates are used to bind clay pigments that are applied to high-quality printing paper in the coating process. Such coatings strengthen paper during formation in the wet state and improve surface properties in the dry state. Coated paper is bright due to the homogeneous dispersion of the clay pigments, while

the flexibility of the starch film gives the paper a glossy appearance. Under the FDA indirect food additive regulations, urea-starch phosphates may be used to coat paper that is used in direct contact with food (Code of Federal Regulations 1981).

Low concentrations of native starch dispersions on heating and subsequent cooling are characterized by association of amylose chains, which ultimately precipitate out of solution. Depending on the cooling conditions, higher concentrations may form gels (Schoch 1968). Introduction of phosphate groups into the amylose chains leads to irregularities that prevent chain association and thereby stabilize the cooked pastes at temperatures below the retrogradation temperature. Clarity of a starch paste is an important attribute that varies considerably with the botanical source of starch. This functional property can also be manipulated by chemical modification of the granules.

Response Surface Methodology (RSM) can be employed as a tool to overcome a number of process optimization problems. In addition, this technique can be used to determine optimal conditions of a particular procedure (Mullen and Ennis 1979). Second-order response surface equations for a response "Y" are determined using multiple regression analysis:

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \beta_{12} AB + \beta_{13} AC + \beta_{14} AD + \beta_{23} BC + \beta_{24} BD + \beta_{34} CD$$

RSM is a powerful tool that can simultaneously consider all variables affecting a desired response and their interrelationships. Despite the power of this technique, ultimately it is the experimental model that has greatest influence upon predictive accuracy. Because of this limitation, residual analysis should be performed after generating the models, and, if necessary, data corrected prior to using the models for predictive purposes.

MATERIALS AND METHODS

Materials

Tapioca and sago starches of 14.67% and 16.75% moisture contents (w.s.b.) were kindly donated by Wah Chang International Group of Companies; a urea-starch phosphate was obtained from a commercial source.

All chemicals were of at least analytical grade and were purchased from either Merck, Darmstadt Co. or Sigma Chemical Co. (St. Louis, MO).

Viscosity measurements were made with a Brookfield Cone/Plate Digital

TABLE 2.
NONCENTRAL COMPOSITE (SAN CRISTOBAL) DESIGN FOR p = 4

Row	A	B	C	D	A^2	B^2	C^2	D^2	AB	AC	AD	BC	BD	CD
1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	1
2	-1	-1	-1	1	1	1	1	1	1	1	-1	1	-1	-1
3	-1	-1	1	-1	1	1	1	1	1	-1	1	-1	1	-1
4	-1	-1	1	1	1	1	1	1	1	-1	-1	-1	-1	1
5	-1	1	-1	-1	1	1	1	1	-1	1	1	-1	-1	1
6	-1	1	-1	1	1	1	1	1	-1	1	-1	-1	1	-1
7	-1	1	1	-1	1	1	1	1	-1	-1	1	1	-1	-1
8	-1	1	1	1	1	1	1	1	-1	-1	-1	1	1	1
9	1	-1	-1	-1	1	1	1	1	-1	-1	-1	1	1	1
10	1	-1	-1	1	1	1	1	1	-1	-1	1	1	-1	-1
11	1	-1	1	-1	1	1	1	1	-1	1	-1	-1	1	-1
12	1	-1	1	1	1	1	1	1	-1	1	1	-1	-1	1
13	1	1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	1
14	1	1	-1	1	1	1	1	1	1	-1	1	-1	1	-1
15	1	1	1	-1	1	1	1	1	1	1	-1	1	-1	-1
16	1	1	1	1	1	1	1	1	1	1	1	1	1	1
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	1.37	0	0	0	1.877	0	0	0	0	0	0	0	0	0
21	0	1.37	0	0	0	1.877	0	0	0	0	0	0	0	0
22	0	0	1.37	0	0	0	1.877	0	0	0	0	0	0	0
23	0	0	0	1.37	0	0	0	1.877	0	0	0	0	0	0

TABLE 3.
COMPARISON OF THE FUNCTIONAL PROPERTIES OF MODIFIED STARCHES

	Viscosity of 5 % sample at 7.5 s^{-1} (cps)	Solubility of 1 % sample at 25 C (mg/ml)	% clarity of 1 % sample at T_{650}
Commercial starch	0	0.20	94.4
Modified sago starch	0	0.18	96.4
Modified tapioca starch	0	0.15	95.2

TABLE 4.
COMPARISON OF VISCOSITY STABILITY OF NATIVE AND MODIFIED SAGO AND TAPIOCA STARCHES AT 25C AND 50C

	Viscosity (cps) of 5 % sample at 37.5 s^{-1}		% viscosity decrease after 24 h	
	(25 C)	(50 C)	(25 C)	(50 C)
Native sago starch	370	174	81.08	77.59
Native tapioca starch	525	202	83.81	78.22
Commercial starch	6.54	3.92	0	0
Modified sago starch	9.82	3.92	0	0
Modified tapioca starch	3.92	1.96	0	0

Viscometer, model RVTDV-II, using spindle CP40. The cone angle was 0.8° and the cone diameter 2.4 cm.

Methods

Moisture contents of the samples were determined as indicated by AOAC (1980).

Preparation Of Urea-Modified Alkali Metal Starch Phosphates (Neukom 1958). 1–3.37 M monobasic ($NaH_2PO_4 \cdot H_2O$) and dibasic ($Na_2HPO_4 \cdot 2H_2O$) sodium phosphates were dissolved in different proportions by warming to ap-

TABLE 5a.
REGRESSION EQUATIONS FOR THE VARIOUS RESPONSES (SAGO)

Response	Equation[a]	R^2_a[b]
Viscosity	$Y_v = 1675.982 + 227.768A - 1234.439A^{\wedge 2}$	0.718
Solubility	$Y_s = 1.624 - 1.089A + 1.714B - 0.939A*B + 1.489A^{\wedge 2} - 1.303B^{\wedge 2}$	0.819
Clarity	$Y_c = 42.886 - 22.164A - 10.777B + 14.239A^{\wedge 2}$	0.728

[a] Where A = pH; B = Temperature.

[b] Significant at the 1 % level.

TABLE 5b.
REGRESSION EQUATIONS FOR THE VARIOUS RESPONSES (TAPIOCA)

Response	Equation[a]	R^2_a[b]
Viscosity	$Y_v = 785.780 + 318.768C - 288.279D - 244.456\ C*D$	0.424
Solubility	$Y_s = 1.255 - 0.935A + 1.288B - 0.925A*B$	0.741
Clarity	$Y_c = 59.724 - 8.052A - 11.293B - 14.607C - 12.844B*C + 10.235A^{\wedge 2}$	0.904

[a] Where A = pH; B = Temperature; C = Urea and D = Phosphate.

[b] Significant at the 5 % level.

proximately 50C to give the desired pH and a total volume of 100 ml. To this solution, urea (0.5–7.61 g) was added; 10 g of either sago or tapioca starch was slurried in the solution and agitated for 10 min. After filtration under vacuum through Whatman glass microfiber filter of pore size 1.6 μm, the mixtures (containing about 15% moisture) were baked at 120–180C for 4 h in a vacuum oven (−30 in. Hg).

Viscosity Measurement (Colas 1986). A 5% starch suspension was heated with stirring in a boiling water bath until it attained 90C, after which it was immediately

TABLE 6.
F VALUES FOR THE LACK-OF-FIT OF THE REGRESSION MODELS

Dependent Variable	Residual Sum of Squares / Degrees of freedom (df_r)	[1] MS_e = Pure Error Sum of Squares / df_e	[2] MS_l = Lack of Fit Sum of Squares / df_l	[3] F_{lof} = MS_l / MS_e	$F_{0.05}$ (df_l, 2)
SAGO :					
Viscosity	2985797 / 20	811266.667 / 2	2174530.333 / 18	0.298	19.4
Solubility	13.3107 / 17	0.231 / 2	13.080 / 15	7.517	19.4
Clarity	3466.42 / 19	21.01 / 2	3403.08 / 17	19.047	19.4
TAPIOCA :					
Viscosity	4219371 / 19	44162.667 / 2	4175208.333 / 17	11.123	19.4
Solubility	16.9912 / 19	0.297 / 2	16.694 / 17	6.591	19.4
Clarity	862.708 / 17	113.66 / 2	749.048 / 15	0.879	19.4

[1] MS_e = mean square of the pure error.

[2] MS_l = mean square of the lack-of-fit for the model.

[3] F_{lof} = F value for lack-of-fit for the model.

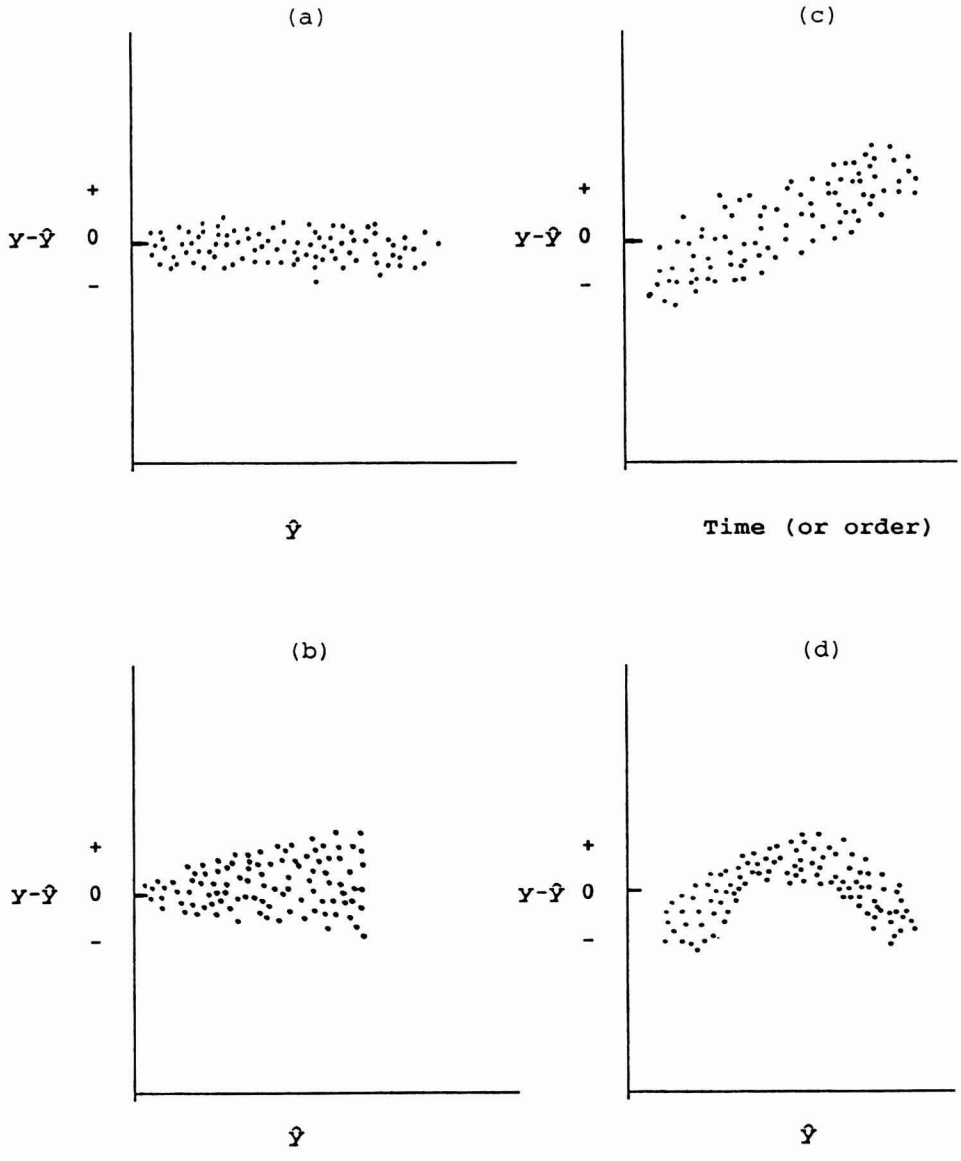


FIG. 1. PLOTS OF RESIDUALS AGAINST FITTED VALUES $\hat{y}$
(a) A normal distribution of residuals. (b) A plot illustrating heteroscedasticity.
(c) A plot showing omission of an important variable. (d) A plot showing curvilinearity.

TABLE 7a.
POINTS FLAGGED WITH r_i, h_i, DFITS AND CD_i VALUES FOR SAGO

	q	Sample	r_i	h_i	DFITS	CD_i
Viscosity	1	S3	2.210	0.124	0.833	0.346
		S17	3.665	0.152	1.552	1.204
Solubility	2	S5	4.404	0.244	2.505	2.087
Clarity	2	S5	1.888	0.181	0.887	0.262

TABLE 7b.
POINTS FLAGGED WITH r_i, h_i, DFITS AND CD_i VALUES FOR TAPIOCA

	q	Sample	r_i	h_i	DFITS	CD_i
Viscosity	2	T7	2.156	0.218	1.139	0.432
Solubility	2	T5	6.036	0.169	2.720	2.470
Clarity	3	T20	1.684	0.320	1.155	0.334

placed in a 25C water bath and equilibrated at this temperature for 5 min. Flow curves were constructed at 25C as a function of increasing and decreasing shear rates in the range 3.75–750 s^{-1}.

Starch Solubility. Suspensions of starch (1%) were incubated at 25C. After 10 min, a 10 ml aliquot of the solution was removed and subjected to centrifugation (10 min at 20C, 4400 rpm). Total sugar content of the supernatant was determined by the method of Dubois *et al.* (1956).

Starch Paste Clarity (Craig *et al.* 1989). 5 ml of a 1% dispersion was pasted by heating in a boiling water bath for 15 min. All dispersions were thoroughly mixed. After cooling to room temperature (5 min), the percent transmittance (% T) of samples at 650 nm was determined, measured against a water blank.

Viscosity Stability. Viscosity of some of the starch pastes was measured over a 24 h period at either 25C or 50C. A constant shear rate of 37.5 s^{-1} was maintained throughout the measurement period. A stock starch paste was kept in suspension at a slow rate of 40 rpm and maintained at either temperature, an aliquot being removed for analysis every hour.

TABLE 8a.
REGRESSION EQUATIONS FOR THE VARIOUS WINSORIZED RESPONSES (SAGO)

Response	Equation[a]	R^2_a[b]
Viscosity	$Y_v = 1597.635 + 223.370A - 149.543B - 1162.117A^{\wedge 2}$	0.806
Solubility	$Y_s = 1.626 - 0.925A + 1.570B - 0.784A*B + 1.305A^{\wedge 2} - 1.262B^{\wedge 2}$	0.884

[a] Where A = pH; B = Temperature.

[b] Significant at the 1 % level.

TABLE 8b.
REGRESSION EQUATIONS FOR THE VARIOUS WINSORIZED RESPONSES (TAPIOCA)

Response	Equation[a]	R^2_a[b]
Solubility	$Y_s = 1.109 - 0.737A + 1.112B - 0.716A*B$	0.895

[a] Where A = pH; B = Temperature.

[b] Significant at the 1 % level.

Response Surface Methodology (RSM)

A 4-variable (p = 4), 4-level Noncentral Composite (San Cristobal) Design proposed by Rojas, 1963 was constructed. A center point, given a value of 0, was included and repeated three times to give information on the error associated with an individual measurement. Table 1 lists the values of the independent variables and their associated coded values: pH, temperature, amount of urea and phosphate concentration. Levels for pH were chosen to include acidic and alkaline values, the center value of 6.5 was chosen as reaction efficiency is highest in the acidic region 5–6.5 (Rutenberg and Solarek 1984); the levels for the other variables were based on literature sources. A temperature range of 120–180C was used as below 120C, the reaction is too slow to be commercially feasible and yet above 180C, charring can become considerable (Neukom 1958). Table

TABLE 9.
F VALUES FOR THE LACK-OF-FIT OF THE WINSORIZED REGRESSION MODELS

Dependent Variable	Residual Sum of Squares / Degrees of freedom (df_r)	[1] MS_e = Pure Error Sum of Squares / df_e	[2] MS_1 = Lack of Fit Sum of Squares / df_1	[3] F_{lof} = MS_1 / MS_e	$F_{0.05}$ (df_1, 2)
SAGO :					
Winsorized Viscosity	1557369 / 19	201666.667 / 2	1355702.333 / 17	0.791	19.4
Winsorized Solubility	6.32354 / 17	0.231 / 2	6.09254 / 15	3.517	19.4
TAPIOCA :					
Winsorized Solubility	3.97514 / 19	0.297 / 2	3.67814 / 17	1.457	19.4

[1] MS_e = mean square of the pure error.

[2] MS_1 = mean square of the lack-of-fit for the model.

[3] F_{lof} = F value for lack-of-fit for the model.

TABLE 10.
POINTS FLAGGED WITH r_i, h_i, DFITS AND CD_i VALUES FOR THE WINSORIZED EQUATIONS

		Sample	r_i	h_i	DFITS	CD_i
Sago	Viscosity	S3	2.560	0.182	1.206	0.486
		S15	2.001	0.151	0.843	0.237
	Solubility	S22	2.614	0.200	1.306	0.569
Tapioca	Solubility	T5	1.671	0.218	0.883	0.259
		T6	1.677	0.218	0.886	0.261

2 shows the experimental design. When the experimentation was completed, Statgraphics vers. 3.0 was used to draw the contour plot of each response and analysis of variance ANOVA (Snedecor and Cochran 1980) was applied to the data.

Verification

After the main experiment was completed and influential outlying observations in the models had been modified, two more experiments were performed. Conditions for making modified sago and tapioca starches with specific responses were chosen at random after superimposing the respective contour plots. Responses were monitored, and results were compared with model predictions.

RESULTS AND DISCUSSIONS

Modified sago and tapioca starches were made with functional properties similar to those of the commercial starch. Conditions for their preparation are: pH 3.5, 120C, 0.5 g urea and 3 M phosphate. Table 3 compares the functional properties of the starches.

Urea-starch phosphate is characterized by its remarkable viscosity stability, while the viscosity of a native starch paste decreases with time (Table 4).

Fitting the Models

Many predictors can be used in multiple correlation analysis, but only a few receive substantial β weights and the rest of the β's will be near zero (Thorndike

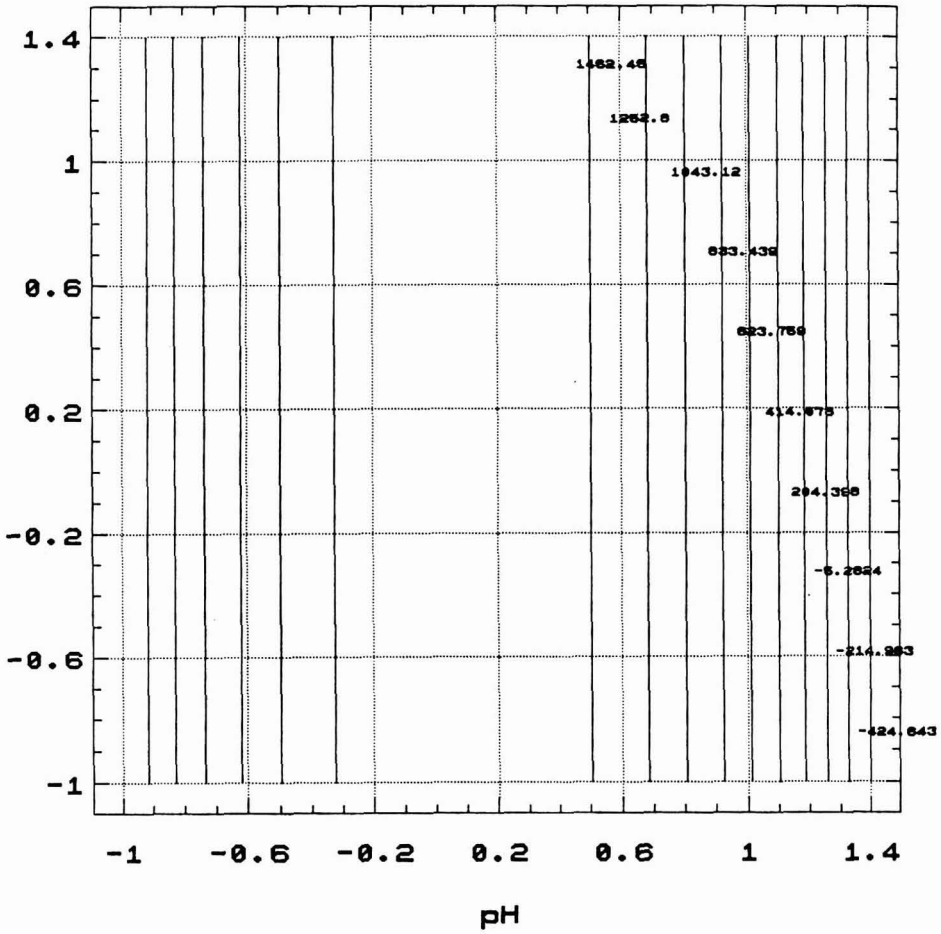


FIG. 2a. CONTOUR PLOT RELATING EFFECT OF pH ON VISCOSITY OF MODIFIED SAGO STARCH
Levels of pH are coded values.

1978). Even when all the independent variables have moderate to large correlations with the criterion, the correlations among the predictors prevent most of them from having much effect on the predictor composite. The use of an optimum subset of the predictors results in simplicity of description as well as a stable, economical regression equation (Thorndike 1978). A smaller number of variables will reduce the possibility of the regression equation reflecting chance relationships (Thorndike 1978).

In this work, the best equation for each response was found using a Step-Up Variable Selection (Draper and Smith 1980). In this method, each variable in

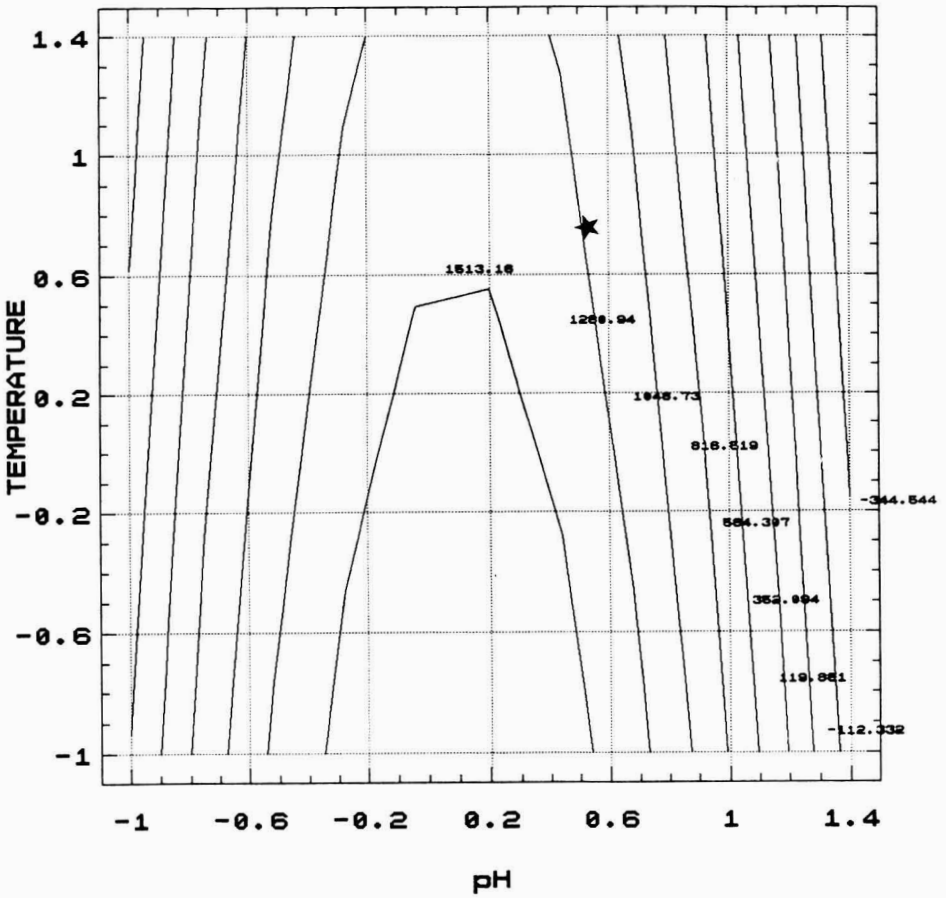


FIG. 2a′. CONTOUR PLOT RELATING EFFECT OF pH AND TEMPERATURE ON VISCOSITY (WINSORIZED) OF MODIFIED SAGO STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.52, temperature 0.74, urea 0 and phosphate 0 to check model for predictive accuracy.

the equation is treated as though it were the most recent variable entered, irrespective of its actual point of entry into the model. Significance of each independent variable in a response is evaluated by its p-value after entering the equation. Significance of a model can be used as an overall measure of attained fit (Thorndike 1978).

All regression equations and their corresponding R^2_a values are given in Tables 5a and 5b.

The residual sum of squares of each regression model was obtained from the ANOVA table. The pure error sum of squares ${}^3\Sigma_{i=1}(y_i - \overline{y})^2$ was calculated

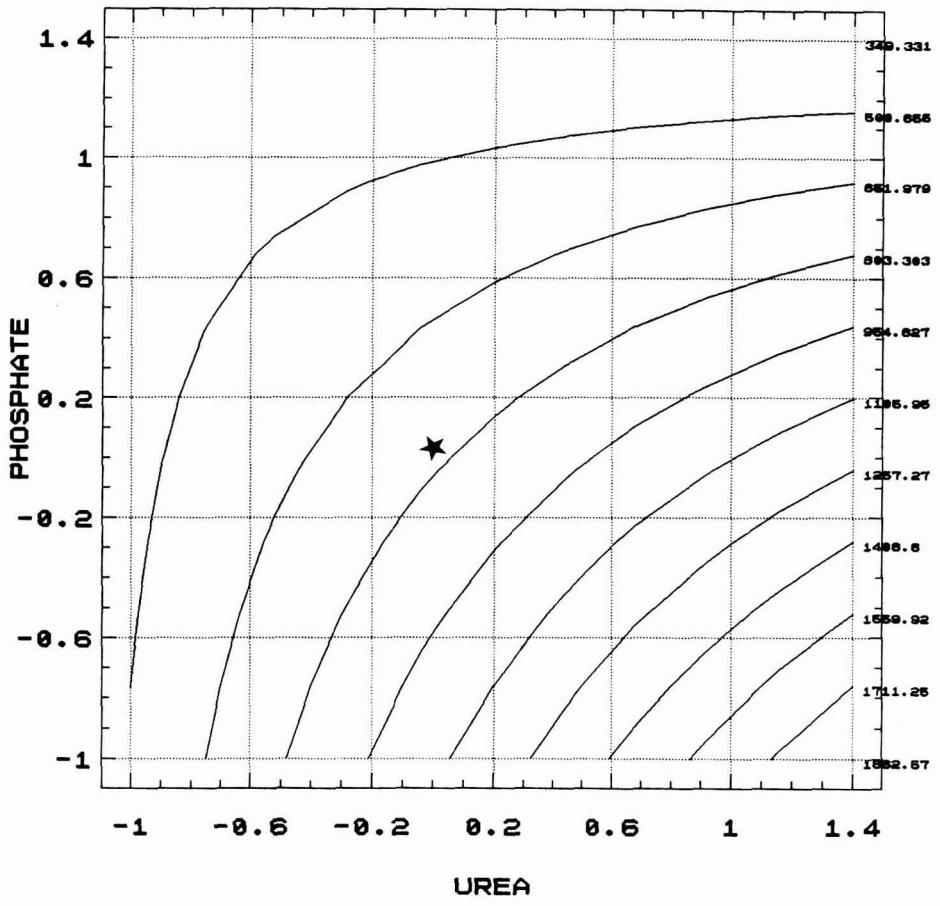


FIG. 2b. CONTOUR PLOT RELATING EFFECTS OF UREA AND PHOSPHATE CONCENTRATIONS ON VISCOSITY OF MODIFIED TAPIOCA STARCHES

Levels of urea and phosphate concentrations are coded values. ★ Sample was made at coded values of pH 0.41, temperature 0.39, urea 0 and phosphate 0.02 to check model for predictive accuracy.

from triplicates of the center point. The difference between these two sums of squares gives the lack-of-fit sum of squares. Refer to Table 6. The F_{1of} values for all models showed that the models gave a good fit [since $F_{1of} < F_{0.05}(df_1,2)$].

Modification of the Models

Residuals were analyzed to check if they were normally distributed. Refer to Fig. 1. Residuals are the differences between observed and the predicted values determined by regression analysis; they help to define the variability not explained

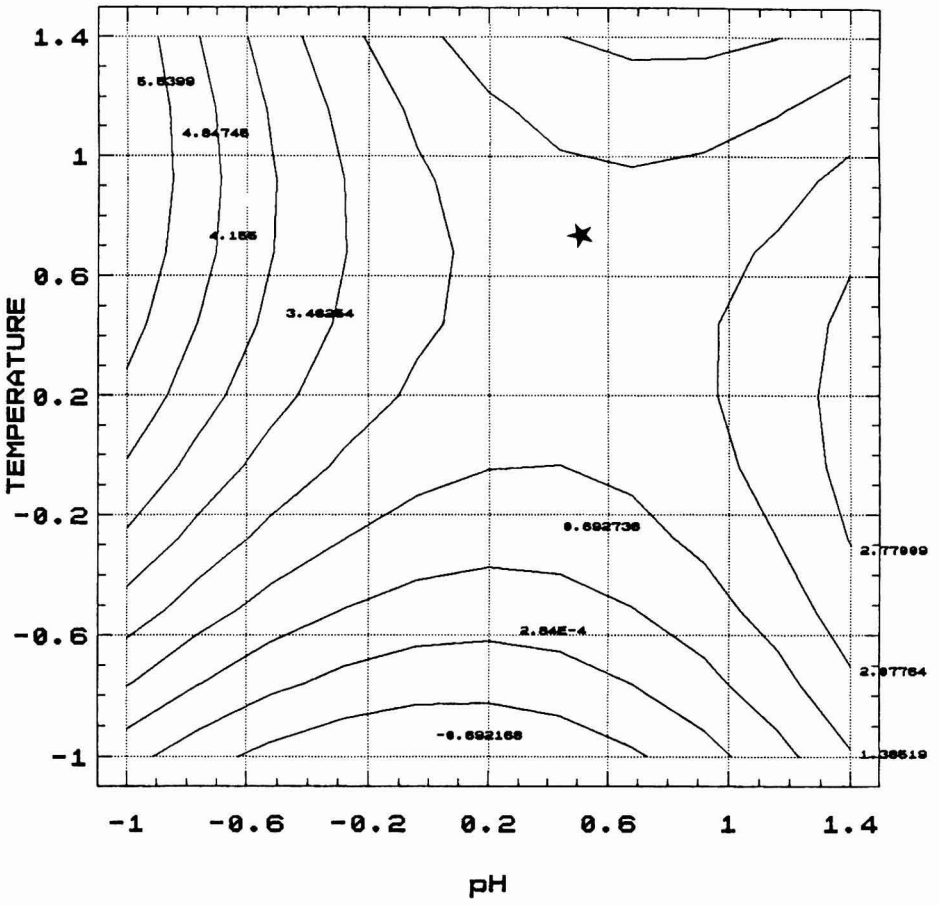


FIG. 3a. CONTOUR PLOT RELATING EFFECTS OF pH AND TEMPERATURE ON SOLUBILITY OF MODIFIED SAGO STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.52, temperature 0.74, urea 0 and phosphate 0 to check model for predictive accuracy.

by the regression equation (Draper and Smith 1980). Plotting residuals against predicted responses showed that plots of the functional properties for sago and tapioca gave normal distributions.

An outlier among residuals is one that is far greater than the rest in absolute value and lies ± 3 standard deviations or more from the mean of the residuals (Draper and Smith 1980). Standardized residuals r_i are residuals divided by their standard errors (Sen and Srivastava 1990):

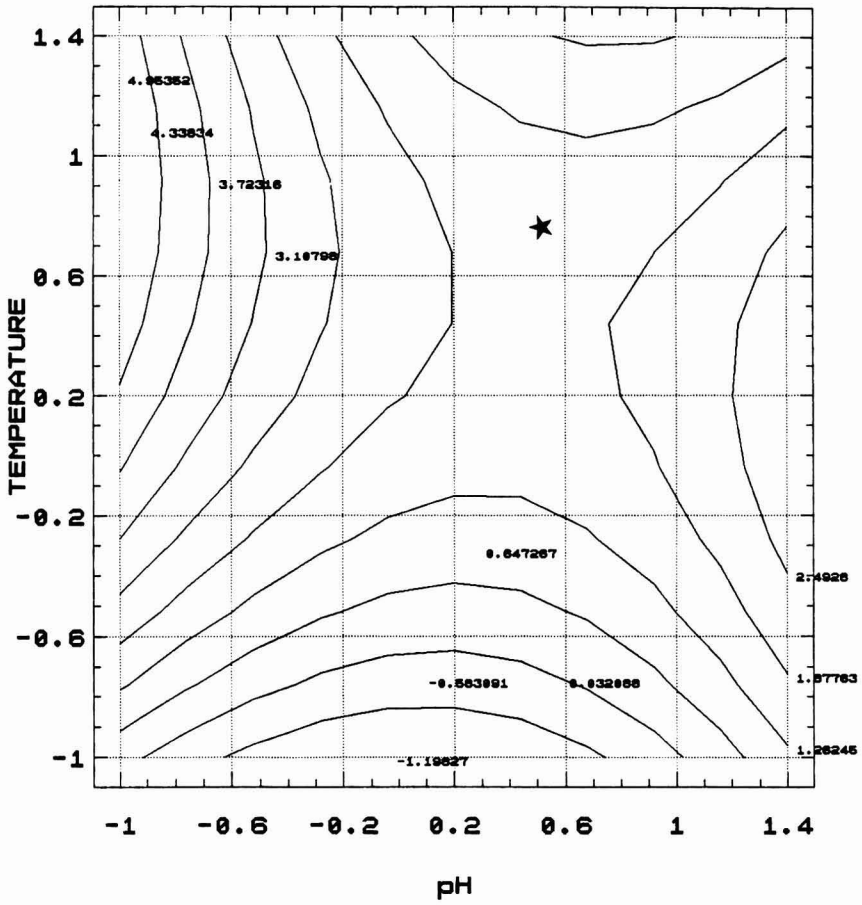


FIG. 3a′. CONTOUR PLOT RELATING EFFECT OF pH AND TEMPERATURE ON SOLUBILITY (WINSORIZED) OF MODIFIED SAGO STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.52, temperature 0.74, urea 0 and phosphate 0 to check model for predictive accuracy.

$$r_i = \frac{e_i}{s\sqrt{(1-h_i)}}$$

Studentized residuals $r_{(-i)}$ can detect outliers on Y and the leverage h_i detects outliers in the space of the predictors. Studentized residuals are the residuals divided by their standard errors after the ith case is deleted (Sen and Srivastava 1990):

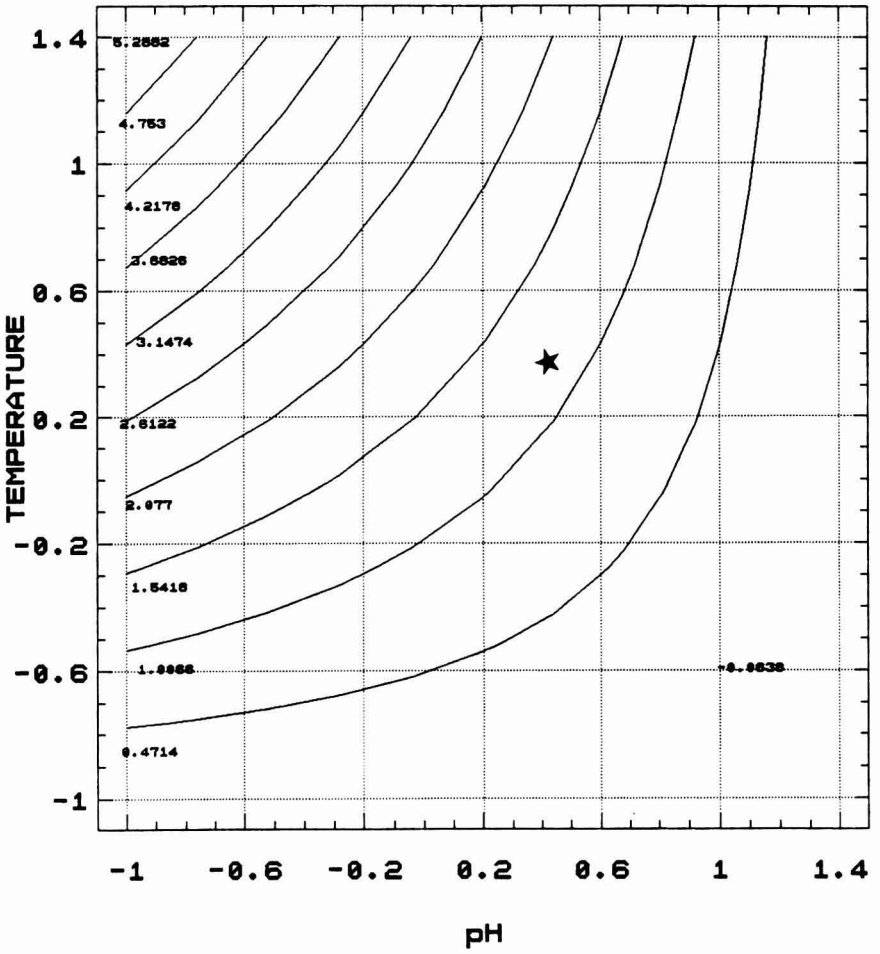


FIG. 3b. CONTOUR PLOT RELATING EFFECTS OF pH AND TEMPERATURE ON SOLUBILITY OF MODIFIED TAPIOCA STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.41, temperature 0.39, urea 0 and phosphate 0.02 to check model for predictive accuracy.

$$r_{(-i)} = \frac{e_i}{s_{(i)}\sqrt{(1-h_i)}}$$

Leverages are diagonal elements of the hat matrix H, which determine predicted values $\hat{y}$, since $\hat{y} = Hy$ (Belsley *et al.* 1980).

The standardized change in fit, DFITS, tells how much the predicted value

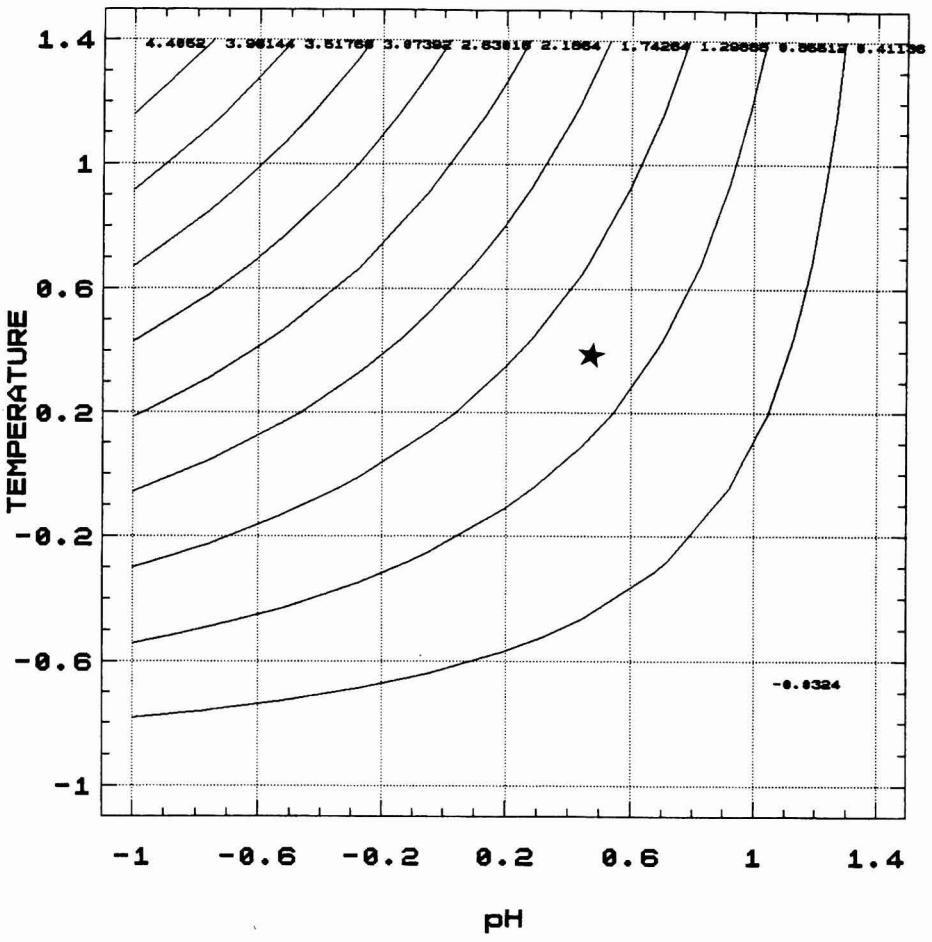


FIG. 3b′. CONTOUR PLOT RELATING EFFECTS OF pH and TEMPERATURE ON SOLUBILITY (WINSORIZED) OF MODIFIED TAPIOCA STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.41, temperature 0.39, urea 0 and phosphate 0.02 to check model for predictive accuracy.

$\hat{y}_i$ at the design point x_i would be affected if the ith case were deleted (Sen and Srivastava 1990):

$$DFITS = r_{(-i)}\sqrt{\frac{h_i}{(1-h_i)}}$$

An observation is flagged if it has a leverage above 2q/n or a DFITS above $2(q/n)^{1/2}$ where q is the number of predictors in the model and n is the number

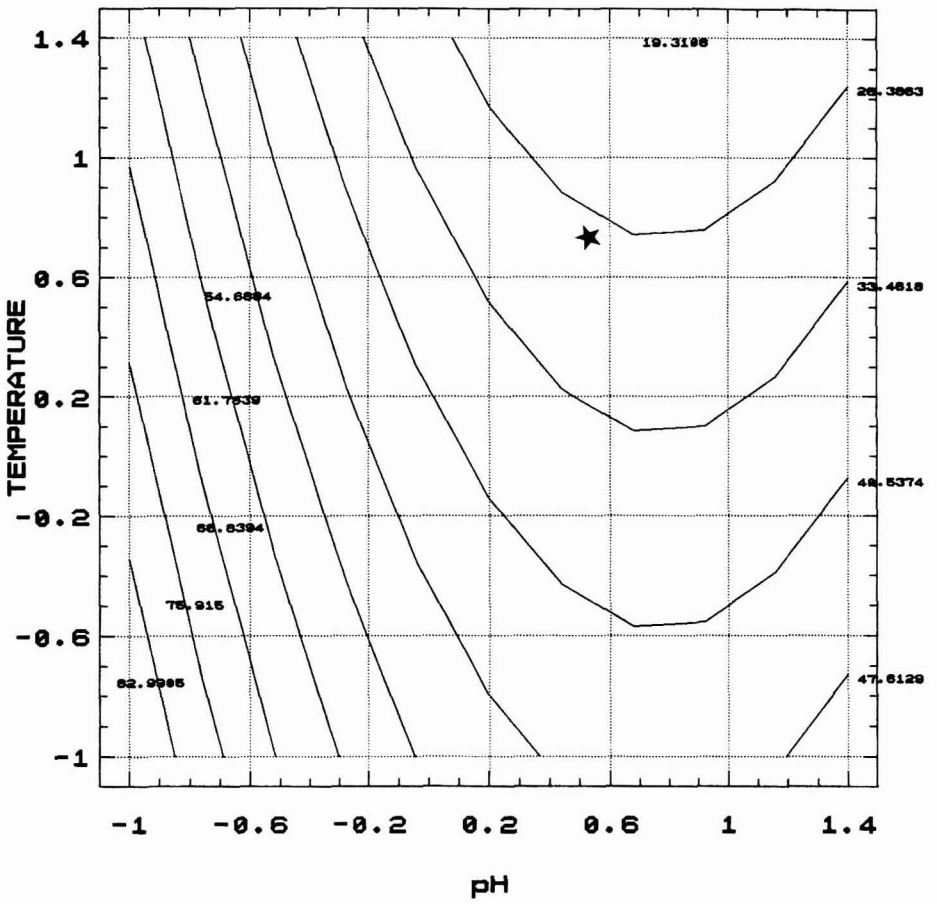


FIG. 4a. CONTOUR PLOT RELATING EFFECTS OF pH AND TEMPERATURE ON CLARITY OF MODIFIED SAGO STARCH

Levels of pH and temperature are coded values. ★ Sample was made at coded values of pH 0.52, temperature 0.74, urea 0 and phosphate 0 to check model for predictive accuracy.

of complete cases (Belsley *et al.* 1980). Large residuals need not be influential points and vice versa. Cook's distance CD_i detects high influence points (Stevens 1984). The two main reasons for identifying outliers are to protect the integrity of the model from the effects of points that do not belong to it and to identify shortcomings in the model.

Points with either leverage or DFITS values above the crucial values were flagged (Tables 7a and 7b). Flagged points were checked to determine if they were high influence points. Influential points have $CD_i > 1$ (Cook and Weisberg 1982):

TABLE 11.
COMPARISON OF PREDICTED AND OBSERVED FUNCTIONAL PROPERTIES OF MODIFIED STARCHES

		Viscosity of 5 % sample at 7.5 s^{-1} (cps)	Solubility of 1 % sample at 25 C (mg/ml)	Clarity of 1 % sample at T_{650}
Sago	Observed	1450	2.50	33.70
	Predicted (original model)	1431.98	2.45	27.64
	Predicted (Winsorized model)	1280.94	2.22	27.64
Tapioca	Observed	839	1.20	52.80
	Predicted (original model)	775.51	1.24	53.96
	Predicted (Winsorized model)	775.51	1.10	53.96

$$CD_i = \frac{h_i \cdot r_i^2}{(q+1)(1-h_i)}$$

Influential outliers were treated to Winsorization (Barnett and Lewis 1978), which enables them to be included in the models in a nondiscordant fashion. Winsorization is the replacement of the lower and upper extreme values by their nearest neighbors, thus making such values appear twice in the data (Barnett and Lewis 1978). Where CD_i (Tables 7a and 7b), the reading for that sample is replaced by the value closest to it. The resulting data is then subjected to Step-Up Variable Selection (Draper and Smith 1980).

Tables 8a and 8b show the Winsorized regression equations for sago and tapioca and their corresponding R^2_a values.

In the case of sago viscosity, B was selected into the regression equation where it was previously not allowed, making q = 2. The resulting Winsorized equation is different from the original while the other Winsorized equations are similar to the original.

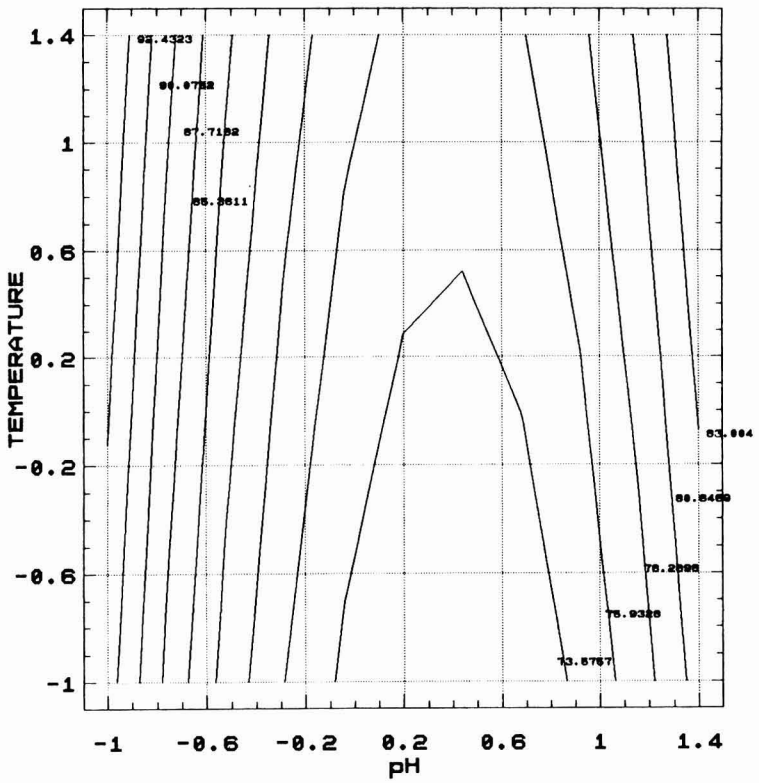
The F_{lof} values for the Winsorized models showed that they gave a good fit (Table 9).

None of the outliers in the Winsorized models were influential points since $CD_i < 1$ (Table 10), and so they were retained in the models.

Verification

In order to check the accuracy of the models for modified sago starch, contour plots for viscosity, solubility and clarify (Fig. 2a, 3a and 4a); and plots for Win-

i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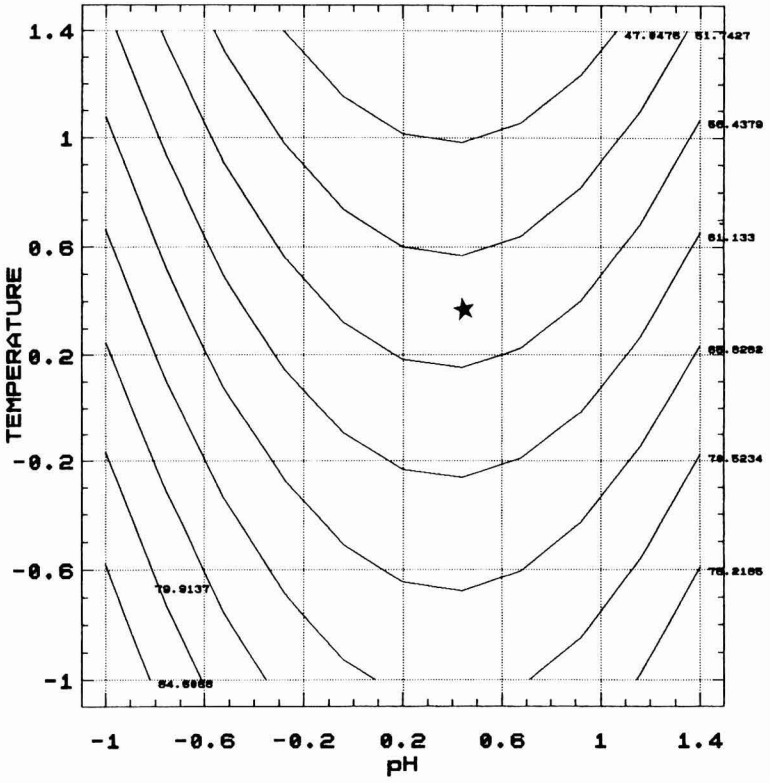
1
0.6
0.2
-0.2
-0.6
-1
-1
-0.6
-0.2
0.2
0.6
1
1.4
93.4323
90.0732
87.7192
85.3611
83.004
80.6469
78.2898
75.9328
73.5757

ii


TEMPERATURE
pH
1.4
1
0.6
0.2
-0.2
-0.6
-1
-1
-0.6
-0.2
0.2
0.6
1
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55.6379
61.133
65.5282
75.5234
79.9137
84.6988

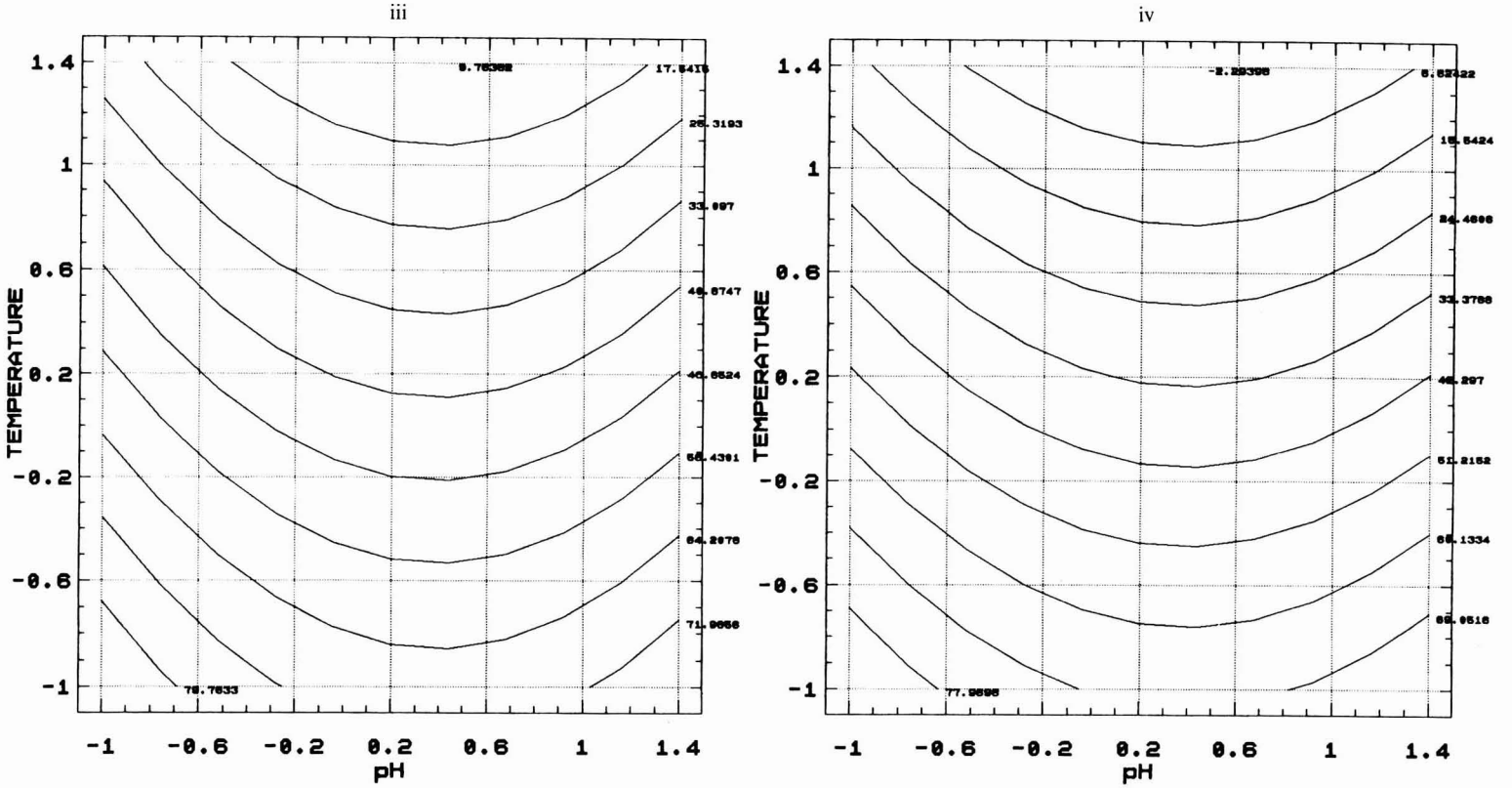

FIG. 4b. CONTOUR PLOT RELATING EFFECTS OF pH AND TEMPERATURE ON CLARITY OF MODIFIED TAPIOCA STARCH

Levels of pH and temperature are coded values. Urea concentration was held constant at (i) 0.5 g, (ii) 3.5 g, (iii) 6.5 g, (iv) 7.61 g.

★ Sample was made at coded values of pH 0.41, temperature 0.39, urea 0 and phosphate 0.02 to check model for predictive accuracy.

sorized viscosity, Winsorized solubility and clarity (Fig. 2a′, 3a′ and 4a) were superimposed. Coded values of pH 0.52, temperature 0.74 were chosen as conditions for making a modified starch. Figures 3a and 3a′ are similar. A coded value, 0, was taken for both urea and phosphate concentrations, these two variables being not significant in the models.

For tapioca, the coded values of urea and phosphate concentrations of 0 and 0.02 were chosen from the contour plot for viscosity (Fig. 2b). The Winsorized solubility and clarity contour plots [see Fig. 3b′ and 4b(ii)] were superimposed to give coded pH and temperature values of 0.41 and 0.39, respectively. Again, Fig. 3b (contour plot for solubility) and Fig. 3b′ are similar.

The actual values may be derived from the coded values (x_i) by the following equation (Floros and Chinnan 1987):

$$x_i = \frac{2(\xi_i - \bar{\xi}_i)}{d_i}$$

where ξ_i = actual value in original units,
$\bar{\xi}_i$ = mean of high and low levels of ξ_i,
d_i = difference between high and low levels of ξ_i.

The actual conditions for making modified sago and tapioca starches respectively are: pH 8.06, 172.2C, 2.5 g urea and 2 M phosphate; and pH 7.73, 154.75C, 2.5 g urea and 2.02 M phosphate.

Table 11 compares predicted (as read of from the contour plots) and observed functional properties of the modified starches.

In general, the observed functional properties agreed well with the predicted values. The original plots of sago viscosity and solubility and tapioca solubility gave better predictions than the Winsorized plots, thus showing that the outliers were not due to experimental error and need not have been modified. The measured tapioca viscosity was somewhat far from the predicted value, perhaps because factors other than phosphate and urea concentrations might be significant in determining the viscosity (R^2_a = 0.424).

CONCLUSIONS

Modified sago and tapioca starches with functional properties similar to the commercial starch were made. The conditions for making these starches are as follow: pH 3.5, 120C, 0.5 g urea and 3 M phosphate.

Contour plots were found to be useful in predicting the functional properties of products made according to the specified conditions. Only in the case of the

viscosity plot for tapioca did the measured value differ significantly from the predicted value, perhaps indicating the significance of other factors not considered in the model, e.g., baking period ($R^2_a = 0.424$).

When the outliers were treated to Winsorization (Barnett and Lewis 1978), R^2_a values improved: for sago viscosity, from 0.718 to 0.806; sago solubility, from 0.819 to 0.884 and tapioca solubility, from 0.741 to 0.895. However, the predictive value of the models decreased, which indicates that the influential outliers were valid observations in the models and not erroneous readings. This latter point is in tandem with the opinion of many authors that outliers should be reported and not discarded (Barnett and Lewis 1978; Stevens 1984; Kleinbaum *et al.* 1987).

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INHIBITION OF THE BROWNING REACTION BY MALTO-DEXTRIN IN FRESHLY GROUND APPLES

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ABSTRACT

Malto-dextrin (DE 10) was able to inhibit the browning reaction in fresh ground apples. The presence of sucrose decreased the inhibitory effect of malto-dextrin. Glucose did not show the inhibitory effect at all. The inhibitory mechanism may involve an unidentified enzymatic reaction(s), which maintains the redox potential at about 320 mv. Potassium ions increased the inhibitory effect of malto-dextrin on the browning reaction, indicating that pyruvate kinase may be involved in this mechanism.

INTRODUCTION

The browning reaction is an undesirable phenomenon in apple processing; however, a small degree of color development is desirable in the production of apple juice. There are several mechanisms that inhibit browning reaction (Macheeix *et al.* 1990). Chloride ions (Taeufel and Voigt 1964) inhibit the activity of phenol oxidase, and amino acids react with phenol compounds. It has not been reported that malto-dextrin has an inhibitory effect in freshly ground apples. The purpose of this report is to quantify the inhibitory effect of malto-dextrin on the browning reaction and survey general information concerning these phenomena. The effects of calcium, sodium, and potassium ions were studied, and the effects of sucrose and glucose on the inhibitory action were compared with malto-dextrin.

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MATERIALS AND METHODS

Materials

Banana (Chiquita, at stage 2) and apples (Golden Delicious and Red Delicious) were purchased from a local grocery during the months of June to August and the months of October to December. Malto-dextrin (Malto dextrin 100, DE 10) was obtained from Grain Processing Company, Muscatine, Iowa. Potassium chloride, calcium chloride, sodium chloride, glucose, and sucrose were purchased from Fisher Chemical Company.

Methods

In order to minimize browning color formation during the sample preparations, only four apples (about 450 g) were used in each sample preparation, and they were processed rapidly. Four replicates were prepared for each sample. The four apples were peeled, decored, cut into 1-in. cubes and then immediately dipped in 1 L of sodium chloride solution (0.15M) at an ambient temperature. As soon as all four apples were processed (about 2 min), the apple cubes were removed from the sodium chloride solutions and rinsed with 2 L of distilled water to remove salt solution from the surface. The apple cubes were then blended in a Waring blender (Model 31BL91), at the lowest speed for 1 min and then at the highest speed for 25 s. Before the blending started, appropriate amounts of starch (0–200 g) were added to the samples. One control sample was prepared without the addition of starch. The blended apples were then transferred to a beaker and covered with parafilm. At each time period, a portion of the sample was placed into a suction flask, and the flask was subjected to vacuum to remove air with an aspirator for 5 min. The vacuumed sample was then placed into a sample holder of colorimeter. Values of L, a, and b were measured with a Hunter color/difference meter (model D25-2 optical head). To eliminate the possibility that malto-dextrin might lighten the sample, malto-dextrin was added to the browned sample, and the samples were measured with the colorimeter.

The pH value of each sample was monitored throughout the entire experiment. Viscosity was measured by a digital Brookfield viscosity meter (model D, V.A.C. 115, spindle No. 1) at 6, 12, 30 and 60 RPM. Relative electromotive potentials were monitored by a pH meter with an Orion redox electrode.

To compare the effects of sucrose and glucose on the inhibition of browning reactions, samples were prepared the same way as described above, except that 150 g of sucrose or glucose were added to the samples instead of malto-dextrin.

The effects of calcium, potassium, and magnesium ions were studied by adding their chloride salt (0.3 N) to the samples along with malto-dextrin.

For microscopic examinations, samples were smeared with a cover glass with illumination from the bottom.

In another experiment, the color development in juice was monitored by measuring the change of optical density at 420 nm. Samples were deaerated by a vacuum (100 mm Hg for 5 min) and centrifuged at 13,800 × g for 20 min at 4C. The supernatant was diluted 10 times with distilled water. A portion of the sample was placed in a cuvette for measuring.

RESULTS AND DISCUSSION

Visual Observation

In samples containing no malto-dextrin, the color became dark brown after 1 h. An inhibitory effect occurred when 50 g of malto-dextrin were added to 400 g of ground apple. When more than 150 g of malto-dextrin were added, the ground apple maintained a light color overnight at an ambient temperature. Eventually the apple turned as dark as the controls. Malto-dextrin was added to the browned sample, and it did not change the color readings. This indicates that maintenance of a light color was not due to a dilution effect of malto-dextrin.

Effect of Malto-Dextrin Concentration on the Inhibition of Browning Reaction

The development of the browning color was monitored by measuring L, a, and b values with a Hunter colorimeter. The effects of the malto-dextrin on the L, a, b values are shown in Fig. 1–3. Here the values represent the average reading from four samples. It was noticed that the initial readings of these values were not identical for each sample. Addition of malto-dextrin decreased the initial readings of L and b values due to a decrease of apple density. The increases of the sample volume by the addition of malto-dextrin is shown in Fig. 4.

In order to quantify the effect of malto-dextrin on the browning reaction, changes of chromaticity of each sample were plotted against time. Figure 5 shows that the inhibitory effect of malto-dextrin on browning reaction is a function of the malto-dextrin concentration. Unfortunately, these methods failed to quantify the inhibitory effect of malto-dextrin on the browning reaction in banana and Red Delicious apples, both rapidly formed a pink color, which is derived from xanthocyanates and interfered with the measurements of browning color formation.

Another method to analyze color formation is to plot logarithm of L values against time. L values were corrected for volume change. The slopes of these

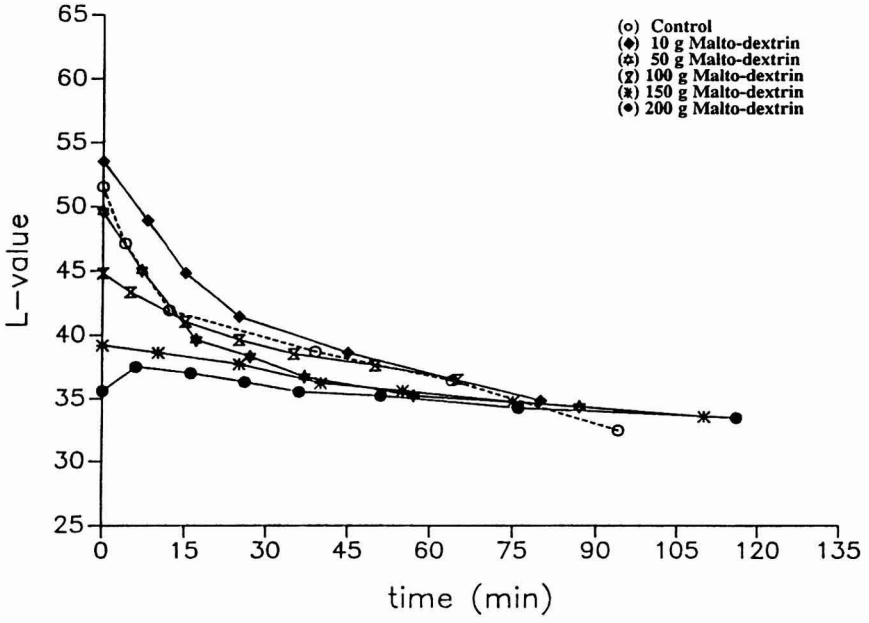

FIG. 1. CHANGES OF "L" VALUE OF GROUND APPLE

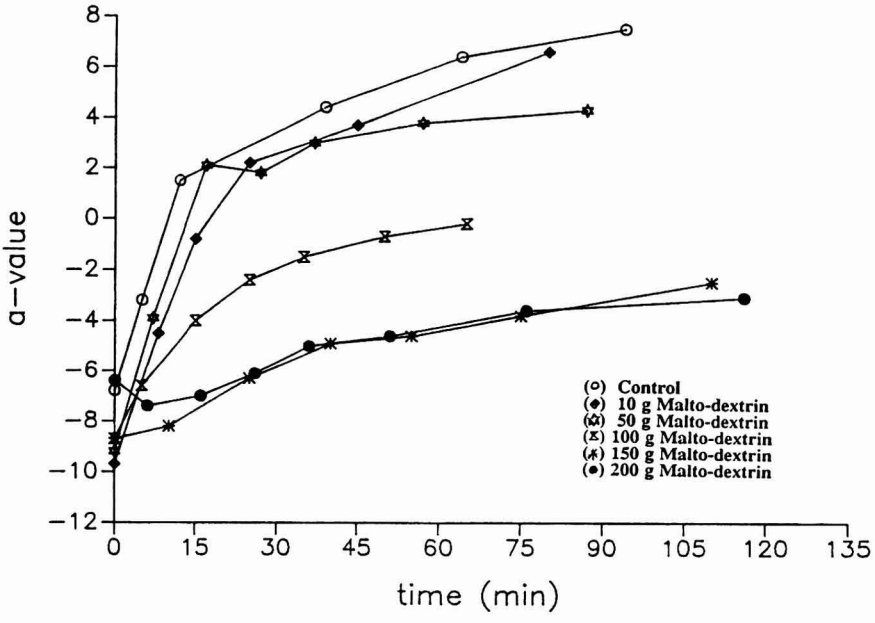

FIG. 2. CHANGES OF "a" VALUE OF GROUND APPLE

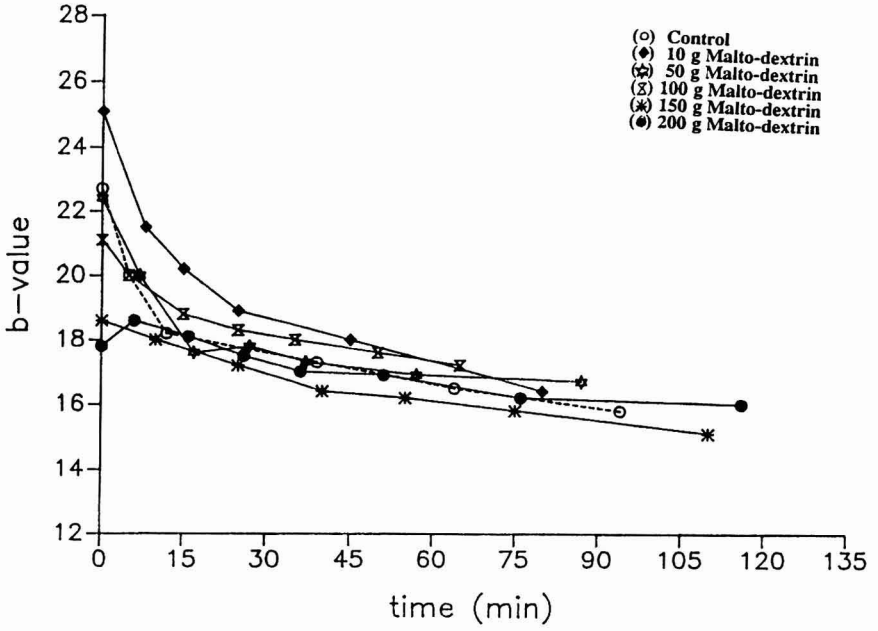

FIG. 3. CHANGES OF "b" VALUE OF GROUND APPLE

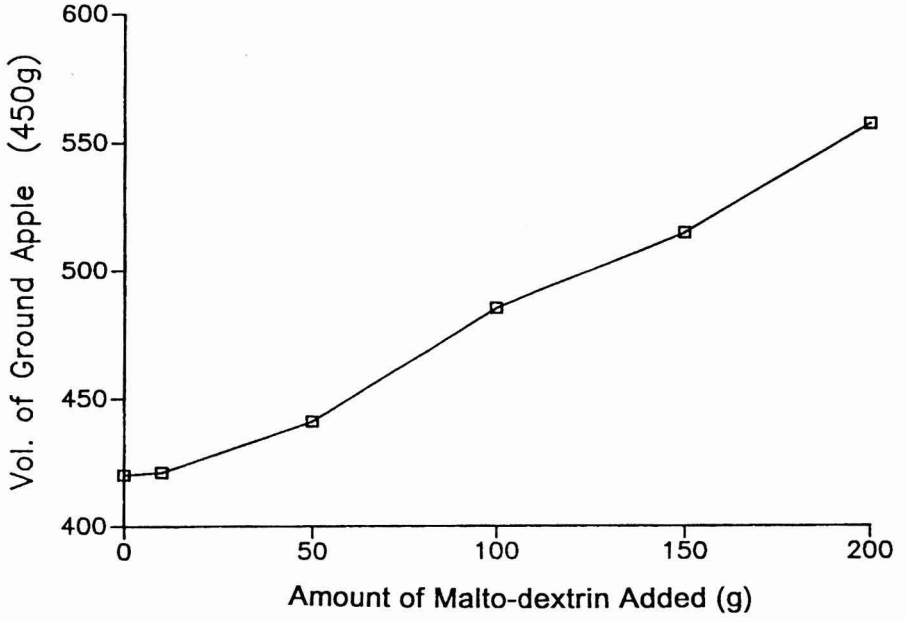

FIG. 4. VOLUME CHANGES IN GROUND APPLE AS A FUNCTION OF THE AMOUNT OF MALTO-DEXTRIN IN THE SAMPLES

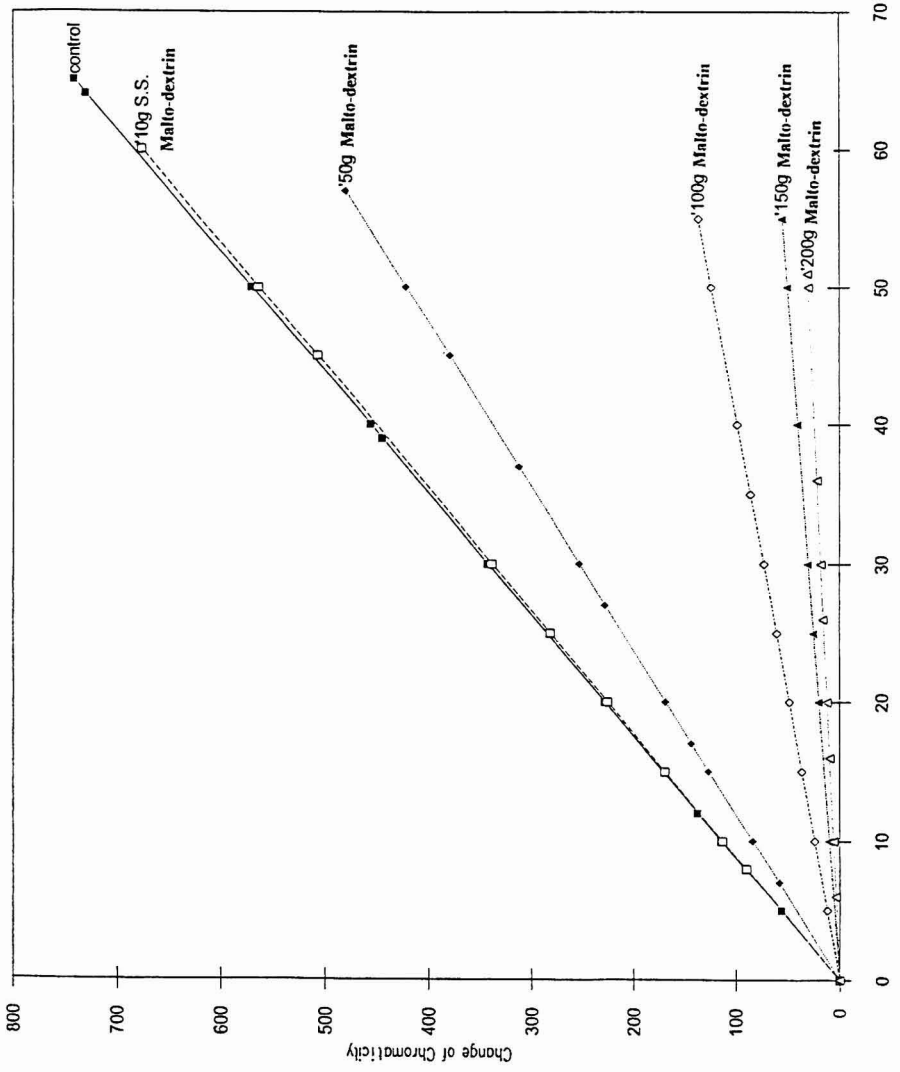

FIG. 5. EFFECT OF MALTO-DEXTRIN CONCENTRATION ON THE CHANGE OF CHROMATICITY

plots were then plotted against the amount of malto-dextrin added to the samples (Fig. 6). Values of "a" were plotted against time to obtain initial reaction rates. When these initial rates of "a" values were plotted against the amounts of malto-dextrin, a result similar to the "L" plots was observed (Fig. 7). The slopes of the "L" plots represent the rate of darkening of the apple sample, and the slopes of the "a" plots represent the formation of red color. Figure 6 and 7 have the same pattern, and it indicates that darkening of the apple is due to the formation of red color.

As shown in Fig. 8 and 9, additions of glucose and sucrose did not have the same inhibitory effect as malto-dextrin.

Effect of Storage Time of Apple on the Inhibitions of Browning Reaction

It was visually observed that apples purchased in December through February turned brown slower than those purchased from June to August. As the storage time for apples increased, ground apples turned brown faster than the freshly harvested apples, and the inhibition of browning by malto-dextrin became more

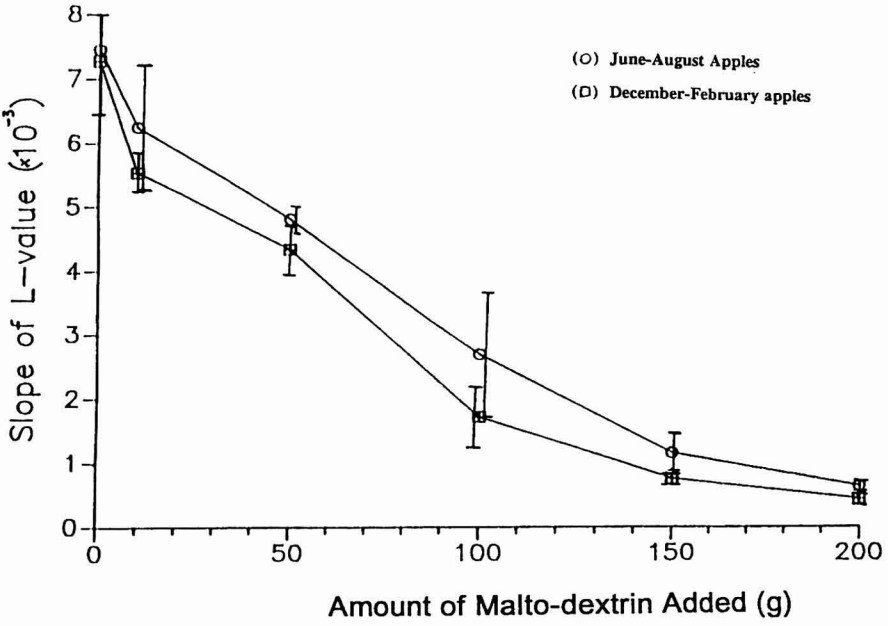

FIG. 6. SLOPES OF log(L)/TIME PLOT VS AMOUNT OF MALTO-DEXTRIN IN 450 g OF GROUND APPLE
Vertical bars represent standard deviations.

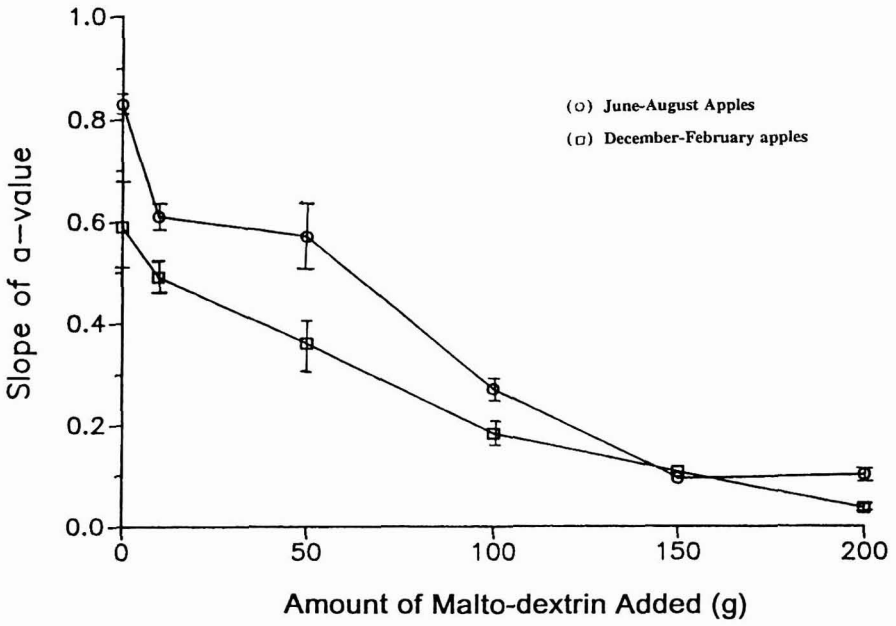

FIG. 7. SLOPES OF "a"/TIME PLOT VS AMOUNT OF MALTO-DEXTRIN IN 450 g OF GROUND APPLE
Vertical bars represent standard deviations.

significant. In the "L" plot and "a" plot, apples purchased in December through February had smaller slopes than that of apples purchased in June through August (Fig. 6 and 7). It was reported that during the ripening of apples, an increasing proportion of phenol oxidase was found in the soluble fraction in the cells. This apparent release of phenol oxidase may be due to fragmentation of the membrane during ripening (Butt 1980). If this is true, the inhibitory effect of malto-dextrin should be related to the reduction of the enzyme activity of phenol oxidase in the juice fraction.

pH Values

The optimal pH for phenol oxidase ranges from 5.0 to 6.5 (Sataque and Wosiacki 1987; Kahn 1977; Chung *et al.* 1984). In all the apple samples, pH values fluctuated in a range between 3.0 to 3.4. Addition of malto-dextrin did not cause any change of pH; therefore, the reduction of phenol oxidase activity was not due to the change of pH. Since pH values were maintained at the same level, the electo-potential differences measured by the pH electrode could be used as

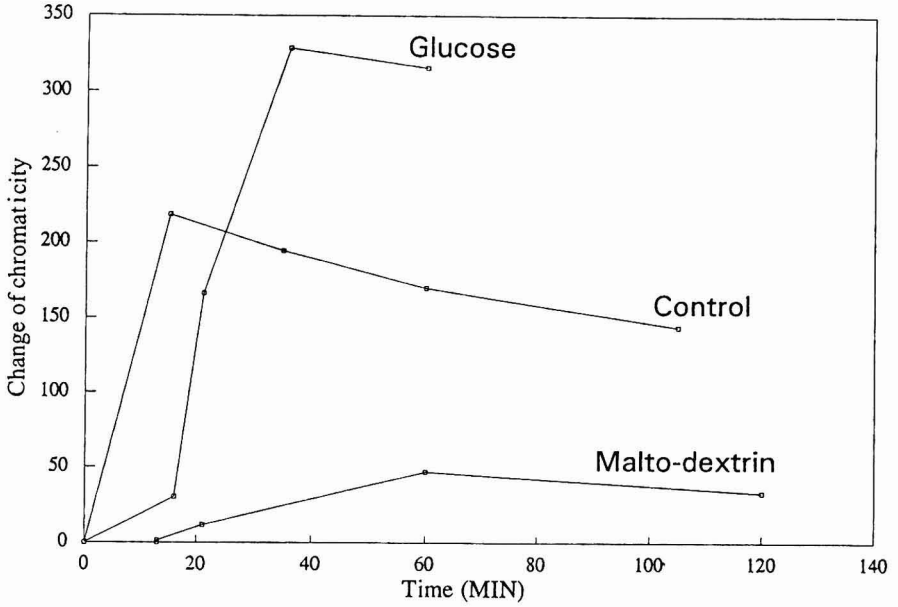

FIG. 8. EFFECT OF GLUCOSE ON THE CHANGE OF CHROMATICITY OF GROUND APPLES

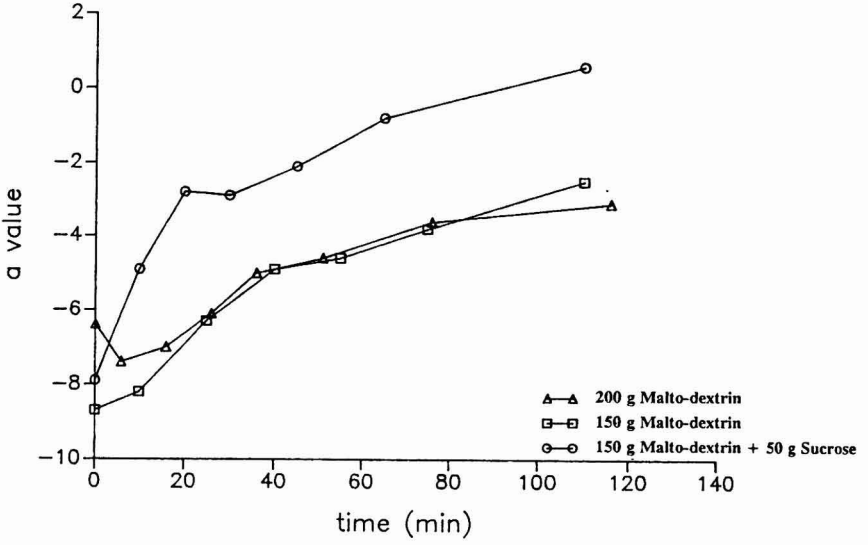

FIG. 9. EFFECT OF SUCROSE ON THE BROWNING OF GROUND APPLES

an indicator for the changes of redox potentials in the samples during the experiments. It was found that during the entire experiment, the redox-potential reading of the sample containing malto-dextrin were maintained at 320 mv, and the redox-potential of the control samples rapidly increased to and remained at 370 mv.

Effect of Salts on the Browning Reaction in the Presence of Malto-Dextrin

When the apple samples contained more than 150 g of malto-dextrin, addition of sodium and calcium chloride did not affect the inhibitory ability of malto-dextrin; however, addition of potassium chloride to ground apple further reduced browning (Fig. 10). If enzyme activity is involved, this enzyme system may need potassium ion. In the glucose metabolic pathway, pyruvate kinase is the only enzyme requiring potassium ion as a cofactor. The involvement of this enzyme in the inhibitory mechanism needs to be studied further.

Effect of Viscosity

Sucrose (60% w/w) has been used to prevent browning reactions (Sataque and Wosiacki 1987). It is believed that sucrose at this concentration provides a viscous

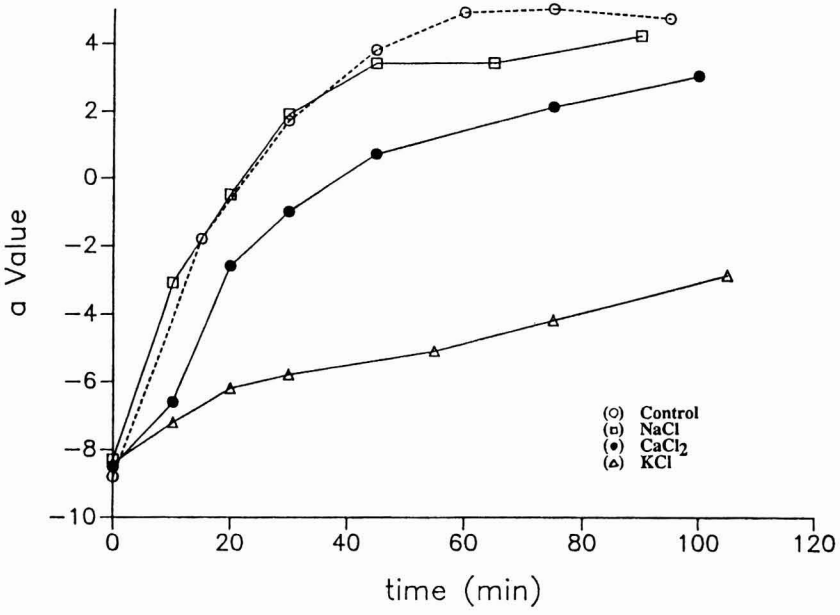

FIG. 10. EFFECT OF CATIONS ON THE BROWNING OF GROUND APPLES

barrier (58 cps) for oxygen to penetrate (Karel *et al.* 1975). This phenomenon probably cannot apply to malto-dextrin because the viscosity of the malto-dextrin, at a concentration of 150 g malto-dextrin per 400 ml of apple juice, was 16 cps. When a sucrose solution of 16 cps (50% w/w) was added to the fresh ground apple, no inhibitory effect was observed. Furthermore, as shown in Fig. 9, addition of sucrose into samples containing malto-dextrin increased the rate of the browning reaction.

Mechanism of Inhibition

Several postulations can be made to explain this inhibitory effect. When cells are ruptured, phenolic compounds or phenol oxidase were separated or absorbed by the malto-dextrin, and thus inhibiting the oxidation reaction. It was reported that phenol oxidase exists in chloroplast and mitochondria of apple fruit (Mayer *et al.* 1964; Harel *et al.* 1965), and most of the phenolic compounds are stored in the vacuoles of the cell (Saigo and Saigo 1983). Microscopic examination of the samples indicated that all of these organelles were ruptured, and there were only small vesicles visible. Possibly, in the presence of malto-dextrin, phenol oxidase may remain to be adsorbed on the membranes and phenolic compounds may remain insoluble. In either case the browning reactions were inhibited. Similar to the phenomenon that when the plant leaf cells were ruptured in a nonisotonic solution, chlorophyll was entrapped in the phospholipid vesicles; malto-dextrin may help phospholipids to form vesicles to entrap phenol oxidase or phenolic compounds. It was not clear whether the enzyme was adsorbed on the membranes or trapped in the vesicles; however, microscopic examination showed that the samples containing malto-dextrin developed distinct yellow spots, while the control sample had a wide spread smear of dark yellow color. This indicates that either enzyme or oxidation products of browning reaction were localized.

The color development in juice showed that juice containing malto-dextrin had a higher optical density (0.46) than that of the control sample (0.32). The differences of optical absorbency in the juice fraction of all samples were within 10% in 6 h; however, the solid fraction turned dark as time elapsed. Obviously, pigment was adsorbed by the solid fraction.

To examine the possibility of enzyme involvement, it was observed that malto-dextrin alone did not inhibit the browning reaction in banana puree, but addition of unheated apple juice containing malto-dextrin was able to slow down the change of L value (Fig. 11). This indicated that unheated apple juice contained an enzyme system that reacted with malto-dextrin, and the product(s) of this enzymatic reaction is then involved in the inhibition of the browning reaction. It was suggested that glucose is utilized by other enzymes to generate NADH or NADPH, which reduces quinone and thus prevents the formation of brown pigments (Butt

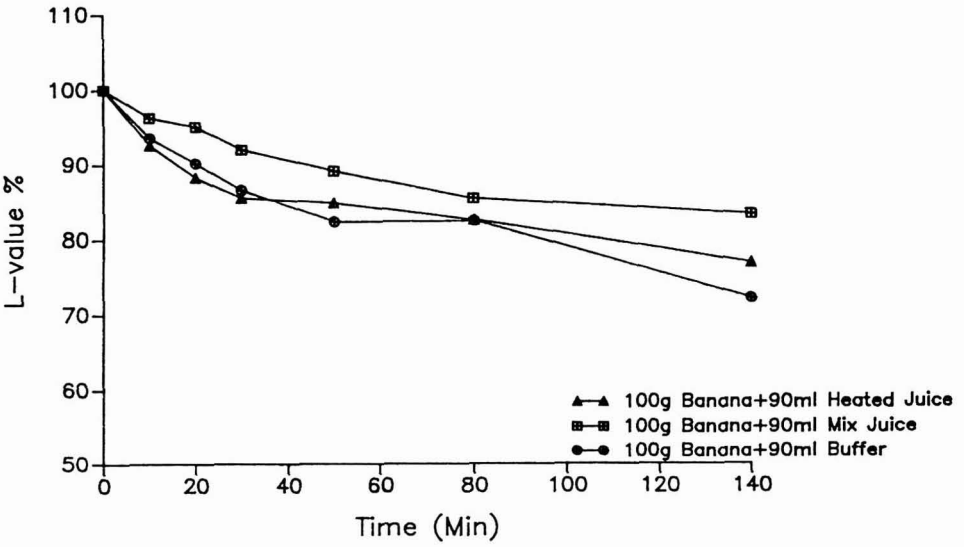

FIG. 11. COMPARISON OF THE INHIBITORY EFFECT BY UNHEATED APPLE JUICE AND HEATED JUICE ON THE BROWNING REACTION OF BANANA PUREE

1980). Quinones are intermediates of the browning reaction. Maintenance of a lower reduction-oxidation potential in the sample containing malto-dextrin provides indirect evidence of this mechanism. Malto-dextrin provides a low level of glucose (about 60 mg/100 ml) in solution through hydrolysis by glucoamylase. Addition of a large quantity of glucose to ground apple reduced water activity to 0.82. At this level, most of the enzymatic activities in the system are impaired.

CONCLUSION

Malto-dextrin can inhibit browning reaction in fresh ground apple. The mechanism may involve localization of phenol oxidase, or it may involve an enzyme system that maintains a low redox potential in ground apples.

The amount of malto-dextrin added to the sample to inhibit the browning reaction was too large for commercial processing of apples, but once the mechanism of inhibition is known, the requirement of malto-dextrin may be reduced to a level that becomes practical in processing apples and other produce.

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THERMAL EXTRUSION AND ALKALI PROCESSING OF DRY BEANS (*PHASEOLUS VULGARIS* L.)

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ABSTRACT

Dry beans are an important source of protein but contain antinutritional factors. An important antinutrient is phytohemagglutinin (PHA), a heat-labile lectin known to depress the nutritional quality of dry beans. This work was undertaken to evaluate the utility of two processes that may aid in the inactivation of PHA, extrusion and cooking in a high pH medium. Extrusion was found to be relatively ineffective in reducing the activity of PHA of whole red kidney or black beans. Extrusion was more effective but highly variable in reducing the PHA activity of bean flours (25–80%). However, soaking and cooking beans at high pH was very effective, significantly reducing the activity of PHA and also reducing the time required to reach a palatable texture. Soaking and cooking dry beans at high pH also caused significant changes in the saline soluble protein extract as determined by gel electrophoresis. High pH cooking treatment may be useful in improving nutritional quality of dry beans.

INTRODUCTION

Dry beans (*Phaseolus vulgaris* L.) are an important source of protein and other nutrients. Although generally deficient in the sulfur-containing amino acids, beans

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supply lysine and are used to complement cereal grains in vegetable-based diets. A major drawback to bean consumption is relatively low digestibility compared to animal proteins (Paredes-Lopez *et al.* 1989; Wolzak *et al.* 1981a,b; Gomez Brenes *et al.* 1975). Another drawback is the presence of antinutritional components and enzyme inhibitors in dry beans (Liener 1976, 1978).

Many processing operations can improve the nutritional quality of *P. vulgaris* varieties for human consumption. Dry bean digestibility can be substantially improved by heating for 10–20 min at 121C (Gomez-Brenes *et al.* 1975). The effect of thermal processing on the antinutritional characteristics is well-recognized (Bender and Reaidi 1982; Kakadi and Evans 1965). The inactivation of dry bean lectins improves the protein quality of dry beans for animals (Jaffe and Hanning 1965; Jaffe and Vega Lette 1968; Jayne-Williams and Burgess 1974). The thermal inactivation of lectins is known (Thompson *et al.* 1983; Coffey *et al.* 1985; Dhurander and Chang 1990). Paredes-Lopez *et al.* (1989) reported the thermal inactivation of hemagglutinating activity of normal and genetically improved common bean varieties. A kinetic model was developed that demonstrated the rate of reduction in hemagglutinating activity of the improved cultivar differed from the normal cultivar only by the temperature constant.

Reddy *et al.* (1979) demonstrated that the nutritive value of dry beans was improved by gamma irradiation. El-Hag *et al.* (1978) found that sprouting increased the digestibility coefficient from 29.5% in raw to 66.4% in cooked red kidney bean. Nielsen and Liener (1984) investigated the degradation of the G1 storage proteins during germination. Chen *et al.* (1977) reported that the hemagglutinating activity of a number of germinating pea and bean seeds decreased to generally less than 10% of the concentration in the ungerminated dry seed.

Alkali, used for centuries in the preparation of corn in indigenous Indian diets, improves lysine availability and therefore improes the protein quality of the diet. According to Coffey *et al.* (1992), alkali treatment of dry beans may be a possible approach for improving the protein quality of beans. However, the alkaline treatment would increase the protein quality primarily by increasing the destruction of phytohemagglutinin in legumes. Little is presently known of the effect of alkali on the quality and processing characteristics of cooked beans.

The per capita consumption of dry beans is decreasing in the United States and is presently approximately 6.8 lb/person/year (The Food Institute 1992). However, interest in ethnic cuisine, especially Mexican, is increasing. The increased popularity of Mexican cuisine may provide an outlet for expanded use of new bean-based products or ingredients providing opportunities for processing beans in novel ways, such as extrusion. However, little information is available on the effect of extrusion cooking on the antinutrients of dry beans.

In this study, the effect of extrusion and alkaline soaking and cooking conditions on the hemagglutinating activity, protein characteristics and texture of dry beans (*P. vulgaris*) was investigated.

MATERIALS AND METHODS

Bean Preparation

Bean Types. The dry beans (*P. vulgaris* L.) used in this study were dark red kidney (Montcalm cultivar), black turtle soup type (Domino cultivar) and pinto (Oletha cultivar). Materials were obtained from Michigan Foundation Seed, East Lansing, MI as certified seed and ranged from 14–16% moisture.

Extrusion. Dry beans were prepared for extrusion in either of two ways: (1) by cleaning and separating the whole seeds; or (2) by grinding the cleaned seeds in a Fitzpatrick mill (Model D Comminuting Machine, Fitzpatrick Co., Chicago, IL) to produce a 50 mesh flour. Whole beans and bean flours were introduced to a Creusot-Loire (Model 2000) commercial extruder and processed at barrel pressures ranging from 500 to 1200 psi, barrel temperatures from 124 to 200C, water feed rate from 9 to 20 ml/min and final product temperature from 116 to 193C. The parameters and product characteristics for each process campaign are presented in Table 1.

High pH Soaking and Cooking. Kidney beans were soaked overnight in physiological buffered saline (PBS) at pH 7.0 and in PBS adjusted to pH 12.0 with sodium hydroxide (beans: soak media, 1:5, W/V). The soaking media was monitored and adjusted as necessary with sodium hydroxide solution to maintain pH 12.0. Following the soak, containers with the beans were placed in water baths at 76 and 93C. At 2, 4 and 8 h intervals, bean samples were withdrawn, cooled immediately, and a saline extract produced. The extracts were then assayed for hemagglutinating activity (Coffey *et al.* 1985). Additional bean samples were simultaneously withdrawn and evaluated for texture.

Hemagglutinating Activity

The method of Coffey *et al.* (1985) was used to determine hemagglutinating activity (HA) in this study. Analyses were performed in triplicate with duplicate determinations. Purified phytohemagglutinin (PHAP) was obtained from Sigma Chemical Co. (St. Louis, MO) and used as a standard.

Bean Texture

The texture of the cooked beans were determined objectively by shearing a 100 g portion of the cooked beans in a Kramer Shear Press (Model TR3 Texturecorder, Food Technology Corp., Rockville, MD) equipped with a 3000 lb transducer and a number C-15 standard multi-blade shear compression cell. Shear peak heights indicating maximum force to shear cooked beans were recorded and expressed as lbs force/100 g bean.

TABLE 1.
SELECTED EXTRUSION PROCESS PARAMETERS AND PRODUCT CHARACTERISTICS FOR EXTRUDED DRY BEAN PRODUCTS

Process Campaign	Water Feed ml/min	Barrel Temp. C	Product Pressure psig	Product Temp. C
		Kidney Bean Flour		
1	20	124	1200	116
2	20	146	1000	126
3	20	150	900	133
4	20	155	800	146
5	15	165	950	149
6	12	175	500	171
7	12	175	500	182
		Black Bean Flour		
8	20	100	500	149
9	12	190	570	177
10	12	200	900	182
		Whole Kidney Beans		
11	20	150	1000	149
12	12	185	800	160
13	9	200	700	171
14	12	200	1000	182
		Whole Black Beans		
15	20	190	900	171
16	10	195	1000	184
		Whole Kidney Beans		
17	10	195	1100	189
18	20	140	1200	177

Electrophoretic Separations

Sodium Dodecyl Sulphate Polyacrylamide Gel Electrophoresis (SDS-PAGE) was performed to resolve the component peptides using the method of Weber and Osborne (1969). Arcylamide gel (10%) was allowed to polymerize in tubes for 24 h before use. The tubes were subjected to 3 mA/tube for 10 min followed by 8 mA/tube for the remainder of the separation. Staining was accomplished

by holding overnight in 0.04% Coomassie Brillian Blue G-250 in 3.5% perchloric acid. Gels were destained and preserved in 7% acetic acid. Relative mobility (Rm) for each band was determined. Molecular weight standards used were: phosphorylase B (94,000), bovine serum albumin (67,000), ovalbumin (43,000), carbonic anhydrase (30,000), soybean trypsin inhibitor (20,000), and alpha-lactalbumin (14,400) (Sigma Chemical Co., St. Louis, MO).

RESULTS AND DISCUSSION

Extrusion

Figure 1 presents the hemagglutinating activity of exturded dry bean products. Extrusion of whole beans resulted in significant inactivation of hemagglutinating activity. Based on a comparison with control (raw beans), whole extruded kidney and black beans retain 82–88% of the original activity of approximately the concentration in unheated whole Montcalm and Domino cultivars (Coffey 1985). Extrusion resulted in no significant difference in hemagglutinating activity between whole kidney and black beans. Pinto beans, which contain relatively low concentrations of lectins, were incorporated in this study for comparative purposes and had significantly less activity (24–26%) than Black or Kidney beans.

The extrudates of whole beans produced under the conditions employed in this study (150–185C, 700–1200 psi) showed the presence of uncooked cotyledon particles and analysis demonstrated limited reduction of HA. The extrusion processing

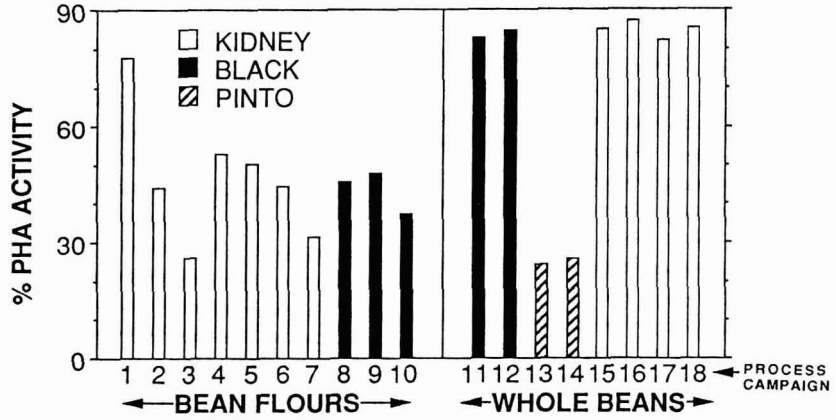

FIG. 1. HEMAGGLUTINATING ACTIVITY OF EXTRUDED BEAN PRODUCTS PRODUCED UNDER DIFFERENT CONDITIONS (PROCESS CAMPAIGNS 1–18) DESCRIBED IN TABLE 1

conditions used were not effective for reducing hemagglutinating activity of whole beans.

Alterations in processing parameters caused considerable variation in hemagglutinating activity in extruded bean flours. No consistent trends were observed with the hemagglutinating activity and barrel temperature, barrel pressure, water feed rate or final product temperature in this experiment. There was also no correlation between hemagglutinating activity and electrophoretic patterns in extruded products (data not shown).

Alkaline Soaking and Cooking

Hemagglutinating Activity. Significant reductions in the HA of purified phytohemagglutinin occur during high pH treatments (Coffey *et al.* 1992). Temperature, pH and cooking time had a significant effect ($p > 0.01$) on hemagglutinating activity in kidney beans. Beans soaked and cooked at pH 7 retained full PHA activity after 8 h at 76C (Fig. 2). However at 93C, beans retained approximately 50% activity after 2 h and no detectable activity at 4 and 8 h. Beans soaked and cooked at pH 12 and at 76C retained full hemagglutinating activity at 4 h, which decreased to approximately 20% at 8 h. However, at 93C no detectable hemagglutinating activity remained after only 2 h.

Texture. An analysis of the cooked bean texture was performed and the results are summarized in Fig. 3. At both temperatures, kidney beans soaked and cooked at high pH were softer than kidney beans soaked and cooked at neutral pH. For beans cooked at 76C, there was a linear correlation of shear force to cooking time. At a cooking temperature of 93C, the same relationship was observed. At every time tested, the pH 12.0 beans were softer than pH 7.0 beans. At 93C, however, shear force was not linearly related to cooking time.

Coffey *et al.* (1985) reported that 250 lb/100 g was the shear force indicative of minimum palatability. Using this figure and the regression equations for 76C, beans cooked at pH 12.0 reached theoretical palatability at:

$$\text{Extrapolated Cooking Time Estimate} = (250\text{–}883)\ \text{lb force}/-62.9\ \text{lb force/hr} = 10.6\ \text{h}$$

For beans cooked at pH 7.0, the time required is:

$$\text{Extrapolated Cooking Time Estimate} = (250\text{–}1140)\ \text{lb force}/-55.2\ \text{lb force/h} = 16.2\ \text{h}$$

To summarize the 76C data, soaking and cooking beans at pH 12.0 decreases the time required to reach palatability by approximately 6 h or by 62.4%.

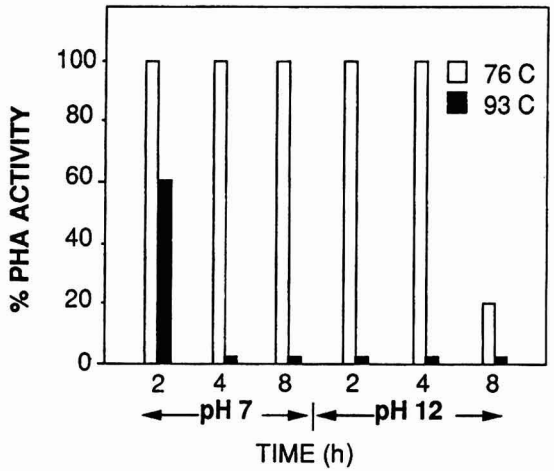

FIG. 2. EFFECT OF PROCESSING CONDITIONS ON THE HEMAGGLUTINATING ACTIVITY OF KIDNEY BEANS

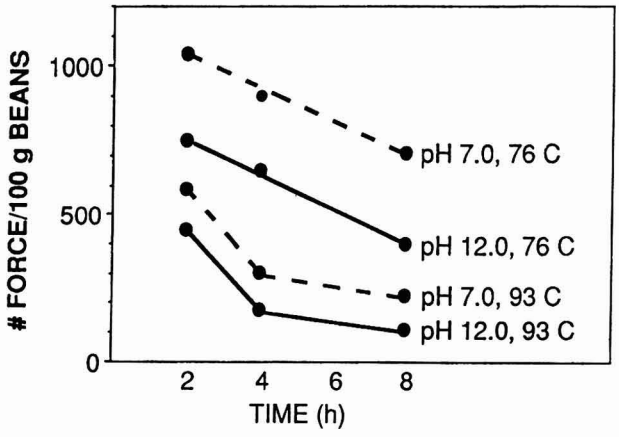

FIG. 3. EFFECT OF pH AND THERMAL TREATMENT ON THE TEXTURE OF COOKED KIDNEY BEANS

For 93C cooking, the palatability can be estimated from Fig. 3. At pH 12.0, a shear value of 250 lb will be expected at approximately 3.5 h, but at pH 7.0 approximately 6 h are required. To summarize the data at 93C, soaking and cooking beans at pH 12.0 decreases the time required to reach minimum palatability by approximately 2.5 h or by 58.3%.

The strong relationship between pH and texture and pH and residual hemagglutinating activity suggest the alkali treatment of beans may be a possible approach to improve the nutritional value of dry beans. A comparison of palatability and hemagglutinating activity indicates that for kidney beans cooked at 76C for 8 h, no reduction in HA is observed if the soaking and cooking media is pH 7.0, whereas approximately 80% of the HA is inactivated at pH 12.0. For beans cooked at 93C, hemagglutinating activity is nondetectable before the beans reach a palatable texture irrespective of pH.

Electrophoretic Analysis

Alkaline Soaking and Cooking. Figure 4 illustrates the SDS-PAGE patterns of extracts of kidney beans soaked and cooked at pH 7 and pH 12. There are differences for both 2 and 8 h cooking times for the beans cooked at pH 12.0.

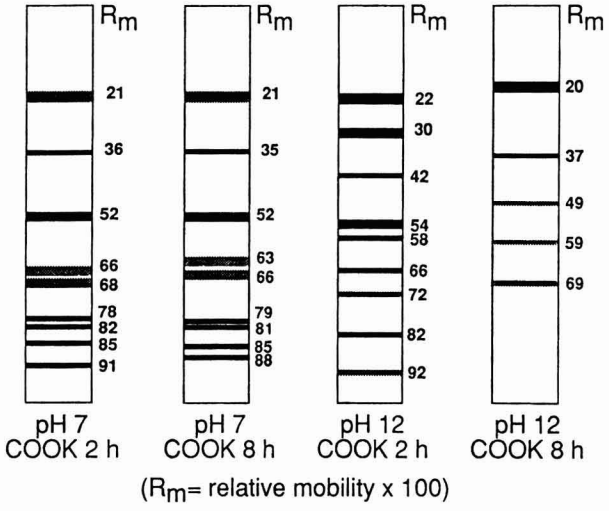

FIG. 4. ELECTROPHORETIC ANALYSIS OF KIDNEY BEANS COOKED AT pH 7 AND pH 12 (SDS-PAGE)

For beans cooked at pH 7.0, the patterns were the same as the control bean extracts throughout the heating period. For beans cooked at pH 12.0 for 2 h, there were major bands at 0.22, 0.30, 0.42, 0.54, 0.66 and 0.82. For beans held for 8 h at pH 12.0, there was one major band at 0.20 and minor bands at 0.32, 0.49, 0.59 and 0.69. This electrophoretic analysis indicates that significant changes occur in the proteins in kidney beans during cooking at pH 12. These changes may be due to hydrolysis of the native proteins or other changes in the proteins that result in decreased detection of the lower molecular weight proteins with this method. The pH 12.0 cook treatment provided rapid decrease in hemagglutinating activity, seed softening and changes in the apparent molecular weight distribution of the extractable proteins.

The increased softening rate observed for beans prepared using alkaline cooking has important ramifications for dry bean utilization. A persistent postharvest problem is the development of hard-to-cook phenomenon in dry beans. The hard-to-cook beans are difficult to eat and therefore represent a dietary and economic loss for the consumers in areas highly dependent on beans as a dietary staple. A simple treatment, like alkaline cooking, which would ameliorate the hard-to-cook phenomenon would represent a significant improvement in the quality of the diet of those consumers. The results of this study indicate that limited reduction of HA was achieved under the extrusion conditions evaluated; however, alkaline soaking and cooking may represent a practical approach to reducing cooking time of beans. However, further research is needed to assess nutritional quality of beans prepared by alkaline cooking.

ACKNOWLEDGMENT

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WATER ACTIVITY AND PHYSICAL STATE EFFECTS ON AMORPHOUS FOOD STABILITY

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ABSTRACT

Water-adsorption data and glass transition temperatures (T_g) of maltodextrins with dextrose equivalent (DE) values ranging from 4 to 38, horseradish roots, and strawberries were used to establish relationships between water activity (a_w), water content (m), and T_g. Critical m values were considered as those depressing T_g to 25C. Corresponding values of critical a_w were obtained from GAB isotherms that were used to model water adsorption. The use of BET isotherms was tested, but the model showed poor correlation with experimental data at high a_w values, especially for low DE maltodextrins. Critical m and a_w values were lowest for strawberries (1.5 g H_2O/g solids; 0.07 a_w). The values increased with decreasing DE, ranging from 7.2 (0.44 a_w) to 11.2 g H_2O/g solids (0.70 a_w). Understanding of water-sorption properties and T_g is valuable in controlling processability and stability, and for determining of food-packaging requirements.

INTRODUCTION

The amorphous state of food materials is a nonequilibrium state that affects material behavior during processing and storage (Troy and Sharp 1930; White and Cakebread 1966; Levine and Slade 1986; Roos and Karel 1991a). Food

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materials may be considered as stable in their solid "glassy" state (Levine and Slade 1986), which is characterized by an extremely high viscosity (10^{12} Pa s). Glasses are able to support their own weight, but they are transformed to more liquid-like "rubbers" in the temperature region of the glass transition (T_g). The glass transition results in dramatic changes in molecular mobility and in mechanical and electric properties (Williams *et al.* 1955; Slade and Levine 1991).

White and Cakebread (1966), Levine and Slade (1986), Roos and Karel (1991a) and Slade and Levine (1991) have related the physical state of amorphous foods to processability and storage stability. Food products that contain low molecular weight sugars are usually difficult to dehydrate, and they exhibit poor stability in the dehydrated or frozen state above T_g (Downton *et al.* 1982; Roos and Karel 1990; Slade and Levine 1991). Typical changes in amorphous food materials, which occur above T_g, include stickiness (Lazar *et al.* 1956; Downton *et al.* 1982; Levine and Slade 1988; Roos and Karel 1991b), collapse (Tsourouflis *et al.* 1976; To and Flink, 1978a,b,c; Levine and Slade 1988; Roos and Karel 1991c), and crystallization (Makower and Dye 1956; Levine and Slade 1988; Roos and Karel 1990, 1992). The increase of molecular mobility above T_g may also affect diffusion and result in increasing rates of deteriorative changes, such as enzymatic reactions (Simatos and Karel 1988; Slade and Levine 1991), nonenzymatic browning (Karmas *et al.* 1992), and oxidation (Simatos and Karel 1988; Roos and Karel 1991a). In products that contain flavor compounds or lipids encapsulated in amorphous matrices, crystallization results in the release of the entrapped compounds (Flink and Karel 1972; To and Flink 1978c). Thus, crystallization is related to loss of flavor compounds and exposure of lipids to atmospheric oxygen, which promotes oxidation (Shimada *et al.* 1991). Changes in food texture, such as loss of crispness, may also be related to water plasticization of amorphous components (Katz and Labuza 1981; Slade and Levine 1991).

Low water contents (m) and temperatures below T_g or T'_g (T_g of maximally freeze-concentrated solutes) are required for stability of amorphous foods (Levine and Slade 1986; Slade and Levine 1991). Most dehydrated foods are hygroscopic and excessively plasticized by water (Roos and Karel 1991a; Slade and Levine 1991). Plasticization leads to the depression of T_g values, which at fairly low water contents, fall below the typical storage temperatures of dehydrated foods (Levine and Slade 1988; Roos and Karel 1991a). Since water activity (a_w) is related to equilibrium relative humidity (ERH), and both T_g and a_w are functions of m, the interrelationships among a_w, m, ERH, and T_g are important in controlling food processability and shelf-life (Slade and Levine 1991). In this study, experimental data on glass transition temperatures, water activities, and moisture contents of food components and dehydrated foods were used to relate their physical state to a_w, m, and T_g.

MATERIALS AND METHODS

Water Adsorption and Physical State

Roos (1987), Pääkkönen and Roos (1990), and Roos and Karel (1991c) reported water activity, water content, and T_g values for strawberries, horseradish roots and maltodextrins [Maltrin M040 (DE 4–7), M100 (DE 9–12), M200 (DE 20–23), M250 (DE 23–27), and M365 (DE 34–38); Grain Processing Corp.]. The amorphous state was produced by freeze-drying, followed by dehydration and storage of the materials over P_2O_5 below T_g. The dehydrated samples were analyzed for "anhydrous" T_g. Materials with various m and a_w were obtained by rehumidification of samples at various relative humidities (RH) over saturated salt solutions in desiccators at 25C. The freeze-dried materials had a large surface area and equilibration occurred within four days. Differential scanning calorimetry (DSC) was used to determine the onset-temperature values of T_g for materials with various m and a_w. A constant T_g at each RH conditions indicated constant m, full equilibration, and constant a_w of the samples. The results (Table 1), based on the assumption that temperatures above T_g result in loss of stability, were used to identify critical a_w and m values for stability at room temperature.

Prediction of T_g

Various studies have shown that the T_g of amorphous carbohydrates, as a function of m, can be calculated with Eq. (1) (Roos and Karel 1991a). The constant

TABLE 1.
GLASS TRANSITION TEMPERATURES OF ANHYDROUS MATERIALS (T_g), k VALUES FOR PREDICTION OF T_g AS A FUNCTION OF WATER CONTENT, CRITICAL WATER CONTENT (m, T_g=25 C), AND CRITICAL WATER ACTIVITY (a_w), AS PREDICTED USING THE BET AND GAB ISOTHERMS

Material	T_g (°C)	k	m (gH_2O/100g solids)	a_w BET	a_w GAB	a_w T_g vs. a_w[a]
Maltrin M040	188	9.118	11.2	0.62	0.70	0.79
Maltrin M100	160	8.298	10.2	0.59	0.64	0.66
Maltrin M200	141	7.741	9.4	0.58	0.55	0.53
Maltrin M250	121	7.155	8.4	0.53	0.52	0.48
Maltrin M365	100	6.540	7.2	0.45	0.44	0.39
Horseradish	58	5.295	3.8	0.11	0.21	0.23
Strawberries	36	4.674	1.5	0.08	0.07	0.08

[a] Estimated by plotting T_g against a_w (Roos 1987; Roos and Karel 1991b)

(k), necessary for T_g prediction with Eq. (1), can be taken as the average value obtained by solving Eq. (1) for experimental T_g values and corresponding solute weight fractions (Roos and Karel 1991d), or by using the values for the change of specific heat at T_g, as was suggested by Couchman (1978). The most recent approach has been based on estimation of k, using the anhydrous T_g values of water-plasticizable carbohydrates (Roos 1992). In this study, T_g values were predicted using Eq. (1), with estimated k values obtained from Eq. (2) according to Roos (1992). The T_g of amorphous water was taken as −135C (Johari *et al.* 1987).

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{1}$$

$$k = 0.0293\ 1/°C\ T_g + 3.61 \tag{2}$$

Sorption Isotherms

The a_w data from Roos (1987), Pääkkönen and Roos (1990), and Roos and Karel (1991c,e) were used to construct sorption isotherms. The data were fitted to the Brunauer-Emmett-Teller (BET) (Brunauer *et al.* 1938) or Guggenheim-Anderson-DeBoer (GAB) (van den Berg and Bruin 1981) sorption-isotherm models. The BET model is given in Eq. (3).

$$\frac{a_w}{(1-a_w)m} = \frac{1}{m_m K} + \frac{a_w(K-1)}{m_m K}, \tag{3}$$

where m_m is the BET monolayer value, and K is a constant.

$$\frac{a_w}{(1-a_w)m} = b\ a_w + c, \tag{4}$$

where $b = (K-1)/m_m K$, and $c = 1/m_m K$.

Equation (3) has the form of a straight line (Eq. 4), with $m_m = 1/(b + c)$ and $K = (b + c)/c$. The BET isotherm was obtained by plotting a_w against $a_w/(1 - a_w)m$ (Labuza 1968). The constants, b and c, were obtained for each material from the linear regression of the experimental data in the a_w range shown in Table 2, which allowed calculation of m_m and K. Equation (1) was used to calculate the moisture content that decreased T_g to 25C. The BET model, derived from the adsorption data, was used to calculate critical a_w and m values.

The GAB isotherm model is given in Eq. (5). As suggested by Bizot (1983), Eq. (5) was transformed to the form of a second-order polynomial (Eq. 6). The constants α, β, and γ in Eq. (6) were obtained by plotting a_w against a_w/m and

TABLE 2.
CONSTANTS b AND c, MONOLAYER VALUE (m_m), AND K FOR THE BET ISOTHERMS

Material	a_w range[a]	n[b]	b	c	m_m	K	R^{2c}
Maltrin M040	0.11-0.52	5	0.1559	0.0476	4.913	4.275	0.907
Maltrin M100	0.11-0.52	5	0.1829	0.0318	4.658	6.744	0.922
Maltrin M200	0.11-0.85	7	0.2312	0.0122	4.107	19.891	0.974
Maltrin M250	0.11-0.85	7	0.1995	0.0286	4.385	7.973	0.978
Maltrin M365	0.11-0.85	7	0.1378	0.0517	5.278	3.664	0.859
Horseradish	0.33-0.85	5	0.2202	0.0082	4.378	27.747	0.942
Strawberries	0.33-0.75	4	0.0574	0.0549	8.904	2.047	0.971

[a] a_w range of experimental adsorption data
[b] Number of experimental data points
[c] R^2 for the linear regression $[a_w/(1-a_w)m] = b\,a_w + c$

from quadratic regression (Bizot 1983). The constants (α, β, and γ) were calculated from the experimental adsorption data for each material in the a_w range shown in Table 3. The constants C and K′ and the monolayer value (m_m) were calculated from Eq. (9), (8) and (7), respectively. The GAB isotherm was solved for the critical water content (T_g = 25C), to obtain the critical a_w.

$$\frac{m}{m_m} = \frac{CK'a_w}{(1-K'a_w)(1-K'a_w+CK'a_w)} \tag{5}$$

$$\frac{a_w}{m} = \alpha a_w^2 + \beta a_w + \gamma, \tag{6}$$

where $\alpha = K'/m_m\,[(1/C) - 1]$, $\beta = 1/m_m\,[1 - (2/C)]$ and $\gamma = 1/CK'm_m$.

$$m_m^2 = -\frac{1}{4\,\alpha\gamma - \beta^2} \tag{7}$$

$$K' = \frac{\beta - (1/m_m)}{-2\,\gamma} \tag{8}$$

$$C = \frac{1}{m_m\,\gamma\,K'} \tag{9}$$

TABLE 3.
CONSTANTS α, β, AND γ, MONOLAYER VALUE (m_m), AND CONSTANTS K' AND C FOR THE GAB ISOTHERMS

Material	a_w range[a]	n[b]	α	β	γ	m_m	K'	C	R^{2c}
Maltrin M040	0.11-0.85	7	-0.0913	0.0843	0.0482	6.362	0.7561	4.310	0.364
Maltrin M100	0.11-0.85	7	-0.0904	0.0940	0.0394	6.582	0.7351	5.248	0.328
Maltrin M200	0.11-0.85	7	-0.1792	0.1638	0.0234	4.790	0.9616	9.291	0.772
Maltrin M250	0.11-0.85	7	-0.1648	0.1337	0.0362	4.894	0.9751	5.786	0.884
Maltrin M365	0.11-0.85	7	-0.1114	0.0567	0.0580	5.866	0.9807	2.998	0.816
Horseradish	0.33-0.75	4	-0.1284	0.1015	0.0380	5.790	0.9362	4.850	0.899
Strawberries	0.33-0.94	6	-0.0304	-0.0280	0.0629	10.890	0.9530	1.533	0.999

[a] a_w range of experimental adsorption data
[b] Number of experimental data points
[c] R^2 for the quadratic regression $(a_w/m) = \alpha a_w^2 + \beta a_w + \gamma$

All data were processed with a Macintosh IIci microcomputer and Cricket Graph 1.3.2 software.

RESULTS AND DISCUSSION

Glass Transition Temperatures

The glass transition temperatures of maltodextrins, horseradish roots, and strawberries were predicted using Eq. (1), with k values derived using Eq. (2), as shown in Fig. 1. The anhydrous T_g values and k values are given in Table 1. Since calculated k values from Eq. (2) were used instead of those calculated as an average of experimental data, the predicted T_g values at various water contents were slightly different from those reported earlier for maltodextrins (Roos and Karel 1991e).

No previous attempts to consider complex amorphous foods as binary blends of solids and water have been reported. The T_g values predicted for horseradish

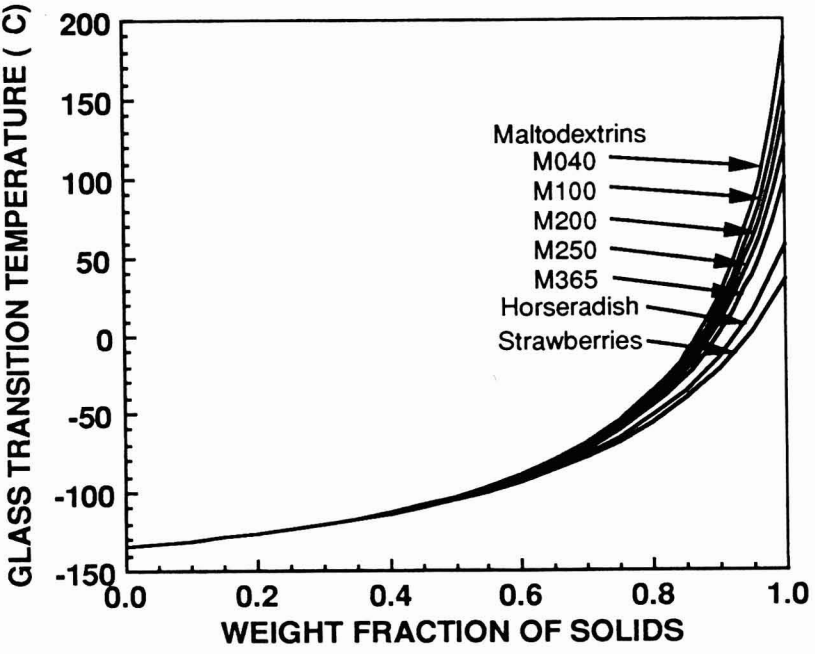

FIG. 1. STATE DIAGRAM OF MALTODEXTRINS, HORSERADISH ROOTS, AND STRAWBERRIES, SHOWING CONCENTRATION-DEPENDENCE OF THE GLASS TRANSITION TEMPERATURE

roots and strawberries showed good correlation with the experimental data, as has been shown for low molecular weight carbohydrates, maltodextrins, and starch (Roos and Karel 1991e; Roos 1992). Therefore, it might be reasonable to assume that the T_g values of food solids with high carbohydrate contents can be predicted with Eq. (1) and (2), which would be important for the evaluation of food behavior during dehydration, freezing, and storage. Both horseradish roots and strawberries have carbohydrates as their main solids. The amounts of fructose, sucrose, and glucose in strawberries are high, being 19.7, 19.0, and 16.5% of solids, respectively (Skrede 1982), which results in a fairly low anhydrous T_g value (Roos 1987; Pääkkönen and Roos 1990). Horseradish roots contain 22.7% sucrose, 15.0% starch, and 2.7% other carbohydrates of total solids (Rastas *et al.* 1989). This could explain the higher T_g value of horseradish, as compared to that of strawberries. The T_g values of various food solids can be similarly related to composition, as was reported by Slade and Levine (1991) and Roos and Karel (1991c) for binary mixtures of sucrose and maltodextrins.

Water Adsorption Models

All materials studied showed substantial water adsorption, even at low relative humidities, and the drastic decrease of T_g with increasing water content typical of water-plasticizable polymers (Slade and Levine 1991). Increasing molecular weight (decreasing DE) increased T_g of maltodextrins (Levine and Slade 1986; Roos and Karel 1991c) and decreased water adsorption (Fig. 2). The constants of the BET isotherms are given in Table 2, and those of the GAB isotherms are given in Table 3.

All materials had the typical BET type II sigmoid water adsorption isotherm, but the GAB isotherms showed better correlation with experimental adsorption data and wider applicable a_w ranges than did the BET isotherms (Fig. 2 and 3). However, for horseradish and strawberries, the applicable GAB isotherm range was only between 0.33 and 0.75 a_w, compared to 0.11–0.84 for maltodextrins. The greatest deviations from the BET isotherm were noticed for the low DE maltodextrins at high a_w values (Fig. 2). Generally, the BET isotherm was applicable at low a_w values, as was reported by van den Berg and Bruin (1981). The GAB isotherm gave good agreement with the experimental adsorption data for maltodextrins over the whole a_w range, in accord with previous findings (van den Berg 1986; van den Berg and Bruin 1981).

The rate of water adsorption of amorphous materials is dependent on various factors including the physical state. Crystallization of amorphous sugars can result in loss of adsorbed moisture (Makower and Dye 1956; Roos and Karel 1990). The sorption isotherms did not indicate such loss of moisture during water ad-

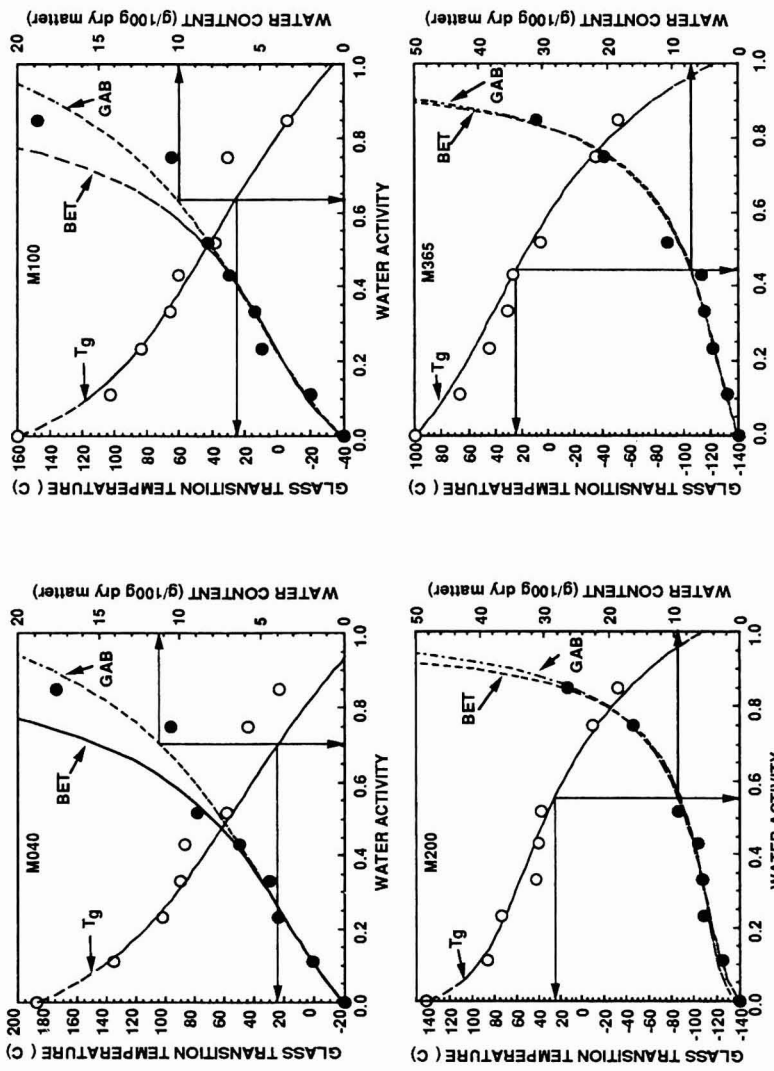

FIG. 2. RELATIONSHIPS BETWEEN WATER ACTIVITY (a_w), GLASS TRANSITION TEMPERATURE (T_g), AND MOISTURE CONTENT (m) FOR MALTODEXTRINS (M040, M100, M200, AND M365)
The locations of critical T_g, a_w and m at 25C are shown with arrows.

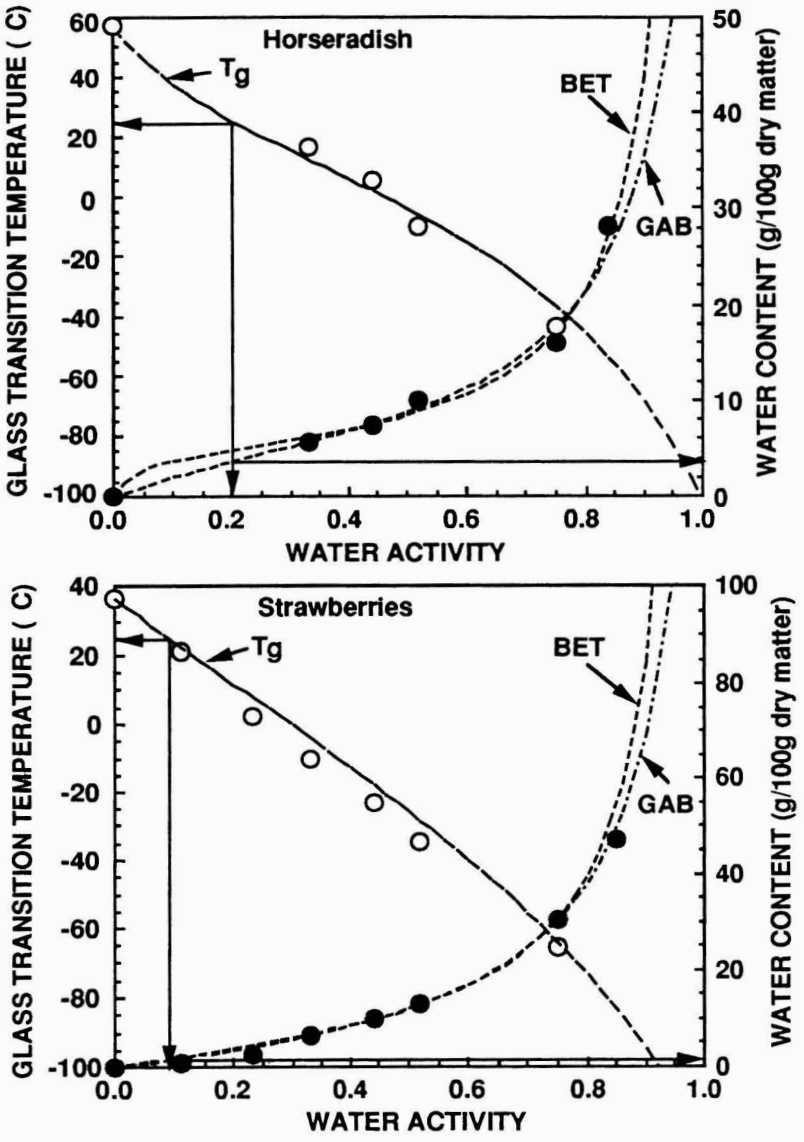

FIG. 3. RELATIONSHIPS BETWEEN WATER ACTIVITY (a_w), GLASS TRANSITION TEMPERATURE (T_g), AND MOISTURE CONTENT (m) FOR HORSERADISH ROOTS AND STRAWBERRIES

The locations of critical T_g, a_w and m at 25C are shown with arrows.

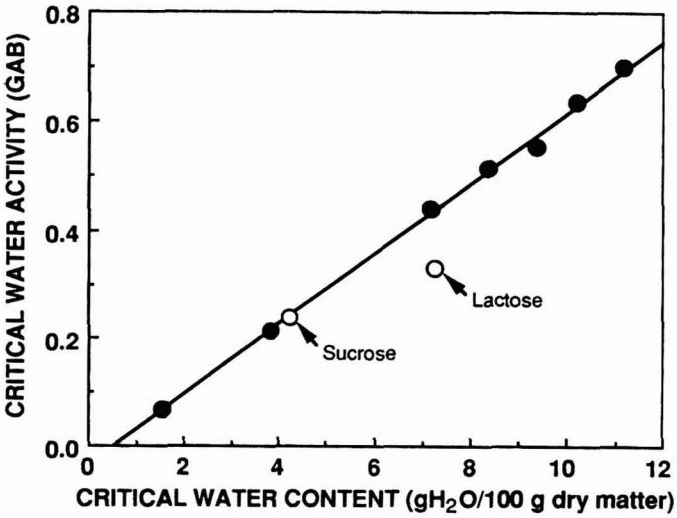

FIG. 4. CRITICAL WATER ACTIVITY (a_w) OF MALTODEXTRINS, HORSERADISH ROOTS, AND STRAWBERRIES AT 25C, AS A FUNCTION OF CRITICAL WATER CONTENT
The data for sucrose and lactose are from Roos and Karel (1991b), with critical water activity obtained from the linear relationship between water activity and glass transition temperature.

sorption, which is typical of pure amorphous sugars and dehydrated milk products, as the T_g is decreased below ambient temperature, due to water plasticization (Bushill *et al.* 1965; Roos and Karel 1990). In products with crystallizing components, the sorption isotherm models used in this study cannot be applied, but the critical a_w values, although less accurate (Table 1), can be obtained from the linear decrease of T_g with increasing a_w (Roos 1987; Roos and Karel 1991b; Slade and Levine 1991).

Critical Water Activity and Water Content

Water activity of foods can be related to stability and to the rates of deteriorative reactions and microbial growth, as suggested by Labuza (1968, 1980) and Labuza *et al.* (1970). It has also often been assumed that the BET monolayer value is the critical water content, below which dehydrated foods are most stable (Labuza *et al.* 1970; van den Berg 1986). The critical moisture contents obtained from the T_g data (Table 1) differed significantly from the BET monolayer values (Table 2). For the maltodextrins, the monolayer values were lower than the critical

moisture contents, but those of strawberries and horseradish were higher. It has been shown that stickiness, collapse, and crystallization of amorphous compounds in dehydrated foods occur as the viscosity decreases above T_g (Levine and Slade 1988; Roos and Karel 1991a,d; Slade and Levine 1991). Since the rates of these changes are related to plasticization by water or temperature, they are not controlled by the monolayer value or water activity, as was pointed out by Slade and Levine (1991). This agrees with the results of Katz and Labuza (1981), who reported critical water contents (at 20C), for crispness of snack foods, above the monolayer value. They also pointed out that the critical water activity range (0.35–0.50) was the same as that at which amorphous-to-crystalline transformations occur in sugars. It should be noted that crystallization of amorphous sugars occurs above T_g, even in the anhydrous state (Roos and Karel 1990). Recent findings on the rates of nonenzymatic browning also indicate that the rates of deteriorative reactions are related to molecular mobility above T_g, rather than to the monolayer value (Slade and Levine 1991; Karmas *et al.* 1992). Thus the critical m and a_w values can be considered as those that depress T_g to ambient temperature.

Under equilibrium conditions (constant T, m, and a_w), the T_g is determined by m (a_w) (Roos 1987; Roos and Karel 1991c). The maltodextrin data showed that the critical m and a_w values increased with increasing molecular weight (decreasing DE). As the critical m increased, the critical a_w also increased. A plot of critical a_w values against critical water contents showed a linear relationship (Fig. 4). Levine and Slade (1986, 1988), Roos and Karel (1991a), and Slade and Levine (1991) have proposed the use of state diagrams for the evaluation of stability of amorphous foods during processing and storage. Such state diagrams can be used to show the dependence of T_g on water content, i.e., T_g can be estimated from the water content of the material. For the materials studied here, the critical water content can be obtained from the state diagram or calculated with Eq. (1), and the corresponding critical a_w can be obtained from Fig. 4. This information would be useful in food-product development, since it can be applied to establish relative humidity limits for the storage of amorphous, low moisture foods.

CONCLUSIONS

T_g of amorphous foods determines their stability, and a_w values can be used to manipulate both T_g and material behavior under various storage conditions. Understanding of water sorption behavior, and its relationship to T_g, provides a valuable tool to control material behavior during processing and subsequent storage, and for the determination of food-packaging requirements.

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