

## VISCOGRAPHIC CHARACTERISTICS OF CHEMICALLY MODIFIED CASSAVA STARCHES ASSESSED BY RVA

## CARACTERÍSTICAS VISCOAMILOGRÁFICAS DE AMIDOS DE MANDIOCA QUIMICAMENTE MODIFICADOS

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### ABSTRACT

Cassava starch presents technological properties that make it a special raw material for the food industry. Its mild flavor, free of the undesirable "cereal flavor" of corn starch as well as its viscographic pattern during cooking are some of these valued characteristics. In the present work a viscographic study of cassava starch modified with oxidative treatments was made in order to verify the effects of the modifications on the apparent viscosity of the starches during cooking at different pH values. The samples studied were produced by reaction with 0.1N potassium permanganate and 1% lactic acid (LACW) or citric acid (CITW). After a short reaction period the starches were recovered, washed and oven dried. Other cassava starches were considered for comparison, including native (NAT) and sour (SOUR) ones. Also 1% lactic acid treated samples were produced, one oven dried (LACOVW) and another one sun dried (LACSUNW). The viscographic analysis was made in a Rapid Visco Analyser (RVA), with 2g (DM) of starch and 28g of solvent (de-ionized water, 0.2M acetate and 0.2M phosphate buffers at pHs 4.0, 5.0, 6.0, 6.5 and 7.0). The results showed that the chemically oxidized samples (LACW and CITW) as well as the LACSUNW and the SOUR ones presented a related viscographic pattern when studied at the different pH values. These samples had lower viscosity peaks and cooking stability when analyzed at the higher pH values. In the case of LACW and CITW, there was no detectable viscosity at pH 7.0, because the pastes presented high fluidity. The other samples (NAT and LACOVW) did not present this pattern. Their lower viscosity peaks appeared when cooked in the lower pH, which can be

explained by the degradative effect of acidity on the starch macromolecules.

Key words: cassava starch, RVA, oxidized starch

## RESUMO

O amido de mandioca apresenta propriedades tecnológicas que o torna matéria-prima de grande interesse à indústria de alimentos. A ausência de “odor de cereal”, típico do amido de milho assim como seu padrão viscoamilográfico durante o cozimento são algumas das características de interesse. Neste trabalho um estudo viscoamilográfico de amido de mandioca modificado por tratamentos oxidativos foi feito com a finalidade de verificar o efeito das modificações na viscosidade aparente dos amidos durante o cozimento a diferentes valores de pH. As amostras estudadas foram produzidas por reação com solução de permanganato de potássio 0,1N e ácido láctico (LACW) ou cítrico (CITW) 1%. Após um curto período de reação, o amido foi recuperado, lavado e seco em estufa. Outras amostras foram consideradas, para comparação, incluindo o amido de mandioca nativo (NAT) e o polvilho azedo (SOUR). Também foram produzidas amostras de amido acidificado com ácido láctico 1%, sendo uma delas seca em estufa (LACOVW) e outra seca ao sol (LACSUNW). A análise viscoamilográfica foi feita com emprego do analisador rápido de viscosidade (RVA), com 2g (MS) de amido e 28g de solvente (água deionizada, tampões acetato e fosfato 0,2M a pH 4,0, 5,0, 6,0, 6,5 e 7,0). Os resultados mostraram que as amostras oxidadas quimicamente (LACW e CITW) e também a LACSUNW e a SOUR tiveram padrões viscoamilográficos relacionados quando considerados os diferentes pHs. Estas amostras apresentaram menores picos de viscosidade e estabilidade ao cozimento quando analisadas nos maiores valores de pH. No caso de LACW e CITW, não houve possibilidade de se detectar viscosidade para o pH 7,0, pois as pastas apresentaram elevada fluidez. As outras amostras (NAT e LACOVW) não se comportaram dessa forma. Nestes dois casos, os menores picos de viscosidade apareceram quando a análise foi feita no menor pH, o que pode ser explicado pela ação degradativa que a maior acidez exerce durante o cozimento sobre as macromoléculas constituintes do amido.

Palavras-chave: amido de mandioca, RVA, amido oxidado

## 1. Introduction

Cassava starch presents technological properties that make it interesting for multiple applications. Among these properties the absence of “cereal flavor” and the viscographic pattern during cooking are valued for applications in the food industry. Another characteristic is the expansion of baked doughs made with cassava starch, mainly when employing sour cassava starch (*polvilho azedo*). The expansion of cassava starch is also very valued for producing extruded snacks. The importance of cassava starch functional properties is

so that led to the development of special kinds of native starches by genetic selection of corn and other cereals (waxy starch series). Lower pasting temperature and susceptibility to syneresis, when compared with regular cereal starches, are some of the properties that differentiate cassava starch for industrial applications.

Sour cassava starch is produced in South America, mainly in Brazil and Colombia (Cereda, 1983a,b; Petruccelli *et al.*, 1993) and is employed exclusively for its expansion property when baked. Both in Brazil and Colombia people consume special kinds of bread-like foods made from sour cassava starch that

present very good taste and are completely free of gluten due to the fact that not contain any amount of wheat flour. There are few papers describing physico-chemical properties of sour cassava starch and some questions about its structural characteristics remain to be answered. Some papers, considering viscographic pattern as well as intrinsic viscosity, show that a decrease on molecular weight occurs (Asquiere *et al.*, 1993; Cárdenas & de Buckle, 1980; Demiate *et al.*, 2000; Mestres & Rouau, 1997; Nakamura & Park, 1975). The presence of lactic acid produced during the fermentation step of sour cassava starch processing was believed to be the principal responsible for the changes on the functional properties, but Nunes & Cereda (1994) showed the importance of sun drying. The authors proposed a drying process using ultraviolet (UV) irradiation that was efficient on modifying cassava starch properties in the same way of sun drying.

Demiate (1999) proposed a chemical modification of cassava starch that resulted in high degree of expansion of the produced samples. In this method the author employed a chemical treatment of cassava starch with 0.1N potassium permanganate associated with 1% (w/w) lactic or citric acid. All modified samples presented baking ability, in the same way as sour cassava starch that was considered for comparison. Demiate & Cereda (2000) produced these samples and evaluated some physico-chemical properties including the baking ability, carboxyl content, intrinsic viscosity, differential scanning calorimetry analysis and microscopy of the granules. The hot paste

behavior was also considered but only the viscosity peaks were discussed. Demiate *et al.* (2000) studied the same samples by using Fourier transform infrared spectroscopy (FTIR). By using multivariate analysis (principal component analysis – PCA) of the spectral data the authors were able to separate the samples in accordance to their content in acid and anionic carboxyls. Also they succeeded in predicting the baking property by exploring the FTIR spectra of the samples by employing partial least squares regression (PLS). In the present work the viscographic pattern of these samples is evaluated and the results discussed.

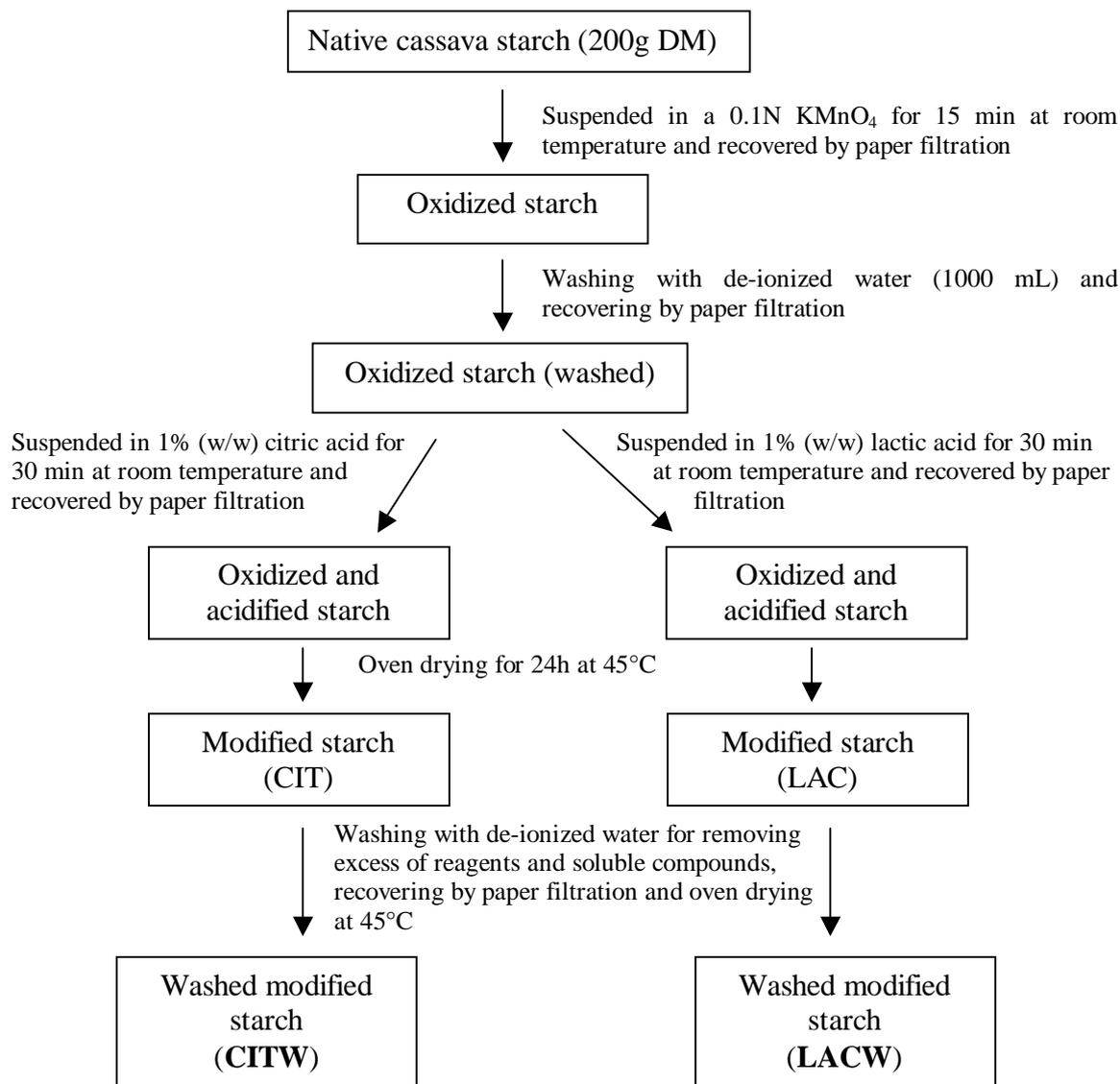
## 2. Material and Methods

### 2.1 Material

The native cassava starch was a gift from an industrial producer (Halotek-Fadel, Palmital SP). It was considered as a standard for comparison and used for the chemical modifications. A commercial sample of sour cassava starch was bought in the local market (Ponta Grossa PR) and also analyzed for comparison. All chemicals used were of reagent grade.

### 2.2 Methods - Production of the modified starches

Chemically modified samples were produced as described in the Figure 1.

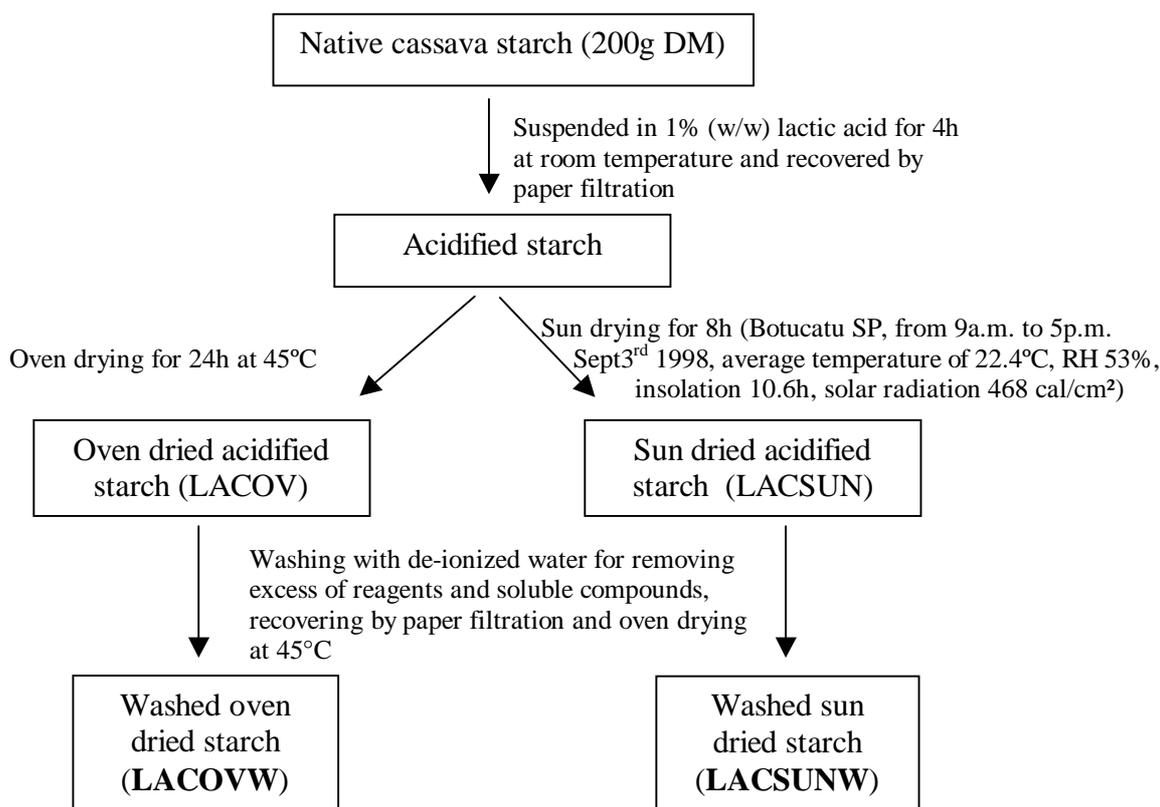


**Figure 1** - Production of chemically modified cassava starches.

In the production of the samples CITW and LACW the relation between the suspended material and the reagent solutions was always of 1:5, and the concentrations showed in Figure 1 are final concentrations.

In order to compare the viscographic patterns,

other two samples were produced in the laboratory. Both samples were made by suspending native cassava in 1% (w/w) lactic acid solution, but dried by different processes. One was oven dried and the other sun dried. In the Figure 2 their production is described.



**Figure 2** - Production of lactic acid treated cassava starch.

The relation 1:5 for the suspensions was also respected in the production of these samples.

### pH

Starch samples of 20g were suspended in 100mL of deionized water and stirred for 30 minutes. After this period the pH was directly measured, at room temperature (20°C), employing a calibrated pH potentiometer (Smith, 1967).

### Viscographic analysis

The viscographic analysis was made using a Rapid Visco Analyser (Newport Scientific, Narabeen, Australia). The samples (2g DM) were suspended in 28g of solvent by using a Ultraturrax T25 (Ika, Staufen, Germany), as described by Mestres & Rouau (1997). De-ionized water, 0.2M acetate and 0.2M phosphate buffers at pHs 4.0, 5.0, 6.0, 6.5 and 7.0 were employed as solvents. The temperature program was: keeping at 35°C for 2min, heating to 95°C at 6°C/min rate, keeping at 95°C for 5 min and cooling to 50°C at 6°C/min rate.

The cooking pattern of the samples was evaluated considering the main points of the viscoamylograms, including the peak viscosity and temperature, pasting temperature, viscosity at 95°C and final viscosity. Six samples were analyzed: native cassava starch (NAT), permanganate/lactic acid modified cassava starch (LACW), permanganate/citric acid modified cassava starch (CITW), lactic acid treated/oven dried cassava starch (LACOVW), lactic acid treated/sun dried cassava starch (LACSUNW) and a commercial sample of sour cassava starch (SOUR).

## 3. Results and discussion

The pH values of the studied samples are shown on Table 1. As expected, the native starch presented a value next to neutrality (6.0) and the sour cassava starch had a value in the acid region, of 3.5.

**Table 1** - pH values of the samples.

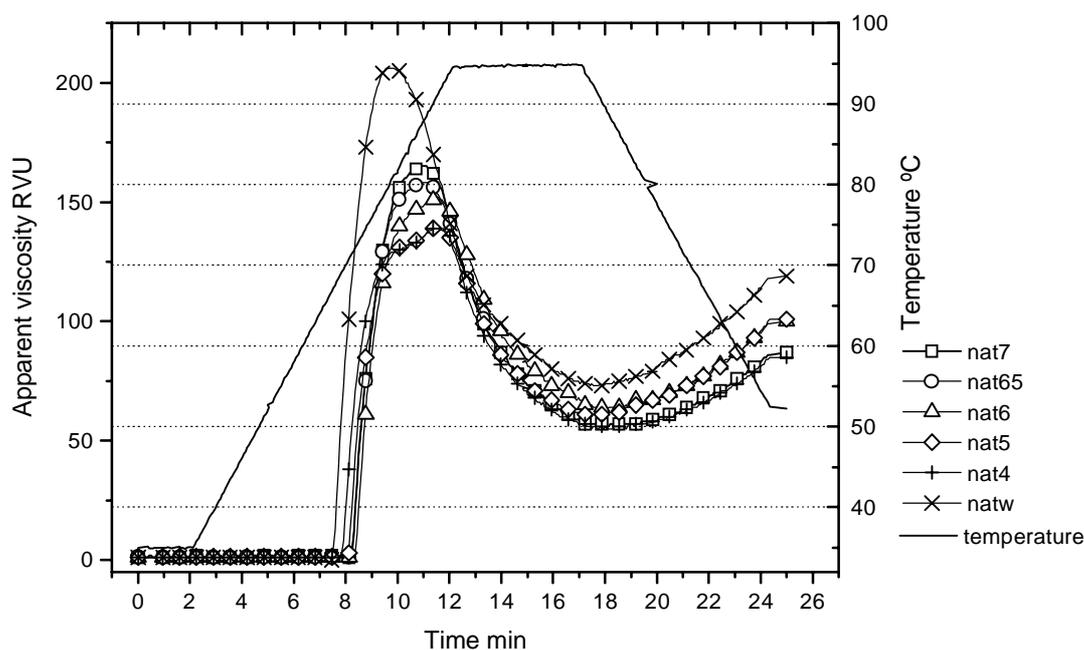
Sample	pH
NAT	6.0
SOUR	3.5
LACOVW	4.7
LACSUNW	4.7
LACW	4.5
CITW	3.9

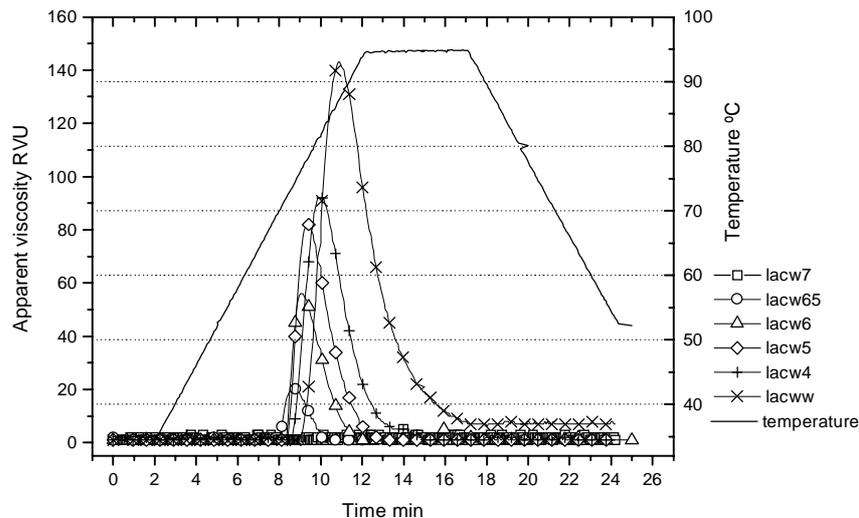
The pH values varied, in the case of the chemically treated starches, from 3.9 (CITW) to 4.7 (LACOVW and LACSUNW).

The results of the cooking patterns of the samples are shown in Figures 3 to 8, as the amylograms. It is possible to observe differences among the samples, especially in terms of viscosity peak and cooking stability. The effect of pH is very pronounced in the

modified samples. As already discussed by other authors (Nunes, 1994; Nunes & Cereda, 1994; Messtres & Rouau, 1997), there is a marked influence of sun drying on lactic acid treated cassava starch, here represented by the sample LACSUNW. This sample presents a different feature when compared to that produced by the same chemical treatment but oven dried (LACOVW). All modified samples, except LACOVW, presented a viscosity profile, mainly when considering the viscosity peak and cooking stability, with a related pattern in the different pHs tested.

The Figure 3 illustrates the amylograms of native cassava starch (NAT) at the different solvents. Although there appears a somewhat higher viscosity peak (*circa* 200 RVU) when this starch was suspended in water, the general profile of all other tested solvents presented a similar behavior for native cassava starch. The viscosity peaks of the native starch analyzed in pH 4.0 to 7.0 was of ca. 150 RVU

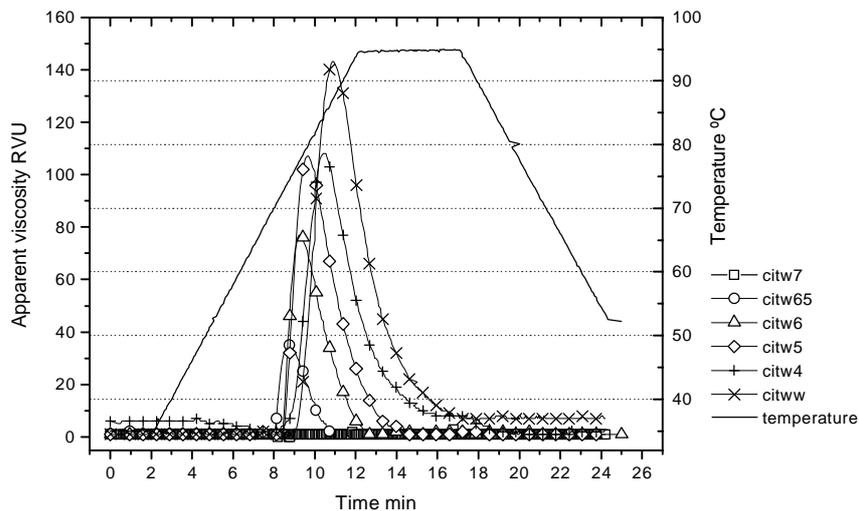
**Figure 3** - Amylograms of native cassava starch (NAT) in different solvents.



**Figure 4** - Amylograms of permanganate/lactic acid modified cassava starch (LACW) in different solvents.

In the Figure 4 the results of the LACW sample are shown and there are evident differences due to the employed solvent. Although the sample presented lower viscosity peaks and cooking stability in all solvents, it was possible to observe that at higher pH the viscosity peaks were very low. In pH 7.0, it was not possible to detect any viscosity during the analysis as the gelatinized starch presented high fluidity.

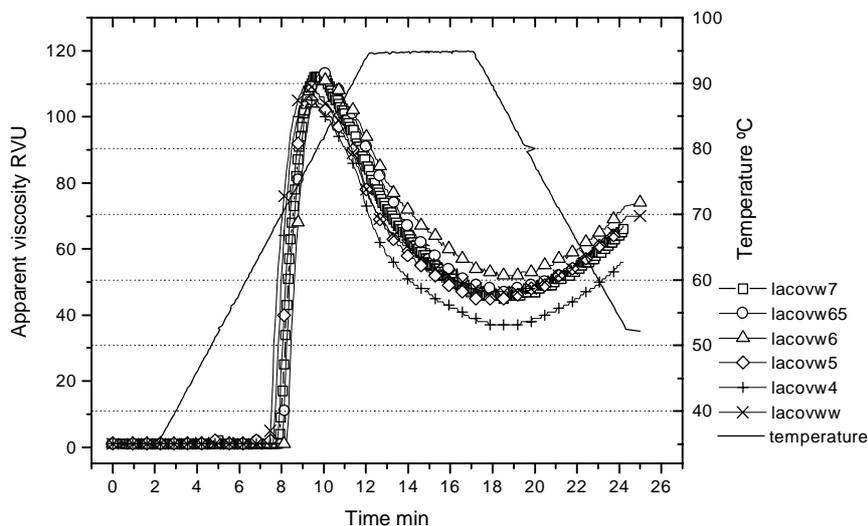
In the Figure 5, the CITW sample presented a viscographic pattern very similar to that of LACW. It seems that there was not any difference between the profile of these samples in relation to their behavior during cooking in excess of water. It was possible to observe a tendency of decreasing pasting temperature at pH 6.5 and also absence of viscosity when the sample was tested with pH 7.0 buffer.



**Figure 5** - Amylograms of permanganate/citric acid modified cassava starch (CITW) in different solvents.

The sample produced only by suspension of native cassava starch in lactic acid solution and oven dried (LACOVW) presented an expected cooking profile (Figure 6). At the lowest pH (4.0) it showed the lowest viscosity peak, what can be attributed to the action of the acidity over the starch macromolecules

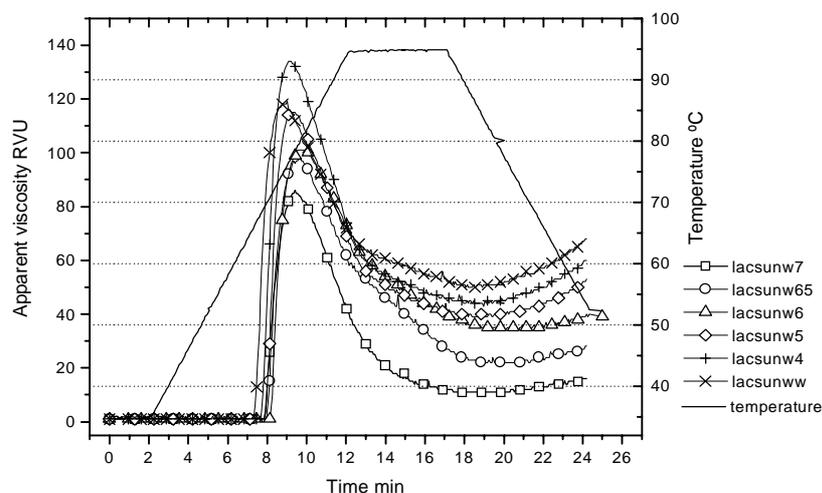
structure. Comparing all the different solvents, it was not possible to detect important differences that should be related with any chemical changing in the starch due to the lactic acid treatment. All viscosity peaks were of around 110 RVU, independently of the solvent.



**Figure 6** - Amylograms of lactic acid treated/oven dried cassava starch (LACOVW) in different solvents.

In the Figure 7 the results of the lactic acid treated and sun dried cassava starch are presented. In this case it seems that the pH has great influence in the cooking profiles. The highest pH resulted in lower viscosity peaks as well as cooking stability, in a manner that can be related with the chemically modified samples (Figures

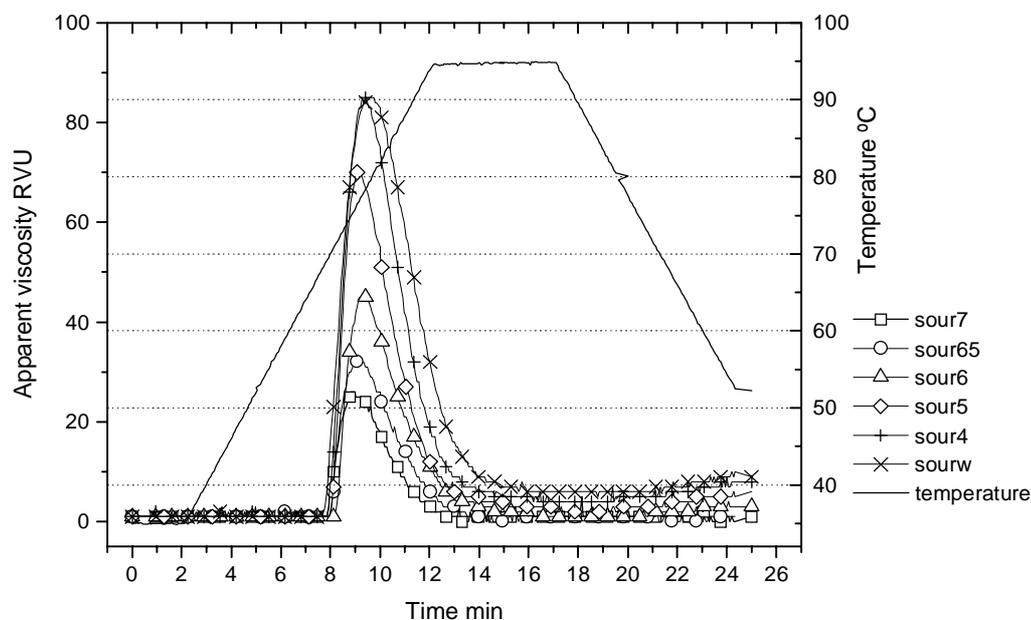
4 and 5). As already stated by others (Demiate, 1999; Demiate *et al.*, 2000; Demiate & Cereda, 2000; Mes-tres & Rouau, 1997; Nunes & Cereda, 1994), sun drying has a decisive paper in this type of starch modification.



**Figure 7** - Amylograms of lactic acid treated/sun dried cassava starch (LACSUNW) in different solvents.

The amylograms of a commercial sample of sour cassava starch were made in order to compare the results with the chemically treated starches. In the Figure 8 it is possible to observe relatively lower viscosity peaks (from ca. 25 to 85 RVU), and a profile that is

comparable to that of the samples LACW, CITW and LACSUNW when considering the influence of the solvent. The buffers with higher pH were associated with the lower viscosity peaks as well as cooking stability.



**Figure 8** - Amylograms of commercial sample of sour cassava starch (SOUR) in different solvents.

Selected points of the viscoamylograms as well as other characteristics calculated from the data are summarized on Table 2. The six samples considered in the present study at the six different solvents, from deionized water to the buffers with pH ranging from 4.0 to 7.0 are shown on Table 2. In this table the values of viscosity peak, viscosity at 95°C (start and end) and

final viscosity or viscosity at 50°C are shown. Also the pasting temperature, here considered as the temperature in which viscosity starts to increase, is indicated. The temperature of the viscosity peak is shown and the stability and setback from peak are calculated as differences between initial and final viscosity at 95°C and final viscosity and peak viscosity, respectively.

Table 2- Selected information from the amylograms.

Sample	Description	Solvent					
		Water	pH 7.0	pH 6.5	pH 6.0	pH 5.0	pH 4.0
NAT	Viscosity peak (RVU)	206	165	158	152	139	139
	Pasting temperature (°C)	68	72	72	73	71	70
	Peak temperature (°C)	80	87	88	90	90	91
	Viscosity at 95°C (start) (RVU)	136	135	137	143	132	130
	Viscosity at 95°C (end) (RVU)	75	58	n.a	67	60	56
	Viscosity at 50°C (RVU)	119	87	n.a	100	100	85
	Stability (RVU) <sup>1</sup>	61	77	n.a	76	72	74
	Setback from peak (RVU) <sup>2</sup>	-87	-78	n.a	-52	-39	-54
LACW	Viscosity peak (RVU)	143	0	20	56	82	92
	Pasting temperature (°C)	77	n.d.	71	73	73	75
	Peak temperature (°C)	87	n.d.	74	76	78	82
	Viscosity at 95°C (start) (RVU)	90	0	0	0	5	19
	Viscosity at 95°C (end) (RVU)	7	0	0	0	0	0
	Viscosity at 50°C (RVU)	7	0	0	0	0	0
	Stability (RVU) <sup>1</sup>	83	0	0	0	5	19
	Setback from peak (RVU) <sup>2</sup>	-136	0	-20	-56	-82	-92
CITW	Viscosity peak (RVU)	143	0	35	77	107	108
	Pasting temperature (°C)	79	n.d.	71	73	74	75
	Peak temperature (°C)	88	n.d.	74	77	79	84
	Viscosity at 95°C (start) (RVU)	100	0	0	5	23	48
	Viscosity at 95°C (end) (RVU)	8	0	0	0	0	8
	Viscosity at 50°C (RVU)	7	0	0	0	0	0
	Stability (RVU) <sup>1</sup>	92	0	0	5	23	40
	Setback from peak (RVU) <sup>2</sup>	-136	0	-35	-77	-107	-108
LACOVW	Viscosity peak (RVU)	110	112	113	112	105	106
	Pasting temperature (°C)	67	70	71	72	70	68
	Peak temperature (°C)	77	80	81	82	79	77
	Viscosity at 95°C (start) (RVU)	75	84	89	92	76	70
	Viscosity at 95°C (end) (RVU)	48	47	49	54	45	39
	Viscosity at 50°C (RVU)	70	66	n.a	74	67	56
	Stability (RVU) <sup>1</sup>	27	37	40	38	31	31
	Setback from peak (RVU) <sup>2</sup>	-40	-46	n.a	-38	-38	-50
LASUNW	Viscosity peak (RVU)	119	86	98	101	115	134
	Pasting temperature (°C)	67	70	70	72	70	69
	Peak temperature (°C)	76	78	80	81	77	77
	Viscosity at 95°C (start) (RVU)	70	40	58	70	66	71
	Viscosity at 95°C (end) (RVU)	52	12	27	39	41	45
	Viscosity at 50°C (RVU)	68	16	28	39	53	60
	Stability (RVU) <sup>1</sup>	18	28	31	31	25	26
	Setback from peak (RVU) <sup>2</sup>	-51	-70	-70	-62	-62	-74
SOUR	Viscosity peak (RVU)	85	26	33	45	70	85
	Pasting temperature (°C)	70	71	71	72	71	70
	Peak temperature (°C)	79	75	77	78	77	78
	Viscosity at 95°C (start) (RVU)	29	3	5	10	11	17
	Viscosity at 95°C (end) (RVU)	6	0	0	0	0	4
	Viscosity at 50°C (RVU)	10	0	0	0	6	8
	Stability (RVU) <sup>1</sup>	23	3	5	10	11	13
	Setback from peak (RVU) <sup>2</sup>	-75	-26	-33	-45	-64	-77

n.a: not analyzed n.d: not detected

<sup>1</sup> viscosity at 95°C (start) minus viscosity at 95°C (end)<sup>2</sup> final viscosity minus peak viscosity

As summarized on Table 2, it is possible to observe that in the case of the samples treated with lactic and exposed to solar radiation, as well as for the samples that reacted with potassium permanganate and organic acids (lactic or citric), the viscographic behavior changed in the same way when analyzed on different pH values. At higher pH values, the viscosity peaks of these samples were lower as well as the final viscosity and consequently the cooking stability.

The oxidative treatment of starch promotes macromolecular partial degradation and also is responsible for the generation of carbonyl and carboxyl groups in the starch macromolecules. As the carboxyl groups may be charged or not depending on pH values, this could be a explanation for the different patterns observed on the amylograms. When the carboxyl groups are negatively charged, the polysaccharides present a polyelectrolyte behavior.

#### 4. Conclusions

- Cassava starch treated with potassium permanganate and lactic or citric acid presented decreasing viscosity peak and cooking stability with increasing pH, from 4.0 to 7.0;

- Cassava starch treated with potassium permanganate and lactic or citric acid did not present detectable apparent viscosity by the employed method, when analyzed at pH 7.0;

- Sour cassava starch and sun dried lactic acid treated cassava starch showed the same viscographic behavior when analyzed in pH range from 4.0 to 7.0;

- Native cassava starch as well as oven dried lactic acid treated cassava starch had lower viscosity peaks when analyzed at the lowest pH, probably due to the fact that higher acidity at cooking has a degradative effect on starch macromolecules.

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#### REFERENCES

- 1 ASQUIERI, E. R.; VILELA, E. R.; CEREDA, M. P. Efeito do processo de extração e da fermentação nas características do polvilho azedo. **Ciência e Tecnologia de Alimentos**, v. 13, n.1, p.67-76, 1993.
- 2 CÁRDENAS, O. S.; de BUCKLE, T.S. Sour cassava starch production: A preliminary study. **Journal of Food Science**, v.45, n.6, p.1509-12/28, 1980.
- 3 CEREDA, M.P. Avaliação da qualidade de duas amostras de fécula fermentada de mandioca (polvilho azedo). **Boletim da SBCTA**, v.17, n.3, p.305-20, 1983a.
- 4 CEREDA, M. P. Determinação de viscosidade de fécula fermentada de mandioca (polvilho azedo). **Boletim da SBCTA**, v.17. n.1, p.15-24, 1983b.
- 5 DEMIATE, I.M. **Desenvolvimento de fécula de mandioca auto-expansível**. Botucatu, Botucatu, 1999. 149p. Tese (Doutorado em Agronomia/Energia na Agricultura) – Faculdade de Ciências Agrônômicas, Universidade Estadual Paulista.
- 6 DEMIATE, I. M.; CEREDA, M. P. Some physicochemical characteristics of modified cassava starches presenting baking property. **Energia na Agricultura**, v.15, n.3, p.36-46, 2000.
- 7 DEMIATE, I. M.; DUPUY, N.; HUVENNE, J.P.; CEREDA, M.P.; WOSIACKI, G. Relationship between baking behavior of modified cassava starches and starch chemical structure determined by FTIR spectroscopy. **Carbohydrate Polymers**, v.42, p.149-158, 2000.
- 8 MESTRES, C.; ROUAU, X. Influence of natural fermentation and drying conditions on the physicochemical characteristics of cassava starch. **Journal of the Science of Food and Agriculture**, v.74, p.147-55, 1997.
- 9 NAKAMURA, I.M.: PARK, Y.K. Some physicochemical properties of fermented cassava starch (*polvilho azedo*). **Die Stärke**, v.27, p.295-7, 1975.
- 10 NUNES, O.L.G.S. **Efeito da radiação ultravioleta sobre as propriedades funcionais da fécula de mandioca tratada com ácido láctico**. Botucatu, 1994. Dissertação de Mestrado, Faculdade de Ciências Agrônômicas/Unesp.
- 11 NUNES, O.L.G.S.; CEREDA, M.P. Effect of drying processes on the development of expansion in cassava starch hydrolyzed by lactic acid. **International Meeting on Cassava Flour and Starch**, Cali/CIAT, January 11-15, p.110, 1994.
- 12 PETRUCCELLI, S., ZAMPONI, R.A., JOVANOVIĆ, G., AÑÓN, M.C. Characterization of fermented cassava starches. **Journal of Food Biochemistry**, v.17, n.3, p.161-72, 1993.
- 13 SMITH, R.J. Characterization and analysis of starches. In: WHISTLER, R.L., PASCHALL, E.F. **Starch: Chemistry and Technology**. New York : Academic Press, v. 2, p. 569-635, 1967.