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Using Carboxymethylated Cassava (*Manihot*) Wastes as Thickeners for Latex Paint

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SUMMARY

*Cassava (*Manihot*) starch wastes carboxymethylated to a degree of substitution in the range of 0·42–0·61 have been prepared and used as thickening agents for the formulation of water-based latex paints. It was found that paint thickened with cassava-waste-based sodium carboxymethyl starch acquires a mechanical strength and drying time comparable to paint formulated with the commercial grade thickeners such as Tylose and Natrosol.*

INTRODUCTION

The ability of natural polymers, especially polysaccharides, to act as binders, viscosity modifiers and flocculants has long been known. A great deal of work has been done on modifying such polysaccharides (including cellulose) from sources other than cassava and their chemistry is reasonably well established. These efforts have not only resulted in the commercial production of cellulose and starch products that could compete with the synthetic polymers, but have also turned them into speciality products. Both cellulose and starch are polyhydroxyl alcohols and offer many possible sites for chemical modification by formation of ester and ether linkages. Although the products from ester linkages have shown the greater promise, those of ether linkages are becoming increasingly important owing to their application in aqueous media. The carboxymethylation reaction (etherification) is one of the viable methods of solubilizing cellulose to

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produce sodium carboxymethyl cellulose (CMC), as described by Savage *et al.* (1954). As a polyelectrolyte of high molecular weight, CMC is useful in aqueous solutions because of its thickening and colloidal action; and it is this property that has made it useful in water-based latex paint formulations. In paint systems, CMC not only increases the viscosity, thereby keeping a large quantity of pigment suspended, but also improves the flow and brushing characteristics. Besides its use in paint manufacture, CMC finds a wide application in soap, crude oil drilling, paper, food and drug industries. Thus there is a constant demand for readily utilizable sources of cellulose.

Cassava (*Manihot*) tuber is an important source of staple food in most African countries, but the by-products emanating from its conversion into the edible form (garri) are normally discarded as wastes. This starchy waste constitutes a valuable source of raw material for industry but has remained largely unused owing to a lack of knowledge as to its effective utilization.

However, under the pressure of the present raw material crisis, it has become necessary to evaluate its commercial usefulness. A literature survey has revealed that carboxymethylated products have been prepared by various workers from wood pulp (Shigenaga *et al.*, 1974), polyvinyl alcohol (Hassan & El-Sabbah, 1974) and cotton linters (Klug, 1977), etc.; however, no work has been reported either on the carboxymethylation of cassava wastes or their subsequent use for latex paint manufacture.

An important objective of this present paper was, therefore, to investigate the preparation of carboxymethyl starch (CMS) from cassava starch wastes for use as a thickening agent in the manufacture of latex emulsion paint. The paints so prepared were evaluated for their physical and mechanical properties. These were compared with unmodified cassava starch wastes and the corresponding commercial grade water soluble cellulose thickeners commonly employed in paint formulation, such as Tylose (methyl cellulose) and Natrosol (hydroxyethyl cellulose).

EXPERIMENTAL

Materials

The cassava starch waste used in this study was obtained as a by-product of the processing of cassava tubers. The process involves crushing of the cassava tuber into a thin pulp, transferring this into a jute bag and then straining to remove water. The water is collected in a receiver, and the fine particles contained in the water are allowed to sediment, and are decanted and then sun dried. The resulting solid particles served as the source of starch. The process described here is typical of a local processing method used for converting cassava tuber into garri.

Carboxymethylation of cassava (starch) waste

Two methods of preparation of CMS from cassava waste which differed essentially only in reaction time and ratio of alkali to monochloroacetic acid were followed.

CMS-1

One-hundred millilitres of an aqueous slurry of 57% w/v cassava starch were reacted with 47·2 g (1·18 mol) sodium hydroxide (dissolved in 100 ml of water) over a period of 50 min at 30°C, and the mixture stirred for an additional 15 min; this was followed by the addition of 108 g (1·13 mol) of monochloroacetic acid. The entire mixture was then stirred for another 1½ h. The resulting dough-like product was allowed to age overnight, dried, pulverized and stored.

CMS-2

A similar preparative method was used as in the case of CMS-1 above except that the duration of the reaction was shorter and the ratio of alkali and acid to cassava starch was lower. Here, 100 ml of 57% w/v of cassava starch slurry was reacted with 35·0 g (0·87 mol) sodium hydroxide dissolved in 100 ml of water and 37·5 g (0·8 mol) of monochloroacetic acid for a reaction time of 30 min initially and finally for 1 h.

Analysis

The starch content of the cassava waste as determined by the iodine method (Radley, 1976) was found to contain about 85% starch. No determination as to the content of cellulose in the cassava waste was carried out.

A 5% solution of the cassava starch was found to have a pH of 8·42. The other characteristics of the cassava starch were: moisture content

18%, apparent viscosity (5% w/v solution) 13 cP, using a Fann Viscometer at 300 rpm, and browning temperature 212°C.

The moisture, carboxyl and sodium chloride contents and degree of substitution of the cassava-based CMS were determined according to ASTM (1973). Similarly, the commercial grades (Tylose and Natrosol) of water-soluble cellulose were analyzed for their moisture content and degree of substitution.

Due to lack of facilities, it was not possible to carry out the determination of the hydroxyethyl cellulose and methyl cellulose contents of Natrosol and Tylose respectively.

CMS — paint formulation

The formulation details for the latex emulsion paints using the cassava-based CMS are given in Table 1 below.

RESULTS AND DISCUSSION

The sodium carboxymethyl starch products based on cassava waste were studied for their degree of substitution or etherification (*DS*),

TABLE 1
Formulation of Latex Paints with Commercial CMC and Cassava-Based CMS

Paint sample code	*A*	*B*	*C*	*D*	*E*	*F*
Emulsion PVA/PVC copolymer	356	356	356	356	356	356
Tioxide	267	267	267	267	267	267
Calcium carbonate	622	622	622	622	622	622
CMS-1	18	—	—	—	—	—
CMS-2	—	18	—	—	—	—
Dowicil 75 (fungicide)	4	4	4	4	4	4
Calgon S	8	8	8	8	8	8
Tylose[a]	—	—	18	—	—	—
Natrosol[a]	—	—	—	18	—	—
Sodium benzoate	13	13	13	13	13	13
Unmodified cassava starch waste	—	—	—	—	18	—
Water (kg)	1	1	1	1	1	1

[a] Commercial grade cellulose thickeners.

moisture, carboxyl and sodium chloride contents. The results showing these are given in Table 2. As can be seen (Table 2), the *DS*, carboxyl and sodium chloride contents of the CMS-2 are higher than those of the CMS-1 product. This is understandable considering the fact that in all cases of etherification the efficiency of the carboxymethylation is increased at high sodium hydroxide concentrations. This is in line with the findings reported by Savage *et al.* (1965). It appears, therefore, that the reaction conditions employed for the production of CMS-2 result in high reaction efficiency, at least in the present study.

Evaluation of the latex paint thickener system

The latex paint systems (at a final pigment/binder ratio of 2·2:1) were prepared according to the formulation given in Table 1. These thickened paints were screened to determine the effects of the thickening agents on the viscosity of the formulations as well as some basic film properties such as their drying characteristics, mechanical properties and water resistance.

Drying characteristics

Since water-based coatings (as in the case of the formulations prepared in this study) dry in air by loss of water, it was important to test their drying characteristics in order to ascertain whether the degree of substitution of cassava CMS as compared to the unsubstituted cassava starch waste thickened paint (sample E) tended to increase or decrease the drying time.

TABLE 2
Characteristics of Cassava-Waste-Based Sodium Carboxymethyl Starch and the Commercial Grades

	CMS-1	*CMS-2*	*Tylose*	*Natrosol*
% Moisture content	6·8	6·5	5·5	5·8
% Carboxyl content	13	25	—	—
% Sodium chloride content	34·7	52	—	—
Degree of substitution (etherification)	0·43	0·61	0·4	2·5

The results given in Table 3 show that the paint sample B thickened with cassava-based CMS-2 (*DS* of 0·61) yields relatively fast-drying films as is the case with sample F (the unthickened formulation). No significant differences in the drying times of sample A (cassava-based CMS-1) and samples D (thickened with commercial grade Natrosol) and C (thickened with commercial grade Tylose) were observed. Minor differences in the drying times of the paint samples could be attributed to the degree of substitution.

Viscosity

The viscosities of the paint samples (Table 3) appear to have no direct correlation with the degree of substitution or the carboxyl content of the cassava thickeners. This is because the magnitudes of the viscosities depend on the molecular weights of the initial starch waste.

Scratch resistance

Scratch resistances of the dried paint films were tested on steel panels with a Sheen Scratch Tester. Scratch resistance (g) data of the paint samples are listed in Table 3. Paint samples A and D had better scratch resistance values than those of samples C and F, with sample E

TABLE 3
Properties of Latex Paint Thickener Systems

Paint sample code	*Viscosity ICI Rotothinner (cP)*	*Solvent resistance (water rubs)*	*Scratch resistance (g)*	*Impact strength*	*Drying characteristics (min)*	
					Dry to touch	*Hard dried*
A	720	69	350	Passed	97	123
B	140	4	50	Passed	33	57
C[a]	880	70	250	Passed	95	119
D[a]	920	71	350	Passed	98	120
E	105	—	20	Failed	112	140
F[b]	50	—	300	Passed	23	50

[a] C and D are paints thickened with the commercial grade thickeners Tylose and Natrosol, respectively.
[b] Unthickened latex paint.

(thickened with the raw cassava starch) offering very little resistance to scratch.

Impact strength

Impact strengths of the dried paint films were tested on steel panels using a Sheen Impact Tester. All the samples (Table 3), excepting paint sample E, passed this test as visual observation showed little damage on the films, indicating good adhesion.

Solvent resistance

The solvent resistance, given by the number of water rubs, indicated that samples A, C and D had comparable solvent resistance levels as seen in Table 3. Sample B showed poorer solvent (water) resistance. It would, therefore, appear that as the *DS* increases the resistance to water decreases. As expected a high *DS* (more water soluble product) results in a lower water resistance.

CONCLUSION

From the results obtained it may be tentatively concluded that the cassava-based CMS-1 thickened paint formulation (sample A) showed good physical properties such as viscosity, scratch hardness, impact strength, drying pattern and water resistance as compared with the paints thickened with the commercial grade thickeners such as Tylose and Natrosol.

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