Effect of Different Types of Surfactants on Cassava Starch Properties[1]

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The effect of anionic, neutral, and cationic surfactants in three different concentrations on cassava starch properties was studied. The iodine affinity of total amylose was reduced by 20–40% by all surfactants, with highest reduction being observed for cetyltrimethylammonium bromide. The iodine affinity of soluble amylose was suppressed by 30–70% by all reagents except cetyltrimethylammonium bromide, which lowered the value to almost zero. There was no significant difference between the concentrations 0.04 and 0.06 mol of surfactant per 100 g of starch. Viscosity was stabilized by potassium stearate and potassium palmitate without greatly affecting the peak viscosity of 660 BU of pure starch, but sodium lauryl sulfate and cetyltrimethylammonium bromide increased the peak viscosity to 900 and 780 BU, respectively, at 0.06-mol concentration and did not show stable viscosity during the holding period. Defatted and raw starch showed similar viscosity patterns on incorporation of surfactants. Pasting temperature was increased to over 90 °C by potassium stearate, palmitate, and glyceryl monostearate, while the increase was only by 3–15 °C over control (65 °C) by the other two reagents. The swelling volume of starch was reduced to nearly half the original value by potassium palmitate and stearate, while glyceryl monostearate did not change it noticeably. Sodium lauryl sulfate and cetyltrimethylammonium bromide increased the value by nearly 50%. Sol stability was improved considerably by all the reagents. The results are discussed in relation to structure of the surfactants.

INTRODUCTION

Surfactants have been in use in food industry since 1920s mainly as dough conditioners, as crumb softeners in breads, buns, and rolls, and as amylose complexing agents in starch-based foods. The crumb-softening effect of the surfactants is based on the formation of surfactant–amylose complex, and good correlation between the amylose complexing index of various surfactants and their crumb softening effect has been found (Krog and Nyobojensen, 1970; Lagendijk and Pennings, 1970; Krog, 1981).

Similarly, use of monoglycerides in the production of dehydrated mashed potato is aimed at binding free amylose to control the stickiness or gluiness of the product. Here also the role of the surfactant as amylose complexing agent has been established (Hoover and Hadziyev, 1981a, 1981b, 1982).

The structure of the amylose–surfactant complex has been investigated in detail. It has been observed early that iodine affinity of starch is reduced drastically by addition of fats and surfactants. Butanol-precipitated corn amylose showed reduction in iodine affinity from 18.7% to 0% by addition of 10% palmitic acid (Schoch and Williams 1944). Osman et al. (1961), however, found that though the iodine affinity of corn starch amylose was reduced by addition of surfactants, it never reached zero value. On the basis of iodine affinity studies, it has been proposed that amylose forms a helical structure that is stabilized by the hydrocarbon part of the surfactant, which fulfills the hydrophobic solvation requirements of the helix (Krog, 1981). Carlson et al. (1979) have used X-ray and Raman spectroscopies to study the complexes, and their results also confirm a helical inclusion complex.

The effect of surfactants on the viscosity of starch pastes has been studied by Osman and Dix (1960) and Krog (1973). The former group observed that the pasting temperature of corn starch was increased in the case of nonionic surfactants. The effect was related to length of hydrocarbon chain in the surfactants. Krog used monoglycerides, steroyl 2-lactylates, and diacetylated tartaric acid esters of monoglycerides (DATE) at 0.5% concen-

trations in his study of their effects on various starches including cassava starch. The peak viscosity of cassava was slightly reduced by all the emulsifiers. The viscosity during the holding period was stabilized by glyceryl monostearate (GMS) while it was destabilized by DATE. The pasting temperature was increased by GMS and sodium steroyl lactylate while calcium steroyl lactylate and DATE had no effect.

Hoover and Hadziyev (1981a, 1981b, 1982) have studied in detail the potato amylose–monoglyceride complex and the effect of this complexing on starch properties like swelling power, water-binding capacity, solubility, and blue value index. They found that swelling power and solubility were reduced by both monoglycerides and the potassium salts of fatty acids and the reduction was dependent on the chain length of the fatty acid portion of the surfactants. Both water-binding capacity and blue value index were suppressed.

Apart from the study on the brabender viscosity pattern and pasting behavior of cassava starch in the presence of various surfactants by Krog (1973), there has been no systematic investigation on the effects of different surfactants on the properties of cassava starch. Hence, the present study was undertaken using cationic, anionic, and neutral surfactants in three concentrations each (0.02, 0.04, and 0.06 mol per 100 g of starch). In addition to the total and soluble amylose binding capacity, the 2% solution viscosity and 6% paste viscosity of cassava starch in the presence of surfactants, the effect on swelling power, and sol stability have been examined, since cassava starch has a high swelling power and low retrogradation tendency compared to cereal starches. Cassava starch finds extensive use in food and industry, and the results can prove useful to find out ways to improve its undesirable properties like unstable viscosity and long cohesive texture of its paste.

MATERIALS AND METHODS

Commercial grade cassava starch obtained from Lakshmi Starch Factory, Kundara, Kerala, India, was used as such or after defatting by hot extraction with petroleum ether (60–80 °C). The five surfactants used for the study include three anionic and one each of neutral and cationic surfactants. The anionic ones were potassium stearate and potassium palmitate with 16- and 18-carbon chains in the

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Table I. Total and Soluble Amylose Content of Surfactant-Incorporated Starch

starch	blue value	
	total amylose: 0.58	sol amylose: 0.35
starch (100 g) + 0.02 mol of potassium stearate	0.45	0.18
starch (100 g) + 0.04 mol of potassium stearate	0.41	0.11
starch (100 g) + 0.06 mol of potassium stearate	0.41	0.13
starch (100 g) + 0.02 mol of potassium palmitate	0.41	0.17
starch (100 g) + 0.04 mol of potassium palmitate	0.38	0.11
starch (100 g) + 0.06 mol of potassium palmitate	0.37	0.10
starch (100 g) + 0.02 mol of GMS	0.42	0.16
starch (100 g) + 0.04 mol of GMS	0.41	0.16
starch (100 g) + 0.06 mol of GMS	0.41	0.14
starch (100 g) + 0.02 mol of sodium lauryl sulfate	0.44	0.22
starch (100 g) + 0.04 mol of sodium lauryl sulfate	0.41	0.20
starch (100 g) + 0.06 mol of sodium lauryl sulfate	0.39	0.18
starch (100 g) + 0.02 mol of cetyltrimethylammonium bromide	0.37	0.05
starch (100 g) + 0.04 mol of cetyltrimethylammonium bromide	0.35	0.02
starch (100 g) + 0.06 mol of cetyltrimethylammonium bromide	0.34	0.01
CD (5%) for interactn	0.021	0.014
CD (5%) for concn	0.009	0.006
CD (5%) for reagents	0.011	0.006

hydrophobic portion and sodium lauryl sulfate with a 12-carbon chain. The neutral surfactant was glyceryl monostearate (18-carbon chain) while the cationic one was cetyltrimethylammonium bromide (with chain length of 16 carbons in the hydrophobic portion). Analar grade reagents were used for preparation of the complex with starch. Three concentrations of each of the surfactants were tried, viz. 0.02, 0.04, and 0.06 mol per 100 g of starch. The concentration factor was fixed as moles/100 g of starch to eliminate the effect of the large difference in molecular weights between the surfactants.

The starch–surfactant complex was prepared by the procedure described by Hoover and Hadziyev (1981a). The surfactant was dispersed in 50 mL of distilled water preheated to 65 °C and stirred for 30 min. The temperature was brought down to 45 °C, 50 g of dry starch in 100 mL of water was added, and the slurry was heated at 45 °C for 6 h with continuous slow stirring. The suspension was filtered, washed thoroughly, and dried at room temperature.

Blue values for total amylose and soluble amylose were determined by the colorimetric procedure described by Sowbhagya and Bhattacharya (1971) and Shanty et al. (1980), respectively, using pure amylose (SIGMA) as standard. Three replications were used for determination of blue values.

Viscosity of the starch and starch–surfactant complex solutions (2%) was determined by the ISI procedure using Redwood viscometer No. 1, (ISI, 1970). A 4-g sample of material was dissolved in 200 g of hot distilled water, heated at 100 °C for 30 min, filtered through cheese cloth, and cooled to 75 °C, and viscosity was taken as the time taken in seconds for 50 mL of the solution to pass through the orifice of the viscometer. Three readings were taken for each sample.

Paste viscosity of a 6% paste of starch and its complexes were monitored on a Brabender viscoamylograph (Model 801020) provided with automatic heating and stirring systems (75 rpm, 1.5 °C/min). 27 g of the material (dry weight basis) was suspended in 450 mL of distilled water in the amylograph cup and heated with stirring at 75 rpm at 1.5 °C/min. At 97 °C, the temperature was maintained constant for 20 min. The pasting temperature range was obtained as the range between the temperature at the start of increase of viscosity and that at which it remains constant.

The swelling volume was obtained by Schoch's method (Schoch, 1964). A 0.5-g portion of dry material in 50 mL of distilled water was heated with stirring to 80 °C in a water bath, maintained at 85 °C for 15 min, cooled, and centrifuged at 2200 rpm for 15 min, and the swelling volume was expressed as the volume of gelatinous sediment per 1 g of dry starch. The sol stability was taken as the time taken by the starch gel to start settling on keeping undisturbed (with a little amount of toluene added to prevent microbial damage).

RESULTS AND DISCUSSIONS

The total iodine affinity and the iodine affinity of soluble amylose are given in Table I in terms of blue values. The maximum reduction in iodine affinity of total amylose is observed in the case of cetyltrimethylammonium bromide. All the other reagents show an almost equal reduction in affinity. Since reduction in iodine affinity value can be taken as a measure of the complex formation, it can be concluded that cetyltrimethylammonium bromide complexes to the maximum extent and potassium stearate and sodium lauryl sulfate the least.

It is also seen from Table I that the differences in blue values at concentrations of 0.04 and 0.06 mol are nonsignificant. The reduction in blue value of amylose with addition of increasing amounts of fatty acids or surfactants is reported by many authors, but the present study indicates that blue values of cassava starch tend to taper off on increase in concentration above 0.04 mol of surfactant per 100 g of starch. Similar results have been obtained for potato starch by Hoover and Hadziyev (1982), who found that the blue value remains constant above a concentration of 0.3% glyceryl monostearate. Hence, at higher concentrations, the surfactant may not be forming an effective complex. The amylopectin molecules may be offering resistance to the surfactant to complex with the amylose molecules, and hence all the amylose is not bound by the surfactants.

The blue values of the soluble amylose in the treated samples give an indication of the preference of the reagents to add to free amylose. The results (Table I) indicate that all the surfactants reduce the value considerably and that the ratio of blue values of total to soluble amylose is in the range 2–2.5 for all reagents except in the case of cetyltrimethylammonium bromide, which imparts a very low blue value for soluble amylose. Here also, there is no significant difference between the concentrations 0.04 and 0.06 mol. Though all the treatments are significantly different, the values with cetyltrimethylammonium bromide point out that this surfactant has a very high affinity for soluble amylose. At a 0.06-mol concentration, the blue value nearby reaches zero, indicating that this reagent is
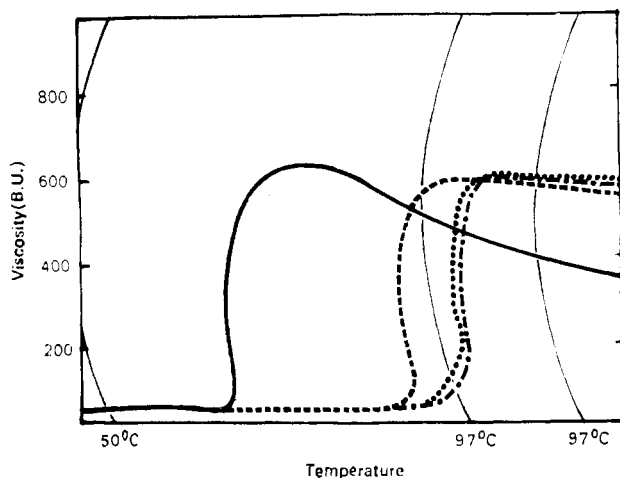
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Figure 1. Effect of potassium stearate on the Brabender viscosity curve of cassava starch: —, cassava starch (raw/defatted); - - -, cassava starch + 0.02 mol of potassium stearate (per 100 g of starch); ⋯ cassava starch + 0.04 mol; –·–, cassava starch + 0.06 mol.
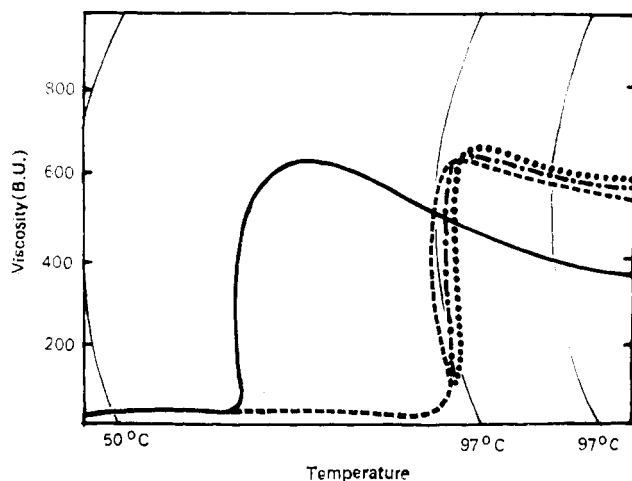

Figure 3. Effect of glyceryl monostearate on the Brabender viscosity curve of cassava starch: —, cassava starch (raw/defatted); - - -, cassava starch + 0.02 mol of GMS (per 100 g of starch); ⋯, cassava starch + 0.04 mol; –·–, cassava starch + 0.06 mol.

Figure 2. Effect of potassium palmiate on the Brabender viscosity curve of cassava starch: —, cassava starch (raw/defatted); - - -, cassava starch + 0.02 mol of potassium palmitate (per 100 g of starch); ⋯ cassava starch + 0.04 mol; –·–, cassava starch + 0.06 mol.

Figure 4. Effect of sodium lauryl sulfate on the Brabender viscosity curve of cassava starch: —, cassava starch (raw/defatted); - - -, cassava starch + 0.02 mol of Sodium lauryl sulfate (per 100 g of starch); ⋯, cassava starch + 0.04 mol; –·–, cassáva starch + 0.06 mol.

binding almost all the soluble amylose. Such high tendency of surfactant to complex with soluble amylose is reported for the first time.

The viscosity of a 2% solution of starch and surfactant-incorporated starch is given in Table II. Treatment with surfactants at all concentrations increases the viscosity, especially with sodium lauryl sulfate and cetyltrimethylammonium bromide. All the treatments and concentration show significant differences in viscosity. However, no direct relation between the increasing concentration and an increase in viscosity could be observed. In the cases of potassium stearate, potassium palmitate, and sodium lauryl sulfate, there is only a slight increase in viscosity at 0.06-mol concentration compared to that of 0.02-mol concentration. Cetyltrimethylammonium bromide, however, exhibits a regular increase in viscosity with increasing concentration. The absence of a regular increase in viscosity with increasing concentration in the case of treatment with GMS may be due to incomplete gelatinization of starch granules, as observed by congo red staining experiments that showed that 20–25% of the granules in the solution remained ungelatinized.

The Brabender viscosity curves for the samples are given in Figures 1–5. The results indicate that different sur-
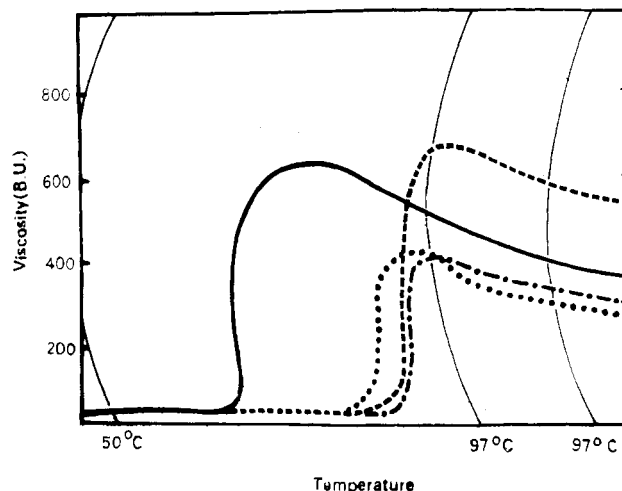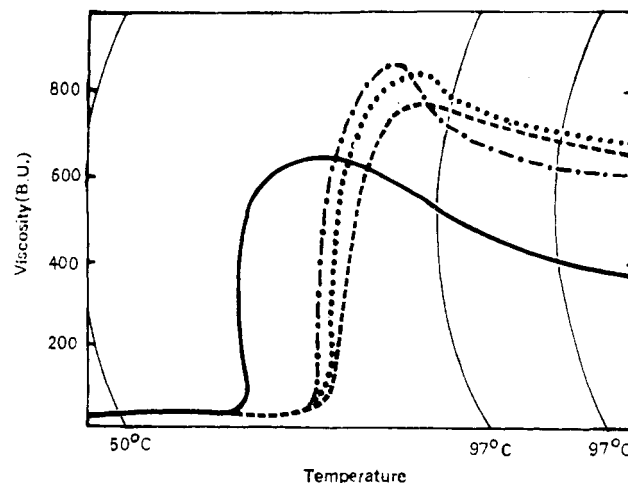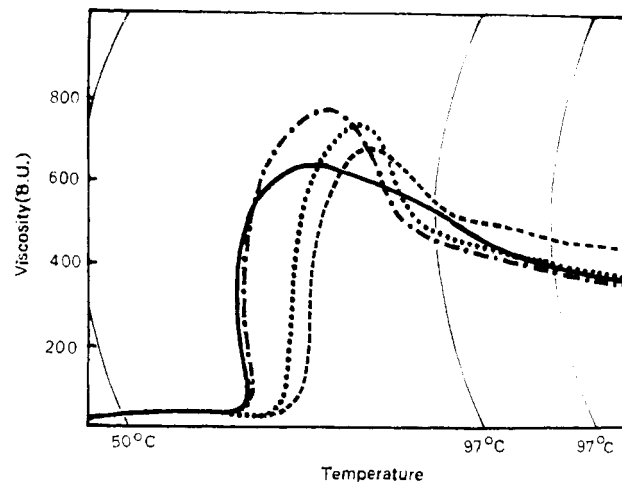

Figure 5. Effect of cetyltrimethylammonium bromide on the Brabender viscosity curve of cassava starch: —, cassava starch (raw/defatted); - - -, cassava starch + 0.02 mol of cetyltrimethylammonium bromide (per 100 g of starch); ⋯, cassava starch + 0.04 mol; –·–, cassava starch + 0.06 mol.

factants show different patterns. Potassium palmitate and stearate suppress the peak viscosity slightly, but the vis-

Table II. Viscosity and Pasting Temperature of Surfactant-Incorporated Starch

	2% visc, s	peak visc, 6% paste, BU	pasting temp, °C
starch	50	660	65–77
starch (100 g) + 0.02 mol of potassium stearate	57	600	95–97
starch (100 g) + 0.04 mol of potassium stearate	55	620	95–97
starch (100 g) + 0.06 mol of potassium stearate	62	600	97
starch (100 g) + 0.02 mol of potassium palmitate	64	640	95–97
starch (100 g) + 0.04 mol of potassium palmitate	72	680	96–97
starch (100 g) + 0.06 mol of potassium palmitate	70	660	97
starch (100 g) + 0.02 mol of GMS	95	680	90–97
starch (100 g) + 0.04 mol of GMS	55	420	88–94
starch (100 g) + 0.06 mol of GMS	70	420	94–97
starch (100 g) + 0.02 mol of sodium lauryl sulfate	84	800	78–94
starch (100 g) + 0.4 mol of sodium lauryl sulfate	90	880	78–92
starch (100 g) + 0.06 mol of sodium lauryl sulfate	87	900	77–88
starch (100 g) + 0.02 mol of acetyltrimethylammonium bromide	69	680	73–85
starch (100 g) + 0.04 mol of acetyltrimethylammonium bromide	90	740	68–83
starch (100 g) + 0.06 mol of acetyltrimethylammonium bromide	96	780	68–80
CD (5%) for interactn	2.41		
CD (5%) for concn	1.08		
CD (5%) for reagents	1.40		

cosity remains almost steady during the holding period. Thus, a slight reduction in swelling along with a good strengthening of the starch granules against shear and temperature is imparted by these reagents. The peak viscosity does not show an increase with increasing concentration of the reagent. The results point out that these reagents can be useful in stabilizing the viscosity of cassava starch. The increased resistance to breakdown under shear and temperature can be useful to prevent the long cohesive nature of the starch paste. The stabilization is achieved even at the lowest concentration (0.02 mol), and the production of the surfactant–starch complex is easier compared to cross-linking by chemical reactions (Srivastava and Patel, 1973; Knight, 1974) or physical treatment (Moorthy, 1980).

Sodium lauryl sulfate increases the peak viscosity considerably, and at a 0.06-mol concentration, it reaches 900 BU. However, during the holding period, the viscosity drops rapidly and reaches the value of pure starch. This result shows that sodium lauryl sulfate binds with starch molecules and allows them to swell considerably, but under shear and temperature, the complex breaks down to release the swollen starch granules that start fragmenting.

Glyceryl monostearate increases peak viscosity slightly at a 0.02-mol concentration, but at higher concentrations, the values fall. These results, as also the 2% viscosity values, show that gelatinization is not complete at 97 °C. The viscosity is maintained during the holding period, and hence this reagent can also be used at a 0.02-mol concentration for viscosity stabilization of cassava starch. Krog (1973) in his study has also found that GMS at 0.5% concentration stabilizes cassava starch viscosity. However, he found a slight decrease in peak viscosity with the reagent at 0.5% concentration.

Cetyltrimethylammonium bromide leads to a steady increase in peak viscosity with increasing concentration, reaching 780 BU at a 0.06-mol concentration. However, the viscosity breaks down during the holding period, similar to the case of sodium lauryl sulfate incorporated starch, indicating that the complex is unstable on heating and stirring.

In order to compare the effects of surfactants on defatted and nondefatted cassava starch, the Brabender viscosity pattern of surfactant-incorporated starch prepared from nondefatted (raw) starch was obtained. It was found that there is practically no difference in the viscosity pattern, peak viscosity, or pasting temperature, between defatted or raw starch treated with surfactants. This can be explained by the low fat content of cassava starch compared to cereal starches.

Taylor and Nelson (1920) reported values of 0.61% and 0.11% fat content, respectively, for maize and cassava starches. Compared to the high lipid content in maize starch (0.87%; Morrison, 1976) or rice starch (0.4%; Maningat and Juliano, 1980), the minor amount of lipid in cassava starch may not be existing as a complex with amylose molecules to be affected by addition of surfactants. The gelatinization temperature is lowered by extraction of lipids from corn, wheat (Melvin, 1979), or rice (Ohashi et al. 1980) starches, but no such effect is observed in cassava starch.

The pasting temperature as observed from the Brabender viscosity curves are given in Table II. Invariably all the reagents increase the pasting temperature, but to different extents. In the case of potassium palmitate and stearate, the pasting temperature initiation is increased by around 30 °C and the pasting temperature range is narrowed to 2 °C. At higher concentrations, the rise in viscosity appears only at 97 °C. It was also found by congo red staining that all the granules do not gelatinize at 97 °C, but only during the holding period. The high pasting temperature indicates the resistance offered by the surfactants that fit into the amylose helix to entry of water molecules. With GMS also, the pasting temperature is enhanced to over 90 °C, but the range is comparatively more than with potassium palmitate or stearate. At higher concentrations, incomplete gelatinization becomes prominent.

Sodium lauryl sulfate and cetyltrimethylammonium bromide increase the pasting temperatures to a lower extent. At higher concentration of the reagents, there is even a drop in the pasting temperature. The results with pasting temperature show that reagents with small hydrophilic groups impart a higher increase in pasting temperature. This may be due to the closer packing these reagents can achieve with the starch molecules. As Carlson has pointed out (1979), part of the hydrocarbon chain lies outside the amylose helix and this length may be dependent on the bulk of the hydrophilic group. Sodium lauryl sulfate and cetyltrimethylammonium bromide having big hydrophilic groups do not fit so closely as the other reagents into the starch molecules and hence cannot prevent entry of water molecules, when compared to the surfactants with the smaller hydrophilic groups. The re-

Table III. Swelling Volume and Sol Stability of Surfactant-Incorporated Starch

	swelling vol, mL	sol stability, days
starch	40.0	2
starch (100 g) + 0.02 mol of potassium stearate	21.0	7
starch (100 g) + 0.04 mol of potassium stearate	19.5	9
starch (100 g) + 0.06 mol of potassium stearate	19.0	9
starch (100 g) + 0.02 mol of potassium palmitate	24.0	8
starch (100 g) + 0.04 mol of potassium palmitate	23.0	7
starch (100 g) + 0.06 mol of potassium palmitate	22.5	8
starch (100 g) + 0.02 mol of GMS	37.0	10
starch (100 g) + 0.04 mol of GMS	40.0	8
starch (100 g) + 0.06 mol of GMS	37.0	9
starch (110 g) + 0.02 mol of sodium lauryl sulfate	64.5	12
starch (110 g) + 0.04 mol of sodium lauryl sulfate	64.0	14
starch (110 g) + 0.06 mol of sodium lauryl sulfate	63.5	14
starch (100 g) + 0.02 mol of cetyltrimethylammonium bromide	57.0	11
starch (100 g) + 0.04 mol of cetyltrimethylammonium bromide	64.5	12
starch (100 g) + 0.06 mol of cetyltrimethylammonium bromide	66.5	11
CD (5%) for interactn	0.94	
CD (5%) for concn	0.42	
CD (5%) for reagents	0.54	

duction in pasting temperature with a higher concentration of the reagents is also indicative of mutual crowding of the surfactant molecules.

The effect of the size of the hydrophilic portion of the surfactant in comparison to the hydrophobic chain has been discussed by Osman and Dix (1960) as well as Krog (1973). The results obtained also confirm the importance of close packing of the hydrophobic group into the amylose helix to render it stable.

The very slight increase observed in the pasting temperatures in the case of cetyltrimethylammonium bromide in contrast to the notable decrease in blue value with the same reagent indicates that this reagent is able to block the entry of bulky I_3^- ion and not the much smaller water molecule.

Swelling volume is an important characteristic of starch, especially for cassava starch, which exhibits high swelling property. A large swelling can lead to reduction in associative forces, resulting in breakdown of granules and simultaneous cohesive texture. The swelling volumes of treated samples are given in Table III. The treatments and concentration show significant variations. It is seen that potassium stearate and palmitate reduce the swelling volume to almost half its original value, even at lowest concentrations. GMS also reduces the swelling volume, but only to a very small extent. Sodium lauryl sulfate, on the other hand, increases the value considerably. A similar result is also obtained with cetyltrimethylammonium bromide.

GMS has been reported to reduce the swelling power of potato starch by 10%, but the value tapers off above 0.3% concentration of GMS (Hoover and Hadziyev, 1982). Such high reduction in swelling volume in the case of potassium stearate or palmitate and increase by over 50% by sodium lauryl sulfate and cetyltrimethylammonium bromide have not been reported so far.

The swelling of starch is determined by the strength of associative forces between molecules and also contributes to the viscosity of the paste. The high paste viscosity obtained for starch incorporated with cetyltrimethylammonium bromide and sodium lauryl sulfate and the high viscosity breakdown are explainable by the high swelling volume of these starch complexes. GMS exhibits almost the same swelling volume and viscosity as pure starch, but potassium stearate and palmitate reduce the swelling volume without reducing the viscosity of starch. Associative forces between starch granules in addition to intermolecular association between starch molecules in the

starch granules may be playing a role in determining these properties.

The sol stability of starch paste was found to be increased by all the reagents (Table III). Among the reagents, sodium lauryl sulfate exhibited highest stability (10 days) while there was not much difference between the other reagents. The reagents act by inhibiting parallel association of linear amylose chains or the outer chains of amylopectin molecules that would otherwise lead to settling of the starch gel.

Thus, the study points out that different types of surfactants modify the properties of cassava starch differently. Cetyltrimethylammonium bromide shows high affinity for soluble amylose compared to other surfactants. Potassium stearate and potassium palmitate stabilize the paste viscosity of cassava starch without affecting the peak viscosity, while sodium lauryl sulfate and cetyltrimethylammonium bromide increase the peak viscosity but do not stabilize the viscosity. The instability of the complexes of amylose with these reagents may be explained as due to the relatively bulky hydrophilic group in them, as suggested by Krog (1973). The lack of difference between viscosity properties of defatted and nondefatted starch on surfactant incorporation may be due to relatively low lipid content of cassava starch. The wide variations in swelling volume of starch imparted by different types of surfactants and the improvement in sol stability are reported for the first time. The study also shows that concentrations above 0.04 mol/100 g of starch do not have much effect on most of the properties.

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Vinclozolin Decay on Different Grapevines in Four Differing Italian Areas

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A comparative study of the decay of Vinclozolin on four different grapevines in four widely differing areas of Italy was carried out. The residues from two different doses of the commercial product were examined by gas chromatography during 3 weeks following each treatment. The decline of the residues in all cases was described by an exponential trend ($Y = Ae^{-KX}$). The theoretical half-life of the original residue (that present after 2 h) varied quite considerably in the four areas (Piedmont, Friuli, Latium, Emilia), whereas successive treatments in the same location varied less. The minimum half-life was 1.2 days for the normal and 2.0 days for the double dose (Emilia); the maximum was 4.6 and 4.9 days (Piedmont).

INTRODUCTION

Vinclozolin, 3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione, is widely used in Italian grape cultivation to control *Botrytis* and has been the object of numerous studies from the purely residual point of view (Molinari et al., 1978, 1983; Barbina Taccheo et al., 1978; Zanini et al., 1980; Del Re et al., 1980, 1981; Flori et al., 1980, 1982; Cabras et al., 1983). One aspect has been rather neglected: the variations of the residues in the treatment parts of the plant induced by the environment. This investigation is important from both an agricultural and a pesticide residue level point of view.

It is normal practice both in Italy and in other countries to establish an interval of time after the final spraying with a pesticide at the end of which the residue in the edible product must not exceed a certain tolerance level. This is fixed for each pesticide without taking into account that it might differ widely from one environment to another, from one crop to another, or even from one variety to another of the same crop. The safety interval, moreover,

is fixed with reference only to the final spraying and does not take into account the fact that the final residue level of an active principle is very often the consequence of several successive treatments carried out according to a time table or in response to particular environmental conditions or particular stages of development of the crop: each treatment could be influenced by those preceding it. On the other hand, the efficacy of many pesticides, especially if systemic or translaminal, is often a function of their persistence. This characteristic can be of extreme practical importance in preventive pest control and when protection is guaranteed only if the pesticide does not decay too rapidly.

With the same crop in different environments the effects of sunlight, daily temperature changes, and rainfall must be carefully evaluated by comparing the degradation curves. The present study was conducted to illustrate the varying behavior of a pesticide: widely differing environments were chosen (Piedmont, Friuli, Latium, Emilia), involving one crop, grapevine, and a single active principle, Vinclozolin, in a sample year, 1983, so as to illustrate a representative situation that can be generalized to a wider context.

MATERIALS AND METHODS

The investigation was carried out during 1983 by the following research units of the Gruppo di Ricerca Italiano Fitofarmaci e Ambiente (Italian Group for Pesticide and Environment Research): A. Piedmont, Istituto di Chimica Agraria and Laboratorio NMR e Spettroscopie Applicate alla Tossicologia, University of Turin; Experimental sta-

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