Microwave-assisted esterification of cassava starch

A.N.Jyothi[1], S.N.Moorthy[1] and K.N.Rajasekharan[2]

[1]Central Tuber Crops Research Institute,Kerala, India
[2]Dept. of Chemistry, University of Kerala, India

email:sreejyothi_in@yahoo.com

Introduction

- Cassava and maize - major commercial sources of starch
- Cassava starch - tropical countries
- Desirable characteristics such as easy extractability, bland flavour, high paste viscosity and clarity
- Major drawback -instablility of paste

- Esterification- derivatives with good viscosity stability and low pasting temperature
- Conventional esterification reactions - aqueous alkaline medium - require long time to attain a desired level of substitution
- Microwave reactions
  - Ultra fast, reproducible and scalable
  - Cleaner products
  - Use of solvent-free systems - Microwaves interact directly with the reagents and can therefore, drive chemical reactions more efficiently

- Microwave irradiation seems applicable to starch processing but it has not yet been used widely
- Dextrinization and some chemical modification of starch by microwave irradiation are reported (Muzimbaranda and Tomasik, 1994; Sikora *et al*., 1997a,b; Lewandowicz *et al*., 1997, 2000; Szepes *et al.,* 2005)
- Systematic studies on the modification of cassava starch by microwave technique are relatively sparse
- Objectives:
  - To study the application of microwave heating for the synthesis of succinic, alkenyl succinic, citric and phosphate esters of cassava starch
  - Characterization of the products

Materials and Methods

- Cassava starch: commercial sample
- Microwave oven: A domestic oven with convection heating (Kenstar, Pune, India)
  - Power: 500 W
  - Frequency: 2450 Hz
- Reagents: Dodecenyl succinic anhydride (DDSA) and Octenyl succinic anhydride (OSA) (Sigma-Aldrich, USA)
- Citric acid, Succinic anhydride,sodium dihydrogen phosphate and disodium hydrogen phosphate (E-Merck, Mumbai)

Synthesis of starch esters

Succinylation

- Concentration of succinic anhydride: 0.25, 0.50 and 0.75 moles/mole of AGU
- Starch was mixed thoroughly with required quantity of succinic anhydride and subjected to microwave irradiation at 100 $^{\circ}\mathrm{C}$ for 5 min
- Cooled and dispersed in ethanol (85 %)
- After pH adjustment, product was washed with 85 % ethanol and finally with absolute ethanol
- Filtered and dried in an air oven at 55 $^{\circ}\mathrm{C}$ overnight

Alkenyl succinylation

Synthesis of dodecenyl succinates

- Concentration of DDSA: 0.06, 0.09 and 0.12 moles /mole of AGU
- Reaction time: 3, 5 and 7 min
- Starch was thoroughly mixed with required quantity of DDSA
- The mixture was irradiated by microwaves with convection heating at 100°C for the required time
- After cooling, samples were slurried in distilled water, pH was adjusted to 6.5
- Washed with distilled water and finally with acetone, filtered and dried at 55°C

Synthesis of octenyl succinates

- Concentration of OSA: 0.0375, 0.075 and 0.15 moles /mole of AGU
- Time of reaction: 3, 5 and 7 min
- Starch was thoroughly mixed with weighed quantity of OSA
- The mixture was microwave irradiated at 100°C for the required time
- After cooling, samples were slurried in distilled water, pH was adjusted to 6.5
- Washed with distilled water and finally with acetone, filtered and dried at 55°C

Synthesis of Starch Citrates

- Concentration of citric acid: 0.15, 0.3 and 0.45 moles /mole of AGU
- Time of microwave exposure: 3, 5 and 7 min
- Temperature: 120, 140 and 160°C
- Citric acid was dissolved in water, pH adjusted to 3.5
- Added to powdered starch and conditioned overnight at room temperature
- Dried in an air oven at 50 $^{\circ}$C to 5- 10 % moisture
- Powdered and subjected to microwave irradiation
- Washed with distilled water several times, filtered and dried at 40°C overnight

Synthesis of Starch Phosphates

- Reagent concentration ($NaH_2PO_4.2H_2O$: Na_2HPO_4) = 0.5 : 1, 1 : 1 and 1.5 : 1 mole per mole of AGU
- Reaction time: 7, 10 and 13 min
- Temperature: 120, 140 and 160 $^{\circ}C$
- Accurate amounts of the reagents were calculated to prepare different molar ratio and dissolved in distilled water, pH-6.0
- Starch was slurried in the salt solution and stirred for 10 min
- Filtered, cake dried overnight at 50 $^{\circ}C$, powdered and dried at 65 $^{\circ}C$ for 90 min
- Subjected to microwave irradiation by convection heating, cooled, slurried in 50 % aqueous methanol, washed and dried at 45 $^{\circ}C$ overnight

Analytical procedures

The products were characterized by determining

- Degree of substitution (DS)
- Scanning Electron Microscopy: Hitachi S/2400 microscope (Hitachi Instruments, Inc., CA)
- Physicochemical properties
  - Swelling Volume and Solubility: standard procedures of Schoch, 1964 and Crosbie (1991)
  - Light Transmittance (% T) or paste clarity: Bello-Perez and Paredes-Lopez (1996)
  - Water Binding Capacity (WBC): Standard method of Yamazaki (1953), modified by Medcalf and Gilles (1965)
  - Viscosity: Rapid Visco Analyzer (RVA-4, Newport Scientific, Australia)

Results and Discussion

Scanning electron microscopy

- Cassava starch granules are spherical with a flat surface on one side containg a pit Figure
- Granule structure was found to be altered for the starch succinate Figure
- Fragmented and deformed granules, inward folding, resulting in channel like appearance
- For DDSA starch, granule surface appeared smoother, deformed granules Figure
- Granule surface of OSA starch became smoother Figure
- Affected granules appeared larger in size; granule rupture

Degree of substitution (DS)

Sample	Reagent conc. (mole/mole of AGU)	Time (min)	Temp (°C)	DS
Succinate	0.75	5	100	0.303
DDSA starch	0.12	5	100	0.02
OSA starch	0.15	7	100	0.061
Citrate	0.45	7	160	0.063
Phosphate	0.5 :1	13	140	0.088

Viscosity parameters (RVA) of native and esterified starches

Sample	PV (cP)	Setback	Br. ratio	Past temp (°C)
Native starch	2880.0	981.0	0.668	69.1
Succinate	14957.0	9225.0	0.983	51.4
DDSA starch	2734.0	1364.0	0.525	66.0
OSA starch	2419.0	1150.0	0.515	67.1
Citrate	7564.5	3533.0	0.553	62.9
Phosphate	403	44.5	0.623	NR

Physicochemical properties

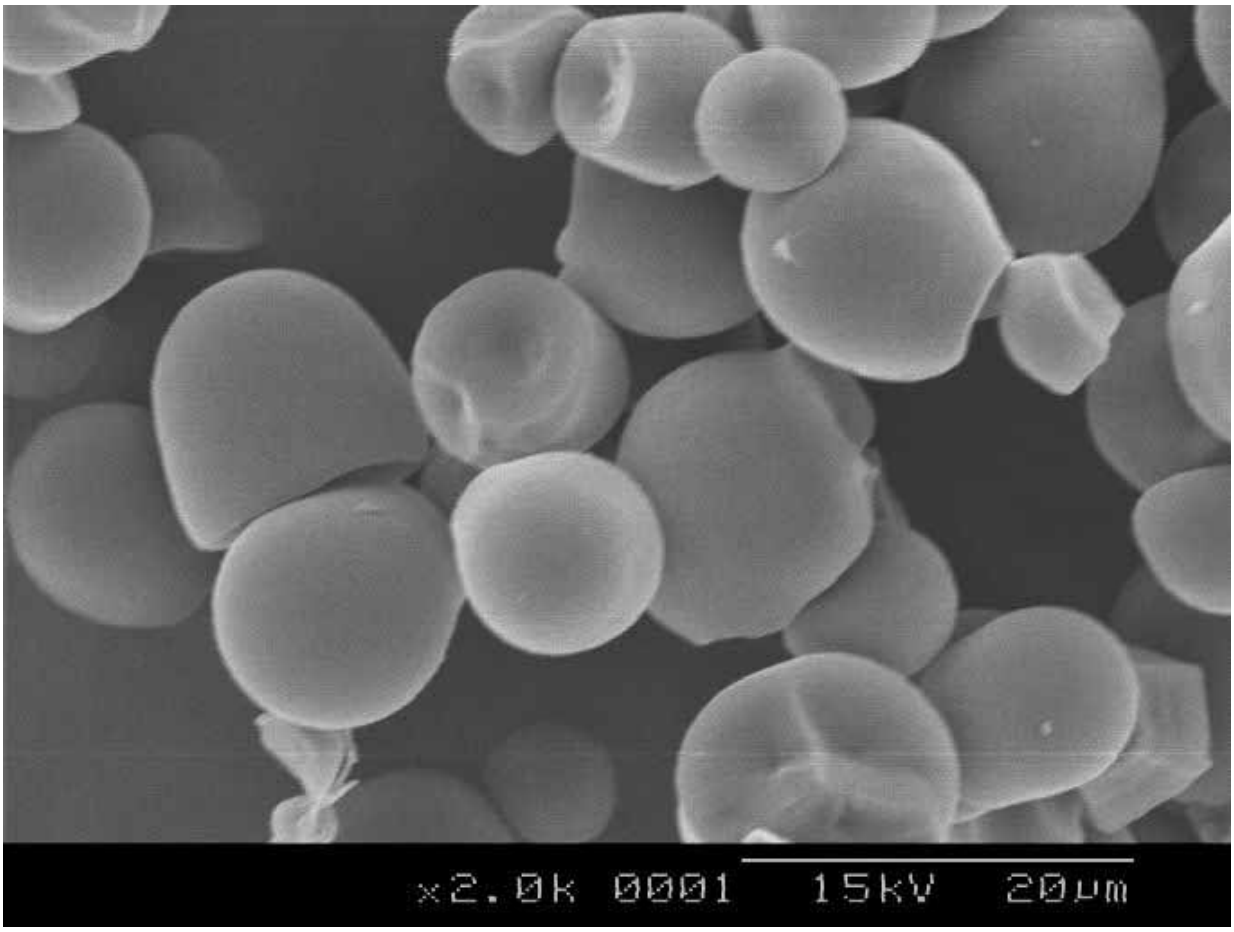
Sample	Swelling vol. (ml/g)	Solubility (%)	Light transmittance (%)	WBC (%)
Native starch	27.0	20.2	22.8	68.3
Succinate	38.5	4.1	7.4	652.7
DDSA starch	22.0	17.8	5.9	98.6
OSA starch	32.0	29.9	10.1	104.3
Citrate	21.5	13.1	9.8	106.4
Phosphate	4.5	76.6	70.0	161.7

- Dodecenyl and octadecenyl derivatives: exhibited hrophilic and hydrophobic properties and free-flow nature
- Succinate starch produced highly opaque gels Figure
- Gel of the dodecenyl succinate starch showed more hardness than native starch, appeared opaque Figure

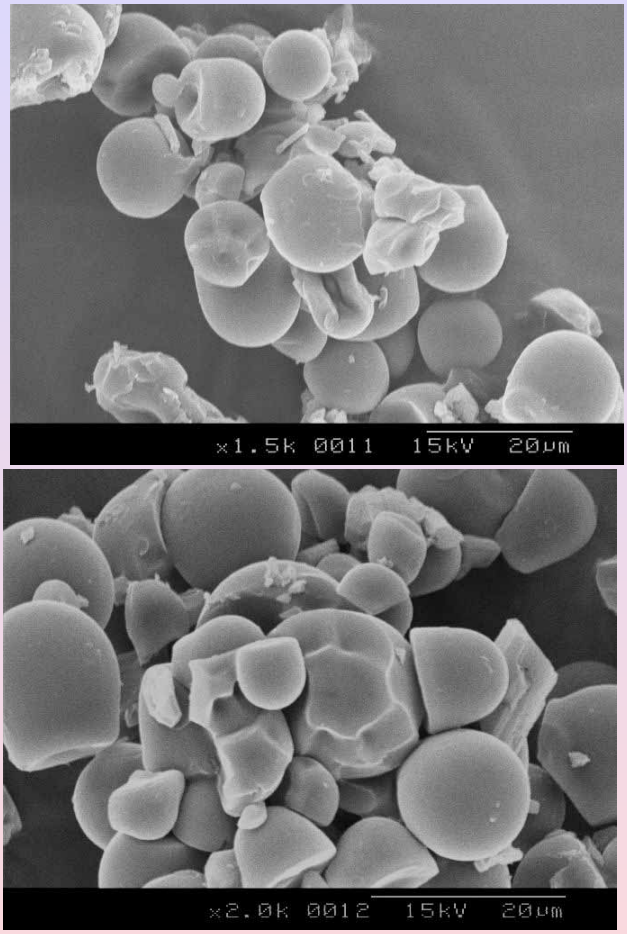
Conclusions

- Esterification of cassava starch was found to be very successful under microwave conditions in the dry state
- Reaction time for esterification could be reduced to a few minutes and higher DS derivatives were obtained than those in conventional reactions
- Succinate and phosphate derivatives showed low temperature swelling properties
- Alkenyl succinylation resulted in derivatives with amphiphilic side chains


Thank You



Back to presentation



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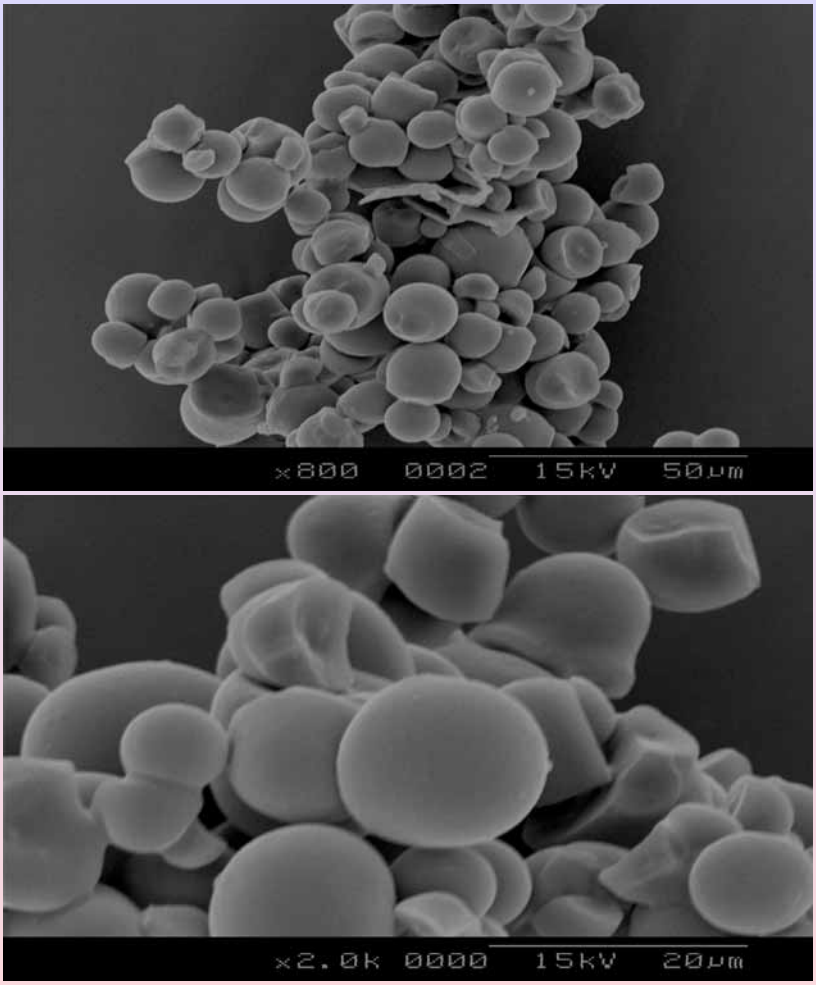

Back to presentation

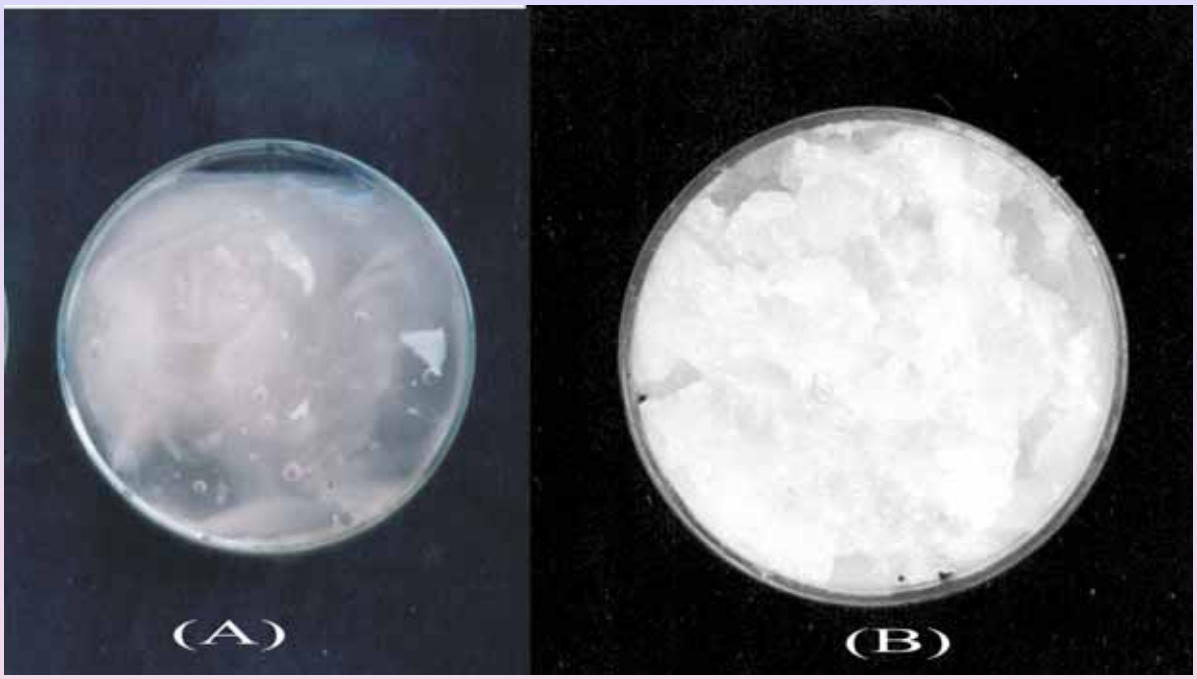

Figure: Gels of native (A) and dodecenyl succinate derivative (B) of cassava starch

Back to presentation

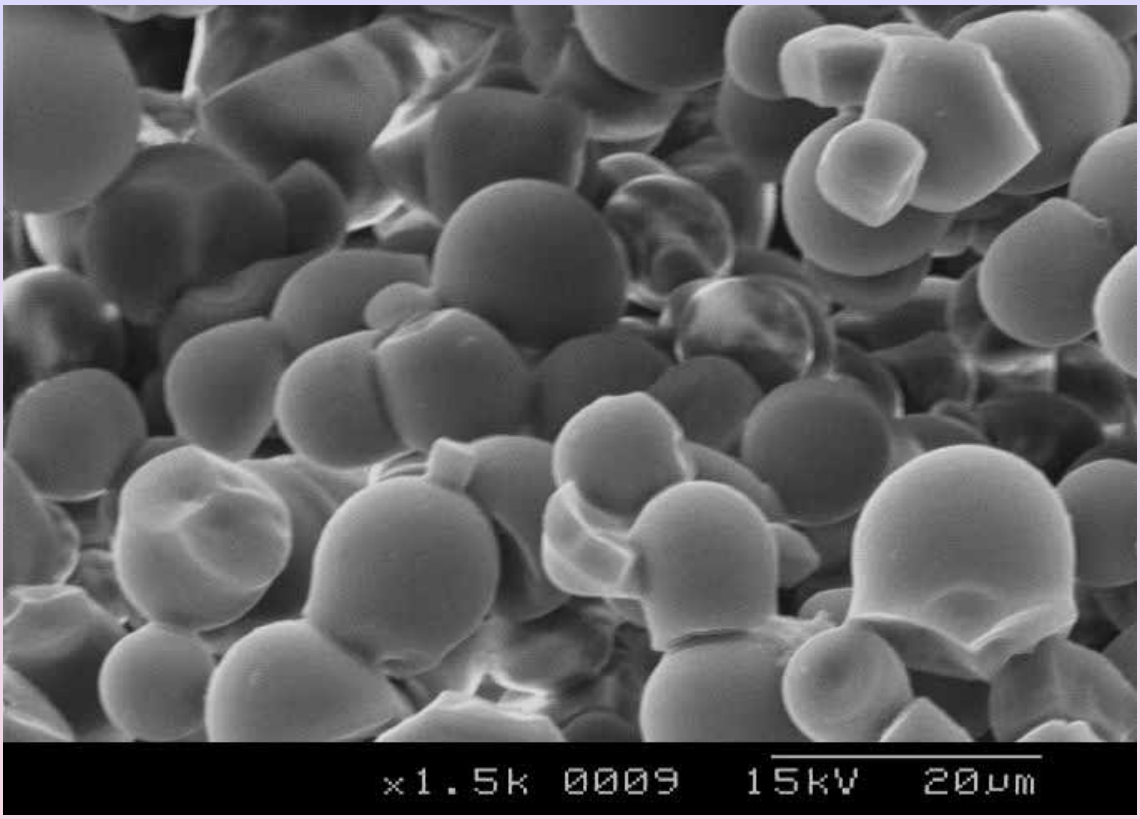

Figure: Scanning electron micrograph of octenyl succinate derivative of cassava starch

Back to presentation