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Preparation of hydroxypropyl corn and amaranth starch hydrolyzate and its evaluation as wall material in microencapsulation

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Abstract

Hydroxypropylation of starches lends it useful physicochemical and functional properties that are industrially important. The literature on hydroxypropylation using organic solvents for obtaining higher molar substitution (MS) is scantily available. The present work reports on hydroxypropylation of corn and a waxy amaranth starch to different MS with propylene oxide in an alkaline-organic medium (isopropanol). The synthesis was followed in terms of MS. The parameters optimized were starch:isopropanol ratio (w/w), reaction temperature, reaction time and the quantity of alkali required in the process. A maximal MS of 0.180 and 0.162 were obtained for hydroxypropyl corn starch (HPSC) and hydroxypropyl amaranth starch (HPSA), respectively. Enzymatic hydrolysis of the HPSC and HPSA of the above MS was carried out on a 30% (w/v) solution at a pH of 6.5 and 95 °C for varying time periods using 0.1% (w/w based on starch) bacterial α-amylase, termamyl. The hydrolysis was terminated by adjusting the pH to 3.5 using 0.1 N HCl. The hydrolyzates were characterized in terms of dextrose equivalent and viscosity. The hydrolyzate obtained after 3 h of hydrolysis was spray dried and compared to gum arabic with respect to encapsulation of model flavourings, orange oil and lemon oil.

Keywords: Encapsulation; Hydroxypropyl starch; Etherification; Enzyme hydrolysis

1. Introduction

Large quantities of starch are chemically and/or physically modified to obtain desired properties for different applications. One important product group is hydroxypropyl starch that has widespread applications in foods. Hydroxypropylation of starch imparts improved shelf life, freeze/thaw stability, cold storage stability, cold water swelling and reconstituting properties to a formulated product. A unique application of specialty food starches is in preparation of oil-in-water emulsions, which can be used for encapsulation of sensitive food ingredients. Granule starch is virtually insoluble in cold water, and has no lipophilic groups. Consequently, it does not form emulsions. Specialty starches that can be used for emulsification are hydrolyzed *n*-octenyl succinic anhydride (OSA)-modified starches from waxy corn starch (Trubiano, 1995; Cadwell & Wurzburg, 1953). These are commercially available under the brand names HiCap, Capsul, NLok, EmCap and Cleargum, Amiogum as gum Arabic substitutes for encapsulation of sensitive food ingredients.

Hydroxypropyl cellulose obtained by etherification of cellulose with propylene oxide is reportedly used as emulsion stabilizer (Belitz & Grosch, 1999). Reports on hydroxypropyl starch having emulsifying properties are also reported (Mitchel, Seidel, & Orozovich, 1997).

Replacement of gum arabic by a combination of hydroxypropyl starch and hydrolyzed collagen in certain food applications has also been described (De Coninck, Valere, L. M. P., van der Schueren, & Freddy, 1996). In this work, an attempt is made to use enzymatically hydrolyzed hydroxypropyl starch for encapsulation of model flavourings, namely lemon oil and orange oil.

Hydroxypropylation of starch can be carried out either in an aqueous, or in a non-aqueous medium, with the

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former being most commonly reported. In a standard process, native granule starch is suspended in water, and the etherification is terminated before starch is swollen to an unfilterable condition. Preparation of hydroxypropyl starch from variety of cereal starches such as rice (Islam & Azemi, 1997; Seow & Thevamalar, 1993; Yeh & Yeh, 1993), wheat (Wootton & Haryadi, 1992; Wootton & Mahdar, 1993) maize (Hoover, Hannonz, & Sosulski, 1988; Leegwater & Luten, 1971; Wootton & Manatsathit, 1983), tuber starches like potato (Lammers, Stanhuis, & Beenackers, 1993; Mchale, 1998), and legume starches like field pea (Hoover et al., 1988) has been reported. A number of patented processes have been developed for preparation of low substituted hydroxyalkyl starch ethers in aqueous phase (Helwig & Wilhelm, 1984; Hjermstad and Rapids 1971). Organic phase hydroxypropylation of starch to obtain high MS (0.40–0.50) is patented in the scientific literature (Hjermstad, Rapids, & Martin, 1964). Organic solvents range from high to low boiling, depending on types and sensitivity of product, reactants and reaction condition. In general, methanol, ethanol, and isopropanol are of commercial interest. The synthesis is followed in terms of molar substitution (MS). The US FDA limits an MS for hydroxypropyl starch for food applications at 0.2 (Dias, Teckchandani, & Mehta, 1997).

The main reaction parameters, which influence the MS of hydroxypropyl starch, are reaction temperature, reagent concentration, starch:isopropanol ratio, alkali concentration, and reaction time. One-factor-at-a time and factorial design was used to optimize the hydroxypropylation of corn and waxy amaranth starch for maximum MS. A full factorial design results in large number of experiments. To reduce the number of experiments to a practical level, only a small set from all possibilities is selected. Minitab constructed a special set of general design guidelines for factorial experiments that cover many applications. The method uses a special set of arrays called orthogonal arrays, which stipulate the way of conducting the minimal number of experiments, and gives full information of all the factors that affect the performance parameter.

Earlier work from our laboratory had explored possibility of hydroxypropylation of waxy starch from *Amaranthus paniculatas* Linn seeds (*Rajgeera*) in an aqueous medium. In continuation, the present work was planned to investigate hydroxypropylation of corn and amaranth starch in an organic (isopropanol) medium, followed by enzymatic hydrolysis. The purpose of hydrolysis was to evaluate the hydrolyzates as wall materials for encapsulation of flavours.

2. Materials and methods

2.1. Materials

Corn starch was obtained from Anil Starch, Baroda, India. Amaranth starch was isolated in the laboratory by alkali steeping method (Yanez & Walker, 1986) from *A. paniculatus Linn* (*Rajgeera*). Termamyl® 120 L DBA 85 was obtained as a gift from Arun & Co., agents of Novozymes, Mumbai, India. Typical characteristics of given sample provided by company were an amylase activity of 120 KNU/g and a specific gravity of 1.20 g/ml. Orange and lemon oils were obtained from Döhler Pvt. Ltd., Pune, India. All other reagents used in this work were of analytical grade obtained from Merck, Mumbai, India.

2.2. Methods

2.2.1. Preparation of hydroxypropyl corn and amaranth starch in organic phase

Preparation of hydroxypropyl starch was based on an earlier report (Pal, Singhal, & Kulkarni, 2000), wherein the reaction was carried out in aqueous slurry. Organic slurry reaction was carried out in a two-neck conical flask provided with mechanical stirring, which was immersed in a water bath at desired temperature. Starch, 2-propanol, and sodium hydroxide were mixed to obtain homogenous slurry, requisite volume of propylene oxide added, neck closed, and reaction carried out for varying temperatures and varying times under constant stirring. On completion of reaction, hydroxypropyl starch was neutralized with glacial acetic acid, washed with ethanol, and air-dried. The product obtained was ground to a powder of mesh size of 60 μm. Process parameters like temperature, time, starch: isopropanol ratio, and alkali concentration were studied with respect to their molar substitution (MS). MS represents the level of substitution in terms of moles of monomeric units in the substituents per mole of anhydroglucose unit in the starch.

2.2.2. Optimization of parameters for organic phase reaction

One-factor-at-a-time-method was chosen to optimize the reaction temperature and propylene oxide concentration. Reaction was carried out at varying temperatures (30, 40, and 50 °C) and propylene oxide concentration (16%, 20%, and 24% based on starch) by keeping the starch: isopropanol ratio, reaction time and sodium hydroxide constant at 1:1, 24 h and 2.8% (based on starch), respectively. Following preliminary trials, the design for L_9 orthogonal array was developed and analyzed using "MINITAB 13.30" software. Table 1 depicts the reaction conditions and L_9 orthogonal array, which was used in the present study. The parameters chosen were starch: isopropanol ratio (25:25, 25:35, and 25:45), reaction time (12, 24, 36 h), and quantity of sodium hydroxide (2.4%, 2.8%, and 3.2% based on starch). As one-third factorial design was used, the number of experiments was reduced from 27 to 9 as shown in Table 1. All experiments were performed in at least triplicates.

2.3. Determination of MS of hydroxypropyl starches

The spectrophotometric determination of hydroxypropyl group using propylene glycol was followed to determine the molar substitution. The method is based on

Table 1
L_9 orthogonal array for optimization of hydroxypropyl corn and amaranth starch[a]

Run	Components			Components			MS	
	A	B	C	A	B	C	Corn	Amaranth
1	1	1	1	25:25	12	2.4	0.0862 ± 0.0018	0.013 ± 0.002
2	1	2	2	25:25	24	2.8	0.109 ± 0.0006	0.135 ± 0.004
3	1	3	3	25:25	36	3.2	0.173 ± 0.007	Gelatinized
4	2	1	2	25:35	12	2.8	0.058 ± 0.001	0.101 ± 0.0008
5	2	2	3	25:35	24	3.2	0.048 ± 0.001	0.163 ± 0.002
6	2	3	1	25:35	36	2.4	0.131 ± 0.009	0.036 ± 0.001
7	3	1	3	25:45	12	3.2	0.078 ± 0.001	0.083 ± 0.0005
8	3	2	1	25:45	24	2.4	0.062 ± 0.0002	0.022 ± 0.0008
9	3	3	2	25:45	36	2.8	0.157 ± 0.009	Gelatinized

Where A = Starch:Propanol ratio (w/w), B = Time (h), C = NaOH (g).
[a] Results are means ± SD of two determinations.

principle given by Johnes and Riddick (1957) to determine propylene glycol and polyoxypropylene. The method involves hydrolysis of the hydroxypropyl group to propylene glycol, which in turn is dehydrated to propionaldehyde, and the enolic form to allyl alcohol. The products were measured spectrophotometrically at 590 nm after reaction with ninhydrin to form a blue colour. The concentration of propylene glycol was then converted to hydroxypropyl group equivalents from which MS was determined as per the method of Rutenberg and Solarek (1984)

$$\mathrm{MS} = \frac{162 \times W}{100M - (M-1)W}$$

where W is % by weight of substituent; 162 is the molecular weight of anhydroglucose unit; M is Molecular weight of the monomeric units of polymeric substituents.For propylene oxide treated starch: W is HP group equivalent in 100 mg of dry starch and M is the Molecular weight of propylene oxide = 58

$$\mathrm{MS} = \frac{162 \times W}{5800 - 57W}$$

2.4. Enzymatic hydrolysis of hydroxypropyl starches

HPSC of MS 0.180 & HPSA of MS 0.169 were suspended in distilled water at 30% (w/v), and pH adjusted to 6.5 with 0.1 N HCl. 0.1% termamyl (w/w) based on starch and 70 ppm calcium as calcium chloride were added, and the resultant slurry heated at 95 °C in a water bath for varying times (1–4 h) for complete gelatinization. Constant stirring was provided with an overhead stirrer for uniform distribution of enzyme, and the reaction was terminated at desired time by adjusting the pH to 3.5–4.5 using 0.1 N HCl and boiling in a water bath for 10 min to inactivate the enzyme. The slurry so obtained was spray dried in JISL, LSD-48 mini spray drier (Mumbai, India) (inside chamber dimension: 100 cm height, 60 cm diameter) equipped with 0.5 mm diameter nozzle. The pressure of compressed air for the flow of the spray was adjusted to 2 bar. The inlet and outlet temperatures were maintained at 180 and 100 °C, respectively. A peristaltic pump was used to feed the spray drier at 400 ml/h.

The hydroxypropyl starch powder was collected from the collecting chamber and filled in airtight, self-sealable polyethylene pouches until further analysis. The powder so obtained was analyzed for viscosity and dextrose equivalents (DE).

2.5. Measurement of viscosity

Viscosities of 30% (w/v) of hydrolyzed HPSC and HPSA were measured using a Brookefield viscometer (Model DV – III (LV), Stoughton, MA, USA) viscometer at room temperature (28–30 °C) on a sample volume of 40 ml and using LV-2 spindle, operated at 60 rpm.

2.6. Degree of hydrolysis as dextrose equivalent (DE)

Dextrose equivalent (DE) is a measure that can be used to follow the extent of starch hydrolysis. It is defined as reducing power of substance expressed in g of D-glucose per 100 g of dry substance. The DE of hydrolyzed HPSC and HPSA was measured by determining reducing sugars using Fehling solution (Guzman, Paredes-Lopez, & Dominguez, 1992). DE was calculated as follows:

$$\mathrm{DE} = \frac{\%\ \text{Reducing sugar} \times 100}{\%\ \text{Dry substance}}$$

2.7. Emulsion studies

The carrier materials (30%, w/v) were taken for emulsion preparation. They were dispersed individually in required amounts of distilled water and rehydrated for about 12 h under refrigeration (4 °C) until emulsion preparation. This dispersion was mixed well with 20% of core material (orange oil and lemon oil), and emulsified in a shear homogenizer for 5 min at 3000 rpm to obtain a complete dispersion.

2.8. Emulsion stability index (ESI)

A sample of liquid emulsion was transferred to a 10 ml measuring cylinder, which was then capped and stored for 24 h. The volume of oil separated from the emulsion

was measured, from which emulsion stability index (ESI) within a possible range from 0 to 1 was recorded. A value of 0 represents poor emulsion stability, while a value of 1 represents high emulsion stability (Cho & Park, 2003)

$$\mathrm{ESI} = 1 - \frac{\text{Total volume of separated oil}}{\text{Total volume of oil in emulsion}}$$

2.9. Emulsion particle size

Emulsion particle size was measured using Biovis Pharma Plus Image Analysis System (Exton, PA). It consisted of a compound microscope, a digital camera (Motic BS 300) and an image analyzing software. A fine drop of emulsion was transferred to a microslide, smeared and then covered with a cover slip. A very thin layer of emulsion was formed onto the surface of the microslide for greater picture clarity. The slide was then kept on the stage of the compound microscope, and 10 snaps were taken at different points of the smear. The Biovis Image Analyser analyzes all the 10 snaps taken, and presents the analyzed results in terms of particle size distribution, maximum, minimum and mean aspect (spheroidal) and, minor and major axes (elliptical) of the particles. In the present study, the mean aspect of the particle was considered, in view of the fact that the particles were spheroidal.

2.10. Preparation of encapsulated products

The encapsulating agents (30 g) were slowly added to 70 g of distilled water with constant stirring to totally dissolve the encapsulating agent. The core material (orange oil and lemon oil at 6 g each, corresponding to 20% of carrier material used) were added with constant stirring. The mixture was emulsified in a shear homogenizer for 5 min at 3000 rpm until complete dispersion. The slurry so obtained was spray dried in JISL, LSD-48 mini spray drier (Mumbai, India) (inside chamber dimension: 100 cm height, 60 cm diameter) equipped with 0.5 mm diameter nozzle. The pressure of compressed air for the flow of the spray was adjusted to 2 bar. The inlet and outlet temperatures were maintained at 150 and 90 °C, respectively. A peristaltic pump was used to feed the spray drier at 400 ml/h.

2.11. Determination of total oil and surface oil in encapsulated powder

Total oil content of powders was determined by Clevenger apparatus by taking 5 g powder dissolved in 125 ml distilled water in 250 ml round bottom flask. Sample was distilled for 3 h and collected oil measured (Anandaraman & Reineccius, 1987). Surface oil was determined by removing it by addition of 100 ml of petroleum ether to 5 g of powder followed by stirring for 10 min. The petroleum ether was then decanted and the residual powder was air dried for 30 min. The true oils encapsulated were determined by Clevenger apparatus.

3. Results and discussion

3.1. Optimization using one-factor-at-a-time

The optimization of hydroxypropylation of corn and amaranth starch was carried out by varying the process parameters. The levels of process parameters were chosen on the basis of the literature reports (Pal et al., 2000). The optimization was started by varying only one parameter at a time, keeping others constant. Hydroxypropyl derivatives so obtained were analyzed for MS. The condition giving the highest MS was kept fixed at that value for next set of optimizations. Initially, the effect of propylene oxide in the concentration range of 16%, 20%, and 24% (v/w) of starch on the MS of HPSC and HPSA was observed. The concentration used were, 1:1 ratio for starch: isopropanol, 2.8% NaOH (based on starch), reaction time of 24 h and reaction temperature of 40 °C. All available literature on hydroxypropylation recommended a reaction temperature of 40 °C (Pal et al., 2000). Hence, for optimization of propylene oxide concentration, the temperature was fixed at 40 °C. For both starches, 24% propylene oxide gave a maximum MS of 0.082 for HPSC, and 0.091 for HPSA (Fig. 1). This is probably due to greater availability of propylene oxide at higher concentration in the proximity of starch granules. The findings are well supported in the literature (Wootton & Manatsathit, 1983). At the same concentration of propylene oxide, MS was found to be higher for amaranth starch as compared to corn starch. It may be due to greater swelling of amaranth starch granules (attributed to its waxy nature), which enables it to remain more dispersible in the suspension. This in turn favours greater diffusion of etherifying agent in the interior of the amaranth as compared to that of corn starch.

In an effort to increase the MS of HPSC and HPSA further, the next parameter chosen was the reaction temperature. The temperature was optimized in the range of 30–50 °C keeping all other parameters constant. The other parameters were a 1:1 ratio of starch: isopropanol, 2.8% NaOH (based on starch), and propylene oxide at 24% based on starch.

As the temperature increased from 30 °C to 50 °C, an increase in the MS of both corn and amaranth starch was observed (Fig. 2). The MS of HPSC and HPSA at 50 °C was 0.109 and 0.135, respectively. A further increase in temperature gelatinizes the starch, and hence is not advisable.

3.2. Optimization of the process parameters using L_9 orthogonal design

Once the reaction temperature and propylene oxide concentration were optimized by one-factor-at-a-time, the reaction was subjected to final optimization using L_9

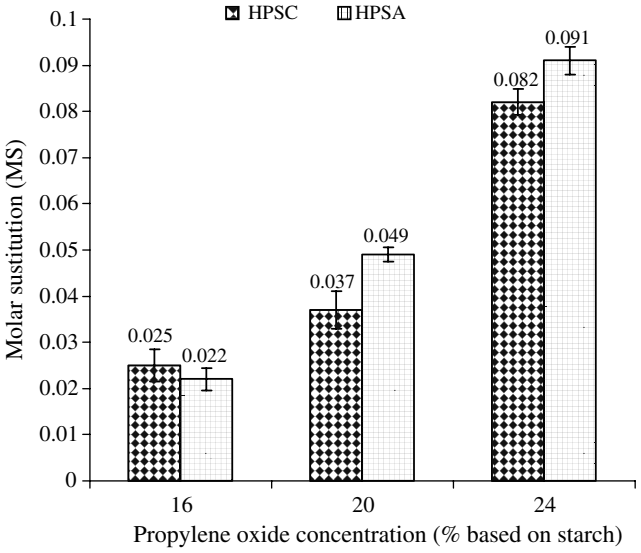

Fig. 1. Effect of propylene oxide concentration (% based on starch) on molar substitution (MS) of hydroxypropyl corn and amaranth starch.

orthogonal array. The parameters optimized involved starch: isopropanol ratio, sodium hydroxide, and reaction time. Table 2 represents the response table for means (larger is better) and for signal to noise ratio obtained with L_9 orthogonal array of HPSC and HPSA. The last two rows in tables document the delta values and ranks for the system. Rank and delta values help to access which factors have greatest effect on the response characteristic of interest. Delta measures the size of the effect by taking the difference between the highest and lowest characteristic average for a factor. A higher delta value indicates greater effect of that component. Rank orders the factor from the greatest effect (based on delta values) to the least effect on the response characteristic. The order in which the individual components selected in the present study effect the MS of HPSC and HPSA are sodium hydroxide > starch: isopropanol ratio > reaction time suggesting sodium hydroxide concentration to have a major effect, and reaction time to have less effect on hydroxypropylation of both corn and amaranth starch.

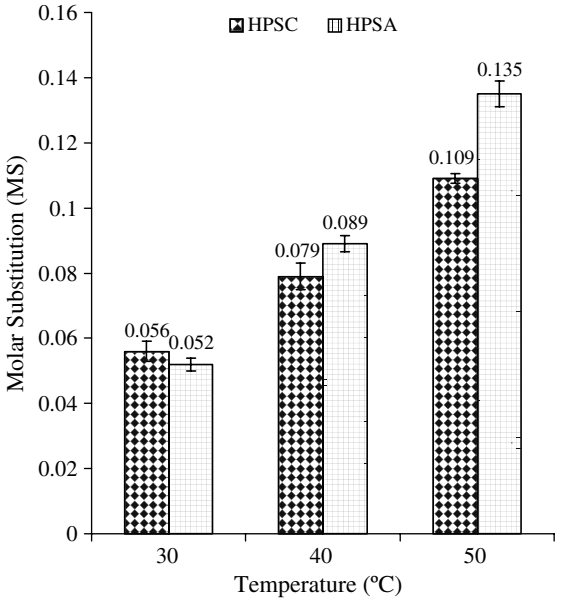

Fig. 2. Effect of reaction temperature (°C) on molar substitution (MS) of hydroxypropyl corn and amaranth starch.

Response tables can also be used to predict the optimum levels of each component used in the study. The optimized level or composition of each factor was predicted by the software, according to the optimal levels of the three parameters for HPSC were starch: isopropanol ratio 25:25, sodium hydroxide of 3.2% and reaction time of 24 h. These conditions gave a maximum predicted MS of 0.183. Similarly for HPSA, starch: isopropanol ratio 25:35, sodium hydroxide 2.8% and reaction time of 36 h gave a predicted MS of 0.165. In order to verify the predicted results, experiments were performed using the optimized levels of the parameters, and the experimental value was 0.189 for HPSC and 0.172 for HPSA, suggesting a good agreement between the experimental and predicted values of MS. It may be noted that hydroxypropylation in aqueous medium has been reported to give similar MS (Pal et al., 2000). Hence, the use of organic solvent may not be necessary to achieve this range of MS.

3.3. Enzymatic hydrolysis of optimized HPSC and HPSA

HPSC of MS 0.18 and HPSA of MS 0.169 were subjected to enzymatic liquefaction to ensure that the starch hydrolyzate thus produced is substantially free of residual starch granules. During liquefaction, starch undergoes saccharification and this increases the DE. The starch hydrolyzates obtained under different conditions of hydrolysis were spray dried, and DE and viscosity was determined. It was observed that an increase in the time of hydrolysis increased the DE and reduced the viscosity for both HPSC and HPSA. For HPSC and HPSA, the DE increased from

Table 2
Response table for means and S/N ratio of hydroxypropyl corn starch

Levels	A		B		C	
	Mean	*S/N*	Mean	*S/N*	Mean	*S/N*
1						
Corn	0.122	−18.59	0.074	−22.72	0.093	−21.03
Amaranth	0.049	65.03	0.065	−26.41	0.023	33.24
2						
Corn	0.079	−22.92	0.073	−23.25	0.108	−20.02
Amaranth	0.1	21.51	0.106	−22.1	0.078	−59.1
3						
Corn	0.099	−20.79	0.153	−16.32	0.099	−21.25
Amaranth	0.035	64.92	0.012	102.95	0.082	59.12
Delta						
Corn	0.043	4.32	0.08	6.93	0.014	1.23
Amaranth	0.065	43.52	0.094	80.85	0.058	25.87
Rank						
Corn	2		1		3	
Amaranth	2		1		3	

Table 3
Effect of enzyme hydrolysis on viscosity and DE of HPSC and HPSA for different time intervals[a]

Time of hydrolysis, h	HPSC		HPSA	
	DE	Viscosity, cPs	DE	Viscosity, cPs
1	0	48.3 ± 2.2	0	54.7 ± 3.4
2	8.2 ± 1.2	30.6 ± 2.3	7.8 ± 0.8	32.4 ± 1.8
3	15.8 ± 0.9	24.4 ± 1.5	15.5 ± 1.1	26.6 ± 2.2
4	18.6 ± 1.8	14.6 ± 3.4	18.1 ± 2.2	16.4 ± 2.7

[a] Results are means ± SD of three determinations.

0 to 18.6 and 18.1, respectively, at the end of 4 h. HPSC after 1 h hydrolysis had a DE of 8.6 and viscosity of 48 cPs, while after 4 h the DE was 18.6 and the viscosity was 14 cPs. Similarly, HPSA had DE of 7.9 and viscosity of 54 cPs after 1 h hydrolysis, while after 4 h it had a DE of 18.1 and viscosity of 16 cPs (Table 3).

3.4. Emulsification capacity and encapsulation properties of hydroxypropyl starch

Thirty percent of wall material (gum arabic, HPSC and HPSA of 16 DE) and 20% loading of core material (orange oil and lemon oil) based on weight of wall material were used for emulsification and encapsulation (Table 4). HPSC of MS 0.18 and HPSA of MS 0.167 were hydrolyzed to 16 DE. The hydrophylic portion comes from the hydrolyzed starch, and the hydrophobic part comes from the hydroxypropyl chains. Gum arabic had an ESI of 1.00 for both orange oil and lemon oil; HPSC and HPSA of DE 16 had ESI of 0.31 and 0.34 for orange oil, and 0.85 and 0.86 for lemon oil, respectively. Flavour compounds could be either of low polarity or high polarity. Low polarity flavour compounds are insoluble in water but soluble in solvents such as *n*-hexane, while high polarity flavour compounds are water-soluble. Gum arabic is an excellent encapsulating agent for low polarity flavour compounds, while cyclodextrins are excellent for flavour compounds of higher polarity (Varavinit, Chaokasem, & Shobsngob, 2001). Higher values of ESI for lemon oil as compared to that of orange oil using HPS as the encapsulating material may be due to differences in polarity of the two oils.

Table 4
Evaluation of hydrolyzed HPSC and HPSC *vis-à-vis* gum arabic for encapsulation of orange oil and lemon oil[a,b,c]

Wall material	ESI	Avgerage size of oil Droplets, μm	% Total retained oil	% Surface retained oil	% Efficiency
Orange oil					
HPSC of DE 16	0.31	3.42	59.45 ± 0.38	4.1 ± 0.08	55.35 ± 0.10
HPSA of DE 16	0.34	3.32	60.12 ± 0.12	3.9 ± 0.04	56.22 ± 0.85
Gum arabic	1.00	1.96	90.50 ± 0.75	7.0 ± 0.12	83.50 ± 0.48
Lemon oil					
HPSC of DE 16	0.85	1.42	86.45 ± 0.38	4.1 ± 0.08	82.35 ± 0.10
HPSA of DE 16	0.86	1.32	87.12 ± 0.47	3.9 ± 0.15	83.22 ± 0.75
Gum arabic	1.00	1.96	92.5 ± 0.75	6.0 ± 0.12	86.5 ± 0.48

[a] Results are means ± SD of three determinations.
[b] The wall material was used at 30% w/w.
[c] The oil was incorporated at 20% based on the weight of wall material.

A good emulsion is a prequisite for spray drying of flavour. A small droplet remains very stable in an emulsion, and can also be thoroughly coated by the film. This gives better protection to oils. The average particle size obtained for orange oil and lemon oil was in the range of 1–5 μm (Table 4), while that of gum arabic was 1 μm. Encapsulation efficiency of HPSC and HPSA of DE 16 were 55% and 56% for orange oil, while that of gum arabic was 83%. For lemon oil, HPSC and HPSA of DE 16 had encapsulation efficiency 82% and 83%, while that of gum arabic was 86%. These results indicate the hydrolyzed hydroxypropyl starches are suitable for encapsulation of lemon oil, but not of orange oil. The starch composition did not influence the encapsulation efficiency of both orange and lemon oil.

4. Conclusions

Optimization of hydroxypropylation of corn and amaranth starch in organic medium using L_9 orthogonal design gave a maximum MS of 0.183 for HPSC, and 0.169 for HPSA. Gum arabic had better encapsulation efficiency for both orange and lemon oil. Hydrolyzed HPSC and HPSA can be used as an excellent encapsulating agent for encapsulation of lemon oil, but were not suitable for orange oil.

References

Anandaraman, S., & Reineccius, G. A. (1987). Analysis of encapsulated orange peel oil. *Perfume and Flavourist, 12*(2), 33–39.

Belitz, H. D., & Grosch, W. (1999). Carbohydrates. In *Food chemistry* (2nd ed., pp. 217–318). Germany: Springer.

Cadwell, C. G., & Wurzburg, O. B. (1953). Polysaccharides derivatives of substituted dicarboxylic acids. US Patent 2,661,349. National Starch and Chemical Corporation, New York, NY.

Cho, Y. H., & Park, J. (2003). Evaluation of process parameters in the O/W/O multiple emulsion method for flavor encapsulation. *Journal of Food Science, 68*(2), 534–538.

De Coninck, Valere, L. M. P., van der Schueren, & Freddy, M. L (1996). Starch composition. US Patent 5,569,480. Cerester Holding B.V, Sas van Gent, Netherland.

Dias, F. F., Teckchandani, H. K., & Mehta, D. (1997). Modified starches and their use by food industry. *Indian Food Industry, 16*(4), 33–99.

Guzman, M. H., Paredes-Lopez, O., & Dominguez, J. (1992). Optimization of an enzymatic procedure for the hydrolytic depolymerization of starch by response surface methodology. *Food Science and Technology, 26*, 28–32.

Helwig, T., & Wilhelm, O. (1984). Process for the production of hydroxypropyl starch. US Patent 4451649, Wolff Walsrode Aktiengesellschaft, Walsrode, DE.

Hjermstad, E. T., Rapids, C., & Martin, L. C. (1964). Etherifying granule starch in aliphatic ketone solvent medium. US Patent 3135739, Penick & Ford Ltd., Iowa.

Hjermstad, E. T., & Rapids, C. (1971). Highly hydroxypropylated granule potato starch. US Patent 3577407, Penick & Ford Ltd., Iowa.

Hoover, R., Hannonz, D., & Sosulski, F. W. (1988). Effects of hydroxypropylation on thermal properties, starch digestibility and freeze–thaw stability of field pea. *Starch/Starke, 40*(10), 383–387.

Islam, N., & Azemi, B. M. N. M. (1997). Rheological properties of calcium treated hydroxypropyl rice starches. *Starch/Starke, 49*(4), 136–141.

Johnes, L. R., & Riddick, J. A. (1957). Calorimetric determination of 1,2-propane-diol and related compounds. *Analytical chemistry, 29*(8), 1214–1216.

Lammers, G., Stanhuis, E. J., & Beenackers, A. A. C. M. (1993). Kinetics of hydroxypropylation of potato starch in aqueous solution. *Starch/Starke, 45*(7), 227–232.

Leegwater, D. C., & Luten, J. B. (1971). A study on in vitro digestibility of hydroxypropyl starches by pancreatin. *Starch/Starke, 23*(12), 430–432.

Mchale, R. H. (1998). A test for endo-amylase activity in the presence of exo-amylase. *Starch/Starke, 40*(11), 422–426.

Mitchel, W. A., Seidel, W. C., & Orozovich, G. A. (1997). Cold water soluble bulked starch. US Patent 4,009,291. General food corporation, White plains, NY.

Pal, J., Singhal, R. S., & Kulkarni, P. R. (2000). A comparative account of conditions of synthesis of hydroxypropyl derivatives from corn and amaranth starch. *Carbohydrate Polymers, 43*, 155–162.

Rutenberg, M. W., & Solarek, D. (1984). In R. L. Whistler, J. N. BeMiller, & E. F. Paschall (Eds.), *Starch derivatives: Production and use*. *Starch: Chemistry and technology* (pp. 344–349). New York: Academic Press (e2).

Seow, C. C., & Thevamalar, K. (1993). Internal plasticization of granular rice starch by hydroxypropylation: Effects on phase transition associated with gelatinization. *Starch/Starke, 45*, 85–88.

Trubiano, P. C. (1995). The role of speciality food starches in flavour encapsulation. *ACS Symposium Series, 610*, 244–253.

Varavinit, S., Chaokasem, N., & Shobsngob, S. (2001). Studies of flavor encapsulation by agents produced from modified sago and tapioca starches. *Starch/Stärke, 53*, 281–287.

Wootton, M., & Haryadi, I. (1992). Effects of starch types and preparation conditions on substituents distribution in hydroxypropyl starches. *Journal of Cereal Science, 15*, 181–184.

Wootton, M., & Mahdar, D. (1993). Properties of starches from Australian wheats part 3: In-vitro digestibility and hydroxypropyl derivatives. *Starch/Starke, 45*(10), 337–341.

Wootton, M., & Manatsathit, A. (1983). The influence on molar substitution on the water binding capacity of hydroxyopropyl starches. *Starch/Starke, 35*(3), 92–94.

Yanez, G. A., & Walker, C. E. (1986). Effect of tempering parameters on extraction and ash of prosomillet flours and partial characterization of proso starch. *Cereal Chemistry, 63*, 164–170.

Yeh, A. I., & Yeh, S. L. (1993). Some characteristics of hydroxypropylated and crosslinked rice starch. *Cereal Chemistry, 70*(5), 596–601.