Carbohydrate Polymers 86 (2011) 1723–1731

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Esterification of guar gum hydrolysate and gum Arabic with *n*-octenyl succinic anhydride and oleic acid and its evaluation as wall material in microencapsulation

Shatabhisa Sarkar, Rekha S. Singhal*

Food Engineering and Technology Department, Institute of Chemical Technology, Matunga, Mumbai 400019, India

ARTICLE INFO

Article history:
Received 20 January 2011
Received in revised form 2 July 2011
Accepted 4 July 2011
Available online 12 July 2011

Keywords:
Guar gum hydrolysate
Gum Arabic
Esterification
Oleic acid
n-Octenyl succinic acid
Wall material

ABSTRACT

The present study was undertaken to introduce hydrophobicity in guar gum hydrolysate (GGH) with a view to develop a suitable alternative to gum Arabic (GA) as wall material for microencapsulation. This was done by esterification with *n*-octenyl succinic anhydride (OSA) and oleic acid. The study was carried out by optimizing three parameters in the esterification process, viz. concentration of the acid, temperature, and time of reaction by response surface methodology (RSM). The reaction was monitored in terms of degree of substitution (DS), and optimized for maximal DS. The maximum DS of GGH oleate, GGH-OSA, and GA-OSA was found to be 0.061, 0.072, and 0.070, respectively. These derivatives were evaluated for their ability to be used as wall materials in microencapsulation with respect to emulsion stability, viscosity and particle size. Our results indicate the wall materials to follow the order GA-OSA > GGH-OSA > GA > GGH-oleate.

1. Introduction

Microencapsulation is a technique by which sensitive ingredients are entrapped in wall materials that protects them against adverse chemical and environmental reactions, loss of volatiles, and also controls their release. It has also become an attractive approach for transforming sensitive liquid food ingredients into stable free flowing powders that are easy to handle and incorporate in dry food mixes (McNamee, O'Riordan, & O'Sullivan, 1998). Among the various techniques that can be employed to microencapsulate food ingredients, spray drying is the most often and industrially used. One of the key aspects in microencapsulation is the selection of an appropriate wall material. Gum Arabic (GA) is the industry standard for encapsulation, and is most frequently used. However, its high cost, inconsistent supply and varying quality has prompted investigations on alternative carrier materials (Kshirsagar & Singhal, 2007). Besides gum Arabic, maltodextrins and emulsifying starches are the other commonly used carrier materials (Reineccius, 1988, 1989).

Guar gum is obtained from the endosperm of the seeds from guar pods (*Cyamoposis tetragonolobus*). Almost 80% of the guar gum is produced in India and it is also exported to other countries (http://www.guargum.biz/). Guar gum, a galactomanan, has a very high viscosity which limits its application as a wall material for encapsulation. Besides, it also does not possess any emulsifying activity that is crucial in microencapsulation of some constituents. Depolymerisation of guar gum to obtain a natural, water-soluble dietary fiber by partial hydrolysis of guar gum has been widely studied by several researchers. Approaches such as acid hydrolysis (Cheng, Brown, & Prud'homme, 2002), using specific enzymes such as mannosidase and/or galactosidase (Mahammad, Prud'homme, Roberts, & Khan, 2006), hydrothermal degradation (Miyazawa & Funazukuri, 2006), microwave mediated free radical degradation (Reddy & Tammishetti, 2004) and irradiation (Jumel, Harding, & Mitchell, 1996) have been used to depolymerise guar galactomannan. The partially hydrolyzed guar gum or guar gum hydrolyzate (GGH) has a lower molecular weight and a markedly lower viscosity than the native guar gum (Slavin & Greenberg, 2003). Since GGH has no hydrophobicity, it does not have emulsifying property which is very important for microencapsulation of lipid-based materials.

Numerous reports on esterification of various starches with *n*-octenyl succinic anhydride (OSA) such as from potato starch (Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009), lima bean starch (Segura-Campos, Chel-Guerrero, & Betancur-Ancona, 2008), waxy maize and amaranth starches (Bhosale & Singhal, 2006), insoluble granular waxy maize starch, granular microporous starch, and soluble maltodextrin (Bai & Shi, 2011) are available in sci-

* Corresponding author. Tel.: +91 22 33612512; fax: +91 22 33611020.
E-mail address: rs.singhal@ictmumbai.edu.in (R.S. Singhal).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.07.003

entific literature. Similarly, esterification of potato starch (Fang, Fowler, Tomkinson, & Hill, 2002) and native and hydrolyzed corn starch (Kshirsagar & Singhal, 2007) with oleic acid is also reported. Low cost acetate, succinate and octenyl succinate derivatives of galactomannans were developed (Savitha Prashanth et al., 2006). Shogren, Viswanathan, Felker, and Gross (2000) reported OSA-starch from waxy maize to have an ampiphilic nature which helped them to stabilize oil/water emulsions by combining the hydrophobicity of the octenyl group with the hydrophilic carboxyl or sodium carboxylate groups broadening their potential uses in the food industry. Wurzburg (1995) reported on potential food applications of succinylated starches as emulsifiers and emulsion-stabilizing agents in products such as beverages, salad dressings, soups, creams and hams, as well as flavour encapsulating agents and clouding agents.

We hypothesized that esterification of GGH with OSA and/or oleic acid would not only introduce hydrophobicity in the backbone but may also be suitable as wall materials for encapsulation. GA and GA ester of *n*-octenyl succinic anhydride (GA-OSA) (also optimized for maximal DS) were used for comparison. The samples were optimized for maximal DS by response surface methodology and evaluated for emulsion stability, particle size and viscosity.

2. Materials and methods

2.1. Materials

GGH was a commercial sample manufactured and gifted by Lucid Colloids Ltd., Mumbai, India. Gum Arabic was obtained from S.D. Fine Chem, Mumbai, India. Octenyl succinic anhydride (OSA) 99.9% was obtained as a gift from Dixie Chemical, USA. Mint oil was gift sample from A.M. Todd, Mumbai. All other reagents used in this work were of analytical grade and procured from reliable sources.

2.2. Methods

2.2.1. Preparation of oleate esters of guar gum hydrolyzate (GGH-oleate)

GGH or GA (25 g) was mixed with 1 g sodium bicarbonate. Oleic acid (0.7, 1.2, 1.7 g) was dissolved in 40 ml of 95% ethanol and mixed with the gum. The above mixture was heated in a water bath at different temperatures (60, 75, 90 °C) for various times (60, 120, 180 min). Reaction parameters like concentration of oleic acid, reaction temperature and duration of reaction were monitored with respect to their DS. Absolute alcohol (100 ml) was added to 15 g of the reaction mixture with constant starring for 10 min for removing untreated oleic acid and pH was adjusted to 7 by adding 1% (w/w) NaOH. The supernatant ethanol was discarded, and the residue rewashed twice with 100 ml ethanol and dried at 60 ± 2 °C for 2 h. These reaction conditions were selected on the basis of prior initial trials (data not reported). Esterification of GA with oleic acid was not successful, and hence only GGH-oleate was selected for further work.

2.2.2. Determination of DS of GGH-oleate

Esterified gum (5 g) was dispersed in 50 ml water containing 25 ml of 0.5 M NaOH followed by shaking on magnetic stirrer at room temperature (30 ± 2 °C) for 30 min. Excess NaOH was then titrated with 1 N HCl using phenolphthalein as an indicator. A blank was simultaneously titrated with unmodified gum.

The DS of esters was calculated according to the equation below (Rutenberg & Solarek, 1984):

$$W = \frac{(\text{blank} - \text{sample}) \times M \times N \times 100}{\text{weight of sample, g} \times 1000}$$

Table 1
Experimental design of guar gum hydrolyzate oleate, guar gum hydrolyzate succinate and gum Arabic succinate.

No.	Coded values and actual values		
	X_{conc}	X_{time}	X_{temp}
1	−1 (0.7)	−1 (60)	0 (75)
2	1 (1.7)	−1 (60)	0 (75)
3	−1 (0.7)	1 (180)	0 (75)
4	1 (1.7)	1 (180)	0 (75)
5	−1 (0.7)	0 (120)	−1 (60)
6	1 (1.7)	0 (120)	−1 (60)
7	−1 (0.7)	0 (120)	1 (90)
8	1 (1.7)	0 (120)	1 (90)
9	0 (1.2)	−1 (60)	−1 (60)
10	0 (1.2)	1 (180)	−1 (60)
11	0 (1.2)	−1 (60)	1 (90)
12	0 (1.2)	1 (180)	1 (90)
13	0 (1.2)	0 (120)	0 (120)
14	0 (1.2)	0 (120)	0 (120)
15	0 (1.2)	0 (120)	0 (120)
16	0 (1.2)	0 (120)	0 (120)
17	0 (1.2)	0 (120)	0 (120)

Actual values are given in parenthesis; X_{conc}, X_{time} and X_{temp} are concentrations of oleic acid/*n*-octenyl succinic anhydride, reaction time and reaction temperature.

Hence, for gum ester:

$$\text{DS} = \frac{162 \times W}{100 \times M - \{(M-1) \times W\}}$$

where

W = % substitution oleic acid;
blank = volume of HCl required for blank titration;
sample = volume of HCl required for sample titration;
N = normality of HCl solution;
M = molecular weight of oleic acid (282);
162 = molecular weight of glucose unit.

2.2.3. Preparation of GGH-OSA and GA-OSA

GGH-OSA and GA-OSA were synthesised as per protocol described in Section 2.2.1 with *n*-OSA as esterifying agent.

2.2.4. Determination of DS of GA-OSA and GGH-OSA

GA-OSA and GGH-OSA were evaluated for DS as reported in Section 2.2.2 with molecular weight (M) of octenylsuccinyl group (210).

2.3. Experimental design for response surface methodology

The levels of the significant parameters (concentration of oleic acid/*n*-OSA, time, temperature) and the interaction between variables which influences the DS were analysed and optimized by Box–Behnken methodology (Box & Behnken, 1960). In this study, the experimental plan consisted of 17 trials and the independent variables were studied at three different levels, low (1), medium (0) and high (+1). The variables and their coded levels used for the study are shown in Table 1. All the experiments were done in triplicate and the average DS obtained was taken as the dependent variable or response. Statistical analysis was performed with the software package 'DESIGN-EXPERT version 6.0.' (Stat-Ease, Inc., Minneapolis, USA). A quadratic polynomial model was defined to fit the response:

$$Y = \beta_0 + \beta_1 X_{conc} + \beta_2 X_{time} + \beta_3 X_{temp} + \beta_{11}(X_{conc})^2 + \beta_{22}(X_{time})^2 + \beta_{33}(X_{temp})^2 + \beta_{12} X_{conc} X_{time} + \beta_{13} X_{conc} X_{temp} + \beta_{23} X_{temp} X_{time}$$

where Y is the response expressed as DS and β_0 is a constant coefficient of the model. The regression coefficients (β_1, β_2 and β_3), (β_{11},

β_{22} and β_{33}) and (β_{12}, β_{13} and β_{23}) respectively represent linear, quadratic, and interaction effects of the model, estimated by multiple regression analysis. X_{conc} (concentration of oleic acid/*n*-OSA), X_{time} (reaction time), and X_{temp} (reaction temperature) are coded variables ranging from −1 to +1.

The goodness of fit of the models was evaluated by coefficient of determination (R^2) and analysis of variance (ANOVA). Quadratic polynomial equations were obtained by keeping one of the independent variables as a constant value and changing the level of other variables.

2.4. Analysis of GA, GA-OSA, GGH-OSA and GGH-oleate as wall materials for microencapsulation

2.4.1. Emulsion stability

Oil-in-water emulsions were prepared by mixing 20% w/v solution of individual esterified gum with 3 g (15% based on the esterified gum) of mint oil. Oil was dispersed in gum solution by shear homogeniser (Indofrench Industries Engineers, Mumbai, Model type-SPM-9) for 10 min at 3000 *g* until complete dispersion of oil. Emulsion was stored at 4 °C for 24 h for complete diffusion of esterified gum and stabilization of the oil–water interface. Emulsion stability index (ESI) was calculated as

$$\text{ESI} = 1 - \frac{\text{oil separated in emulsion}}{\text{total oil in emulsion}}$$

The stability of the emulsions was further evaluated by measuring its turbidity (Pearce & Kinsella, 1978). A 10 μL aliquot of the emulsion was diluted to 1 ml with water and the absorbance (A) was measured at 650 nm using a U-2001 spectrophotometer (Hitachi) in a 1 cm path length cell. Emulsions were prepared in triplicate to check its reproducibility. Equation given below shows the relation between turbidity (τ) and absorbance (A) at 630 nm

$$\tau = \frac{2.303 \times A}{l}$$

2.4.2. Viscosity

Viscosity of the emulsions was measured using Brookefield LV spindle set (Stoughton, MA, USA) viscometer at room temperature (27 ± 2 °C) with a sample volume of 65 ml and using LV-2 spindle, operated at 60 rpm.

2.4.3. Particle size of the emulsion

BioVis Image analyzer plus (Expert Vision Labs Pvt. Ltd., Mumbai, India) was used for determining particle size of dispersed oil in emulsion at 0 h and after 24 h. A smear of emulsion was prepared and observed under compound microscope. A digital camera associated with this instrument was used to take 10 snaps of the emulsion. Particle size of dispersed oil in emulsion was determined with the help of image analysing software. Emulsion was analysed in terms of particle size distribution, maximum, minimum and mean aspect (spheroidal) and, minor and major axes (elliptical) of the particles. In this study, the mean aspect of the particle was considered, since the particles were spheroid.

2.5. Statistical analysis

IBM® SPSS® statistic package was used for analysis of data of turbidity, viscosity and particle size of emulsions. Analysis of variance (ANOVA) by Fisher's least significant difference was performed to examine effect of esterification on emulsifying property of gums.

3. Result and discussion

3.1. Combined effect of concentration of oleic acid/n-OSA, reaction time and reaction temperature on DS

A 17-run Box–Behnken design with three factors and three levels, including five replicates at the centre point, was used for fitting a second-order response surface. The five centre point runs were added to provide as a measure of process stability and inherent variability (Table 1). GGH reacted with oleic acid forming GGH oleate via esterification reaction (Fig. 1). GGH or GA reacts with *n*-OSA (which is strong electrophile) to desirable products formed (GGH-OSA and GA-OSA), even in the presence of weak base (Figs. 2 and 3). The actual DS obtained in experiments and predicted DS produced by the model are given in Table 2. The mathematical equation expressing relationship of DS with variables X_{conc}, X_{time} and X_{temp} (concentration of oleic acid/*n*-OSA, reaction time and reaction temperature, respectively) is given below in terms of coded factors.

For GGH oleate:

$$\begin{aligned}\text{DS} = {} & -0.30 + 0.040 \times X_{conc} + 1.59 \times 10^{-3} \times X_{time} + 5.84 \times 10^{-3} \\ & \times X_{temp} - 0.018 \times X_{conc}^2 - 5.10 \times 10^{-6} \times X_{time}^2 - 4.65 \times 10^{-5} \\ & \times X_{temp}^3 - 3.85 \times 10^{-4} \times X_{conc} \times X_{time} + 8.98 \times 10^{-4} \times X_{conc} \\ & \times X_{temp}\end{aligned}$$

For GGH-OSA:

$$\begin{aligned}\text{DS} = {} & -0.72 + 5.56 \times 10^{-3} \times X_{conc} + 9.38 \times 10^{-3} \times X_{time} \\ & + 6.02 \times 10^{-3} \times X_{temp} - 9.06 \times 10^{-3} \times X_{conc}^2 - 2.22 \times 10^{-2} \\ & \times X_{time}^2 - 1.73 \times 10^{-2} \times X_{temp}^2 - 9.95 \times 10^{-3} \times X_{conc} \times X_{time}\end{aligned}$$

For GA-OSA:

$$\begin{aligned}\text{DS} = {} & -0.78 + 0.18 \times X_{conc} + 1.71 \times 10^{-3} \times X_{time} + 1.65 \times 10^{-2} \\ & \times X_{temp} - 4.90 \times 10^{-2} \times X_{conc}^2 - 6.7 \times 10^{-6} \times X_{time}^2 \\ & - 1.1 \times 10^{-4} \times X_{temp}^2 - 2.2 \times 10^{-4} \times X_{conc} \times X_{time} \\ & - 4.7 \times 10^{-4} \times X_{conc} \times X_{temp} + 4.49 \times 10^{-6} \times X_{time} \times X_{temp}\end{aligned}$$

In order to determine whether the quadratic model was significant, it was necessary to run ANOVA analysis. The results of the second order response surface model fitting in the form of ANOVA are given in Table 3. The ANOVA of quadratic regression model demonstrated the model to be significant, as is evident from Fisher's *F*-test value being 128.49, 39.10 and 191.92 for GGH oleate, GGH-OSA and GA-OSA, respectively. The *P*-values were used as a tool for checking the significance of each coefficient. It also indicated the interaction strength of each parameter. The smaller the *P*-values, the larger is the significance of corresponding coefficient (Murthy, Swaminathan, Rakshit, & Kosugi, 2000). Here, the *P*-value of the model was smaller than 0.0001, for GGH oleate, GGH-OSA and GA-OSA which indicated that the model was suitable for use in this experiment. The fitness of the model was further confirmed by a satisfactory value of determination coefficient (R^2). In these experiments, it was calculated to be 0.993 for GGH oleate, 0.980 for GGH-OSA and 0.995 for GA-OSA indicating that 99.3% for GGH oleate, 98% for GGH-OSA and 99.5% for GA-OSA in the response could be predicted by the model. The value of adjusted determination coefficient $R^2_{adjusted}$ (0.986 for GGH oleate, 0.955 for GGH-OSA and 0.990 for GA-OSA) established high significances of the model. At same time, relatively low value of the coefficient of variation 3.84% for GGH oleate, 8.18% for GGH-OSA and 3.97%

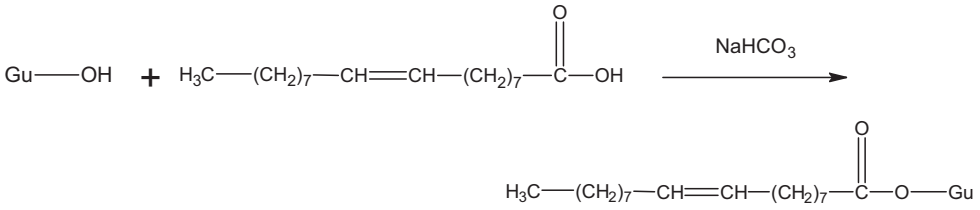

Fig. 1. Schematic representation of the esterification reaction between guar gum hydrolysate and oleic acid.

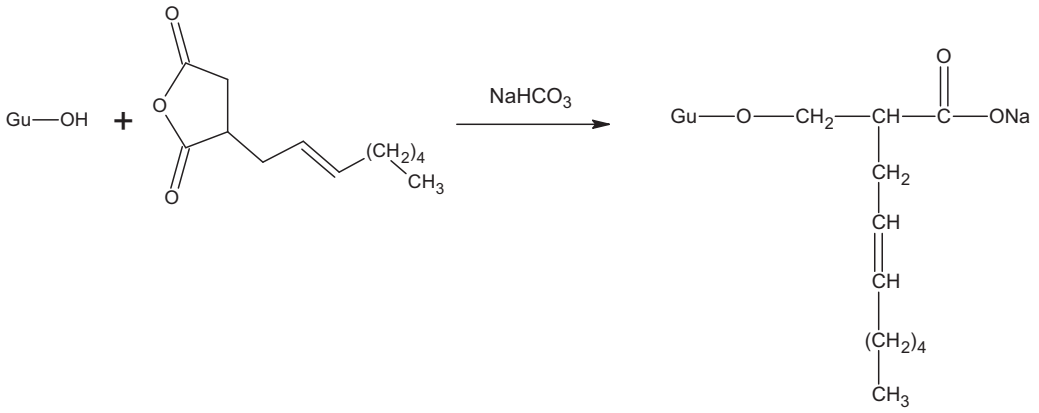

Fig. 2. Schematic representation of the esterification reaction between guar gum hydrolysate and *n*-OSA.

for GA-OSA indicated accuracy and reliability of the experiments. The significance of each term was determined by Student's *t*-test and *P*-values which is listed in Table 4. *P*-values were used to check the significance of each coefficient, as well as the interaction effects between each independent variable. Coefficients are significant for corresponding higher and lower magnitude of *t*-values and *P*-values.

For GGH oleate the coefficient estimates and the corresponding *P*-values suggest that, among the test variables used in the study, X_{conc} (oleic acid concentration), X_{time} (reaction time), X_{temp} (reaction temperature), $X_{conc} \cdot X_{time}$ (oleic acid concentration · reaction time), $X_{conc} \cdot X_{temp}$ (oleic acid concentration · reaction temperature), X^2_{conc} (oleic acid concentration)^2, X^2_{time} (reaction time)^2, X^2_{temp} (reaction temperature)^2 were significant model terms with *P*-values of less than 0.05. However oleic acid concentration, square of oleic acid concentration and reaction time, and interactive term of oleic acid concentration and reaction time ($P < 0.001$) had largest effect on DS.

For GGH-OSA, linear terms X_{conc} (*n*-OSA concentration), X_{time} (reaction time), X_{temp} (reaction temperature), $X_{conc} \cdot X_{time}$ (*n*-OSA concentration · reaction time), X^2_{conc} (*n*-OSA concentration)^2, X^2_{time} (reaction time)^2, X^2_{temp} (reaction temperature)^2 were significant model terms with *P*-values of less than 0.05. Reaction time and square of reaction time, and reaction temperature term with ($P < 0.0001$) had largest effect on DS.

Similarly for GA-OSA, the linear terms X_{conc} (*n*-OSA concentration), X_{time} (reaction time), X_{temp} (reaction temperature), their squares and interactive term were significant model terms with *P*-values of less than 0.05. However model terms squares of X_{conc} (*n*-OSA concentration), X_{time} (reaction time), X_{temp} (reaction temperature) with *P*-values of less than 0.0001 had largest effect on DS.

The 3D plots are the graphical representations of the regression equation, and are presented in Figs. 4–6, from which the values of DS for different variables can be predicted. These graphs are plotted as a function of two of factors while keeping the third as

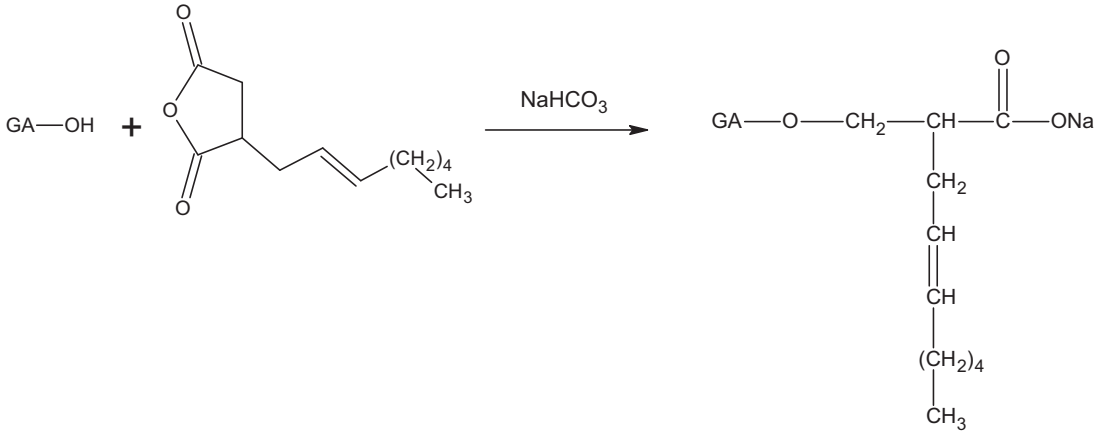

Fig. 3. Schematic representation of the esterification reaction between gum Arabic and *n*-OSA.

Table 2
Experimental design and responses for the DS of guar gum hydrolyzate oleate, guar gum hydrolyzate succinate, gum Arabic succinate and predicted values of DS.

No.	Actual values			Degree of Substitution (DS × 10^{-2})					
	X_{conc}	X_{time}	X_{temp}	GGH oleate		GGH-OSA		GA-OSA	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.7	60	75	1.33 ± 0.07	1.44	1.57 ± 0.17	1.61	2.48 ± 0.11	2.44
2	1.7	60	75	5.69 ± 0.15	5.49	4.21 ± 0.11	4.71	4.25 ± 0.05	4.49
3	0.7	180	75	4.53 ± 0.23	4.72	5.99 ± 0.18	5.48	6.14 ± 0.02	5.88
4	1.7	180	75	4.27 ± 0.06	4.15	4.65 ± 0.04	4.60	5.22 ± 0.07	5.24
5	0.7	120	60	4.32 ± 0.12	4.22	3.21 ± 0.04	3.55	3.04 ± 0.02	3.25
6	1.7	120	60	4.41 ± 0.18	4.61	4.53 ± 0.11	4.41	4.71 ± 0.00	4.66
7	0.7	120	90	3.73 ± 0.08	3.52	4.39 ± 0.04	4.50	4.98 ± 0.01	5.03
8	1.7	120	90	6.51 ± 0.06	6.61	6.22 ± 0.10	5.87	5.26 ± 0.08	5.03
9	1.2	60	60	2.78 ± 0.11	2.76	2.45 ± 0.05	2.05	2.32 ± 0.02	2.13
10	1.2	180	60	3.41 ± 0.08	3.31	3.12 ± 0.05	3.28	3.41 ± 0.01	3.42
11	1.2	60	90	2.91 ± 0.08	3.00	2.77 ± 0.07	2.60	3.00 ± 0.00	2.39
12	1.2	180	90	4.35 ± 0.10	4.37	4.75 ± 0.07	5.14	5.13 ± 1.00	5.30
13	1.2	120	75	6.23 ± 0.18	6.24	7.22 ± 0.09	7.23	8.10 ± 0.05	8.15
14	1.2	120	75	6.25 ± 0.08	6.24	7.25 ± 0.06	7.23	8.10 ± 0.03	8.15
15	1.2	120	75	6.22 ± 0.01	6.24	7.22 ± 0.09	7.23	8.17 ± 0.01	8.15
16	1.2	120	75	6.27 ± 1.18	6.24	7.23 ± 0.06	7.23	8.15 ± 0.02	8.15
17	1.2	120	75	6.27 ± 0.20	6.24	7.24 ± 0.06	7.23	8.15 ± 0.03	8.15

All values are mean ± SD of three determinations.

Table 3
ANOVA for quadratic model.

Source	SS × 10^{-4}			DF			*F*-value			*P* > *F*		
	GGH oleate	GGH-OSA	GA-OSA	GGH oleate	GGH-OSA	GA-OSA	GGH oleate	GGH-OSA	GA-OSA	GGH oleate	GGH-OSA	GA-OSA
Model	37	57	76	9	9	9	128.49	39.10	191.92	<0.0001	<0.0001	<0.0001
Residual	1.14	1.14	0.31	7	7	7						
Lack of fit	1.14	1.14	0.30	3	3	3						
Pure error	6.8×10^{-8}	6.8×10^{-8}	3.28×10^{-7}	4	4	4						
Total	58.7	58.7	76.81	16	16	16						

SS, sum of squares; DF, degree of freedom; R^2 = 0.99, adj R^2 = 0.98, CV = 3.84% for GGH oleate. R^2 = 0.98, adj R^2 = 0.95, CV = 8.18% for GGH-OSA. R^2 = 0.99, adj R^2 = 0.99, CV = 3.97% for GA-OSA.

constant at its mean level. Figs. 4A, 5A and 6A depict the effect of oleic acid/*n*-OSA concentration and reaction time on DS maintaining reaction temperature at its mean level. The maximum DS was attained near the central of experimental domain, beyond which even if the concentration of modifying agent and reaction time were to be increased, the DS would decrease. Song, He, Ruan, and Chen (2006) in their work on OSA-modified early *Indica* rice starch explained that with the progress of esterification, the concentration of modifying agent depleted due to esterification reactions yielding low DS starch. Figs. 4B, 5B and 6B demonstrate the effect of *n*-OSA/oleic acid concentration and reaction temperature on DS. It was observed that after the central region of experimental parameters, the DS decreased. These results are in line with previous study on modification of native and hydrolyzed corn starch with oleic acid (Kshirsagar & Singhal, 2007). Figs. 4C, 5C and 6C demonstrate the effect of reaction temperature and reaction time on DS at a fixed concentration of *n*-OSA/oleic acid. In this set of experiments, since the concentration of reactants was held constant, the DS decreased beyond the optimum time and temperature of reaction which could be due to depletion of the modifying reagent.

As per the model, optimum values of selected variables were obtained by solving regression equation and validated experimentally. For GGH-oleate, 1.4 g oleic acid per 25 g starting material, a reaction time of 120 min at 80 °C gave a maximum DS of 0.061. For GGH-OSA, 1.6 g *n*-OSA per 25 g starting material, a reaction time of 160 min at 85 °C, a maximum DS of 0.072 was obtained. The corresponding values for GA-OSA were an *n*-OSA concentration of 1.5 g per 25 g starting material, a reaction time of 123 min at 77 °C, which

Table 4
Model fitting results for DS.

Model	Coefficient			*P* value		
	GGH oleate	GGH-OSA	GA-OSA	GGH oleate	GGH-OSA	GA-OSA
Intercept	6.24×10^{-2}	7.23×10^{-2}	8.15×10^{-2}	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
X_{conc}	8.70×10^{-3}	5.56×10^{-3}	3.52×10^{-3}	$<1.0 \times 10^{-4}$	6.0×10^{-3}	2.1×10^{-3}
X_{time}	4.82×10^{-3}	9.38×10^{-3}	1.05×10^{-2}	1.0×10^{-4}	3.0×10^{-4}	$<1.0 \times 10^{-4}$
X_{temp}	3.22×10^{-3}	6.02×10^{-3}	5.37×10^{-3}	1.4×10^{-3}	4.0×10^{-3}	2.0×10^{-4}
X_{conc}^2	-4.57×10^{-3}	-9.06×10^{-3}	-1.22×10^{-2}	1.2×10^{-3}	2.5×10^{-3}	$<1.0 \times 10^{-4}$
X_{time}^2	-1.83×10^{-2}	-2.22×10^{-2}	-2.40×10^{-2}	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
X_{temp}^2	-1.04×10^{-2}	-1.73×10^{-2}	-2.42×10^{-2}	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_{conc} \cdot X_{time}$	-1.15×10^{-2}	-9.95×10^{-3}	-6.72×10^{-3}	$<1.0 \times 10^{-4}$	1.7×10^{-3}	4.0×10^{-4}
$X_{conc} \cdot X_{temp}$	6.73×10^{-3}	1.27×10^{-3}	-3.50×10^{-3}	1.0×10^{-4}	5.48×10^{-1}	1.27×10^{-2}
$X_{time} \cdot X_{temp}$	2.04×10^{-3}	3.27×10^{-3}	4.03×10^{-3}	5.74×10^{-2}	1.49×10^{-1}	6.4×10^{-3}

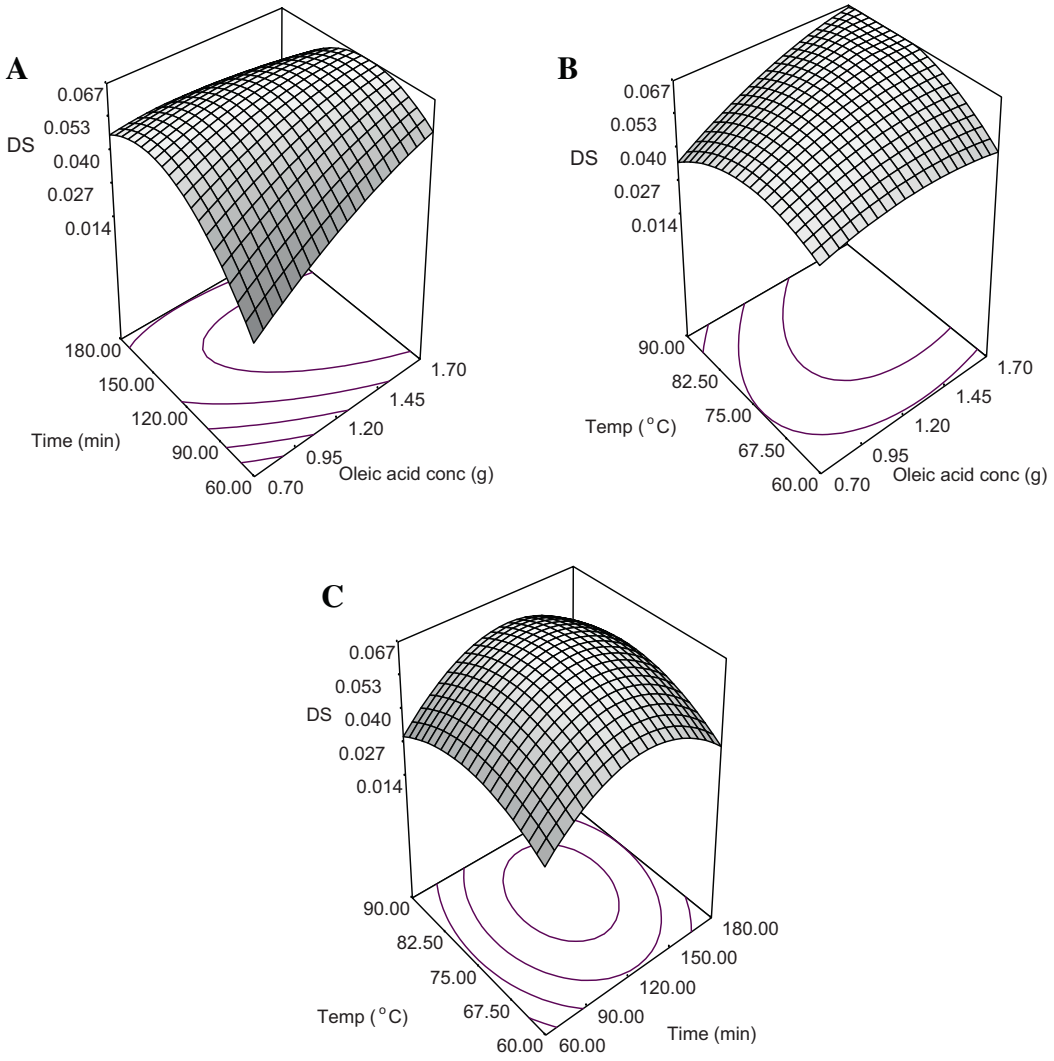

Fig. 4. Response surface plot for guar gum hydrolysate oleate: (A) effect of oleic acid concentration and reaction time on DS, (B) effect of oleic acid concentration and reaction temperature on DS, (C) effect of reaction time and reaction temperature on DS.

gave a maximum DS of 0.070. Model predicted values of DS for GGH oleate, GGH-OSA and GA-OSA were 0.067, 0.074 and 0.072, respectively. The actual DS of the esters were quite close to predicted model values which confirmed the validation of the models.

3.2. Analysis of GA, GA-OSA, GGH-OSA and GGH-oleate as wall materials for microencapsulation

3.2.1. Emulsion stability

Emulsions of GGH-oleate of DS 0.01 and 0.06, GGH-OSA of DS 0.02 and 0.07, and GA-OSA of DS 0.02 and 0.07 were prepared as detailed in Section 2.4.1, and stored for 24 h prior to measurement of emulsion stability index (ESI). All the emulsions showed an ESI of 1 demonstrating good emulsion stability. This method could not distinguish between the esters. Hence, turbidity measurements were made as an indicator of emulsion stability. Turbidity has been reported to be an indicator of emulsion stability by earlier researchers (Erni et al., 2007; Savary, Hucher, Bernadi, Grisel, & Malhiac, 2010). Our results showed GGH-oleate to show least turbidity among the samples evaluated, suggesting a relatively lower emulsifying property as compared to GGH-OSA and GA-OSA. The modified gums showed better emulsifying property than native gum, suggesting that the new functional group attached to the gum during the modification reaction improved their ability to stabilize oil-in-water emulsions. Segura-Campos et al. (2008) reported improved emulsion stability in octenylsuccinic starch from *Phaseolus lunatus* compared to native starch and attributed improved emulsion stability to a combination of the hydrophobic octenyl group and sodium carboxyl group. For GGH-oleate, DS played a significant role in improving emulsion stability. This is seen from higher turbidity of the emulsion prepared from GGH-oleate of DS 0.06 as compared to that of DS 0.01 (Table 5). A higher DS indicates a better substitution of hydrophobic group in the gum which in turn improves its emulsifying activity. However for GGH-OSA and GA-OSA, an increase in DS did not improve their emulsifying activity. Viswanathan (1999) explained in his study on octenylsuccinate starch that overall hydrophobic characteristic of starch did not improve with increasing DS as octenyl chain folded itself toward central region of granule, resulting in decreased interaction between oil phase and hydrophobic part of the chain.

3.2.2. Viscosity

Viscosity of emulsions prepared from gum esters with various DS is tabulated in Table 5. Emulsion with GA showed lowest viscosity (33 ± 0.56 cP), while that with GA-OSA and GGH-OSA showed viscosity of 37 ± 0.13 cP and 62 ± 0.12 cP, respectively.

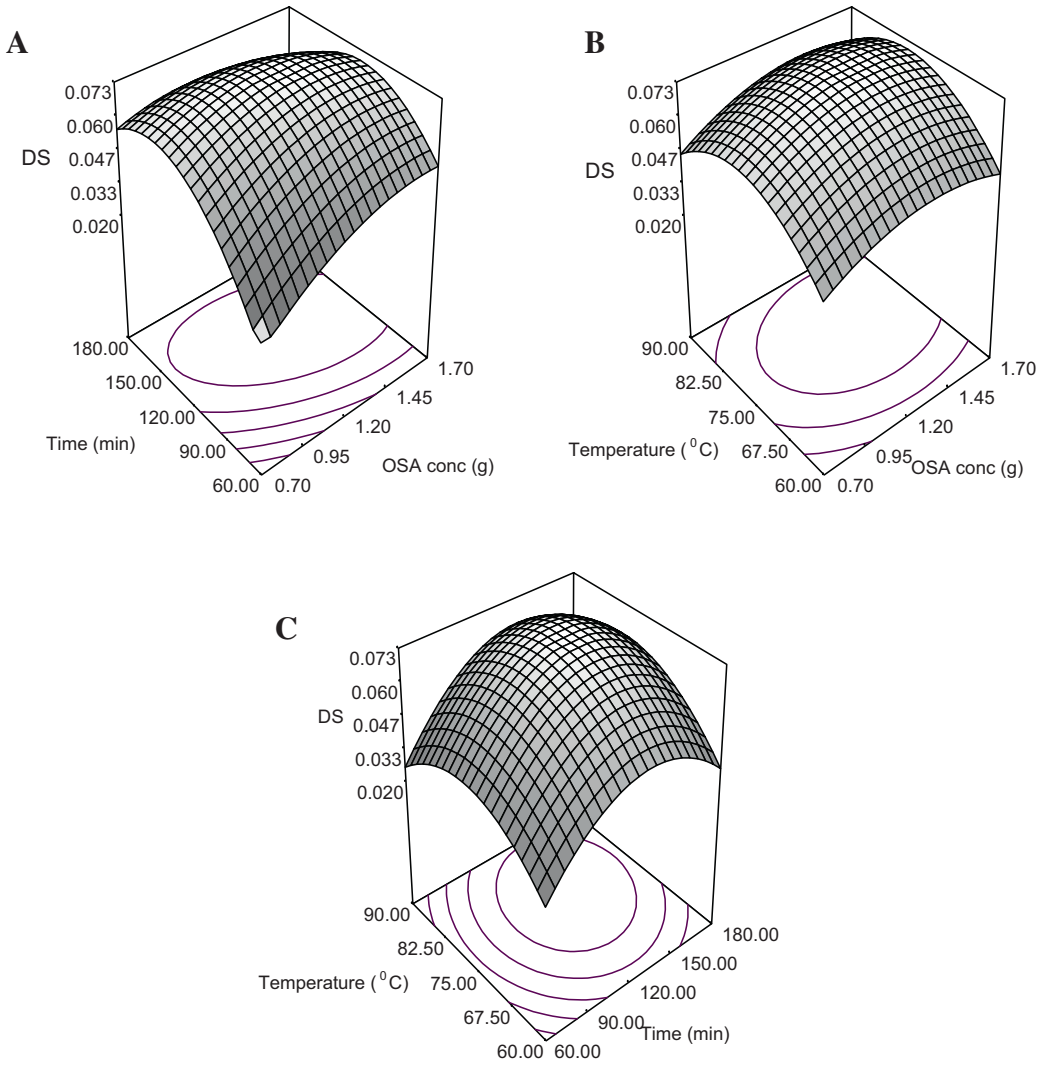

Fig. 5. Response surface plot for guar gum hydrolyzate succinate: (A) effect of OSA concentration and reaction time on DS, (B) effect of OSA concentration and reaction temperature on DS, (C) effect of reaction time and reaction temperature on DS.

3.2.3. *Particle size analysis*

Particle size of the emulsions was analysed and the results are shown in Table 5. Particle size analysis is also an indicator of emulsion stability. As the particles have a tendency to agglomerate, the size of the suspended oil particles increases after certain period and subsequently the emulsion breaks. However, in this study we found the particle size of the gum esters to increase only marginally after 24 h suggesting them to be stable and suitable for spray drying. Emulsion with small mean emulsion particle size is reported to have better flavour retention and stability of entrapped flavour in microencapsulated powder so, emulsion property is very crucial for microencapsulation (Risch & Reineccius, 1988; Sheu & Rosenberg, 1995; Soottitantawat, Yoshii, Furuta, Ohkawara, & Linko, 2003).

The work reported in this paper could be extended to other galactomannans that are abundantly available in different geographical regions, and merits attention.

Table 5
Turbidity, viscosity and emulsion particle size of emulsion with different DS of guar gum hydrolyzate oleate, guar gum hydrolyzate succinate, gum Arabic succinate.

Sample		Turbidity (Γ)	Viscosity (cP)	Emulsion particle size (μm)	
				0 h	24 h
GA	–	0.56 ± 0.10^{a}	33 ± 0.56^{a}	12.76 ± 0.29^{a}	13.56 ± 0.34^{a}
GHH	–	ND	ND	ND	ND
GA-OSA	DS, 0.02	0.97 ± 0.02^{b}	36 ± 0.40^{b}	13.44 ± 0.31^{a}	14.06 ± 0.20^{b}
	DS, 0.07	0.91 ± 0.03^{c}	37 ± 0.25^{c}	13.5 ± 0.18^{a}	13.88 ± 0.14^{c}
GGH oleate	DS, 0.01	0.20 ± 0.11^{d}	45 ± 0.43^{d}	14.68 ± 0.30^{b}	15.32 ± 0.28^{d}
	DS, 0.06	0.47 ± 0.10^{a}	49 ± 0.85^{e}	13.86 ± 0.15^{c}	14.80 ± 0.18^{e}
GGH-OSA	DS, 0.02	0.81 ± 0.06^{e}	58 ± 0.70^{f}	12.84 ± 0.49^{a}	13.46 ± 0.23^{a}
	DS, 0.07	0.77 ± 0.03^{f}	62 ± 0.20^{g}	13.04 ± 0.24^{a}	13.36 ± 0.20^{a}

ND: not determined, since the emulsion was not formed. All values are mean ± SD of three or more determinations. Means in same columns with same superscripts do not differ significantly ($P < 0.05$).

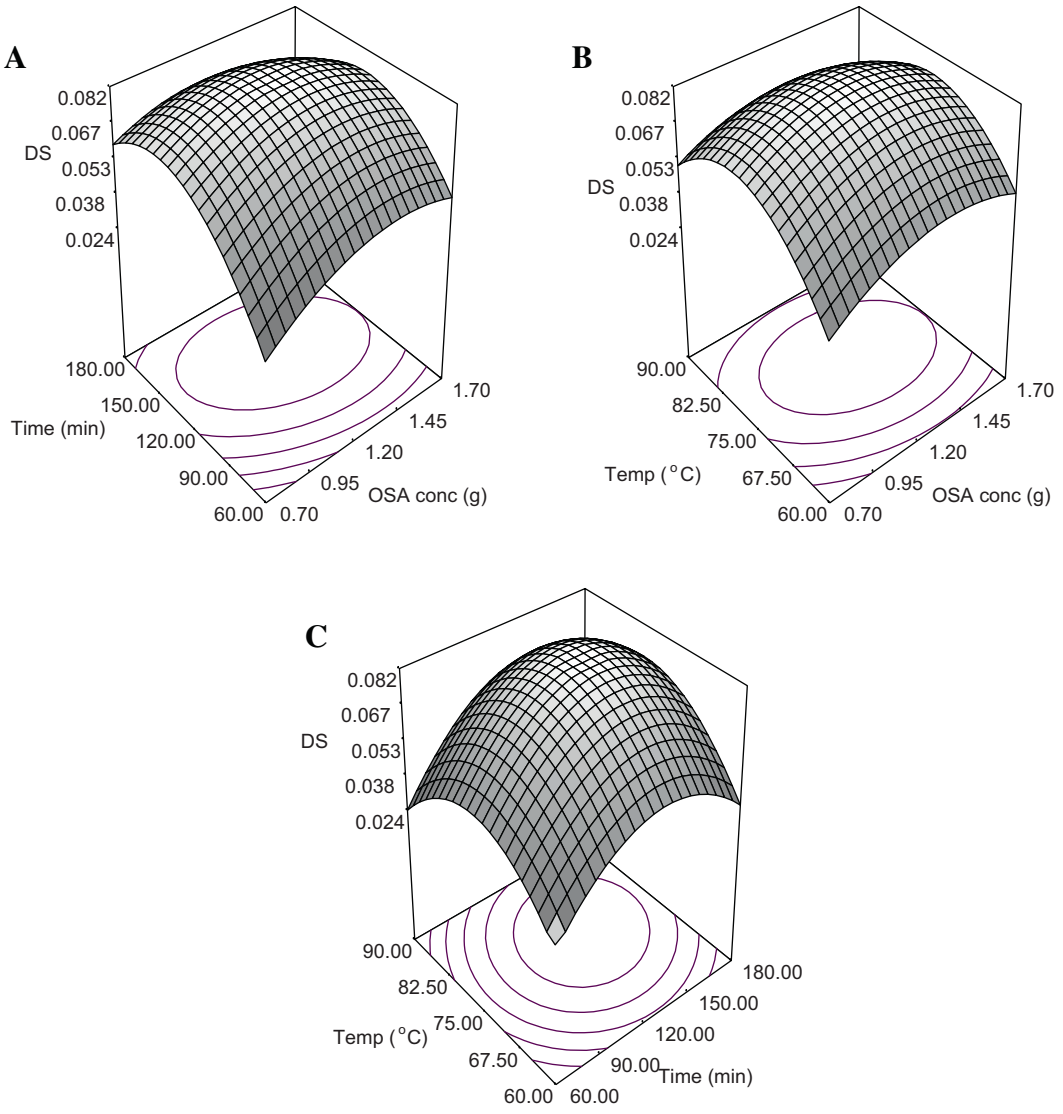

Fig. 6. Response surface plot for gum Arabic succinate: (A) effect of OSA concentration and reaction time on DS, (B) effect of OSA concentration and reaction temperature on DS, (C) effect of reaction time and reaction temperature on DS.

4. Conclusion

Esterification of gum Arabic and guar gum hydrolysate with oleic acid and *n*-octenyl succinic acid improved the emulsification with a desirable range of particle size and viscosity that makes it suitable as a wall material for encapsulation. In particular, *n*-octenyl succinate ester of guar gum hydrolysate could open up avenues in value addition of this important bioresource as a promising alternative to gum Arabic for microencapsulation of sensitive food components showed good emulsifying property which ensures their potential future in microencapsulation. Further studies to understand the effect of DS on microencapsulation of sensitive food ingredients are in progress.

Acknowledgement

Authors are grateful to University Grants Commission, Government of India, for providing financial assistance during the course of this investigation.

References

Bai, Y., & Shi, Y. (2011). Structure and preparation of octenyl succinic esters of granular starch, microporous starch and soluble maltodextrin. *Carbohydrate Polymers*, *83*, 520–527.

Bhosale, R., & Singhal, R. (2006). Process optimization for the synthesis of octenyl succinyl derivative of waxy corn and amaranth starches. *Carbohydrate Polymers*, *66*, 521–527.

Box, G. E. P., & Behnken, D. W. (1960). Some new three level design for study of quantitative variables. *Technometrics*, *2*, 455–476.

Cheng, Y., Brown, K. M., & Prud'homme, R. K. (2002). Preparation and characterization of molecular weight fractions of guar galactomannans using acid and enzymatic hydrolysis. *International Journal of Biological Macromolecules*, *31*, 29–35.

Erni, P., Windhab, E. J., Gunde, R., Graber, M., Pfister, B., Parker, A., et al. (2007). Interfacial rheology of surface-active biopolymers: Acacia senegal gum versus hydrophobically modified starch. *Biomacromolecules*, *8*, 3458–3466.

Fang, J. M., Fowler, P. A., Tomkinson, J., & Hill, C. A. S. (2002). An investigation of the use of recovered vegetable oil for the preparation of starch thermoplastics. *Carbohydrate Polymers*, *50*, 429–434.

Hui, R., Qi-he, C., Ming-liang, F., Qiong, X., & Guo-qing, H. (2009). Preparation and properties of octenyl succinic anhydride modified potato starch. *Food Chemistry*, *114*, 81–86.

Jumel, K., Harding, S. E., & Mitchell, J. R. (1996). Effect of gamma irradiation on the macromolecular integrity of guar gum. *Carbohydrate Research*, *282*, 223–236.

Kshirsagar, A. C., & Singhal, R. S. (2007). Optimization of starch oleate derivatives from native corn and hydrolyzed corn starch by response surface methodology. *Carbohydrate Polymers*, *69*, 455–461.

Mahammad, S., Prud'homme, R. K., Roberts, G. W., & Khan, S. A. (2006). Kinetics of enzymatic depolymerization of guar galactomannan. *Biomacromolecules*, *7*, 2583–2590.

McNamee, B. F., O'Riordan, E. D., & O'Sullivan, M. (1998). Emulsification and microencapsulation properties of gum Arabic. *Journal of Agricultural and Food Chemistry*, *46*, 4551–4555.

Miyazawa, T., & Funazukuri, T. (2006). Non catalytic hydrolysis of guar gum under hydrothermal conditions. *Carbohydrate Research*, *341*, 870–877.

Murthy, M. S. R. C., Swaminathan, T., Rakshit, S. K., & Kosugi, Y. (2000). Statistical optimization of lipase catalyzed hydrolysis of methyloleate by response surface methodology. *Bioprocess Engineering*, *22*, 35–39.

Pearce, K. N., & Kinsella, J. E. (1978). Emulsifying properties of proteins: Evaluation of a turbidimetric technique. *Journal of Agricultural and Food Chemistry*, *26*, 716–723.

Reddy, T. T., & Tammishetti, S. (2004). Free radical degradation of guar gum. *Polymer Degradation and Stability*, *86*, 455–459.

Reineccius, G. A. (1988). Spray drying of food flavours. In S. J. Risch, & G. A. Reineccius (Eds.), *Flavour encapsulation* (pp. 55–66). Washington, DC: American Chemical Society.

Reineccius, G. A. (1989). Carbohydrates for flavour encapsulation. *Food Technology*, *45*, 144–149.

Risch, S. J., & Reineccius, G. A. (1988). Spray-dried orange oil—Effect of emulsion size on flavor retention and shelf life. In S. J. Risch, & G. A. Reineccius (Eds.), *Flavour encapsulation* (pp. 67–77). Washington, DC: American Chemical Society.

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

Savary, G., Hucher, N., Bernadi, E., Grisel, M., & Malhiac, C. (2010). Relationship between the emulsifying properties of acacia gums and the retention and diffusion of aroma compounds. *Food Hydrocolloids*, *24*, 178–183.

Savitha Prashanth, M. R., Parvathy, K. S., Susheelamma, N. S., Hari Prashanth, K. V., Tharanathan, R. N., Cha, A., et al. (2006). Galactomannan esters—A simple, cost-effective method of preparation and characterization. *Food Hydrocolloids*, *20*, 1198–1205.

Segura-Campos, M., Chel-Guerrero, L., & Betancur-Ancona, D. (2008). Synthesis and partial characterization of octenylsuccinic starch from *Phaseolus lunatus*. *Food Hydrocolloids*, *22*, 1467–1474.

Sheu, T. Y., & Rosenberg, M. (1995). Microencapsulation by spray drying ethyl caprylate in whey protein and carbohydrate wall systems. *Journal of Food Science*, *60*, 98–103.

Shogren, R. L., Viswanathan, A., Felker, F., & Gross, R. A. (2000). Distribution of octenyl succinate groups in octenyl succinic anhydride modified waxy maize starch. *Starch/Starke*, *52*, 196–204.

Slavin, J. L., & Greenberg, N. A. (2003). Partially hydrolyzed guar gum: Clinical nutrition uses. *Nutrition*, *19*, 549–552.

Song, X., He, G., Ruan, H., & Chen, Q. (2006). Preparation and properties of octenyl succinic anhydride modified early *Indica* rice starch. *Starch/Starke*, *58*, 109–117.

Soottitantawat, A., Yoshii, H., Furuta, T., Ohkawara, M., & Linko, P. (2003). Microencapsulation by spray drying: Influence of emulsion size on the retention of volatile compounds. *Journal of Food Science*, *68*, 2256–2262.

Viswanathan, A. (1999). Effect of degree of substitution of octenyl succinate starch on emulsification activity of different oil phases. *Journal of Environment & Polymer Degradation*, *7*, 191–196.

Wurzburg, O. B. (1995). Food polysaccharides and their applications. In M. S. Alistair (Ed.), *Modified starches* (pp. 67–97). USA: Marcel Dekker Inc.