WALAILAK JOURNAL
http://wjst.wu.ac.th Engineering and Physical Sciences

Microencapsulation of Citronella Oil with Carboxymethylated Tamarind Gum

Keonakhone KHOUNVILAY[1], Berta Nogueiro ESTEVINHO[2], Fernando Alberto ROCHA[2], José María OLIVEIRA[3], António VICENTE[3] and Wancheng SITTIKIJYOTHIN[1,*]

[1]Department of Chemical Engineering, Faculty of Engineering, Burapha University, Chonburyi 20131, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering, University of Porto, Porto 4200-465, Portugal
[3]Centre of Biological Engineering, University of Minho, Campus de Gualtar, Braga 4710-057, Portugal

([*]Corresponding author's e-mail: wancheng@buu.ac.th)

Received: 29 November 2016, Revised: 1 August 2017, Accepted: 26 September 2017

Abstract

Tamarind gum (TG) and carboxymethylated tamarind gum (CTG) were used as wall material to prepare citronella oil microcapsules by spray-drying. The aim of this work was to study the effect of wall-to-core ratio and fluid viscosity on emulsion droplet and microcapsule size, in order to maximize encapsulation efficiency (EE). EE was directly influenced by gum-to-oil ratio variations. Results showed that emulsion droplet size (D_{32}) of CTG ranged between 0.18 to1.31 μm, smaller than those obtained for TG, which ranged from 0.87 to 2.91 μm. CTG microcapsules had a smooth surface and a spherical shape, as observed by scanning electron microscopy (SEM). Surface oil content and total oil content affected encapsulation efficiency. TG microcapsules showed lower EE than CTG microcapsules, which was related to the viscosity of gum to oil ratio. The maximum EE occurred at 1.14 gum to oil ratio for CTG microcapsules (87 %).

Keywords: Citronella oil, tamarind gum, microencapsulation, carboxymethylation, spray-drying

Introduction

Citronella oil is an essential oil obtained from citronella grass- the common name of plants of genus *Cymbopogon*. The main chemical components of citronella oil are citronellal (33.9 %), geraniol (18.1 %), and citronellol (11.1 %) [1]. These components have been reported to exhibit antimicrobial and anti-parasitic effects against bacteria, yeasts, filamentous fungi, and viruses [2]. Nowadays, citronella oil is one of the most extensively used natural insect repellents on the market, used at concentrations of 5 - 10 % [3]. Citronella oil is known for rapidly evaporating, causing loss of efficiency with time [4]. The use of encapsulation allows slower release profiles of citronella oil and, at the same time, prevents the evaporation of essential oils, resulting in a higher protection time, as well an increase in shelf life [5,6]. The most used technique for the encapsulation of essential oils/volatile compounds is spray-drying, mainly due to the low cost and the availability of equipment when compared to other techniques [7]. A good wall material for microencapsulation by spray-drying should display high solubility, effective emulsification, and film forming characteristics [8]. Previously, Baranauskienė *et al.* [9] and Specos *et al*. [10] used gum arabic for citronella oil encapsulation through spray-drying for the protection of oil release.

Tamarind gum (TG) is a group of storage or structural heteropolysaccharides from tamarind plants (*Tamarindus indical* L.), and its structure is composed by a 1,4-linked β-D glucan main chain that is

partially substituted with α-D xylan side chains at the O-6 atom [11]. The main chemical structure is the glucose unit (**Figure 1A**). The major component of tamarind gum has been identified as natural, non ionic heteropolysaccharides, consisting of glucose, xylose, and galactose [12]. TG has been used in many industrial applications, such as a natural flocculant in water treatment [13], glue and paper adhesive manufacturing, and textile thickener [14], and in novel applications, such as controlled drug delivery [15]. However, several drawbacks have been presented when using TG, such as low solubility in cold water, rapid biodegradability, unpleasant odor, and dull color [16].

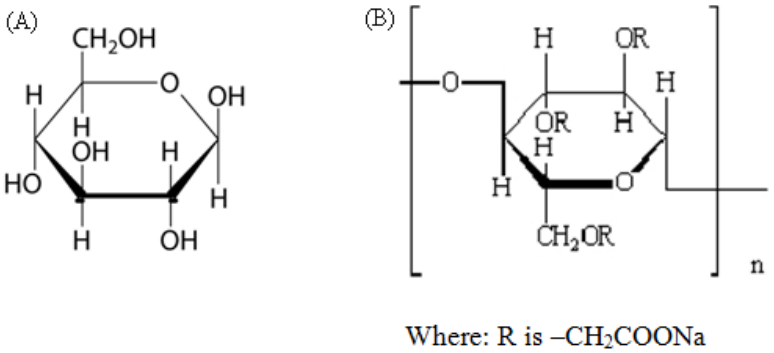

Figure 1 Glucose unit of crude gum (a) and modified gum with carboxymethyl group (b).

Therefore, the carboxymethylation process for crude TG has been used to overcome these disadvantages and to make it more useful for a wider range of industries [17]. Carboxymethylated tamarind gum (CTG) (**Figure 1B**) confers an anionic nature to the biopolymer. Replacement of a hydroxyl group by a carboxymethyl group disrupts the organization of the structure, thereby exposing the polysaccharide network to hydration and resulting in higher solubility in aqueous media, higher viscosity, and lower biodegradability, thus enhancing its shelf life as compared to crude gum [18].

The carboxymethylation of tamarind gum results in etherified tamarind. The hydroxyl groups of tamarind molecules are etherified by carboxymethyl groups. Carboxymethylation tamarind gum is reacted with sodium monochloroacetic acid in the presence of sodium hydroxide. In the main reaction, the sodium hydroxide first reacts with the hydroxyl group of the tamarind gum to give alkoxide groups, as in Eq. (1). In the second step, the glucose units in tamarind molecules are etherified by the carboxymethyl group, as shown in Eq. (2).

$$\text{Tamarind-OH} + \text{NaOH} \xrightarrow{\text{Alcohol}} \text{Tamarind gum-ONa} + H_2O \quad (1)$$

$$\text{Tamarind-ONa} + ClCH_2COONa \longrightarrow \text{Tamarind-O}CH_2COONa + NaCl \quad (2)$$

Recently, carboxymethylated polysaccharide gums were selected as adequate encapsulating materials to be applied in the encapsulation processes [19]. Modified gums are widely used in industry as stabilizers or emulsifiers for the controlled release of products, as previously reported in numerous research studies: carboxymethylcellulose [20], carboxymethylated guar gum [21], and CTG [22].

The aim of this work was to use TG and CTG as wall material to produce citronella oil microcapsules by spray-drying, and to evaluate how different ratios of gum/oil (w/w) influence microcapsule size and encapsulation efficiency (EE). The morphology of all microcapsules was observed by scanning electron microscopy (SEM).

Materials and methods

Materials

TG was kindly supplied from GM Ichihara Co., Ltd. (Thailand). CTG (Degree of Substitution = 0.204) was produced by an adaptation of the method described by Goyal *et al*. [16]. Citronella oil from *Cymbopogon winterianus* was purchased from Thai-China Flavors and Fragrances Industry Co., Ltd. (Thailand).

Determination of chemical compositions

Moisture and ash contents are determined according to the American Society for Testing and Materials methods (ASTM-D2974-87) and the AOAC Official Method 923.03, respectively. Protein content was obtained from the total nitrogen content (N×5.7) by the Kjeldahl method, as described in the AOAC Official Method of Analysis 981.10. Fat content was determined according to the AOAC Official Method of Analysis 923.06.

Fourier-transform infrared (FTIR) spectroscopy

To investigate the effect of the carboxymethylation process on the gum modification, the crude and modified tamarind gums were pulverized and blended with KBr, then compressed. The measurements on prepared discs were carried out using a FT-IR spectrophotometer (Magna-IR system 750, Nicolet Biomedical Inc., USA).

Intrinsic viscosity measurement

The intrinsic viscosities of dilute solutions of TG and CTG were measured with a capillary Cannon Fenske viscometer, using 10 ml of the solutions. Temperature was maintained at 20.0±0.1 °C during all measurements. Relative viscosities ranging between 1.2 and 2.0 were used to assure good accuracy and linearity of extrapolation to zero concentration. The limiting viscosity number ('intrinsic viscosity'), $[\eta]$, was obtained by double extrapolation to zero concentration of the Huggins and the Kraemer equations, respectively;

$$\frac{\eta_{\mathrm{sp}}}{C} = [\eta] + \mathrm{k}'[\eta]^2 C \tag{3}$$

$$\frac{(\eta_{rel})}{C} = [\eta] + \mathrm{k}''[\eta]^2 C \tag{4}$$

where C is the concentration of diluted solution, k', k'' are the Huggins and Kraemer coefficients, respectively, η_{sp} is the specific viscosity, and η_{rel} is the relative viscosity.

Emulsion preparation and spray-drying

Emulsions were prepared at different total solid contents, as shown in **Table 1**. The emulsion process was carried out as previously reported by Koocheki & Kadkhodaee [23]. Briefly, the carrier solution was prepared by dissolving gum into distilled water containing 0.5 g of Tween 80 and 0.5 g of Span 80. The mixture was left overnight under magnetic stirring for a complete hydration at room temperature, after which citronella oil was added drop by drop with a glass dropper. Subsequently, the mixtures were homogenized using an Ultra-Turrax homogenizer (T-25, IKA-Werke, Germany) at 16,000 rpm for 7 min.

Table 1 Emulsion conditions.

Code	Total solid content (g)			Gum-to-oil ratio
	Gum	Oil	Water	
I	5.0	4.0	91	1.25
II	3.2	2.8	94	1.14
III	1.4	1.6	97	0.87

Emulsions were transformed into microcapsules with a mini spray-dryer BÜCHI B-290 advanced (Flawil, Switzerland) with a standard 0.5 mm nozzle. The dried microcapsules were recovered and stored at 0 °C for further analyses.

Emulsion size analysis

Emulsion droplet size was determined by Dynamic Light Scattering (DLS) (Zetasiszer Nano ZS, Malvern Instruments, UK). Before measurement, samples were diluted with distilled water in 1:100 proportions, in order to avoid the multiple scattering effect. Triplicate measurements were performed, with 3 readings for each determination. The mean diameter (D_{32}) represents the surface average diameter [24], and was calculated using Eq. (5);

$$D_{32} = \frac{\sum_i Z_i D_i^3}{\sum_i Z_i D_i^2} \quad (5)$$

where z_i is the number of droplets with diameter D_i.

Emulsion viscosity determination

Viscosity of emulsions was measured using a Brookfield digital rheometer (Model RV-DVII, Brookfield, USA) at 20±2 °C.

Microcapsule size analysis

The size of microcapsules was determined using a laser scattering particle size analyzer (Mastersizer 2000, Malvern Instrument Co., Malvern, UK). This equipment detects particles in a size range from 0.04 to 2,000 μm. Ethanol was used as a dispersant. Before measurement, the sample was diluted in 1:100 proportions to avoid the multiple scattering effect.

Microscopy and morphology of microcapsule observation

Optical microscopy (Olympus, BX51, Japan) was used to confirm the presence of emulsion droplets and microcapsule appearances. Emulsions were diluted with distilled water, whereas microcapsules were dispersed and diluted with 2-propanol, in order to avoid dried microcapsule swelling.

SEM (LEO 1450VP, England) was used to observe the morphology of the microcapsules. The dried microcapsules were placed on the SEM stubs using 2-sided adhesive tape (Polaron, SC 7620) and then sputtered-coated with gold. The morphology of the microcapsules was observed at an accelerating voltage of 10 kV.

Efficiency of encapsulation

Total oil content

The total oil content was determined as described by Soottitantawat *et al*. [25]. Firstly, 4 mL distilled water were added to the dried microcapsules in a closed tube. The sample was mixed with a vortex mixer for 1 min. Then, hexane was used as an organic solvent to extract the oil from the microcapsules, being

heated at 90 °C for 30 min. The mixture in the tube was mixed every 10 min using a vortex mixer. Then, the mixture was centrifuged (Force 1624 microcentrifuge, USA) at 1,400×g for 10 min to separate the organic phase from the water, and the organic phase was then analyzed by gas chromatography.

Surface oil content

Surface oil content was evaluated as described by Tonon *et al.* [26]. Hexane was added as a solvent to the microcapsules, which were slowly shaken for 2 min at room temperature to extract superficial oil. The solvent mixture was then filtered with a 0.2 μm polyethersulfane membrane filter (Whatman, USA). Then, 1 μL of the organic phase was injected into the gas chromatograph. EE was calculated using Eq. (6);

$$\%\text{EE} = \frac{\text{Total oil content} - \text{surface oil}}{\text{Total oil content}} \times 100 \quad (6)$$

Gas chromatography analyses

Gas chromatography-mass spectrometry (GC-MS) analysis was performed using a Varian 3800 Chromatograph (Varian Inc., CA, USA), with a 1079 injector, and an ion-trap mass spectrometer Varian Saturn 2000 (Varian Inc., CA, USA). 1 μL of sample was injected (split ratio of 30 mL/min) into a capillary column, coated with VF-Wax ms (30 m × 0.15 mm i.d., 0.15 μm film thickness, Varian Inc., CA, USA). Both injector and transfer line temperatures were set at 250 °C. Helium was used as a carrier gas at a flow rate of 1.3 mL/min.

Statistical analyses

One-way analysis of variance (ANOVA) and Tukey test were used to determine statistically significant differences. $p < 0.05$ was considered to be statistically significant.

Results and discussion

Chemical composition

Table 2 presents the chemical compositions of TG and CTG. Due to using high temperatures and acidic and base solvents during the carboxymethylation process, the impurities (protein and fat contents) of CTG could be eliminated, as compared to TG. The polysaccharide content of CTG increased from about 78 to 93 % due to the effective removal of impurities. In addition, after carboxymethylation, moisture content was increased, due to CTG displaying more water absorption than TG.

Table 2 Chemical compositions of TG and CTG.

Components (%)	TG	CTG
Moisture	2.7±0.04	5.14±0.97
Ash	0.05±0.00	0.05±0.01
Protein	15.30	6.86
Fat	6.56	0.19
Polysaccharide (by difference)	78.09	92.90

All values (%) are mean ± standard deviation of 3 determinations.

FTIR

Infrared spectroscopy spectra of TG and CTG, shown in **Figure 2**, gave the same functional groups; for example the band at 3434 cm^{-1} is due to -OH stretching, the band at 1049 cm^{-1} is due to –CH-O-CH2 stretching, and the band at 2935 cm^{-1} is due to C-H stretching vibration. Moreover, the band around 1749 cm^{-1} could be the C=O stretching of the fatty acid. The amide group of proteins is C=O stretching at 1640 cm^{-1} and N-H stretching at 1540 cm^{-1} in crude tamarind gum. From the representative spectrum of a synthesized CTG sample, the strongest peaks were at 1441 and 1634 cm^{-1}. This result indicated the presence of carboxymethyl substituent from CTG synthesis at COO^-. Similar observations were reported for carboxymethylated *sesbania* gum [27], carboxymethylation of polysaccharides from *Tremella fuciformis* [28], and carboxymethylation of polysaccharide from *Cyclocarya paliurus* [29].

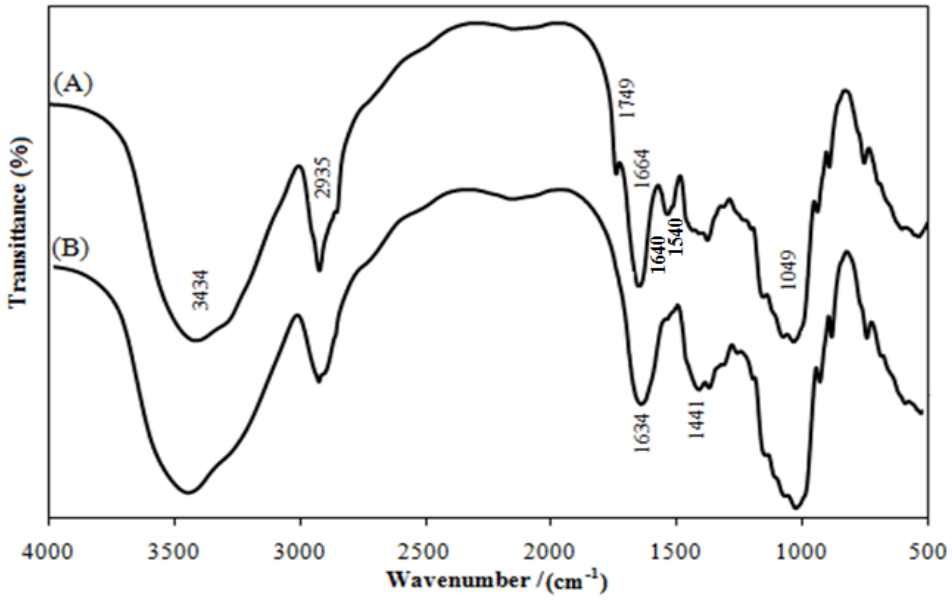

Figure 2 FTIR spectra of TG (A) and CTG (B).

Emulsion droplet and microcapsule sizes

Table 3 shows the emulsion and microcapsule sizes according to the emulsion viscosity and gum-to-oil ratio, evaluated in order to optimize the emulsion process. CTG emulsion presented higher values of viscosity than the TG emulsion when compared at the same gum-to-oil ratio. Moreover, for the CTG emulsion at 1.25 of gum-to-oil ratio (CTG I), the viscosity could not be measured, as it was very high. Since the physicochemical properties of both gums affect the emulsion viscosity, CTG showed a higher viscosity than TG, which was confirmed by intrinsic viscosity determination (**Figure 3**). Also, TG was not completely dissolved in cold water, as compared to CTG, which clearly dispersed in cold water due to the incorporation of the carboxymethyl group onto the TG backbone. After carboxymethylation, 2 adjacent negatively charged groups (i.e. COO−) repelled each other and, hence, the chains were expanded, increasing their hydrodynamic volume (i.e., intrinsic viscosity). In general, the carboxymethylation increases the intrinsic viscosity of polysaccharide. This behavior has been observed for carboxymethyl guar gum; the intrinsic viscosity of native guar gum was 11.09 dL/g, while carboxymethyl guar gum was 27.52 dL/g [30]. Therefore, the higher viscosity values of emulsions from CTG resulted in some degree of aggregation during the feeding of the spray-dryer, which likely explains the higher D_{32} values obtained for CTG microcapsules in comparison with those obtained for TG microcapsules.

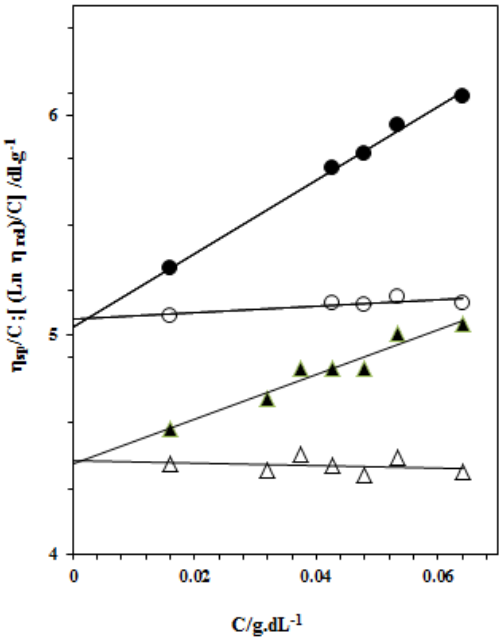

Figure 3 Determination of the intrinsic viscosities for TG (Δ) and CTG (○) by combined Huggins (full symbol) and Kraemer (open symbol) extrapolations to zero concentration, at 20 °C.

Table 3 Emulsions viscosity and sizes of emulsions and microcapsules.

	Code	Gum:Oil	Viscosity at shear rate of 20.4 s^{-1} (Pa.s)	D^*_{32} (µm)	
				Emulsion droplet size	Microcapsule size
TG	I	1.25	0.107	2.91±0.82	5.12±0.05
	II	1.14	0.036	1.87±0.54	4.35±0.04
	III	0.87	0.020	0.87±0.18	3.40±0.01
CTG	I	1.25	n.d.	1.31±0.11	6.30±0.05
	II	1.14	0.295	0.77±0.04	3.82±0.02
	III	0.87	0.032	0.18±0.01	4.82±0.02

*Significantly different values within the same group of values ($p < 0.05$).
n.d. could not be measured, due to excess viscous solution.

Table 3 shows D_{32} for the emulsions as determined by DLS. Results indicated that increasing the proportions of the gum-to-oil ratio results in an increase in the size of emulsion droplets, which can be explained by the increase of the wall material thickness around the oil droplets. However, the corresponding microcapsules obtained after spray-drying present higher size values for increasing gum concentrations. This is in agreement with the results obtained by Lim & Roos [31]; an excess of coating material may also increase the viscosity of the emulsion prior to spray-drying, resulting in a slightly larger particle size. Moreover, materials with higher viscosity (such as CTG) could make a protective layer around the emulsion droplet, resulting in a greater resistance to the movement of the oil droplet, thus avoiding coalescence [32]. Microcapsules obtained by spray-drying presented D_{32} values ranging from

3.40 to 5.12 µm for microcapsules that used TG as wall material, and ranging from 3.82 to 6.30 µm for microcapsules using CTG. Botrel *et al.* [33] also reported small scatter values (2 - 3 µm) for oregano essential oil microcapsules produced by spray-drying. **Figures 4A** and **4B** show the size distribution of emulsion droplets, with values ranging from 0.02 to 10µm, approximately. The bigger emulsion droplet size is due to the viscosity of the gum-to-oil ratio. At higher viscosities, larger droplets are formed during homogenization.

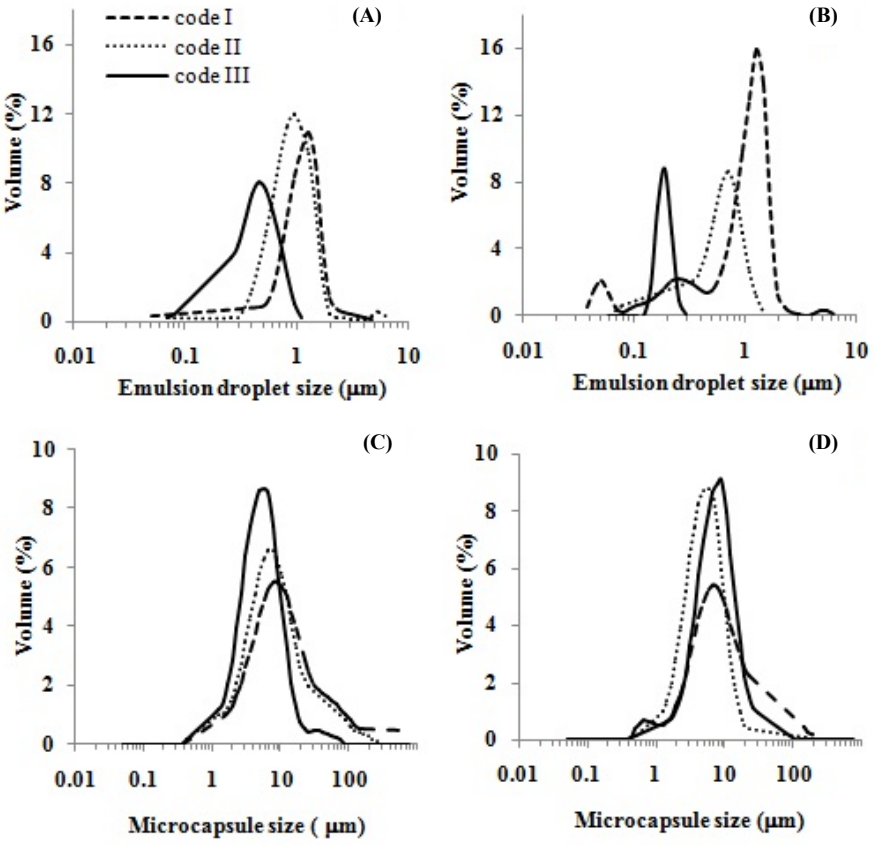

Figure 4 Size distributions of emulsion droplets: TG (a) and CTG (b), and microcapsules: TG (c) and CTG (d). Codes I, II, and III represent different gum-to-oil ratios: 1.25, 1.14, and 0.87, respectively.

The microcapsule size distribution at different conditions is illustrated in **Figures 4C** and **4D**. Microcapsule sizes varied between 0.04 and 100 µm, approximately, with 1 or 2 distinct peaks of size distribution. This is mostly interesting in the case of microcapsules, as once the population of smaller particles can penetrate into the spaces between the bigger ones, they therefore occupy less space [34]. Microcapsule size values were higher than emulsion droplets size values due to the aggregation of emulsion droplets during spray-drying. The microcapsules had a tendency to form agglomerates, which are also relatively common in powders produced by spray-drying [35].

Emulsion droplets and microcapsules were observed under an optical microscope; the shape of the droplets and microcapsules was approximately the same for all samples (**Figure 5** shows examples for CTG II).

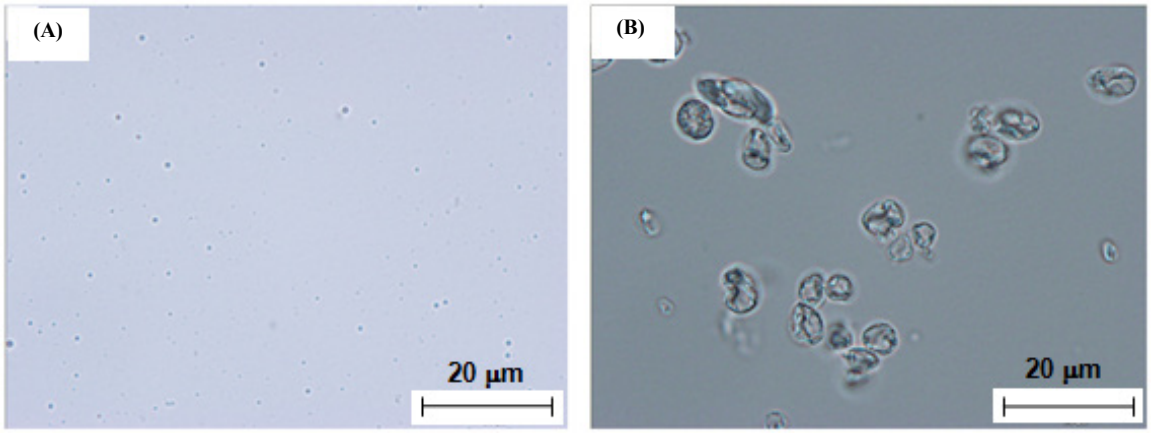

Figure 5 Optical microphotographs of diluted emulsion system (a) and microcapsules (b) for CTG II.

Microcapsule morphology

The morphology of microcapsules was evaluated by SEM (**Figure 6**). Citronella oil microencapsulated in TG had a rough surface for all tested conditions. Additionally, it was observed that microcapsules presented small holes, spread all over their surface. It could be that the TG contained impurities, such as protein and fat inclusions, so that the cross-links between tamarind gum molecules could be interrupted at those sites. This is corroborated by the observation that the microcapsules prepared from TG presented many holes, resulting in citronella oil leak.

Citronella oil CTG microcapsules had a spherical shape and a smoother surface and were apparently not fissured or cracked, which is important to provide lower oil permeability and to increase oil retention. This is more evident in CTG II; however CTG III showed a rougher surface shape, presumably due to the lower gum-to-oil ratio, which can be explained by the fact that there was not enough emulsifier to coat the oil droplet during the spray-drying process. This evidence confirms that CTG was a significantly better material to perform encapsulation than TG, in agreement with the work of Pal *et al.* [22], where TG and CTG were compared for drug encapsulation. Results indicated that the drug microencapsulated in CTG presented good stability, possibly due to the fact that CTG behaves as an anionic biopolymer.

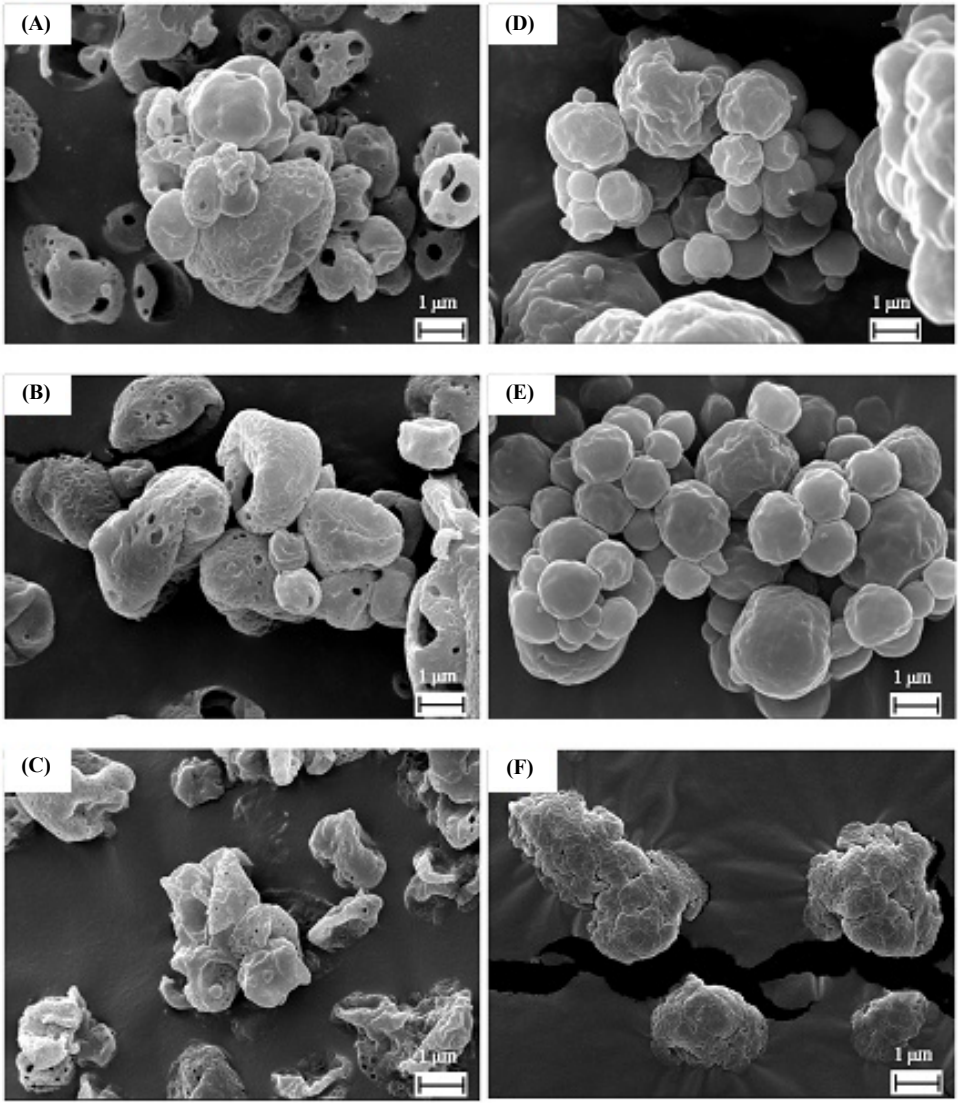

Figure 6 SEM micrographs of TG and CTG microcapsules: TG I (a), TG II (b), TG III (c), CTG I (d), CTG II (e), and CTG III (f).

Encapsulation efficiency

Evaluation of EE was based on the quantification of citronellal as one of the main components of citronella oil [36]. The efficiency of citronella oil retention in microcapsules was evaluated by Eq. (4) and is shown in **Table 4**.

Table 4 EE of both TG and CTG microcapsules.

	Code	Gum-to-oil ratio	EE* (%)
TG	I	1.25	44.93±1.13
	II	1.14	44.60±0.60
	III	0.87	34.64±0.71
CTG	I	1.25	83.48±0.80
	II	1.14	88.87±0.38
	III	0.87	20.85±1.03

*Significantly different values within the same group of values ($p < 0.05$).

According to **Table 4**, the EE values of the samples was significantly influenced by the gum-to-oil ratio used, since the emulsion prepared with lower gum-to-oil ratio (i.e., lower gum or higher oil content) resulted in microcapsules with considerably lower EE than in the emulsions prepared with other gum-to-oil ratios. Thus, the lack of gum associated with higher oil contents may lead to increased droplet aggregation during emulsification, eventually leading to the disruption of the emulsion [37], resulting in lower EE. Results are in agreement with the work of Roccia *et al.* [38], concerning encapsulated sun flower oil in modified cellulose. The wall to core ratio variation from 2/1 to 4/1 had an influence on EE, A low ratio probably led to an unacceptable increase of surface oil, while a high ratio resulted in a powder with a very low oil content.

Comparing the EE values of microcapsules produced with TG and CTG gums in the present study allowed the conclusion that the highest EE value was obtained for TG II and CTG II microcapsules, increasing up to 44 and 88 %, respectively, for the same gum-to-oil ratio. Results showed that the EE of CTG microcapsules was higher than that of TG microcapsules, due to chemical structure changes caused by the carboxymethylation process, clearly evidenced by microcapsule morphological differences (**Figures 6B** and **6E**).

Conclusions

Citronella oil microcapsules were produced from TG and CTG. Emulsion droplets from CTG were smaller than emulsion droplets from TG. The same trend was observed for the corresponding microcapsule sizes. Despite TG and CTG microcapsule appearances being seemingly similar when observed under an optical microscope, SEM micrographs clearly showed differences in the surface of TG and CTG microcapsules, i.e., TG II and CTG II microcapsules (1.14, gum-to-oil ratio). A gum-to-oil ratio of 1.14 of CTG was the best among those tested, producing spherically-shape and smooth-surfaced microcapsules and higher microencapsulation efficiency, due to an adequate emulsion viscosity.

Acknowledgements

The work presented in this paper was financially supported by the Faculty of Engineering, Burapha University, under Grant No. 12/2556. The author, K. Khounvilay, acknowledges the Fellowship of the One More Step: Erasmus Mundus Action 2 project, provided by the European Commission.

References

[1] X Huang, Y Feng, Y Huang and H Li. Chemical composition, antioxidant and the possible use as skin-care ingredient of clove oil (*Syzygium aromaticum* (L.) Merr. & Perry) and citronella oil (*Cymbopogon goeringii*) from China. *J. Essent. Oil Res.* 2013; **25**, 315-23.
[2] LS Nerio, J Olivero-Verbel and E Stashenko. Repellent activity of essential oils: A review. *Bioresour. Technol.* 2010; **101**, 372-8.
[3] MF Maia and SJ Moore. Plant-based insect repellents: A review of their efficacy, development and testing. *Malar. J.* 2011; **10**, S11.
[4] B Solomon, FF Sahle, T Gebre-Mariam, K Asres and RHH Neubert. Microencapsulation of citronella oil for mosquito-repellent application: Formulation and in vitro permeation studies. *Eur. J. Pharm. Biopharm.* 2012; **80**, 61-6.
[5] WC Hsieh, CP Chang and YL Gao. Controlled release properties of chitosan encapsulated volatile citronella oil microcapsules by thermal treatments. *Colloids Surf. B Biointerfaces* 2006; **53**, 209-14.
[6] SN Rodrigues, I Fernandes, IM Martins, VG Mata, F Barreiro and AE Rodrigues. Microencapsulation of limonene for textile application. *Ind. Eng. Chem. Res.* 2008; **47**, 4142-7.
[7] A Gharsallaoui, G Roudaut, O Chambin, A Voilley and R Saurel. Applications of spray-drying in microencapsulation of food ingredients: An overview. *Food Res. Int.* 2007; **40**, 1107-21.
[8] TY SHEU and M Rosenberg. Microencapsulation by spray drying ethyl caprylate in whey protein and carbohydrate wall systems. *J. Food Sci.* 1995; **60**, 98-103.
[9] R Baranauskien, PR Venskutonis, K Dewettinck and R Verhé. Properties of oregano (*Origanum vulgare* L.), citronella (*Cymbopogon nardus* G.) and marjoram (*Majorana hortensis* L.) flavors encapsulated into milk protein-based matrices. *Food Res. Int.* 2006; **39**, 413-25.
[10] MM Specos, JJ García, J Tornesello, P Marino, M Della Vecchia, MD Tesoriero and LG Hermida. Microencapsulated citronella oil for mosquito repellent finishing of cotton textiles. *Trans. R. Soc. Trop. Med. Hyg.* 2010; **104**, 653-8.
[11] TA Jó, DF Petri, LM Beltramini, N Lucyszyn and MR Sierakowski. Xyloglucan nano-aggregates: Physico-chemical characterisation in buffer solution and potential application as a carrier for camptothecin, an anti-cancer drug. *Carbohydr. Polym.* 2010; **82**, 355-62.
[12] Y Ren, DR Picout, PR Ellis, SB Ross-Murphy and JSG Reid. A novel xyloglucan from seeds of Afzelia africana Se. Pers.--extraction, characterization, and conformational properties. *Carbohydr. Res.* 2005; **340**, 997-1005.
[13] S Pal, S Ghosh, G Sen, U Jha and RP Singh. Cationic tamarind kernel polysaccharide (Cat TKP): A novel polymeric flocculant for the treatment of textile industry wastewater. *Int. J. Biol. Macromol.* 2009; **45**, 518-23.
[14] MH Abo-Shosha, NA Ibrahim, E Allam and E El-Zairy. Preparation and characterization of polyacrylic acid/karaya gum and polyacrylic acid/tamarind seed gum adducts and utilization in textile printing. *Carbohydr. Polym.* 2008; **74**, 241-9.
[15] N Dilbaghi, H Kaur, M Ahuja and S Kumar. Evaluation of tropicamide-loaded tamarind seed xyloglucan nanoaggregates for ophthalmic delivery. *Carbohydr. Polym.* 2013; **94**, 286-91.
[16] P Goyal, V Kumar and P Sharma. Carboxymethylation of tamarind kernel powder. *Carbohydr. Polym.* 2007; **69**, 251-5.
[17] G Lu, L Kong, B Sheng, G Wang, Y Gong and X Zhang. Degradation of covalently cross-linked carboxymethyl chitosan and its potential application for peripheral nerve regeneration. *Eur. Polym. J.* 2007; **43**, 3807-18.
[18] KS Parvathy, NS Susheelamma, RN Tharanathan and AK Gaonkar. A simple non-aqueous method for carboxymethylation of galactomannans. *Carbohydr. Polym.* 2005; **62**, 137-41.
[19] H Kaur, M Ahuja, S Kumar and N Dilbaghi. Carboxymethyl tamarind kernel polysaccharide nanoparticles for ophthalmic drug delivery. *Int. J. Biol. Macromol.* 2012; **50**, 833-9.
[20] N Devi and TK Maji. Study of complex coacervation of gelatin a with sodium carboxymethyl cellulose: Microencapsulation of neem (Azadirachta indica A. Juss.) seed oil (NSO). *Int. J. Polym. Mater.* 2011; **60**, 1091-105.

[21] T Reddy and S Tammishetti. Gastric resistant microbeads of metal ion cross-linked carboxymethyl guar gum for oral drug delivery. *J. Microencapsul.* 2002; **19**, 311-8.
[22] S Pal, G Sen, S Mishra, RK Dey and U Jha. Carboxymethyl tamarind: Synthesis, characterization and its application as novel drug-delivery agent. *J. Appl. Polym. Sci.* 2008; **110**, 392-400.
[23] A Koocheki and R Kadkhodaee. Effect of Alyssum homolocarpum seed gum, Tween 80 and NaCl on droplets characteristics, flow properties and physical stability of ultrasonically prepared corn oil-in-water emulsions. *Food Hydrocoll.* 2011; **25**, 1149-57.
[24] TV Huynh, N Caffin, GA Dykes and B Bhandari. Optimization of the microencapsulation of lemon myrtle oil using response surface methodology. *Dry. Tech.* 2008; **26**, 357-68.
[25] A Soottitantawat, K Takayama, K Okamura, D Muranaka, H Yoshii, T Furuta, M Ohkawara and P Linko. Microencapsulation of l-menthol by spray drying and its release characteristics. *Innov. Food Sci. Emerg. Tech.* 2005; **6**, 163-70.
[26] RVTonon, CR Grosso and MD Hubinger. Influence of emulsion composition and inlet air temperature on the microencapsulation of flaxseed oil by spray drying. *Food Res. Int.* 2011; **44**, 282-9.
[27] J Tian, J Yin, X Tang, J Chen, X Luo and G Rao. Enhanced leaching process of a low-grade weathered crust elution-deposited rare earth ore with carboxymethyl sesbania gum. *Hydrometallurgy* 2013; **139**, 124-31.
[28] X Wang, Z Zhang and M Zhao. Carboxymethylation of polysaccharides from *Tremella fuciformis* for antioxidant and moisture-preserving activities. *Int. J. Biol. Macromol.* 2015; **72**, 526-30.
[29] ZJ Wang, JH Xie, MY Shen, W Tang, H Wang, SP Nie and MY Xie. Carboxymethylation of polysaccharide from *Cyclocarya paliurus* and their characterization and antioxidant properties evaluation. *Carbohydr. Polym.* 2016; **136**, 988-94.
[30] S Wang, L He, J Guo, J Zhao and H Tang. Intrinsic viscosity and rheological properties of natural and substituted guar gums in seawater. *Int. J. Biol. Macromol.* 2015; **76**, 262-8.
[31] ASL Lim and YH Roos. Spray drying of high hydrophilic solids emulsions with layered interface and trehalose-maltodextrin as glass formers for carotenoids stabilization. *J. Food Eng.* 2016; **171**, 174-84.
[32] SM Jafari, P Beheshti and E Assadpoor. Rheological behavior and stability of D-limonene emulsions made by a novel hydrocolloid (Angum gum) compared with Arabic gum. *J. Food Eng.* 2012; **109**, 1-8.
[33] DA Botrel, SV Borges, RVB Fernandes, AD Viana, JMG da Costa and GR Marques. Evaluation of spray drying conditions on properties of microencapsulated oregano essential oil. *Int. J. Food Sci. Tech.* 2012; **47**, 2289-96.
[34] HC Carneiro, RV Tonon, CR Grosso and MD Hubinger. Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combinations of wall materials. *J. Food Eng.* 2013; **115**, 443-51.
[35] AACT Hijo, JMG da Costa, EK Silva, VM Azevedo, MI Yoshida and SV Borges. Physical and thermal properties of oregano (*Origanum vulgare* L.) essential oil microparticles. *J. Food Process Eng.* 2015; **38**, 1-10.
[36] R Timung, CR Barik, S Purohit and VV Goud. Composition and anti-bacterial activity analysis of citronella oil obtained by hydrodistillation: Process optimization study. *Ind. Crops Prod.* 2016; **94**, 178-88.
[37] EC Frascareli, VM Silva, RV Tonon and MD Hubinger. Effect of process conditions on the microencapsulation of coffee oil by spray drying. *Food Bioprod. Process.* 2012; **90**, 413-24.
[38] P Roccia, ML Martínez, JM Llabot and PD Ribotta. Influence of spray-drying operating conditions on sunflower oil powder qualities. *Powder Tech*. 2014; **254**, 307-13.