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Preparation of *Acorus calamus* L. Microcapsules

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Abstract. *Acoruscalamus* Linn.extract containing the active compounds were known for insect repellent and antimicrobial activity. The encapsulation of *A. calamus* extract has potential for application asinsect repellent agent orantimicrobial finishing textile. The aim of this study was to encapsulate the extract of*A. calamus* by *in situ* polymerization of urea-formaldehyde. Microcapsules containing *A.calamus* extract were prepared by varying the weight ratio of extract to urea into four ratios ($W_{extract}/W_{urea}$); 0:5, 1:5, 3:5, and 5:5. The prepared microcapsules were characterized using FT-IR,SEM, particle analyzer and TGA to confirm the existing of *A. calamus* extract in microcapsules.

Introduction

Microcapsules (MCs) are the product from microencapsulation process. The definition of microencapsulation is preferred to a process by which very tiny droplets or particles of liquid or solid material are surrounded or encapsulated with a continuous film of a polymeric material [1]. Some microcapsules/microspheres which their diameter is in the nanometer range are referred to as nanocapsules/nanospheres to emphasize their smaller size [2].

Microencapsulation technique is used to protect the active agents from the environment and to control release of the active components for long-acting release.Therefore, this technique has long used for the preparation of capsules containing an active ingredient in various industries, for example, pharmaceutical, agricultural, food, cosmetic and textile industries [3].In recent years, a number of commercial applications of microencapsulation in textile are growing. Microcapsules can be applied to silk, cotton, synthetic fiber, etc. This technique is widely spread technique using for developing new product.Because the shell or wall material can contain various core materials such as perfumes, dyes, antimicrobials, phase change materials, vitamins and other substancesfor application in the functional textile [4,5].

The rhizomes of *AcorusCalamus* Linn. (*A. calamus*) contained beta-asarone which was a trimethoxy derivative of propenylbenzene as the major component [6]. In the rhizomes of *A.calamus* extract was served as an insecticide and insect repellent [7]. Moreover, the extract also exhibited antioxidant and antibacterial properties [8,9]. These activities were of interest to applications in textile to produce a functional fabric, for example, insect repellent, antioxidant or antimicrobial finishing textiles.

The aim of this work was focused on the encapsulation of *A.calamus* extract into urea-formaldehyde MCs by *in situ* polymerization to be developing an eco-friendly natural functional finish in textiles. The prepared MCs were analyzed using Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM) and particle size analyzer to investigate the existing of *A.calamus* extract in urea-formaldehyde shell.

Materials and methods

Materials. Urea and 36 wt% formaldehyde used as wall materials were obtained from VMR International S.D.S., Belgium. Polyvinyl alcohol used as surfactant was purchased from Ajax

Finechem Pty Ltd., Australia. Ammonium chloride was purchased from RFCL, India. Resorcinol was purchased from Himedia Laboratories Pvt. Ltd., India.

Plant material and extraction. The rhizomes of *A. calamus* were collected from Chiang Mai and Uttaradit. The rhizomes were washed to remove debris, cut into small pieces anddried at room temperature. After completely dried, the rhizomes were blended in an electrical blender. Samples were extracted with distilled water in a ratio of 1:15 at 60°C for 1 hr. The extracts were sieved through cheesecloth and centrifuged at 3000 RPM for 10 min. Then, the supernatant were concentrated by evaporating water and freeze-dried at -20°C. The extract of *A. calamus* was stored in 4°C.

Antibacterial activity assessment of *A. calamus*extract.*A. calamus* extract were determined by agar well diffusion method against *Eschericia coli* (*E. coli*) and *Stepphylococcusaureus* (*S. aureus*) to assess the antibacterial activity of the extract. The lower agar layer consisted of approximately 10.0 ml and the upper layer consisted of approximately 5.0 ml agar inoculated with bacteria of $1x10^7$ – $3.0x10^7$ CFU/ml. Then, the agar plate was punched with the help of flamed cork borer and 0.2 ml of the extract (500 mg/ml) was filled in the hole. After incubation at 37°C for 24 hr, the zone of inhibition was observed.

Preparation of *A. calamus* microcapsules.Poly(urea-formaldehyde) (PUF)MCs containing *A. calamus* extract were synthesized by *in situ* polymerization to according the procedure of Suryanarayana [10] with modifications. Briefly, 5 g of urea, 0.5 g of ammonium chloride, 0.5 g of resorcinol were dissolved with 260 ml of distilled water in 500 ml beaker. Then, the solution was mixed with 10 ml of 5%wt aqueous solution of polyvinyl alcohol (PVA). After the pH was adjusted to 3.5 with 5%wt solution of hydrochloric acid, the extract were loaded in the solution with four weight ratios of extract to urea (0:5, 1:5, 3:5 and 5:5). After the stabilization for 10 min, 12 ml of 36%wt formaldehyde solution was added. The reaction was constantly stirred at 800 rpm and heated at 55°C for 4 hr. The obtained microcapsules were filtered under vacuum and thoroughly washed with distilled water. Microcapsules were dried at room temperature and stored under vacuum.

Analyses of *A. calamus* microcapsules.First, the composition of microcapsules and extract were obtained to identify the chemical structure using a FTIR spectrometer (Perkin Elmer), was prepared by grinding the sample with a potassium bromide (KBr) and analyzed in KBr pellet form. The test samples were *A. calamus*extract, MCs without extract, MCs containing *A. calamus*extract (at 5:5 weight ratio of extract to urea).

Second, the morphology and surface of microcapsules was observed by scanning electron microscope (SEM, 5410LV JEOL).MC samples were dispersed in distilled water and sonicated for 30 min. After that, one drop of MCs dispersion was placed on the surface of a double-faced black adhesive tape that attached to a stainless steel stub and dried at 50 °C for 1 hr. The samples were sputtered with a thin layer of gold.The sample was sputtered with a thin layer of gold.

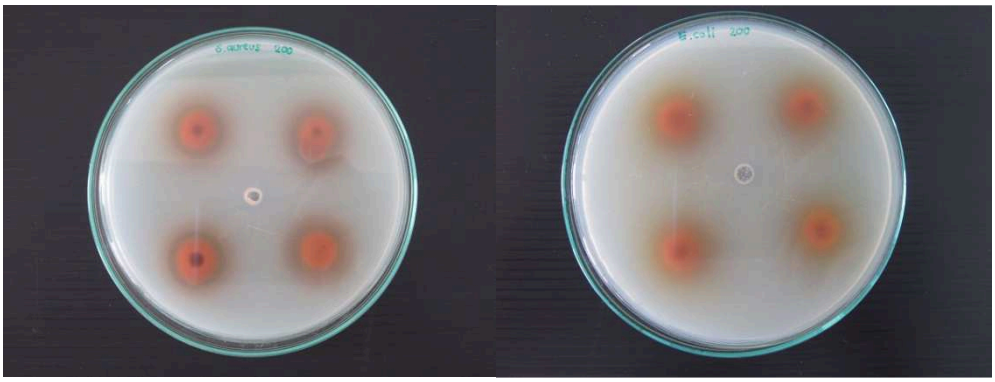
Third, the MC particle size distribution was carried out using particle size analyzer (Mastersizer, MALVERN) based on light scattering apparatus.This equipment has a sample dispersion accessory which allows the system to be used for particle-in-liquid particle sizing. The dispersion unit consists of an electronic motor that drives a stirrer and an impeller in the tank to provide a simultaneous stirring and pumping action. Distilled water was used as dispersant since it does not have interaction with the particles.MCs without *A. calamus*extract and MCs containing *A. calamus*extract were analyzed to compare the distribution.

Last, MCs without extract and MCs containing extract at 1:5, 3:5 and 5:5 weight ratio of extract to urea were analyzed using thermogravimetric analyzer (TGA, Thermoplus TG 8120, Rigaku, Japan). The samples were analyzed at a heating rate of 10 °C/min from 27-500 °C in nitrogen environment.

Results and Discussion

A. calamus rhizomes were extracted with hot water (1:15 ratio (wt/v)). First, crude extract was screened for antibacterial activity by agar diffusion test.The inhibition zone was observed (as seen

in Fig. 1). The inhibition was observed against *S.aureus*and *E.coli*with a zone of inhibition around extract of 5.0 and 3.0 mm diameter, respectively.



(a) (b)

Fig. 1 Antibacterial activities of *A. calamus* extract by agar diffusion method against (a) *S.aureus* and (b) *E.coli*

MCs were prepared by *in situ* polymerization using urea and formaldehyde as a wall materials. First of all, encapsulation of guava leaf extract in a PUF shell was carried out when the pH becomes acidic, was heated to 55 °C, and reacted with urea and formaldehyde resulting in a PUF. In the initial step of polymerization, the urea-formaldehyde molecule was rich in polar groups and was water compatible. The product of this step was called methylol urea. Next, the number of polar groups was gradually reduced as the molecular weight of the polymer increases. Finally, the hydrophilicity of the PUF molecule was reduced leading to separation from the aqueous phase, and droplets of MC powder were received[11]. Fig. 2 presents the suggested reaction of PUF. MCs without extract showed white color. MC powder containing *A. calamus* extract is yellow and the darker of color powder is attributed to the extract content in MCs.

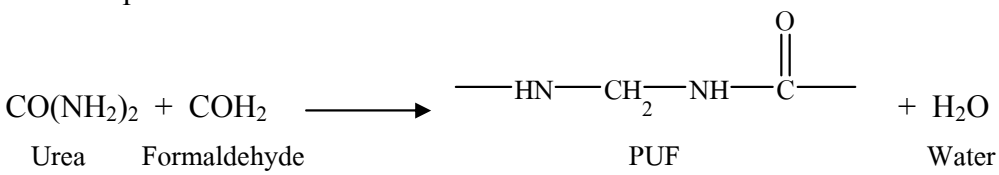


Fig. 2 The reaction scheme of formation of PUF

The information of MCs containing *A. calamus* extract was analyzed using FTIR. From the Fig. 2, the main components of PUF were –NH, C=O and –C-N-. Whereas, the main components of beta-asarone were C=C and C–OMe group. The FTIR spectrum of the *A. calamus* extract, PUF shell, and PUF MCs containing *A. calamus*extract are presented in Fig.3. The spectra of the PUF shell and PUF MCs containing*A. calamus*extract showed a similar pattern: peaks of C=O stretching vibration at 1650 cm^{-1}, N-H stretching vibration at 1554 cm^{-1}, and C-N stretching vibration at 1245 cm^{-1}. These spectrums confirmed the formation of the PUF wall of the MCs. Furthermore, the presence of bands at 1680 cm^{-1} in the spectrum of PUF MCs containing *A. calamus* extract corresponded to the C=C bending vibration in the spectrum of *A. calamus* extract. Along with the O-H peak at 3700-3000 cm^{-1}, it shows a broader band which corresponds to the –OH group in phenolic compounds. It shows that the *A. calamus* extract is encapsulated in the PUF shell.

However, the results from FTIR spectrum did not completely clear to confirm the existence of the extract in PUF MCs. Therefore, additional experimented evidence was under taken using scanning electron microscopy (SEM) and particle size analyzer.

In the preparation of *A. calamus*MCs, the weight ratio of extract to urea ($W_{extract}/W_{urea}$) was varied into three ratios: 1:5, 3:5 and 5:5. The surface morphologies of obtained microcapsules are illustrated in Fig. 4. MCs without *A. calamus*extract showed spherical particles in Fig.4a.When the *A. calamus*extract was loaded at the ratio of 1:5, MCs exhibited a larger shapethan MCs without

extract (Fig. 4b). Furthermore, when the ratio of core to wall was increased to 3:5 and 5:5, MCs were consisted of small and large particles (Fig.4c and 4d). The results of SEM images showed important to the shape and size of the final MCs.This may be due to the overloading of the core in these particular MCs.These results were similar with the report of Yaun et al. [12]. When the weight ratio of UF was lower, the content of free formaldehyde was higher, although the network density of PUF decreased the condensation rate of urea and formaldehyde increased which resulted in quick deposition of PUF nanoparticles on the surface of MCs, forming rougher and more porous outer layer of the PUF shell.

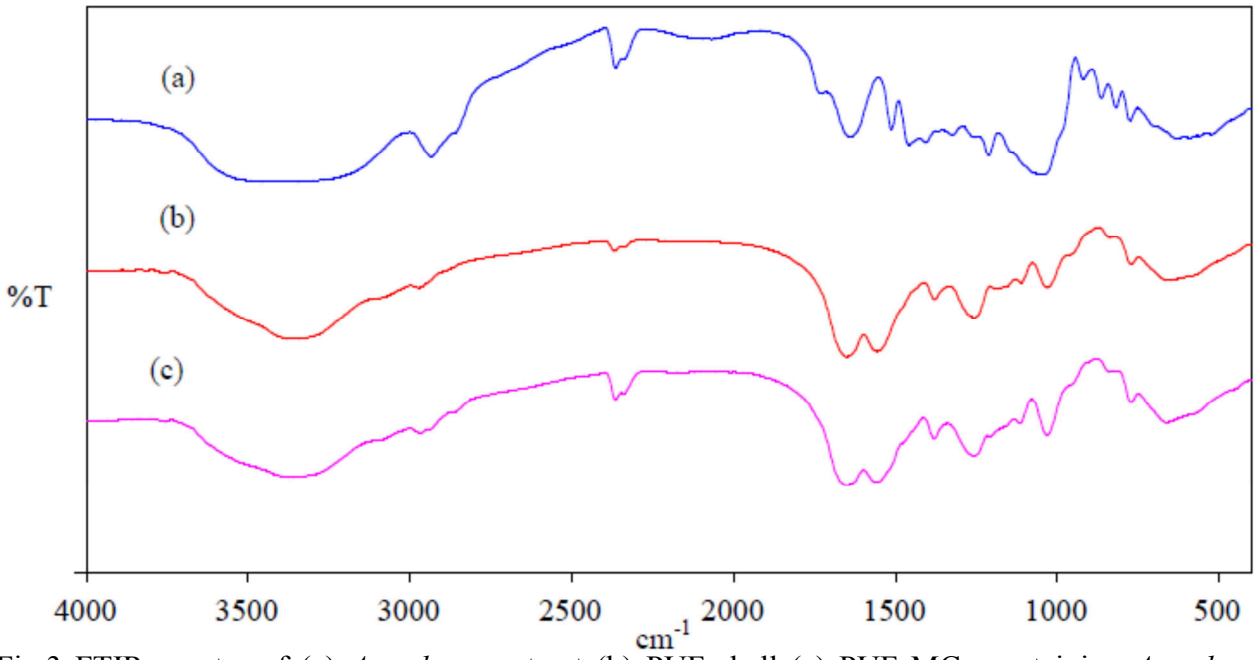
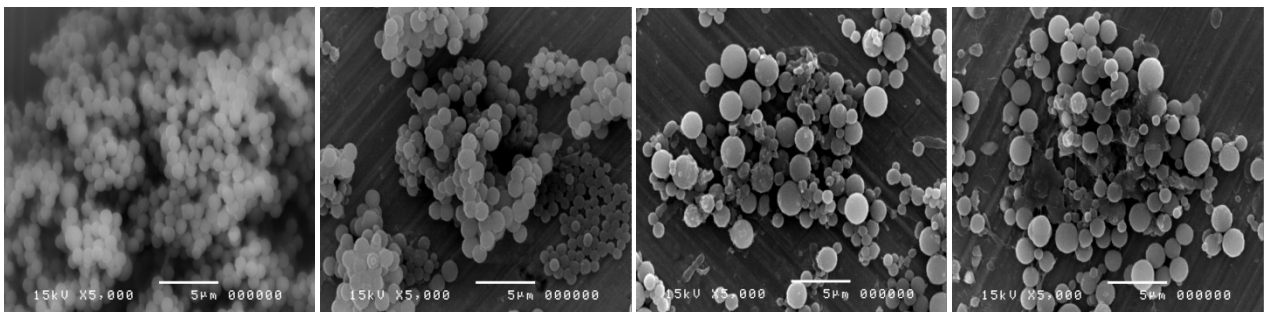


Fig.3 FTIR spectra of (a) *A. calamus*extract (b) PUF shell (c) PUF MCs containing *A. calamus* extractat 5:5 weight ratio



(a) (b) (c) (d)

Fig. 4 SEM images of PUF MCs containing *A. calamus*extract at different weight ratios of extract to urea (a) 0:5, (b) 1:5, (c) 3:5 and (d) 5:5

After that, four MC samples which were MCs without extract and MCs containing *A. calamus*extract at 1:5, 3:5 and 5:5 weight ratio of extract to urea were analyzed by particle size analyzer. The process was run from room temperature to 500 °C. The results of MC size distribution were described by plotting particle diameter (micrometers) versus the percentage of volume.In Fig. 5**,** the results of MCs containing *A. calamus* extract is illustrated. Accordingly in Fig. 5, the particle diameter of MCs without extract was distributed into 2 ranges: a large group of 8-50 micrometers and a smaller group of 50-140 micrometers. When the *A. calamus* extract was added at 1:5 weight ratio of extract to urea into MCs, the diameter of MCs was in a wide ranged from 10-150 micrometers and the average diameter was increased. Otherwise the curve of MCs containing *A. calamus*MCs, the weight ratio of extract to urea ($W_{extract}/W_{urea}$) is important to the

shape and size of the final extract at 3:5 and 5:5 weight ratios was similar and the particle diameter was distributed into 2 groups: a small group was approximately around 10-50 micrometers and a large group wasranged of 50-150 micrometers. The size of MCs was increased according to the weight of the extract in MCs, thus this may be caused by encapsulation of the extract by PUF. Moreover these results were also corresponded with the result from SEM that MCs was larger when an increasing the *A. calamus*extract.

The diameters of MCs increased with the increasing of weight ratio of extract to urea (core to wall material).The main reason was thatthe size of core droplet in emulsion was larger when the weight ratio of core to wall was higher and the other processing parameters were kept constant.Increasing the core material can form larger size core droplet, and accordingly, the MC size became larger. But excess core materials caused poor dispersion, promoting aggregation of core droplets.

Fig. 6showed TGA diagrams of *A. calamus* extract, MCs without extract, MCs containing *A. calamus* extract at 1:5 weight ratio of extract to urea, MCs containing *A. calamus* extract at 3:5 weight ratio of extract to urea and MCs containing *A. calamus*extract at 5:5 weight ratio of extract to urea. Weight loss of *A. calamus*extract occurred at temperature of 130 °C and did not conclude until 450 °C. TGA curve of all MCs (including without and containing *A. calamus*extract) showed the same weight loss occurred at temperature of 30-80 °C due to the evaporation of free formaldehyde and water on MCs surface. Following on with a second weight loss occurred at temperature of 230 °C was as a consequence from the decomposition of the PUF shell. Afterward TGA curves of them were different. For the result of MCs without extract the residue of PUF shell was observed the decomposition temperature at approximate 270 °C. The rate of weight loss was quick at around 240-300°C, later the slope was slow down until 500 °C. Comparing the results of TGA diagram of MCs containing *A. calamus*extract (at 1:5, 3:5 and 5:5 weight ratio of extract to urea) found weight loss temperature of the MCs containing *A. calamus*extract at 1:5, 3:5 and 5:5 occurred approximate at 270 °C, 265 °C and 260 °C, respectively, because *A. calamus*extract was decomposed. The weight loss temperature of MCs containing *A. calamus*extract with three ratios was decreased with increasing the content of extract or decreasing the content of UF shell in MCs. It was indicated that the higher weight ratio of extract was encapsulated in MCs, the shell of MCs was thinner. Resulting in the weight loss temperature of MCs containing *A. calamus*extract was lower according to the weight ratio of extract to urea.

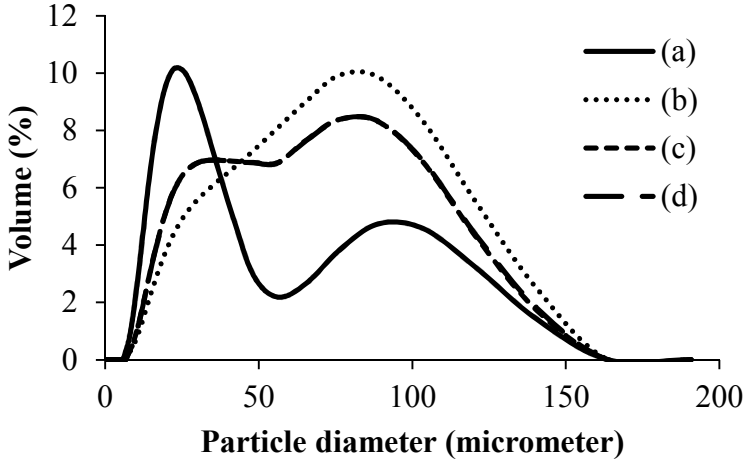


Fig.5 Particle size distribution of MCs containing *A. calamus* extract at three weight ratios extract to urea (a) — is MCs without extract, (b) … is MCs containing *A. calamus*extractat 1:5 weight ratio (c) --- is MCs containing *A. calamus* extract at 3:5 weight ratio and (d) — - is MCs containing *A. calamus* extract at 5:5 weight ratio

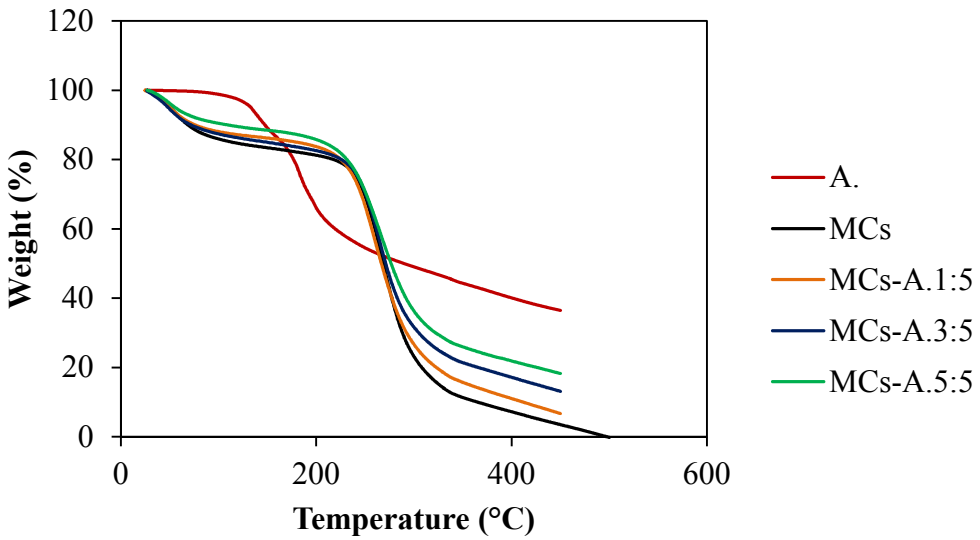


Fig. 6 TGA diagrams of *A. calamus* extract (red line), MCs without *A. calamus*extract (black line), MCs containing *A. calamus*extract at 1:5 weight ratio of extract to urea (blue line), MCs containing *A. calamus*extract at 3:5 weight ratio of extract to urea (yellow line) and MCs containing *A. calamus*extract at 5:5 weight ratio of extract to urea (green line)

Summary

Microcapsules containing *A. calamus*extract were constructed with using urea-formaldehyde resin as shell by *in situ* polymerization. The different weight ratios of extract to urea were varied into five ratios: 1:5, 3:5 and 5:5. The composition of MCs containing the extract was investigated by FTIR. FTIR spectra confirmed the encapsulation of *A. calamus*extract in MCs due to the presence of the absorption band at 1680 cm^{-1} and 3700-3000 cm^{-1} in the spectrum band of MCs containing *A. calamus*extractwere broader than MCs without *A. calamus*extract. The morphology of MCs without *A. calamus* extract was spherical particles. The size of MCs containing *A. calamus*extract was increased according to the weight of the extract in MCs, thus this may be caused by encapsulation of the extract by PUF.Moreover, the results of TGA diagrams showed that microcapsules containing *A. calamus* extract (at 1:5, 3:5 and 5:5 weight ratio of extract to urea) presented weight loss at temperatures of 270, 265 and 260 °C, respectively. In this study, it was successful for encapsulation of the extract from *A. calamus*into urea-formaldehyde wall. In further study, MCs containing *A. calamus* extractwill beapply as the antibacterial andinsect repellent agent in finishing textile.

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