

## Mechanism of Microencapsulation with Urea-Formaldehyde Polymer

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**Abstract: Problem statement:** Microcapsule is one of important fine chemical products in the current chemical industries. Better understanding of microencapsulation process is useful to properly design of microcapsule with specific characteristics. The aim of this research is to study the mechanism of Urea-Formaldehyde (UF) microcapsules formation. **Approach:** Microcapsule was prepared in two steps. The first step was the preparation of oil in water emulsion, which was carried out by mixing of UF pre-polymer solution with refined palm oil at 50-70°C, using high speed homogenizer. The second step was microcapsule shell formation, where the pH of emulsion was adjusted to 3 and the process was run for 3-6 h. At the end of the process, the microcapsule product was cooled with ice and distilled water, filtered, washed and finally dried at 40°C under vacuum condition. The diameter and size distribution of the microcapsule product was measured using optical microscope. **Results:** Microcapsule with the diameter of 20-220 µm, together with UF micro particles. **Conclusion:** UF polymerization reaction took place simultaneously in the solution and at the microcapsule surface. UF reaction in the solution produced UF polymer micro particles, while UF reaction at the microcapsule surface forms microcapsule shell. The UF polymer micro particles precipitated in the form of fine powder, attach to the microcapsule shell. Higher microencapsulation temperature reduced the amount of microcapsule product and increased the amount of micro particles. The microcapsule diameter distribution shifts to smaller diameter and the average diameter  $D_{avg}$  tends to decrease as the homogenization and microencapsulation time increase. Based on oil and resin efficiencies as well as microcapsule characteristics, the process is best conducted at 50°C, 30 min of homogenization and 3 h of microencapsulation time.

**Key words:** Urea-formaldehyde, pre-polymer, microencapsulation, controlled release, micro particle, homogenization

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### INTRODUCTION

Microencapsulation has been widely applied in various areas such as pharmaceutical industry, fragrance, perfumery, coating as well as pesticides. One of the microcapsule applications is to enlave active chemical solution, in which this active compound can be slowly released through the shell of microcapsules. This is commonly known as controlled release, as the rate of release can be controlled by selecting the material and thickness of the microcapsule shell.

Various method of microencapsulation have been well known in chemical industry, generally are still in state of the art. Numerous researches have described microencapsulation qualitatively, but only few have been concerned with quantitative description of microencapsulation process, such as the effect of process variables upon the size of microcapsules.

Hence, better understanding of microencapsulation process can help proper design of microcapsule with specific characteristics.

The purpose of this research is to study the mechanism of urea-formaldehyde microcapsules formation, including the effect of some variables upon the characteristics of microcapsules. In this research, palm oil is encapsulated with urea-formaldehyde resin. The main goal of this research is microencapsulation of pesticide solution, with vegetable oil as a solvent.

Mayya *et al.* (2003) have encapsulated paraffin oil with gelatin and Arabic gum by complex coacervation. Dibutyltin dilaurate as a catalyst of EVA crosslinking in ester-silane exchange reaction has been encapsulated with polycarbonate (Deyrail *et al.*, 2004). Smart method of microencapsulation has been described by Sukhorukov *et al.* (2005) by selection of material and properties condition. Brown *et al.* (2003) have

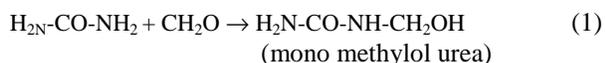
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encapsulated dicyclopentadiene by in situ polymerization of urea-formaldehyde. Salaun and Vroman (2008) have investigated the effect of core material upon thermal properties of melamine-formaldehyde microcapsules. Multilayer of microcapsule shell formation has been described by Radtchenko *et al.* (2002) as well as Antipov and Sukhorukov (2004). Sun and Zhang (2002) studied the mechanical strength of microcapsules in which the wall was made of melamine-formaldehyde resin, urea-formaldehyde resin and gelatin-Arabic gum. Yin *et al.* (2007) have encapsulated epoxy with urea-formaldehyde resin for self-healing epoxy composites. Yang and Pan (1996) have patented the method to microencapsulate pesticide solution with urea-formaldehyde resin.

Encapsulation method applied in this research is in situ polymerization of urea-formaldehyde under low pH (acidic condition). There are 2 steps of process during microcapsule formation. The first step is emulsion of palm oil (vegetable oil) in urea-formaldehyde resin solution, in which palm oil is as a dispersed phase. High rotation speed of stirring is conducted to emulsify palm oil. In this case, high rotation speed homogenizer is used as a stirrer. The second step is microcapsule shell formation. In this step, the pH of emulsion liquid is adjusted into acidic condition. This promotes the reaction of urea with formaldehyde in the interface of emulsion bubbles, producing a film of urea-formaldehyde polymer as a microcapsule shell.

Two reactions take place when urea reacts with formaldehyde, i.e., addition and condensation:



Reaction (1) is an addition reaction, where formaldehyde reacts with H of amine to form methylol. Condensation occurs between OH of methylol and H of amine, forming methylene link between amines of 2 urea molecules, as shown in Eq. 2. This condensation reaction results in urea-formaldehyde polymer chain. Addition and condensation reactions are catalyzed either by  $\text{OH}^-$  or  $\text{H}^+$ . The rate of addition reaction in basic condition is as high as the rate in acidic condition. However, the rate of condensation reaction is much faster in acidic condition, compared with that in basic condition. As urea has four H atoms in amines, it is most possible to produce crosslink or network polymer during condensation reaction. This network polymer is

good for microcapsule shell due to its high strength, in which microcapsule is not easy to break up during its application.

## MATERIALS AND METHODS

The experiment of microencapsulation consists of urea-formaldehyde pre-polymer preparation and microencapsulation process. Pre-polymer Urea-Formaldehyde (UF) resin was prepared under basic condition ( $\text{pH} > 7$ ), in order to produce methylol urea that dissolve in water. Microencapsulation process comprises two steps, i.e., emulsion process and microcapsule shell formation.

**Materials:** Urea was obtained as a fertilizer, which was recrystallized before used as a reagent. Formaldehyde was as 37% solution. The solution contains around 10% of methanol. Sodium hydroxide solution (around 1 N) and citric acid solution (10%) were employed to adjust the pH of solution. Palm oil was obtained as refined palm oil (frying vegetable oil), with its density  $0.906 \text{ g cm}^{-3}$  and its viscosity 28 cP at room temperature.

### Methods:

**Pre-polymer preparation:** One hundreds and twenty grams of recrystallized urea and 225 mL of 37% formaldehyde solution were charged into a three neck flask, equipped with mechanical stirrer, reflux condenser and water bath. The pH of solution was adjusted to 8-8.3 by adding of NaOH solution. The solution was then heated to temperature of  $70^\circ\text{C}$ . The reaction was run for 1 h, while its temperature was maintained at  $70^\circ\text{C}$ . At the end of the reaction, this urea-formaldehyde pre-polymer resin was cooled and diluted with distilled water to be 500 mL of UF resin solution. The resin concentration was  $0.42 \text{ g mL}^{-1}$ .

**Microencapsulation process:** Microencapsulation process consists of 2 steps: Emulsion step and microcapsule shell formation step. In the emulsion step, UF resin was added with a certain amount of distilled water to make specified concentration of resin. Refined palm oil and UF resin solution were heated in water bath to  $50\text{-}70^\circ\text{C}$ . As the temperature was reached, the mixture was stirred with ULTRA TURRAX homogenizer at the rotation speed of 15600 rpm for 10-50 min. White milky viscous liquid was produced. After homogenizing process, the homogenizer was replaced with a helical type stirrer. In the step of microcapsule shell formation, the stirring speed was maintained around 100 rpm, in order to keep homogeneous phase. Very low stirring speed could

result in coalescence of oil bubble (which leads to phase separation), but high speed stirring would break up microcapsule shell formation. Citric acid solution was then added to the liquid mixture, to adjust its pH to 3. This process was run for 3-6 h, while its temperature was maintained constant. At the end of the process, the liquid mixture was cooled by addition of ice and cold distilled water. After one h of cooling, microcapsules product appeared as white solid. Some solid product floated at the top of liquid and the other settled at the bottom. These two solid products were filtered, washed with distilled water and then dried at 40°C under vacuum condition.

Dried top and bottom microcapsule products were weighed and analyzed its oil content. Certain amount of dried microcapsules was grounded and N-hexane was added to extract the palm oil from ground microcapsules. The remaining ground solid was then filtered, dried in an oven at 100°C and finally weighed. The oil content can then be determined.

A sample of microcapsule product to be measured its diameter was prepared by attaching a thin layer of microcapsule paste on a microscope slide glass. The microcapsules image was captured by optical microscope provided with digital camera. The resulting image (picture) was interpreted using Image Pro Plus software, in which the diameter of around 100 or more microcapsule bubbles (in one picture) could be measured.

## RESULTS

There were two parts of suspensions exist, after cooling the microcapsule product with ice and distilled water. The first was floating suspension as upper layer (top product) and the second was settling suspension (bottom product). Few experiments had only one layer product, either floating suspension or settling one at the bottom. This kind of product, however, was poor quality microcapsule particle. In the case of floating suspension product only, microcapsule was unstable, which was easy to break up and coalesce, due to soft shell of microcapsule. In the case of settling solid product only, the settling solid was apparently fine solid powder, not microcapsule.

The top product was mainly floating microcapsules with a density less than 1 g cm<sup>-3</sup>. The bottom product was settling solids, a mixture of microcapsules and fine solid powder (called as UF polymer micro particles). It seems that some UF polymer micro particles attach to microcapsule bubble. These UF polymer micro particles have irregular shape; sometimes they agglomerated. The density of UF polymer from

microcapsule shell was measured and its value was around 1.29-1.38 g cm<sup>-3</sup>. Because microcapsule bubble was attached by several UF micro particles, the microcapsule bubble then settled down. Brown *et al.* (2003) also mentioned this phenomenon, where a number of micro particles attached to microcapsule shell.

The effect of temperature upon the characteristics of microcapsules is shown in Table 1 and Fig. 1. In this case, the efficiency of microencapsulation in Table 1 is defined as:

$$\text{Oil efficiency} = \frac{\text{Weight of oil in microcapsule}}{\text{Initial weight of palm oil}} (100\%) \quad (3)$$

$$\text{Resin eff.} = \frac{\text{Weight of resin in product}}{\text{Initial weight of resin in solution}} (100\%) \quad (4)$$

The experiments were conducted at 50-70°C, 30 min of homogenization, 3 h of microencapsulation process and pH of 3. UF pre-polymer solution 150 mL (concentration 0.294 g mL<sup>-1</sup>) was mixed with 42 mL of refined palm oil.

Table 2 provides the characteristics of microcapsule product and Fig. 2 shows the physical appearance of microcapsule produced at 10 and 20 min of homogenization time. During the emulsion step, homogenization time was varied from 10-50 min. The experiments were conducted at 50°C, 3 h of microencapsulation process and under pH of 3.

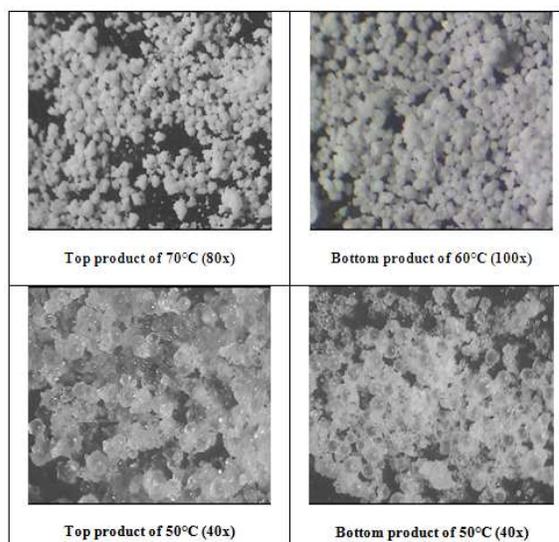


Fig. 1: Physical appearance of microcapsule produced at 50-70°C

Table 1: Characteristics of solid microcapsules produced at 50°-70°C

Temperature (°C)	Oil efficiency (%)			Resin eff. (%)	Oil content (weight fraction)		Particle shape
	Top	Bottom	Total		Top	Bottom	
70	5.31	8.43	13.74	49.24	0.381	0.148	Irregular
60	9.61	10.11	19.72	50.32	0.508	0.171	Irregular
50	36.48	40.14	76.62	47.62	0.661	0.524	Spherical

Table 2: Characteristics of microcapsules, top and bottom products at various homogenization time

Time (min)	Oil efficiency (%)			Resin eff. (%)	Oil content (wt. fraction)		Shell thickness (µm)	D <sub>avg</sub> (µm)
	Top	Bottom	Total		Top	Bottom		
10	13.74	29.37	43.12	21.72	0.701	0.603	3.34	63.87
20	24.04	56.66	80.69	43.70	0.675	0.592	3.16	51.37
40	24.36	61.30	85.66	48.81	0.630	0.592	3.43	45.58
50	28.22	56.42	84.64	49.95	0.621	0.581	4.09	49.97

Table 3: Effect of the microencapsulation time upon the microcapsule characteristics

Time (h)	Oil efficiency (%)			Oil content (wt. Fraction) (%)	Resin Eff. Bottom	Shell thickness (µm)	D <sub>avg</sub> (µm)	
	Top	Bottom	Total					
3	36.48	40.14	76.62	47.62	0.661	0.524	7.61	108.16
4	39.86	43.74	83.59	46.83	0.679	0.553	5.22	66.12
5	56.23	32.23	88.46	49.30	0.750	0.456	4.92	47.84
6	59.31	25.27	84.58	53.82	0.776	0.359	4.25	70.99

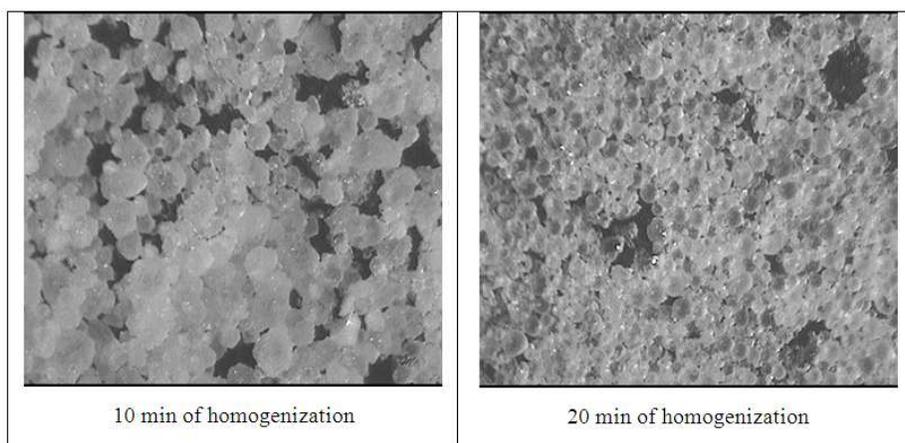


Fig. 2: Microcapsule appearance produced at 10 and 20 min of homogenization

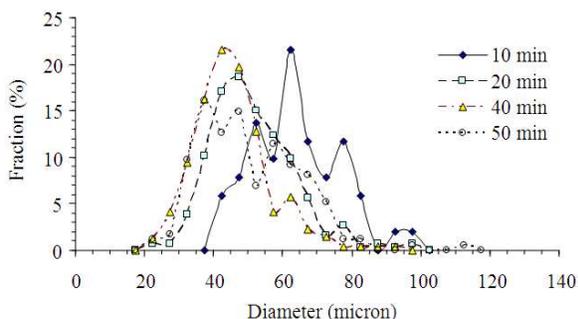


Fig. 3: Distribution of microcapsule diameter at 10 and 20 min of homogenization

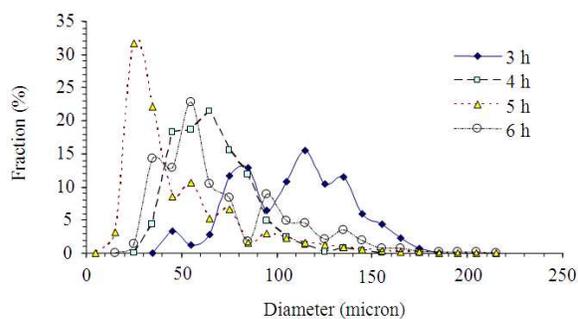


Fig. 4: Distribution of microcapsule diameter at several microencapsulation time

Microencapsulation time was varied from 3-6 h in the second step of microencapsulation process. The experiments were conducted at 50°C, 30 min of homogenization, under pH of 3, with pre-polymer solution 150 mL and refined palm oil 42 mL. Table 3 provides the characteristics of top and bottom products.

Distribution of microcapsule diameter is shown in Fig. 3 and 4 for various homogenization and microencapsulation time.

## DISCUSSION

The microcapsule product showed that besides microcapsule was formed, micro particle was also produced, as shown in Fig. 1. It can be concluded that during microencapsulation process, two simultaneous processes occurred: reaction of UF in the solution to produce UF micro particles and reaction of UF resin at the emulsion interface to form microcapsule shell. The mechanism of microencapsulation process is proposed as follows. During the emulsion step, palm oil bubbles adsorb some amount of UF pre-polymer resin at the bubble interface. When the pH of pre-polymer solution was changed into acidic condition (in the microcapsule shell formation step), urea-formaldehyde condensation reaction took place at high rate, both in the solution (yielding UF micro particle) and at the emulsion interface (forming microcapsule shell). The overall UF reaction rate  $R_p$  is then proposed as follows:

$$R_p = k_r \cdot (C_{UF})^2 + k_{c,a} (C_{UF} - C_{UF,s}) \quad (5)$$

Where:

- $k_r$  = The reaction rate constant
- $k_{c,a}$  = The mass transfer coefficient
- $C_{UF}$  = UF pre-polymer concentration in the aqueous phase
- $C_{UF,s}$  = UF pre-polymer concentration at the microcapsule surface
- $k_r \cdot (C_{UF})^2$  = The rate of UF polymer micro particles formation
- $k_{c,a} (C_{UF} - C_{UF,s})$  = The rate of microcapsule shell formation.

The rate of condensation reaction is high in acidic condition. In this experiment, microencapsulation process was carried out at low pH, which could lead to solid UF polymer production. It was observed in the experiment of pH variation (from 2-5), microencapsulation process at lower pH produced higher amount of solid UF micro particles, compared to that at higher pH. In this case, the reaction rate constant

$k_r$  is proportional to the concentration of  $H^+$ : high  $H^+$  concentration (low pH) means high  $k_r$ . On the other hand, the mass transfer coefficient  $k_{c,a}$  is not influenced by  $H^+$  concentration. Hence, the rate of UF micro particles formation at low pH can be higher than the rate of microcapsule shell formation, or the amount of solid UF micro particles is higher at low pH.

**Effect of temperature:** Table 1 show that total oil efficiency of microencapsulation process of palm oil was 76.62% at 50°C and decreased to 13.74% at 70°C. This means that the amount of oil encapsulated at 70°C is less than the amount of oil encapsulated at 50°C. Meanwhile, the unencapsulated oil floated at the top of UF pre-polymer solution. Resin efficiency remains constant (around 50%) at 50-70°C, or it is independent of temperature. This indicates that the amount of total solid UF polymer in the product (as micro particles and as microcapsule shell) is constant. This also means that the overall rate of UF reaction  $R_p$  is constant. According to the theory,  $k_r \cdot (C_{UF})^2$  (micro particles formation) increases with the increase of temperature. Consequently, the increase of temperature causes the decrease of microcapsule shell formation (as shown by the second term in Eq. 3). This is in line with the trend of total oil efficiency, as shown in Table 1. It is also clearly shown in Fig. 1 that the top product of 70°C and the bottom product of 60°C is dominated by white UF micro particles, while microcapsules produced at 50°C (in the top and bottom product) contains less white UF micro particles.

**Effect of homogenization time:** Table 2 shows that total oil and resin efficiencies gradually rise as the homogenization time increases up to 40 min and then remain constant after 40 min (total oil efficiency around 85% and resin efficiency around 49%). In this case, the amount of UF pre-polymer resin adsorbed at the emulsion interface increases as homogenization time increases, until the oil in emulsion is saturated with UF pre-polymer at around 30-40 min of homogenization. When the oil in emulsion is saturated with UF pre-polymer resin, the resin efficiency is at maximum and it remains constant for longer homogenization time. On the other hand, the increase of resin efficiency reduces the oil content both at the top and bottom products, as also shown in Table 2. Although the increase is not prominent, longer homogenization time also causes thicker microcapsule shell (from 3.34  $\mu\text{m}$  at 10 min-4.09  $\mu\text{m}$  at 50 min). Figure 2 shows the appearance of microcapsule produced at 10 and 20 min of homogenization time. It is clearly appeared that the quality of microcapsule produced at 10 min is poor and

the microcapsule is apparently sticky, while microcapsule produced at 20 min shows good quality. It can be concluded that homogenization time is sufficient at 30-40 min. Average microcapsule diameter  $D_{avg}$  also seems to be constant after 20 min of homogenization, i.e., around 50  $\mu\text{m}$ .

**Effect of microencapsulation time:** Table 3 shows that the increase of microencapsulation time only slightly increases resin efficiency, from 47.62% at 3 h to 53.82% at 6 h for resin efficiency. This means that after 3 h of microencapsulation process, the overall rate of UF reaction  $R_p$  is very low, or the amount of UF micro particles and microcapsule shells only slightly increase. It can be concluded that basically no more UF micro particles and microcapsule shells were formed.

However, oil efficiency and oil content at the top product show different trend with oil efficiency and oil content at the bottom. As the microencapsulation time rises, oil efficiency and oil content at the top product increases, but oil efficiency and oil content at the bottom product decreases. It seems that there is migration of small diameter microcapsules from the bottom product to the top product, which is probably caused by detachment of some micro particles from microcapsule surface due to turbulent action of stirrer. Because the stirring process takes place for a long time, some attaching micro particles at the microcapsule surface are gradually released, both at the top and bottom products. At the bottom product, small diameter microcapsule will rise to float at the top layer, after releasing some micro particles. On the other hand, some released micro particles at the top product will settle down to the bottom. This causes oil efficiency and oil content at the top product increases, while oil efficiency and oil content at the bottom product decreases. The microcapsule average diameter  $D_{avg}$  shows the same trend with the top product, which decreases from 108  $\mu\text{m}$  at 3 h-around 70  $\mu\text{m}$  at 6 h. This phenomenon may be caused by breaking-up of some big microcapsule bubbles into smaller diameter microcapsules due to the effect of extended stirring time. This is also followed by reduction of microcapsule shell thickness, from 7.61  $\mu\text{m}$  at 3 h to 4.25  $\mu\text{m}$  at 6 h. Although the stirring speed is low (around 100 rpm), the shearing force of stirring is likely to influence the microcapsule shell strength. Apart from the microcapsule size, it can be concluded that 3 h of microencapsulation process is sufficient to produce a good quality microcapsule.

**Distribution of microcapsule diameter:** Figure 3 and 4 show the distribution of microcapsule diameter at

various homogenization and microencapsulation time. The distribution of microcapsule diameter in both Fig. 3 and 4 has the same trend that the size distribution is dominated by smaller diameter or it is skew distribution, not Gaussian distribution. This may be due to the characteristics of homogenization process, where some small emulsion bubbles coalesce to form large bubbles as soon as emulsion bubbles exit from the homogenizer.

The microcapsule diameter distribution also shifts to smaller diameter as the homogenization and microencapsulation time increases, as also shown by the decrease of average diameter  $D_{avg}$ . It seems that equilibrium between turbulent force and interfacial tension will be reached at a long time, because the distribution of microcapsule diameter and average diameter  $D_{avg}$  tend to be constant as the homogenization and microencapsulation time increases. Based on the diameter distribution, microcapsule diameter generally ranges from 20  $\mu\text{m}$  to almost 220  $\mu\text{m}$ .

## CONCLUSION

Based on the experimental results, it is concluded that UF polymerization reaction takes place simultaneously in the solution and at the microcapsule surface. UF reaction in the solution produces UF polymer micro particles, while UF reaction at the microcapsule surface forms microcapsule shell. The UF polymer micro particles precipitate in the form of fine powder, attach to the microcapsule surface.

Higher microencapsulation temperature reduces the amount of microcapsule product and increase the amount of micro particles. The microcapsule diameter distribution shifts to smaller diameter and average diameter  $D_{avg}$  tends to decrease as the homogenization and microencapsulation time increase. Microcapsule diameter ranges from 20  $\mu\text{m}$ -around 220  $\mu\text{m}$ . Based on oil and resin efficiencies as well as microcapsule characteristics, the process is best conducted at 50°C, 30 min of homogenization and 3 h of microencapsulation time.

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