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Controlled release properties of Chitosan encapsulated volatile Citronella Oil microcapsules by thermal treatments

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Abstract

This research uses modified orifice method to prepare the O/W type Chitosan encapsulated volatile Citronella Oil microcapsules. In this article, we investigated the forming condition of microcapsules and the influence to sustained release effect of volatile Citronella Oil by applying thermal pretreatment to microcapsules. The results suggest that the forming of microcapsules should be processed under the fundamental conditions of: (1) the concentration of Chitosan is at least 0.2 wt%, (2) NaOH is greater than 0.1 wt%, and (3) with the additive of coconut oil as natural surfactant, so that we could obtain final product of microcapsules with better formation and dispersion. The changes in concentration of Chitosan will affect the encapsulation efficiency of the volatile Citronella Oil. When the concentrations of Chitosan are 0.5%, 1.0% and 1.5%, the encapsulation efficiencies are 98.2%, 95.8% and 94.7%, respectively. The particle size of Chitosan microcapsules would decrease as the emulsification stirring speed increases. When the stirring speeds are 400 rpm, 800 rpm, and 1500 rpm, the average particle sizes of microcapsules produced are 225 ± 24 μm, 131 ± 20 μm, and 11 ± 3 μm, respectively. If the microcapsules were thermal pretreated at 80 °C, the structure of Chitosan wall membrane would shrink and thus achieve the effect of sustained release. The sustaining effect would increase along with treatment time increases.
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Keywords: Chitosan microcapsule; Volatile Citronella Oil; Modified orifice method; Sustained release

1. Introduction

In recent years out of the fear of SARS, Dengue Fever, and Avian Influenza (Bird Flu), people start to take personal hygiene, health care and other protective measures seriously. The volatile essential oils that have efficacies of antibiosis, insect repelling and stress reducing are valued by many [1–3].

The release speeds of these volatile essential oils are usually affected by different application environment conditions. Thus released too little and causes ineffectiveness, or released excessively and causes the uncomfortable feelings [4–8]. Therefore how to control these volatile essential oils to have constant release in various application environment conditions is a good subject quite worth investigation and discussion. Utilizing micro-encapsulation technology to achieve the goal of constant release is one of the most effective methods thus far [9–11]. However at present time there is infrequent study and research related to the technology of encapsulate volatile material in microcapsules and discuss its sustained release property for application in personal hygiene and health care domain [12–14]. Therefore this research elects the Citronella Oil which possesses mood lifting, depression and restless reducing, deodorizing, sterilizing, bug repelling properties as the core material [15], and the Chitosan as the wall membrane material. Chitosan has excellent biodegradable and biocompatible characteristics, and is a naturally occurring polysaccharide. Due to its unique polymeric cationic character, gel and film forming properties, Chitosan has been extensively examined in the pharmaceutical industry for its potential use in the development of drug delivery systems [16–19]. Other than that, Chitosan also possesses heat shrinking property, thus by using this unique property to change the pore space between the Chitosan wall membrane molecules, and achieve the controlled release effect of the content within the microcapsules [20,21]. Study the forming and manufacturing conditions of microcapsules such as the amount of the wall membrane material added, the concentration of cross-linking

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agent, the emulsification stirring speed, the thermal treatment temperature and treatment time, and their influence to the effect of sustained release of the volatile Citronella Oil. Anticipating, we could achieve the goal of controlling the releasing speed of volatile oil liberally by changing simple microcapsule manufacturing conditions.

2. Experimental procedure

2.1. Preparation of microcapsules

Chitosan (80% deacetylated) and volatile Citronella Oil were purchased from Wako, Japan and Siegal Chemical, Taiwan, respectively. Yellow oily dye (Auramine, C.I. Basic Yellow 2), NaOH, and natural coconut oil which contains no phosphorus, fluorescent agent, bleach, and petrified complexes, that act as amphoteric surfactant, were purchased from First Chemical, Taiwan. The procedures of manufacturing microcapsules are as follows: first add 0.5 wt% yellow oily dye in the Citronella Oil for tracing purpose; then pour 2 ml of the yellow Citronella Oil into 20 ml of solutions consisting of 0.2%, 0.5%, 1.0%, and 1.5% Chitosan, respectively; using homogenizer (HG-300D + K12S, Shuang-Tai, Taiwan) to stir 10 min in 400–1500 rpm speed that cause the intermixture emulsification; then drip in 0.1–1.5 wt% NaOH while stirring slowly. Thus form the Chitosan wall membrane on the surface of the Citronella Oil particles and create the microcapsules sample. After wash the microcapsules samples with distilled water twice and then dislodge other unwanted substances with a centrifuge, then place into 5 wt% natural coconut oil amphoteric surfactant solution for 10 days. The resultant Chitosan microcapsules samples were dried in a vacuum oven (TK30, Young-Chen, Taiwan) at 30 °C overnight to evaporate any remaining water on the microcapsule surface. The sample weight was then measured and defined as W_m. Then observe the formation and dispersion of the microcapsules afterward under optical microscope.

2.2. Determination of microcapsule size

The particle sizes of the prepared microcapsules were determined by using particle diameter and particle size analyzers (MSS, Malvern Instruments, UK). The sizes of the microcapsules were determined in chloroform as a non-dissolving dispersion medium and the particles were mechanically suspended by magnetic stirring during the measurement.

2.3. Determination of controlled release and data analysis

The release of Citronella Oil from the microcapsules at the incubation process was estimated by measuring the time course of the weight $W_m(t)$ of the microcapsules placed in an Infrared Moisture Determination Balance (IMDB) (AD-4715, AND) at 40 °C. Here, t is the incubation time. Even tiny amount of vaporization of solvent could be detected by IMDB, as it is commonly used to determine the water content of fibers. The sample in the open box of IMDB was heated by using infrared set at desired temperatures. Temperature and weight of the sample were measured continuously and recorded automatically. The oil release content was defined as:

$$\psi(\%) = \left[\frac{W_m - W_m(t)}{W_m - W_0}\right] \times 100 \quad (1)$$

where W_0 denotes the weight of microcapsules measured after complete evaporation of Citronella Oil at 120 °C for 3 h. Therefore, the encapsulation efficiency can be defined as:

$$\varphi(\%) = \frac{W_m - W_0}{W_m} \times 100 \quad (2)$$

The Citronella Oil release curves were expressed by the exponential equation [22,23]:

$$\psi(t) = C_{eq}(1 - e^{-t/\tau}) \quad (3)$$

where $\psi(t)$ represents the variant of Citronella Oil concentration in the operation environment, C_{eq} the equilibrium state, t the release time and τ is time constant. Thus τ is the significant factor pertaining to the Citronella Oil release properties.

3. Results and discussion

3.1. The formation and encapsulation efficiency of microcapsules

In order to discuss the optimum formation condition of the microcapsules, the change factors we use are the concentration of Chitosan in 0.2 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, and the concentration of NaOH in 0.5 wt%, 1.0 wt%. Fig. 1 is the microscopic picture of microcapsules manufactured under the condition of 0.5 wt% Chitosan, 0.5 wt% NaOH, and with 0.5 wt% natural coconut oil as amphoteric surfactant. Under this manufacturing condition, good formation and dispersion of microcapsules can be obtained. We have discovered that when the Chitosan concentration is lower than 0.2 wt%, there is lot of Citronella Oil floating on the top layer of the emulsion. Obviously in the formation process of the microcapsules, the wall

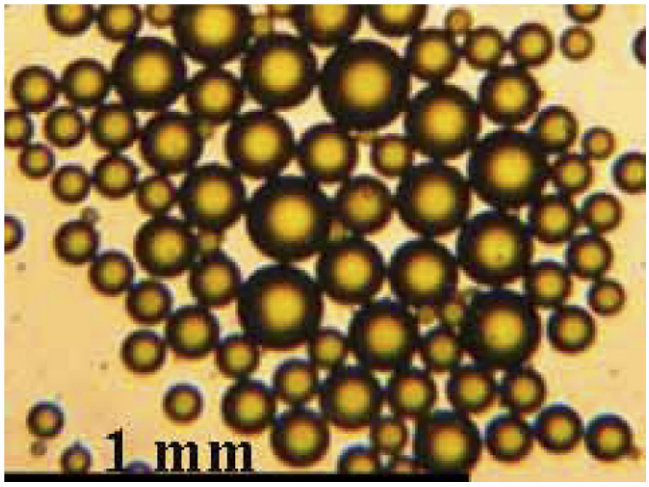

Fig. 1. Microphotographs of Chitosan microcapsules (×80). The microcapsules were prepared at the concentrations of 0.5 wt% Chitosan and 1.0 wt% NaOH at 800 rpm stirring rate.

membrane of the microcapsules is too thin to completely cover the Citronella Oil. On the contrary, when the Chitosan concentration is higher than 0.5 wt%, there is no sign of Citronella Oil on the surface of the emulsion. NaOH plays the role of hardening agent in this experiment. Applying too little NaOH cannot effectively separate out the Chitosan to achieve good encapsulation, on the other hand applying too much NaOH can actually cause excessively high viscosity of the entire emulsification system and produce microcapsules in a bulky group formation. The research shows that the Chitosan microcapsules have very good dispersion result with this natural coconut oil amphoteric surfactant. Adding 0.5–1.0 wt% natural coconut oil amphoteric surfactant and stir slowly using magnetic agitator, then set aside for 10 days to observe the microcapsules' dispersion effect. The probable causes should be that Chitosan solution contains $-CH_3COO^-$ and $-NH_4^+$ structures, the amphoteric surfactant added, which has both positive and negative ion, will react with $-CH_3COO^-$ and $-NH_4^+$ in the same time, therefore achieve good dispersion effect. We can conclude from the results of above experiments and obtain the basic formation and dispersion conditions of Chitosan microcapsules.

3.2. Release effect of concentration of wall membrane and particle size

Fig. 2 shows microcapsules manufactured with Chitosan wall membrane in 0.5 wt%, 1.0 wt%, and 1.5 wt% concentrations, and their influences of release effects to the encapsulated volatile Citronella Oil. The chart demonstrated the sustained release rate of micro-encapsulated volatile Citronella Oil is obviously slower than that of not micro-encapsulated volatile Citronella Oil; moreover, the thicker the Chitosan concentration, the slower the release rate of volatile Citronella Oil. This is because the thicker the Chitosan concentration, the thicker the microcapsules' wall membrane, and smaller the pore space between Chitosan molecules, therefore causes difficulties for the volatile

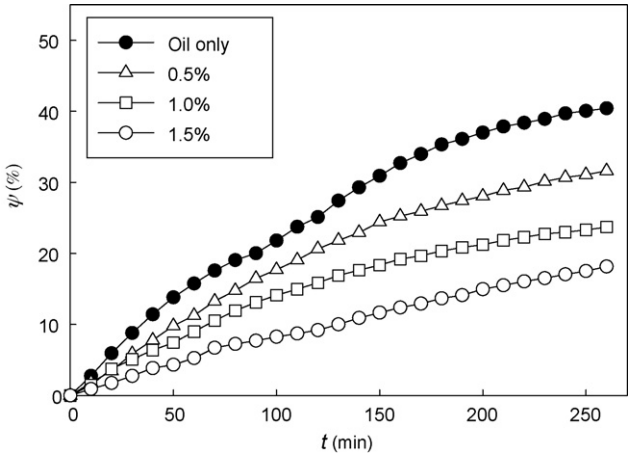

Fig. 2. Time courses of oil release from microcapsules at different concentrations of Chitosan. The samples prepared at NaOH 1.0 wt%, 800 rpm stirring rate. The symbols (black circle), (triangle), (square) and (white circle) denote concentrations of Chitosan of 0 wt% (oil only), 0.5 wt%, 1.0 wt% and 1.5 wt%, respectively.

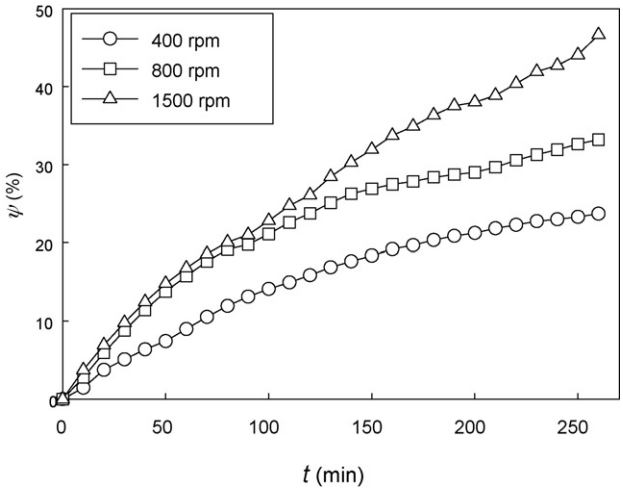

Fig. 3. Time courses of oil release from microcapsules at various stirring rate. The samples prepared at Chitosan 0.5 wt%, NaOH 1.0 wt%. The symbols (triangle), (square) and (circle) denote stirring rate 1500 rpm, 800 rpm and 400 rpm, respectively.

Citronella Oil to release from microcapsules. Thus we could have better control over the sustained release effect by changing Chitosan wall membrane thickness.

In order to observe the influence of the microcapsules' particle size to the release effect of the volatile Citronella Oil, we fix the microcapsules manufacturing condition with Chitosan concentration in 0.5 wt% and NaOH concentration in 1.0 wt%, and change the emulsion stirring speed at 400 rpm, 800 rpm and 1500 rpm. The results are microcapsule samples with average particle sizes of 225 ± 24 μm, 131 ± 20 μm and 11 ± 3 μm, respectively. Then continue the volatile Citronella Oil release experiments with these different sizes samples, and study the influences to the release behavior of microcapsule encapsulated volatile Citronella Oil. The experimental data were plotted in Fig. 3. From the chart it appears that increase the emulsion stirring speed could produce microcapsules with small particle size, and small particle size can increase the release rate of the volatile Citronella Oil. This outcome is consistent with the research of the relation between particle size and sustained release rate by Yamamoto et al. [22]. The reason should be that smaller particle size microcapsules would have larger total specific surface area, therefore causes its release rate to be faster than that of larger particle size microcapsules.

3.3. Release effect of Chitosan microcapsules after thermal treatment

For investigating the influences of: (1) changes in operation environment temperature and (2) changes in thermal pretreatment temperature and thermal pretreatment time, to the release effects of Chitosan microcapsule encapsulated volatile Citronella Oil.

First we set the operation environment temperatures in 40 °C, 60 °C and 80° C; conduct the sustained release property measurement with microcapsule samples that has not been thermal pretreated, and plotted the results in Fig. 4. The

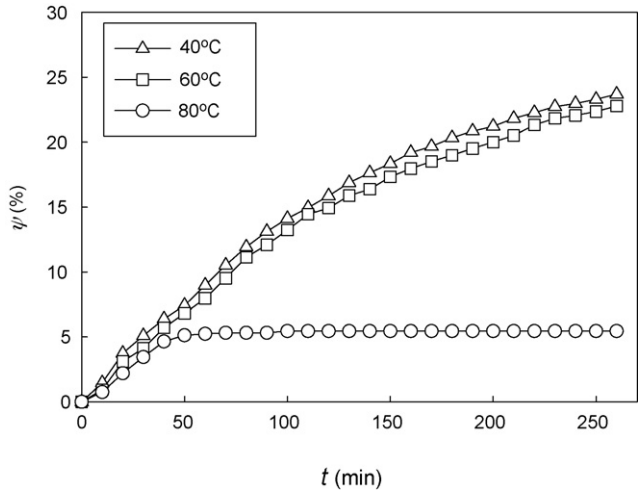

Fig. 4. Time courses of oil release from microcapsules at various operation environment temperatures. The samples prepared at Chitosan 0.5 wt%, NaOH 1.0 wt%. The symbols (triangle), (square) and (circle) denote operation environment temperature 40 °C, 60 °C, and 80 °C, respectively.

manufacturing conditions of the test samples were set at Chitosan wall membrane concentration 0.5 wt%, NaOH concentration 1.0 wt%, hardening time 1 h, and emulsification stirring speed 800 rpm. From the graph we could see under the 40 °C and 60 °C operation environment, the oil release rate of encapsulated Citronella Oil of the latter (60 °C) is slightly higher than the former (40 °C) but there is little difference between the two. Yet if the operation environment temperature were increased to 80 °C, the microcapsule encapsulated Citronella Oil has initial low release rate, and declining to nearly none when operation time is close to 50 min. The reason is that the Chitosan molecule chains gradually contract because the microcapsule wall membrane was heated, intermolecular space is then reduced; therefore slow down the Citronella Oil release rate gradually. So along with the operation time increase, the wall membrane structure highly contracted causing the pores nearly completely seal off and the volatile Citronella Oil unable to continue to release.

Follow by investigating the release behavior of the encapsulated Citronella Oil after thermal pretreatment in 40 °C, 60 °C and 80 °C for 1 min. The results are shown in Fig. 5(a). The microcapsules manufacturing conditions are: Chitosan 0.5 wt%, NaOH 1.0 wt%, hardening time 1 h, stirring rate 800 rpm. From the chart we could find the encapsulated Citronella Oil microcapsules release rates after thermal pretreatment in 40 °C and 60 °C have little difference. It is obvious that Chitosan wall membrane structure were not greatly affected when thermal pretreatment in 40 °C and 60 °C for 1 min. But when the thermal pretreatment temperature increased to 80 °C, the release rate of microcapsule encapsulated Citronella Oil rapidly descended. The reason should be as aforementioned that high heat contracted the microcapsule wall membrane structure and close the pores. Fig. 5(b) shows that when other conditions are fixed, with 80 °C thermal pretreatment temperature for 1 min, 5 min, and 10 min, the release states of the encapsulated Citronella Oil. From the graph we could find that the release rate of

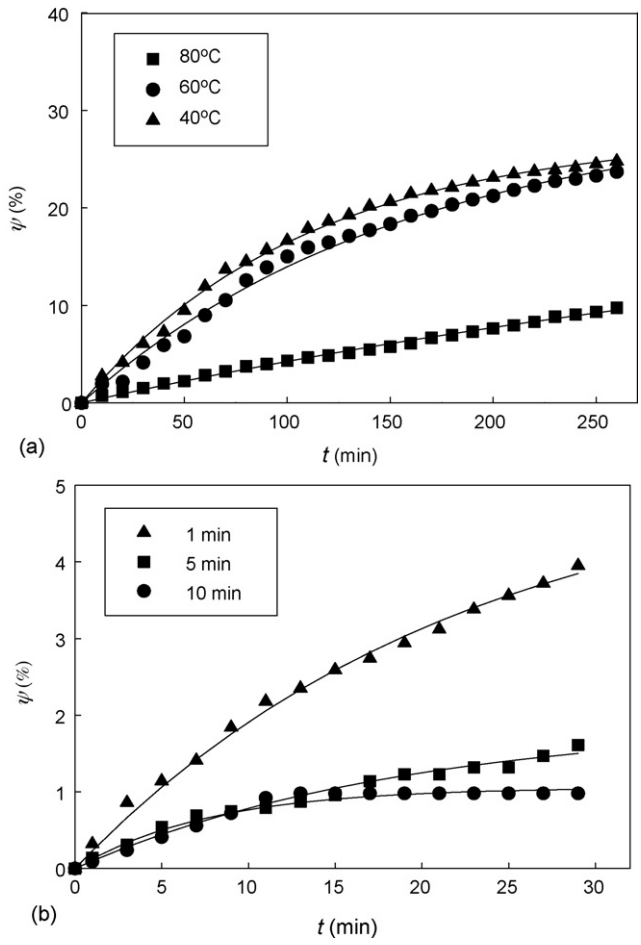

Fig. 5. Time course of oil release from microcapsules at various treated temperatures (a) and treated times (b). The samples were prepared at the condition of 0.5 wt% Chitosan, 1.0 wt% NaOH. The solid lines are calculated using Eq. (3).

Citronella Oil slows down when thermal pretreatment time increases. Especially after thermal pretreated at 80 °C for over 5 min, we can find the release rate of the microcapsule encapsulated Citronella Oil approaching zero, the Chitosan wall membrane almost completely seals up. Therefore we could utilize this method of increase the thermal treatment temperature and treatment time to control the sustained release rate of the microcapsules.

If the experiment data were placed into the exponential function Eq. (3) to generate the solid line in the figure, the results are generally consistent with values obtained from the experiment. Thus the oil release curves are fitted well to the exponential function as aforementioned.

It demonstrated that the analysis data are reliable because all the correlation coefficient in the exponential function are greater than 0.97, where C_{eq} means the concentration of oil released at the equilibrium state, τ the time constant and t is the release time. As shown in Fig. 6(a and b), increasing the pretreatment temperature and pretreatment time would increase the value of τ. Thus the results indicated that the release rate of volatile Citronella Oil depends on the pretreatment temperature and the pretreatment time considerably.

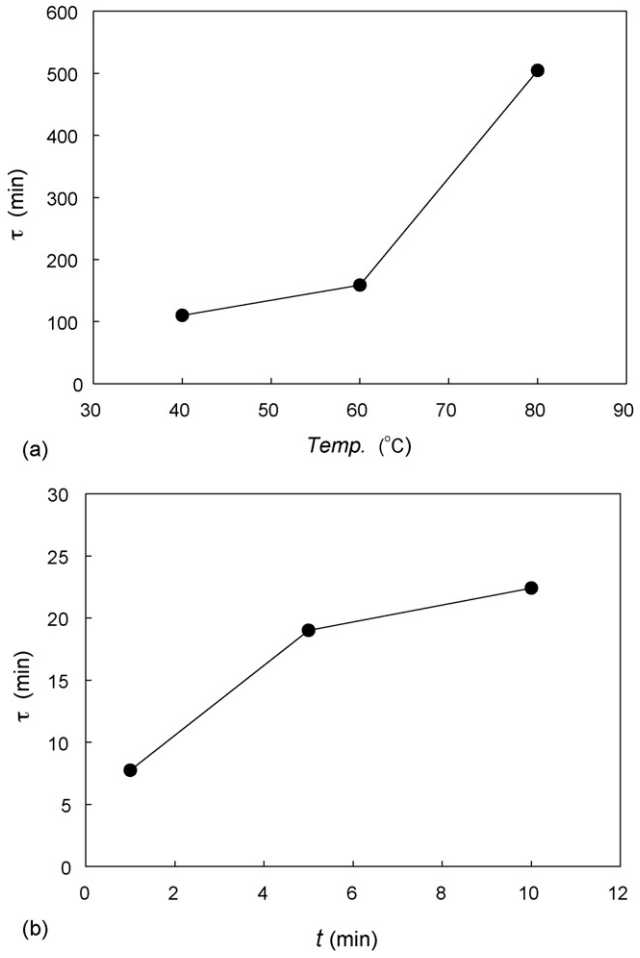

Fig. 6. Oil release from microcapsules at the effective time constant as a function of pretreated temperature (a) and pretreated time (b).

4. Conclusions

The research uses Chitosan as the wall membrane material, volatile Citronella Oil as inner core material and uses modified orifice method to manufacture O/W type microcapsules. Discuss and investigate ways to control the constant release of volatile Citronella Oil by changing the manufacturing conditions of microcapsules. The results indicated that the basic effects of formation and dispersion of microcapsules could be attained under the conditions of Chitosan concentration is higher than 0.2 wt%, NaOH concentration is higher than 0.5 wt%, and natural coconut oil was added as the amphoteric surfactant. When the concentration of Chitosan wall membrane material are 0.5 wt%, 1.0 wt% and 1.5 wt%, the encapsulation efficiency of microcapsules are 98.2%, 95.8%, and 94.7%, respectively. The oil release rate increases when the diameter of microcapsules decreases. If the microcapsules have been thermal pretreated in 80 °C temperature, the Chitosan wall membrane will shrink and causes difficulties for the Citronella Oil to release. This effect is even more noticeable if the time of thermal treatment is longer. Therefore by controlling the concentrations of Chitosan and NaOH, the particle sizes of the microcapsules, the pretreatment temperature and pretreatment time, we could control the oil release rate of the volatile Citronella Oil from the Chitosan wall membrane.

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