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Effect of Nano-montmorillonite on Properties of Spray-dried Cinnamon Oil Microcapsules

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Abstract. Proper dispersion of layered nano-clay within the wall of oil microcapsule is a strategy for improving encapsulation properties. In the present study, cinnamon oil microcapsules with addition of nano montmorillonite (MMT) in wall materials were prepared by spray drying, encapsulation efficiency (EE) and loading capacity (LC) were measured. The release properties of microcapsules at different humidity and high temperature were investigated. The results show that the emulsion with 12% MMT content has the highest stability and shows the lowest droplet mean diameter. The EE and LC increase with the increase of MMT content and reach the maximum at 12% MMT content as a function of compact wall membrane structure formed from MMT dispersed in polymer. The addition of MMT decreases cinnamon oil release rate and improves the barrier property of wall membranes due to the less water absorption. Thermal stability of microcapsules is also enhanced.

1. Introduction

Essential oils are volatile aromatic substances extracted from perfume plants. They are used as natural aromas in food, cosmetics and, due to medicinal properties, many of them are used in conventional medicine and aromatherapy. However it has some shortcomings, such as short retention time, uncontrollable release, due to its volatility and vulnerability to oxygen, light, heat and moisture. The encapsulation can much improve stability of essential oils, which can not only protect against losses and chemical changes, but also apply them in the form of powders and effectively control release of the aroma during consumption [1,2]. The encapsulation technology of plant essential oil mainly includes spray drying, complex coacervation, sharp hole method and saturated aqueous solution method [3].

Spray drying is the most commonly used microencapsulation technology in industrial production. The main characteristics of spray drying are simple process, large production capacity, low cost. As carriers for aroma microencapsulation, carbohydrates and proteins are mainly used [4]. However, low encapsulating efficiency is the problems of spray drying. The rapid evaporation of water causes the rupture of microcapsule wall materials, which makes the oil easy to lose and the storage stability of products decline. In the literature, various attempts have been made to maximise the retention of the essential oil after the drying process is completed, including applying multi-layered capsule wall [5], decreasing the core loading [6] and varying the properties of capsule wall by crosslinking [7] and Maillard reaction [8].

Attempts on utilization of nanomaterials for the preparation of microcapsules have been increased significantly for several applications. The nanoclays offer remarkable improvement in various properties including permeability with incorporation of small amount in polymer matrix. Cracks, bubbles and other defects caused by drying of the wall materials can be significantly reduced due to



the size effect and surface effect of nanoclays, and the bonding between macromolecular chains can be promoted [9-11].

The aim of this study was to prepare cinnamon oil microcapsules coated by materials with addition of nano montmorillonite (MMT). The microcapsules were prepared by spray drying, and the effects of MMT on the encapsulation efficiency (EE) and loading capacity (LC) of microcapsules were studied. The sustained release properties of microcapsules were explored.

2. Materials and Methods

2.1. Materials

MMT was obtained from Zhejiang Fenghong New Materials Co., Ltd. (Zhejiang, China); cinnamon oil was from Hongxing Natural Medicinal Oil Factory, Jishui County (Jiangxi, China); arabic gum, gelatine, maltodextrin were from Sinopharm Group Chemical Reagent Co., Ltd. (Beijing, China); other reagents are all analytically pure. All the reagents and materials were used as received without any further purification.

2.2. Experimentals

2.2.1. Preparation of spray-dried cinnamon oil microcapsules. Gelatin (3%), arabic gum (10%) and maltodextrin (7%) as wall materials were dissolved at 20% (w/w) in water at 60°C. The solution was then cooled to room temperature, added with cinnamon oil (1:1 core and wall ratio), and homogenized at 10000 r/min for 10 min. The uniform and stable microencapsulated emulsion can be formed. The emulsion was spray-dried with inlet temperature of 170°C and outlet temperature 90°C.

For the preparation of microcapsules with MMT in wall materials, MMT was dispersed in water by ultrasonic for 10 min and added in the solution of wall materials with 4%, 8%, 12%, 16% (w/w) content (based on wall materials). The microcapsule preparation steps are the same as above.

2.2.2. Determination of emulsion stability. The emulsion was loaded into a graduated measuring cylinder and placed at room temperature for 2 h to observe the volume of emulsified layer and free layer. The stability index of emulsion was calculated. Emulsion stability index (%) = (total emulsification volume - free layer volume) / total emulsification volume × 100%. Emulsion droplet sizes were measured by dynamic light scattering, using 1.5 mL emulsion samples, diluted 1000× with water to avoid multiple light scattering effect.

2.2.3. Determination of encapsulation efficiency (EE) and loading capacity (LC). Standard Curve of Cinnamon oil in anhydrous ethanol was drawn, and EE and LC were determined as following method: Free cinnamon oils in the microcapsule surface were determined by washing from 0.3g precisely weighed microcapsules with ethanol in test tube. Total oils were determined by extracting the dried microcapsules in ethanol for 10 min by ultrasound, and fixing the volume of solution to 100 mL. The absorbance of the solution was determined at 276 nm, and the cinnamon oil contents were determined according to the standard curve. The EE and LC were calculated as the following formula:

$$EE (\%) = (Oil_{total} - Oil_{surface}) / Oil_{total} \times 100\%$$

$$LC (\%) = Oil_{total} / (\text{Amount of microcapsules}) \times 100\%$$

Oil_{total} is total amount of oil in microcapsule, $Oil_{surface}$ is amount of oil in the microcapsule surface. All the results are the means of at least three separate experiments.

2.2.4. Determination of mechanical property of wall material membrane. The sample was cut into rectangular specimens (20 mm × 100 mm), and the tensile strength and elongation at break were measured by electronic tensile testing machine. The test fixture spacing is 50 mm and the drawing rate is 10 mm/min.

2.2.5. Determination of release rate of microcapsules under different humidity. The microcapsules were accurately weighed and evenly spread on a surface dish and placed in a dryer. A certain amount of saturated salt solution was placed in the dryer to form different relative humidity (saturated sodium chloride for 75% RH and 98% of saturated potassium sulfate). The dryer was placed at 30°C and opened every 12 hours for 5 minutes, and the content of cinnamon oil in the microcapsules was determined at regular intervals.

The moisture adsorption kinetics of microcapsules was determined by evaluating the increase in the amount of moisture over time. Approximately 1 g of microcapsules was placed in a NaCl-saturated solution (75% relative humidity) at 30°C. Samples were weighed after 4,8,12,16,20,24 and 24 h. The hygroscopic values were expressed as percentages.

2.2.6. Determination of thermal stability of microcapsules. The microcapsules weighed accurately were laid in a surface dish and stored in an oven of 80°C. The cinnamon oil content in the sample was determined after a certain period of heat treatment.

3. Results and Discussion

3.1. The Effect of MMT Content on Emulsion Stability

The stable emulsifier is the basis of the preparation of essential oil microcapsules because the emulsifier system is thermodynamically unstable. The droplets tend to self-coalesce and the poor stability of the emulsifier results in oil separation in the upper layer of the tube. The effect of MMT content in wall materials on the stability of emulsion is shown in Fig. 1. It can be seen that the stability of emulsion increases with the increase of MMT content when MMT content is less than 12%, and the stability of emulsion reaches the highest at 12% MMT content. It can be explained that the colloidal suspensions of anionic MMT platelets form as a result of exfoliation of the layered MMT in water. These MMT platelets have the function of stabilizing emulsion in the system when their contents are small. However, MMT can not disperse well in water as the increase of MMT content with the settle of some MMT.

The droplet mean diameter of the emulsion prepared with different MMT contents is presented in Fig.2. The increase in MMT contents leads to a reduction in the oil droplet size, which can be attributed to the stability effect of MMT platelets, as in Fig.1. The emulsion with 12% MMT content has the highest stability and shows the lowest droplet mean diameter (4.15 μm).

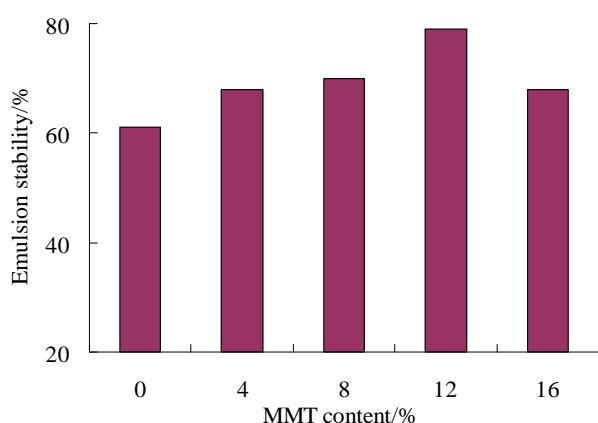


Figure 1. The effect of MMT content on emulsion stability.

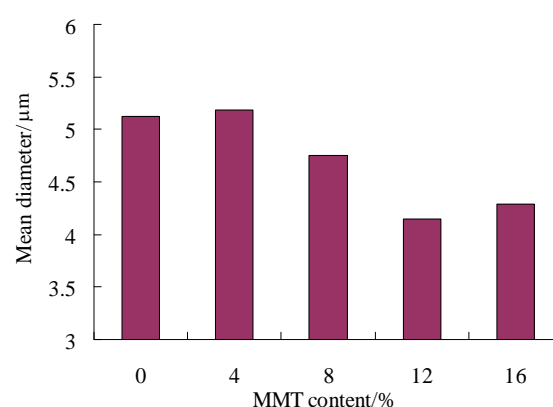


Figure 2. The droplet mean diameter of the emulsions prepared with different MMT contents.

3.2. The Effect of MMT Content on EE and LC during Spray-dried Microencapsulation

Table 1 is the effect of MMT content on EE and LC during spray-dried microencapsulation. The EE and LC increase with the increase of MMT content and reach the maximum at 12% MMT content.

The microcapsule wall with compact membrane structure formed from MMT dispersed in macromolecules is thought to be responsible for the EE increase. The size and surface effect of MMT can promote the bonding between side chains of macromolecules, resulting in significant reduction of the cracks in wall film and the leakage of surface oil. MMT can be easily dispersed uniformly in the wall material with the lower MMT content, resulting in the remarkable enhancement effect. However, when the MMT content go beyond 12%, some of MMT will agglomerate and form stress concentration points, which will result in the decrease of the wall membrane strength. Table 2 shows the effect of different MMT content on the mechanical properties of wall membranes. It can be seen that the tensile strength of wall membranes is the highest when MMT content is 12%, and the tensile strength of wall membranes decreases with further increase of the MMT content.

The addition of 12% MMT in wall material was used in microcapsule preparation with MMT in the following experiments.

Table 1. The effect of MMT content on EE and LC during spray-dried microencapsulation.

MMT content/%	0	4	8	12	16
EE/%	56	61	72	81	75
LC/%	29.4	29.1	30.8	31.6	30.3

Table 2. The effect of MMT content on mechanical properties of wall membranes.

MMT content/%	0	4	8	12	16
Tensile strength/MPa	51	62	65	66	61
Elongation at break/%	5.5	4.8	4.5	3.8	5.8

3.3. Microcapsule Release at Different Humidity

The release curves of cinnamon oil microcapsules with time in different humidity environments are shown in Fig. 3. The release rate of cinnamon oil is fast at the initial stage of release and accelerates with the increase of humidity. The release of oil from the microcapsule without MMT is much faster than that of microcapsule with 12% MMT, indicating that the wall structure with MMT provides a better protection and prevents the leaking of core materials from the microcapsules. For microcapsule with 12% MMT after 10 days of exposure to 95% humidity conditions, the oil loss is 21 wt%, while the oil loss of microcapsule without MMT is 31 wt%.

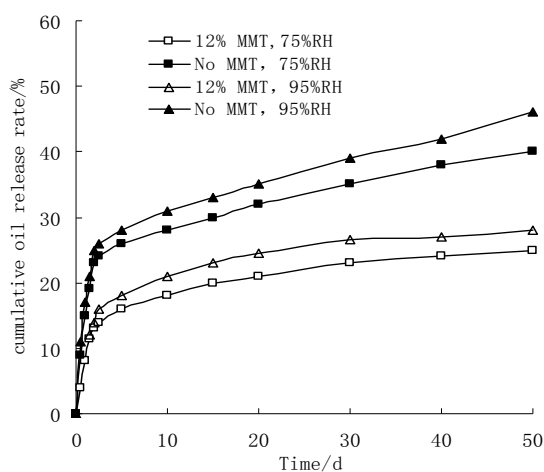


Figure 3. Cumulative oil release rate at different relative humidity.

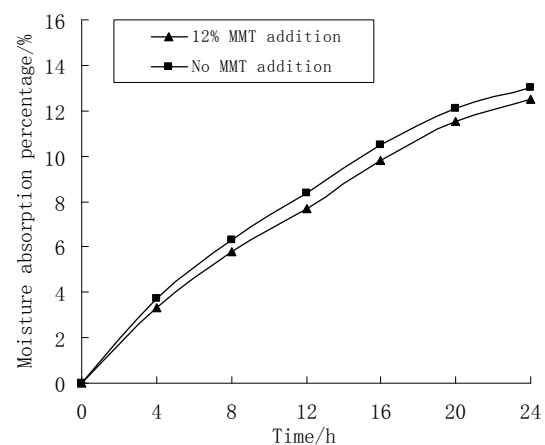


Figure 4. Moisture absorption percentage of microcapsules.

The hygroscopicity of microcapsules at 30°C and 75% humidity was observed within 24 hours, and results are shown in Fig. 4. Two microcapsules have similar hygroscopicity curves, and the initial hygroscopicity rate is relatively fast, because at first, the moisture content in the air is higher than that on the surface of microcapsules, and microcapsules tend to absorb more water in the air; over time, the moisture content in the air is similar to that on the surface of microcapsules, and the surface moisture of microcapsules needs to pass through. At 24 h, the water absorption of the microcapsules without MMT is 13% and was 12% with MMT addition. The less water absorption of the microcapsules with MMT is associated with slow release of oil.

3.4. Thermal Stability

Fig.6 is the Retention Rate of Cinnamon Oil in Microcapsules at 80°C. The results showed that the volatilization rate of essential oil in microcapsules with MMT was lower than that without MMT. This is thought to be associated with higher thermal resistance of wall membrane with MMT.

All the test results of oil release at different humidity and thermal stability have shown that microcapsules with MMT have significantly better barrier property than those without MMT addition. Since the release behavior depends heavily on the microstructure of the microcapsule wall, the microcapsule wall with compact membrane structure formed from MMT dispersed in macromolecules is thought to be responsible for the good release behavior of microcapsules with MMT addition.

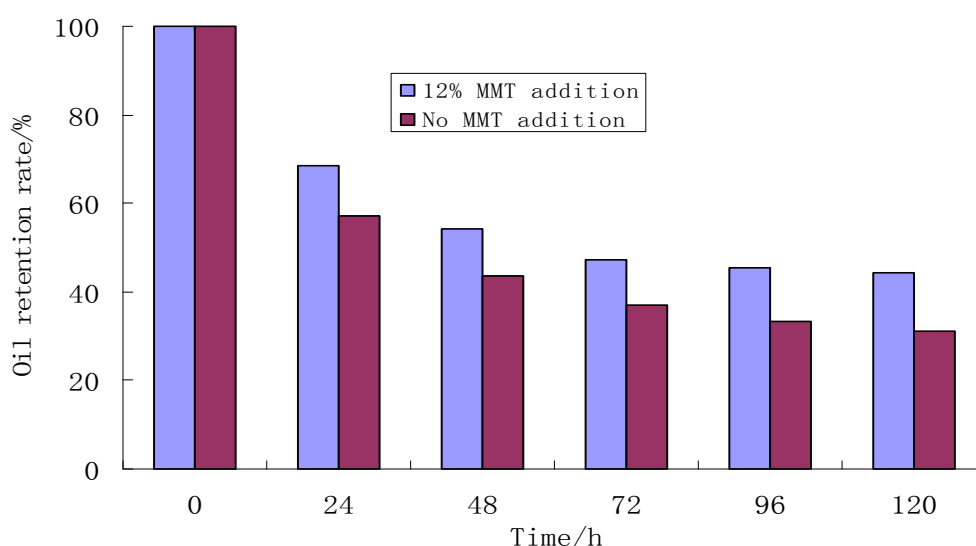


Figure 5. Retention Rate of Cinnamon Oil in Microcapsules at 80°C.

4. Conclusions

In this paper, we have studied the effect of the addition of nano-MMT on the wall material for encapsulating cinnamon oil. Nano-MMT platelets have the function of stabilizing emulsion in the system. The EE and LC increase with the increase of MMT content during spray-dried microencapsulation and reach the maximum at 12% MMT content. The compact structure of wall membrane formed from addition of nano-MMT significantly reduces the cracks and oil leakage. Measurement of microcapsules release has shown that addition of nano-MMT improves barrier property of the wall membrane due to the less water absorption of the microcapsules, decreases cinnamon oil release rate and enhances thermal stability of microcapsules.

5. Acknowledgments

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