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Melamine resin microcapsules containing fragrant oil: synthesis and characterization

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Abstract

Melamine resin microcapsules with long self-life containing fragrant Migrin oil were prepared by in situ polymerization from Migrin oil as core material, melamine and formaline as wall materials, sodium lauryl sulphate as emulsifier and poly(vinyl alcohol) as protective colloid. Melamine resin microcapsules were characterized on structure, a mean particle size and size distribution, morphologies, thermal properties and release behavior.

Keywords: Melamine resin; Microcapsules; Fragrant oil; In situ polymerization; Fragrant fabric; Release behavior

1. Introduction

Recently, functional fibers have been studied to satisfy the needs for the comfort and safety of consumers. Diverse functional fibers related with sensitivity of consumers have been developed, and thus, needs for long-term durability of functional fibers brought about the introduction of microencapsulation technique [1,2]. Microcapsules have the ability to be shaped in their desired form, release of the active substance by an appropriate mechanism, stability and adequate mechanical strength and non-toxicity of the material itself and of its degradation production [3,4]. Microcapsules have been used in carbonless copying paper, liquid crystals, adhesives, cosmetics, insecticides, etc. [5–7]. Especially, the protection of fragrant oil as susceptible material from outer phase by microencapsulation is paid attention, to increase its stability.

In this study, microencapsulation technique was applied by using melamine–formaldehyde as wall material in order to increase the durability of fragrance oil onto substances, such as coating liquid, film, and fiber. In the first step, melamine–formaldehyde prepolymer was prepared to obtain polymer wall composed of thermosetting resin. The prepolymer was added into the aqueous solution with emulsifier. The hydrophobic Migrin oil as core material was added to the solution and stirred vigorously to result in microemulsion. With heating and acidification (lowering pH of the solution down to 3–5), the prepolymer cross-linked and polymer membranes with high durability for heat were prepared successively.

2. Experimental

2.1. Materials

Melamine and 37% formaldehyde as wall materials, sodium lauryl sulfate (SLS) as emulsifier, poly(vinyl alcohol) (PVA, Mw. 1500) as protective colloid, acetic acid and sodium carbonate anhydrous as pH controller were obtained from Junsei Chemicals, Japan without any further purification. Fragrant Migrin oil (Mw. 250) as core material was obtained from Seil Perfume Co., Korea. 1,4-diaminoanthraquinone (DDA, Mw. 253) as penetrator with same molecular weight as Migrin oil, was used to determine loading amount of core material. Cotton fabrics were used to produce fragrant fabrics. All of the chemicals used in this study were a reagent grade.

2.2. Preparation of microcapsules

0.1 M melamine and 0.25 M 37% formaldehyde in 100 ml of distilled water were adjusted to pH 9 with 10% Na_2CO_3 aqueous solution. The step of preparing the melamine–formaline precondensate is effected under alkaline

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conditions. The preferred pH range for this step is from about 7.0 to 9.0. Even more preferably, the pH range is from about 8.5 to 9.0. Melamine–formaline precondensate was prepared by stirring at 70°C for 10 min. Simultaneously, same amount of o/w emulsion of Migrin oil and 0.002 M DAA in 100 ml of 0.5 wt.% SLS aqueous solution was prepared. DAA was used as penetrator with same molecular weight as Migrin oil, to investigate loading content of Migrin oil in the microcapsule. O/w emulsion was added into melamine–formaline prepolymer. Typically, a water soluble melamine–formaline precondensate is dissolved in an aqueous solution (known as the external phase). A discontinuous phase of a material to be encapsulated (known as the internal phase or core material) is emulsified in the external phase using a water soluble PVA as a protective colloid. Generally, the internal phase will consist of droplets of an oily solution. The resultant emulsion lowered the pH to 5.0 and 100 ml of distilled water with 0.001 M PVA was poured into the solution to prevent agglomeration among the prepared emulsion globules, subsequently. The resolution was stirred at 70°C for 30 min. The step of causing the second melamine–formaldehyde precondensate is also effected by decreasing the pH of the emulsion to below about 5.0 and adding heat thereto. The pH can be lowered by adding an acid to the emulsion. After in situ polymerization on o/w emulsion surface, microcapsules slurry was decanted, washed with 30% ethanol to remove Migrin oil on the surface, and dried under the reduced pressure at room temperature for 24 h.

2.3. Characterization

Infrared spectra of core material and microcapsules were obtained with Nicolet Impact 400D Fourier transform infrared spectrophotometer. Differential scanning calorimetry (DSC) and thermogravity (TG) measurements were carried out utilizing DSC Mettler Model TA-3000 (Thermal science PL-STA). The samples of about 5 mg each were heated at the rate of 10°C min^{-1} up to 550°C under constant N_2 flow. Scanning electron microscopy was performed using a JSM-5400 (JEOL Co., Japan). Microcapsules were sprinkled onto a double sided tape, sputter-coated with gold and examined in the microscope. Mean particle size and size distribution of microcapsules were determined using Image Analyzer Galai CIS-100 (Galai Production, Israel). The test with a few drops of suspension was carried out after dispersion by sonicator for 3 min.

2.4. Loading amount and release test

Loading amount of DAA as penetrator and disperse dyes from 100 mg of melamine resin microcapsules with Migrin oil and DAA were determined with dispersion into 100 ml of methanol, and stirred slowly till the complete release of DAA for 24 h at 20°C. The solution was assayed for the amount of the released 1,4-DAA by utilizing UV–Vis spectrophotometer. The obtained DAA amount was calculated along with below equation, and described as loading content (%).

Loading content (%) = (initial concentration of DAA − Encapsulated concentration of DAA) × 100.

Also the microcapsules were put under drier for 60 days at 25°C and 65°C to investigate weight loss (%) of core material released from melamine resin microcapsules. The weight of empty microcapsule was calculated by crushing, drying and weighing the microcapsules completely released for 24 h in methanol.

2.5. Preparation of fragrant functional fabric

Washing durability of fragrant fabric was investigated up to 15 times, after their preparation by treatment of printing paste of fragrant microcapsules, small content of acrylic binder, reactive dyes, and 5% distilled water at room temperature. The surface and durability of fabric after laundry test was observed by SEM.

3. Results and discussion

3.1. Structure of microcapsules

Fig. 1 shows FTIR spectra of Migrin oil as core material and melamine resin microcapsules containing fragrant oil. Strong band of N–H stretching vibration at 3300 cm^{-1}, C–H stretching vibration at 3100–3000 cm^{-1}, C–N absorption band at 1380 cm^{-1} and C–O stretching at 1100 cm^{-1} are observed. This presents the formation of melamine prepolymer, and specific absorption bands of Migrin oil and melamine resin were also shown in the resultant microcapsules. Therefore, core material and wall material of microcapsules were proved as Migrin oil and melamine resin, respectively.

3.2. Thermal properties

TG and DSC results shown in Fig. 2 shows the thermal properties of microcapsules containing fragrant oil. Accord-

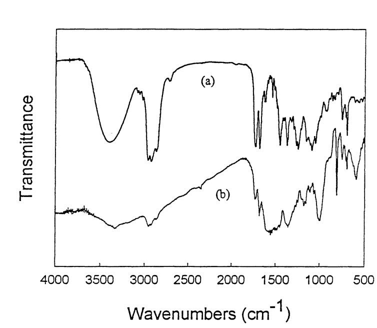

Fig. 1. FT-IR spectra of (a) Migrin oil and (b) melamine resin microcapsules with Migrin oil.

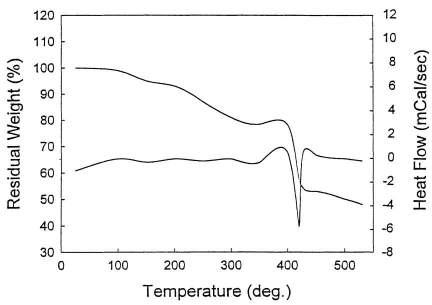

Fig. 2. TG and DSC thermograms of melamine resin microcapsules with Migrin oil.

ing to TG analysis presenting residual weight (%) of material by temperature change, microcapsule weight was decreased with increasing temperature and weight loss was up to about 50%. First small weight loss by slow release of core material entrapped in the microcapsule wall was shown up to 420°C, and any further weight loss was not shown as there was great weight loss at 420°C.

DSC result presenting additional information about polymer properties, such as changes of melting temperature and heat capacity of polymer corresponds with the result of TG thermal analysis. Thermal change was not shown up to 420°C, and sudden absorption peak appeared at around that temperature. This is related to the properties of melamine resin microcapsules as thermosetting polymer, and thus, durable microcapsules containing fragrant functional material seems to be prepared successfully. In addition, core volume in the melamine resin microcapsules seems to be above 50% according to TG result.

3.3. Particle size distribution

Fig. 3 shows the particle size distribution of the prepared melamine resin microcapsules containing fragrant oil. The size of all the resulted particles was below 10 μm by stirring at the rate of 3000 rpm, and their size distribution was narrower. Thus, the prepared microcapsules in this study seem to be adequate for the preparation of fragrant fabric, due to their monodispersed size distribution.

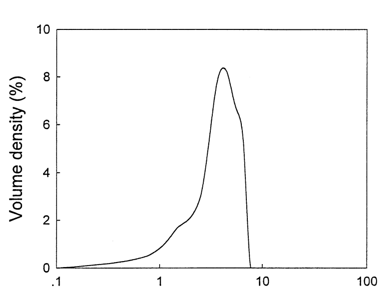

Fig. 3. Particle size distribution of melamine resin microcapsules with Migrin oil.

(a)

(b)

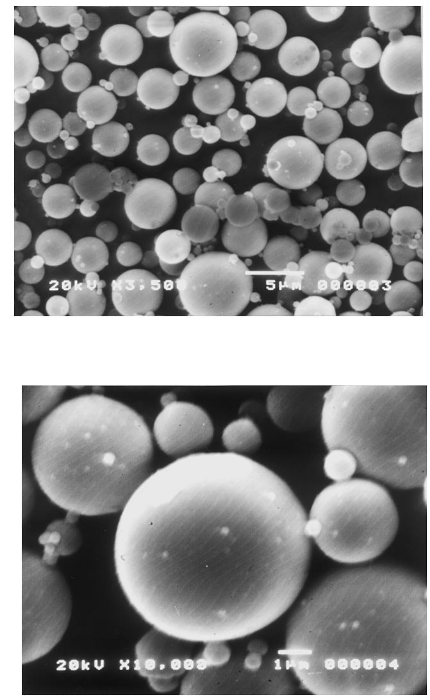

Fig. 4. SEM photographs of melamine resin microcapsules with Migrin oil (a) × 3500 and (b) × 10 000.

3.4. Morphologies

SEM photograph of surface morphologies of the microcapsules prepared at 70°C, 3000 rpm, for 30 min are shown in Fig. 4. As shown in the figure, surface morphology of the microcapsules has sustained releasable membrane due to its great surface smoothness. Thus, melamine resin microcapsules can be used in the purposes of the protection and the sustained release of interior core materials, due to their surface morphologies. Moreover, the microcapsules are

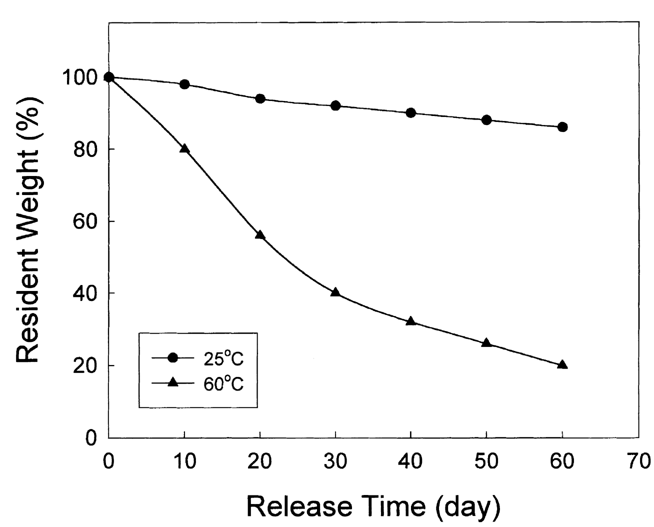

Fig. 5. Resident weight (%) of melamine resin microcapsules after the release for 60 days at 25°C and 60°C.

(a)

(b)

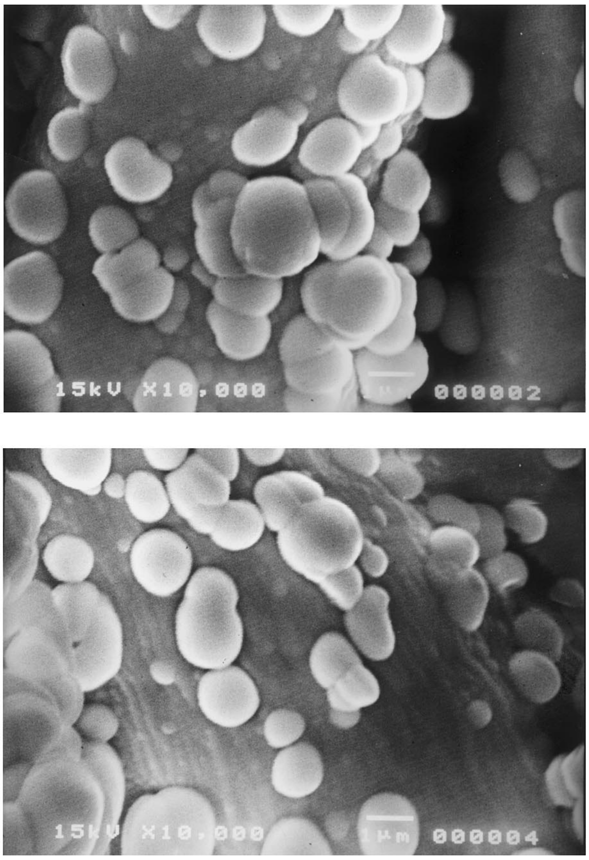

Fig. 6. SEM photographs of fragrant cotton fabric treated with the microcapsules after laundry test: (a) original and (b) 15 times.

concluded to be heat-resistant containers with superior thermal properties.

3.5. Loading amount and release behavior

It was concluded that the microencapsulation efficiency (%) of the resultant melamine resin microcapsules was about 87%, and the loading amount of Migrin oil in the microcapsules was about 53 wt.%. This data of loading amount correspondeds with the TG result.

Fig. 5 shows a resident weight (%) after release test for 60 days at 25°C and 65°C to investigate weight loss of core material in the melamine resin microcapsules. As expected, the release at 65°C was progressed swiftly up to 42% and release at room temperature was progressed up to about 8% of microcapsule weight. This indicates that the durable microcapsules with long self-life were prepared.

3.6. Preparation of fragrant fabric

Fragrant functional fabrics were prepared by the treatment of the microcapsules on cotton fabric, and then, SEM photographs after laundry test of original and for 15 times are shown in Fig. 6. As shown in the pictures, the fabric is coated uniformly by the printing paste with microcapsules, and has almost uniform particle size in itself. Most of the particles, especially fine ones with particle size below 10 µm remains even after 15 times of laundry test. This resulted in the fragrant fabric with washing durability.

4. Conclusions

In this study, melamine resin microcapsules with long self-life were prepared and the size distribution, thermal properties, morphologies, and release behavior of the microcapsules were investigated. Also, fragrant functional cotton fabrics with washing durability were prepared by the treatment of microcapsule solution. The resultant melamine resin microcapsules have thermosetting walls, a narrow size distribution, and surface morphology with great smoothness, capable of preserving fragrant oil for long self-life.

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