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Smooth, stable and optically transparent microcapsules prepared by one-step method using sodium carboxymethyl cellulose as protective colloid

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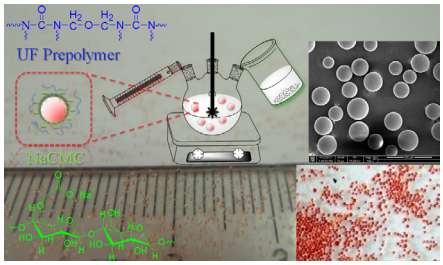
HIGHLIGHTS

- Stable, elastic and transparent urea–formaldehyde microcapsules containing tetrachloroethylene.
- Sodium carboxymethyl cellulose: protective colloid in one-step method.
- The surfactant amount and some crucial synthesis conditions have been optimized.

GRAPHICAL ABSTRACT



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ABSTRACT

Stable, elastic and optically transparent microcapsules containing tetrachloroethylene (TCE) as internal phase were prepared by in situ polymerization of urea–formaldehyde (UF) using the one-step method. For the first time, sodium carboxymethyl cellulose (NaCMC) was applied into the one-step system as a protective colloid. Microcapsules prepared under different conditions were characterized by scanning electron microscopy, optical microscopy, and thermogravimetric analysis. The results show that NaCMC-based microcapsules can exhibit better thermal and barrier properties than Gum Arabic (GA)-based ones. By formation of capsule wall with more compact microstructures, the NaCMC-based microcapsules can give potential application in encapsulated electrophoretic display systems. The system combining sodium dodecyl sulfate (SDS) and NaCMC together was also investigated. It is suggested that SDS can play an important role during the microencapsulation process, by improving the yield as well as the barrier properties of the products, but also resulting in negative effects at higher ratios of SDS-NaCMC. Other operation conditions such as different molar ratio of reactants (formaldehyde/urea) and addition of ammonium chloride (NH_4Cl) were been studied as well.

1. Introduction

Microencapsulation is a technique which solid, liquid or gaseous active ingredients are wrapped within another material for the purpose of shielding the active ingredient from the surrounding environment. This technique has potential applications in a diverse range of fields including chemical and pharmaceutical applications

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[1,2] cosmetics [3], phase change materials (PCMs) [4,5], self-healing systems [6,7] and electronic ink [8,9].

Since the concept of encapsulated electrophoretic ink was first reported by Joseph in 1997 [10], it has been a promising technique in mobile flat panel displays. The encapsulated electrophoretic display (EPD) technique has not only reduced the unwanted particle movement such as particle clustering and agglomeration on a scale larger than the microcapsule size, but also improved the stability of the system and prolonged its service life. The microcapsules for EPD can be produced through in situ polymerization [11], interfacial polymerization [12] and complex coacervation [13]. Most commonly, microcapsules need to have desirable optical characters as well as good barrier properties for high performance in EPD applications. As a flexible and transparent resin with highly cross-linked structures, urea–formaldehyde has been widely used as wall materials to fabricate microcapsules by in situ polymerization [14,15]. Usually, the polycondensation of urea and formaldehyde are achieved in two different ways. First is the traditional two-step process [16,17], which generally involves preparation of pre-condensate under alkaline conditions (pH 8–9) and then encapsulation on the interface under acidic conditions. The condensation products will deposit on the surface of the core material droplets, giving a cross-linked and water-insoluble capsule shell. Second, a one stage method using the above chemistry was developed by Brown [18], Yoshizawa [19], and Cosco [20], where the entire process happens under acidic conditions without having to prepare the pre-condensate under basic conditions. Compared to the two-step process, the one stage method is time-saving and easy-handling as it does not require the preparation of pre-condensate and the precise adjustment of pH during the condensation period. Based on our knowledge, most of the urea–formaldehyde microcapsules (UFM) for EPD reported were fabricated by traditional two-step methods. Few were carried out using the one-step method since the emulsifiers or protective colloids were limited to poly (ethylene-alt-maleic anhydride) (poly (E-MA)) [21], Gum Arabic (GA) [22], and polyvinyl acetate (PVA) [23]. Some of these protective colloids, such as poly (E-MA), cannot be used in the one-step method to prepare urea–formaldehyde microcapsules due to the resulting "hedgehog" morphologies [24] that will influence the optical behaviors when used for EPD. Furthermore, most of the products prepared by one-step method have the same problems including adhesion between the capsules, low optical transparency, etc.

Here we apply a new kind of protective colloid, sodium carboxymethyl cellulose (NaCMC), into the one-step UFM fabrication system. To the best of our knowledge, this is the first time that a water-soluble ionic derivative of cellulose, an abundant, physiologically harmless and biocompatible additive[25], is used as a stabilizer in the one-step system. Compared to the former products using GA as a protective colloid, the microcapsules prepared with NaCMC (see Fig. S-I) are more stable, transparent and smooth with better barrier properties. This method can be served as a basis for fabricating well-defined microcapsules for various applications including phase-changing materials, self-healing, and EPD systems, etc.

2. Experimental

2.1. Materials

Urea (NH_2CONH_2) and formalin (37% formaldehyde in water) solution was used as monomer and condensation agent, respectively. Additional wall-forming materials ammonium (NH_4Cl), sodium chloride (NaCl), and resorcinol (C_6H_4-1,3-$(OH)_2$), were purchased from Shanghai Lingfeng Chemical Regents Factory, China. Tetrachloroethylene (TCE) used as core material was purchased from Shanghai Resin Plant, China.

Gum Arabic (GA) and sodium dodecyl sulfate (SDS) were purchased from Shanghai Lingfeng Chemical Regents Factory, China. Sodium carboxymethyl cellulose (NaCMC) was CR grade product of Sinopharm Chemical Regent Co. Ltd., China, with an average degree of substitution (average number of carboxymethyl groups per glucose unit) of 0.6–0.8. Oil red was received from Tongling Road Chemicals Co., Ltd., Anhui, China. All Chemicals were used without further purification. Single-distilled deionized water was used in all experiments.

2.2. Preparation of urea–formaldehyde microcapsules

100 mL TCE was dyed using 0.20 g oil red and then kept in a sealed bottle for further use. Microcapsules containing a mixture of oil red and TCE were prepared by an in situ urea–formaldehyde microencapsulation procedure. The encapsulation method was adapted from that of our former studies [22,24] (protocol shown in Fig. 1). 100 mL of deionized H_2O was introduced into a 250 mL beaker at room temperature, along with different weight and kinds of protective colloids. The solid wall-forming materials of 2.50 g urea, 0.25 g ammonium chloride, 0.25 g resorcinol was added to the aqueous solution, and 2.5 g sodium chloride as electrolyte. After addition of the solid wall-forming materials, the pH was adjusted by addition of HCl solution from approximately 6.8 to 3.5. The encapsulated phase (TCE) was measured as 20 ml, and dispersed in the beaker at a agitation speed of 450 rpm for 20 min to form the oil-in-water (O/W) emulsions. After 20 min, the polycondensation reaction was started by adding 37 wt% formalin solutions and raising the temperature at a rate of 1 °C/min to a target of 55 °C. The reaction proceeded under continuous agitation with the temperature held at 55 °C for 4 h. The spherical-shaped microcapsules with proper mechanical strength were separated from aqueous solution by suction filtration (filter pore size is about 11 μm) and collected by containers.

2.3. Characterization of urea–formaldehyde microcapsules

Particle size distribution was performed based on our former statistical methods. Microcapsule size analysis was performed with an optical microscope (LV100POL, Nikon) and image analysis software (Motic image plus 2.0). Mean diameter was determined from data sets of at least 800 measurements.

Surface morphology and wall thickness of the microcapsules were observed using a scanning electron microscope (SEM, JSM-6360, FEI). Prior to being observed under the SEM, samples were covered with a gold layer.

Thermogravimetric analysis (TGA) was carried out on TA SDT-Q600, scanning from room temperature to 623.15 K with a scanning rate of 10 K/min under constant N_2 flow.

Yield (Y) of the microcapsules was defined as the proportion of the mass of the microcapsules obtained to the total mass of ingredients used. Before weighing, the microcapsules were washed several times with deionized water and air-dried.

To study the barrier properties of microcapsules prepared under different conditions in the atmosphere, 1.0 g (W) of washed and dried microcapsules were put into a tare bottle. Then the lid was opened and the bottle was put swiftly into an oven with a temperature setting of 50 °C. The samples were cured for the first setting time of 6 h to remove the absorbed water. The bottle was taken out, weighed and the net weight of bottle was subtracted when it cools down and this was recorded as W_1. The bottle without lid was put into the oven again and then the bottle was taken out at a time period of 1 h and weighed. The net weight of the bottle was subtracted and this was recorded as W_2. This procedure was repeated