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SHORT COMMUNICATION

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Synthesis and characteristics of microcapsules containing electrophoretic particle suspensions

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Abstract A microcapsule containing titanium dioxide (TiO_2) and halocarbon oil was synthesized via an in situ polymerization using urea, melamine, and formaldehyde (UM/F) as a wall material to examine its potential application as a microcapsule-based electronic ink display technique. Poly (sodium styrene sulfonate) was used as an anionic polymeric surfactant to stabilize a droplet of the suspension, and easily combined with the UM/F prepolymer through ionic adsorption. The microcapsules obtained had an average diameter and wall thickness of approximately 50 μm and 500 nm, respectively. The electrophoretic TiO_2 particles in the microcapsules responded to electric fields with a response time of few seconds.

Keywords Electronic ink · Microcapsule · Urea–melamine–formaldehyde · Nanoparticle

Introduction

Microcapsulation is an effective method to insert either the liquid or solid material into a microcapsule. Their shells (wall) protect, release, and/or cover the inner materials known as core materials. This technology, which is known as microencapsulation, has been widely adopted in many engineering and industrial areas such as cosmetics, pesticides, pharmaceutical and medical applications, foods, electrorheological materials, and carbonless copying paper [1–4]. However, compared with the microcapsules with a one-phase core (solid and liquid), there have been few studies on microcapsules with two or more phase microcapsules. Recently, a microcapsule-based electronic ink display technique, which uses the microencapsulation of an electrophoretic dispersion, was developed for a direct-view portable display technology [5–10]. Among the many recently developed displays, the electrophoretic display, which is one of the most promising new display techniques, has an important role on account of its potential in the field of mobile flat panel displays. The electrophoretic display has been developed to replace conventional paper owing to its reflective paper-like performance, lower power consumption, flexibility, lightweight, good contrast ratio, and wide-angle view. The electrophoretic display utilizes electrically charged pigment particles that are dispersed in a dyed dielectric medium. The optical contrast is achieved by moving the particle in a dyed medium under an applied electric field. However, the main disadvantage of an electrophoretic display is the lack of long-term stability of the electrophoretic particles as a result of the clustering, agglomeration, and lateral migration [11]. The microencapsulation technique can solve some of these negative aspects.

In this paper, electrophoretic particles with an average size of 200 nm TiO_2 (Dupont, R104) with hydrophobic surface characteristics as a core material were dispersed in a low dielectric medium. A charge control agent was also added to the nanoparticle suspension in the dielectric medium to improve the mobility of the suspended TiO_2 nanoparticles. Various materials have been used as the shell materials of microcapsules such as melamine–formalde-

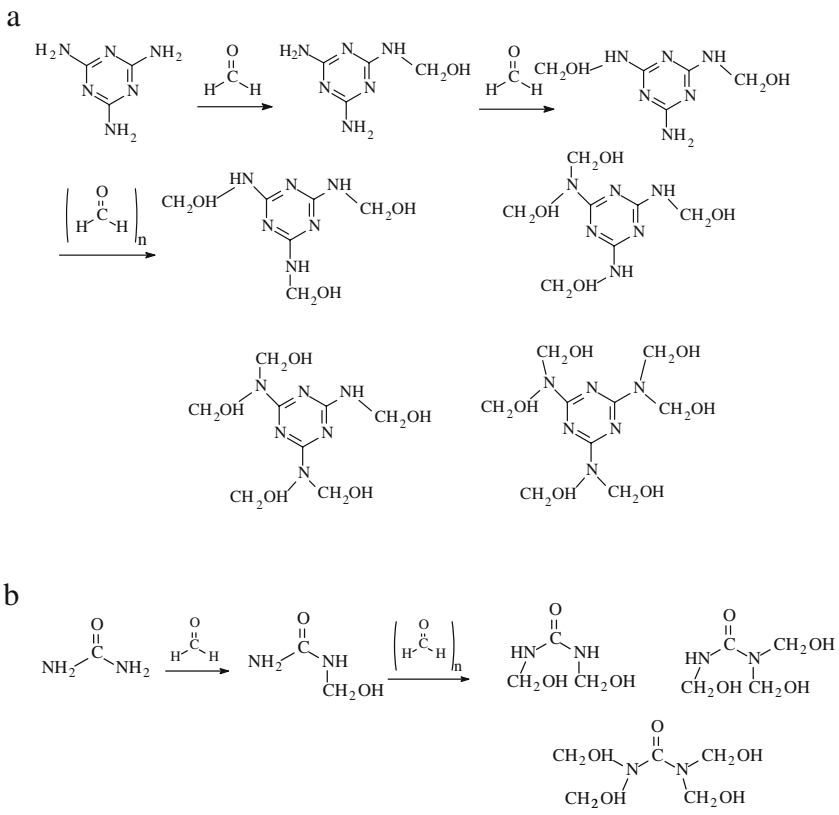

Fig. 1 Schematic of the methylolation reaction scheme of melamine and urea with formaldehyde

hyde [12–14], urea–formaldehyde [15–17], gelatin [18], polyurethane [19], and wax. For electrophoretic displays, the wall of the microcapsules requires not only the properties of a solid to retain its interior materials but also transparency such that the core can be observed during the migration of particles and be relatively inexpensive to produce. The UM/F resin was chosen as a wall material, which was prepared by an in situ polymerization [20, 21], occurring at the interface formed by dispersed core materials and a continuous phase. In addition, the response behavior of the TiO_2 nanoparticles in the microcapsules to an electric field was also characterized.

Experimental

Materials and sample preparation

As a dielectric dye solution, Oil Blue N (Sigma Aldrich, USA) and halocarbon oil (Halogenated Hydrocarbon Products, USA) were mixed together and stirred at 60°C for several hours. The mixture was cooled to room temperature and filtered. A 1.0 g of TiO_2 particles with 200 nm in diameter (DuPont, USA) was added to the dye solution containing 0.3 wt% of charge control agent (CCA), OLOA 1200 (Chevron, USA). The mixture was then sonicated using an ultrasonic generator (G2806, Kyungil Ultrasonic, Korea), which has a nominal frequency of 28 kHz, with a power of 600 W for approximately 20 min [22]. Emulsification and polymerization were performed sequentially in a 700 ml double-wall reactor. Two hundred grams of 10 wt% Poly(sodium styrene sulfonate) (PSSS) (Mw~200,000 g/mol, Aldrich, USA) aqueous solution was introduced in the reactor. Thirty grams of the prepared oil suspension was then poured into the PSSS solution with constant stirring, and the speed of agitation was increased gradually up to 350 rpm. For the wall materials of the microcapsules, 70 g of the prepolymer aqueous solutions including 12 g of melamine (Junsei

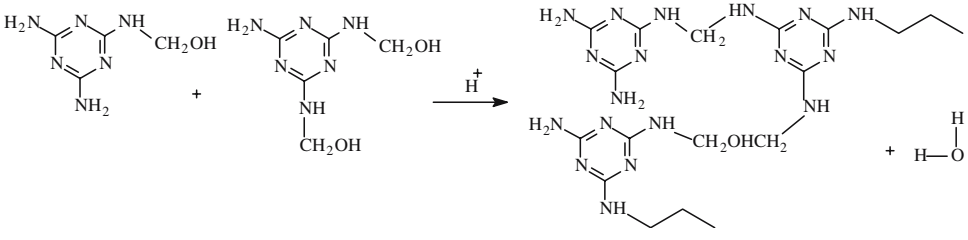

Fig. 2 Schematic of the condensation reaction scheme of melamine with formaldehyde

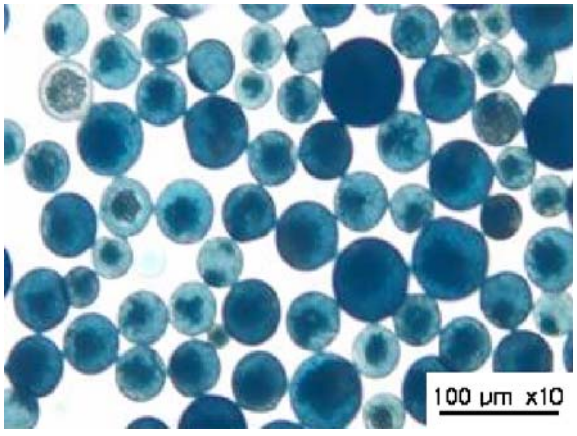

Fig. 3 Optical microscopy image of the microcapsules

Chemical, Japan), 6 g of urea (Duksan, Korea), and 18 g of formaldehyde (Daejung, Korea) were prepared at 60°C. The pH of this solution was adjusted to approximately 9~10 with the proper amount of a 10 wt% aqueous NaOH (Aldrich, USA) solution. The UM/F prepolymer, which changed from opaque to transparent, was added to the oil/aqueous phase emulsion. The pH of the mixture was adjusted to 4.5 with a 10 wt% citric acid (Aldrich, USA) solution at 60°C. After 4 h, the final microcapsule slurries produced were washed with deionized water to remove the unreacted chemicals.

Characterization

Images of the emulsion droplet and microcapsule were taken using optical microscopy (OM, Olympus BX51, Japan). Both the morphology and the wall thickness of the microcapsules as a function of the molar ratio of formaldehyde were investigated via scanning electron microscopy (SEM, Hitachi S-4300, Japan) at 15 kV of an acceleration voltage. The sample was gold-coated to minimize the charging effect. A simple electrophoretic display cell was fabricated, and both the color change and the response time of the display were investigated. It was made of two parallel, ITO-coated transparent electrodes with a 210-μm gap space, and the gap was filled by the microcapsules containing TiO_2 particles in a low dielectric medium. The electrophoretic migration of the TiO_2 particles in the capsules was monitored in different electric fields.

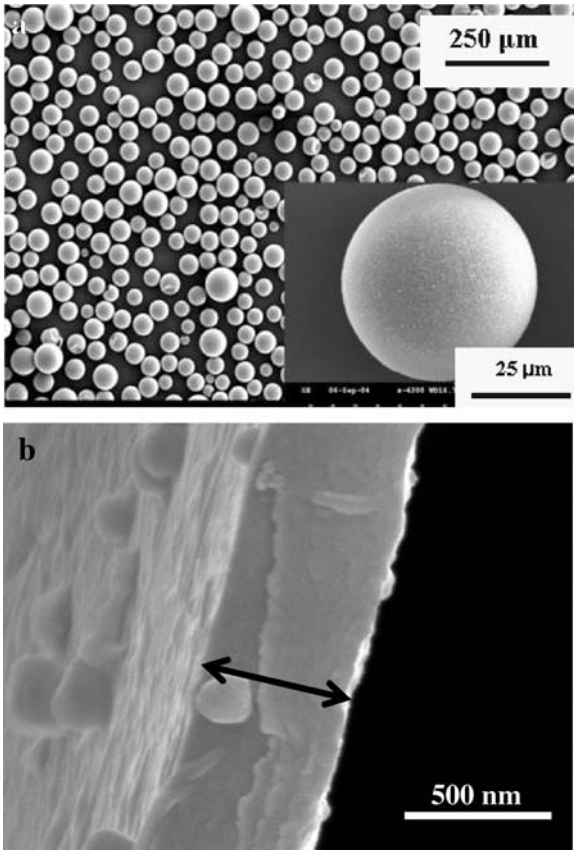

Fig. 4 SEM image of the microcapsule surface (**a**) and the wall structure (**b**)

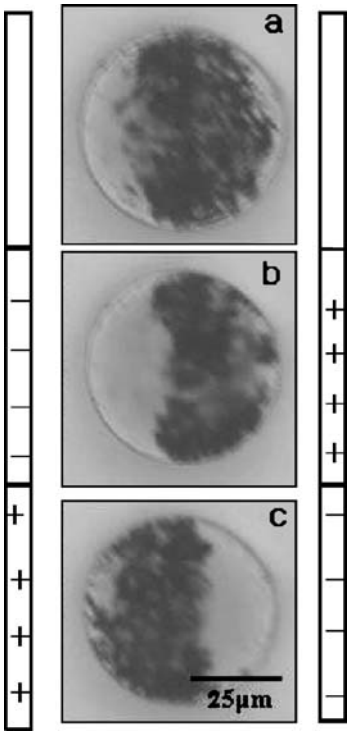

Fig. 5 Optical microscopy image of microcapsules under no electric field (**a**). Microcapsules under an electric field: E=+50 V/mm (**b**) E=−50 V/mm (**c**)

Results and discussion

Polymerization of the UM/F resin involved a two-step process: methylolation and condensation. Therefore, the proper mole ratio of urea, melamine, and formaldehyde and pH are important for the formation of microcapsules. The addition of formaldehyde to melamine and urea leads to a methylolation reaction, as shown in Fig. 1 (melamine), and a condensation reaction, as shown in Fig. 2. The surface morphology and transparency of the microcapsule wall affect the optical and electrical behavior of the electrophoretic display microcapsules. The smooth surface morphology and high degree of transparency of the capsules' wall are major factors for electrophoretic display microcapsules. In our previous work, melamine–formaldehyde resins were also utilized as wall materials to encapsulate polyaniline particles for electrorheological (ER) applications [13], in which the ER fluids are suspensions of polarizable particles dispersed in insulating liquids. They exhibit a rapid and reversible transition from a liquid-like to a solid-like state with a remarkable change in their rheological properties upon the application of an electric field [23–25]. It was confirmed that the melamine–formaldehyde resins were excellent materials to form capsules which can contain solid materials.

Figure 3 shows an OM image of the fabricated microcapsules. The black domains inside the microcapsules indicate the TiO_2 nanoparticles dispersed in the dyed oils inside the microcapsule. The wall of the microcapsules formed from the UM/F precondensates was found to be transparent. Therefore, the optical contrast achieved by the moving particles in the dyed medium under an applied electric field can be clearly identified [26].

Figure 4a shows SEM images of the microcapsule. The average size of the microcapsules is approximately 50 μm with a narrow particle size distribution. The surface of the fabricated microcapsules is smooth, which makes it suitable for examining the optical behavior of the microcapsules. Figure 4b shows the wall thickness of the microcapsules, which were fractured and dried previously to confirm a wall structure of approximately 500 nm.

Figure 5 shows the electric responses of the TiO_2 nanoparticles in the microcapsules. When an electric field was applied, the particles migrated to the opposite electrode [27]. Figure 5a shows a photograph of the microcapsules under no electric field. Figure 5b,c shows photographs of the microcapsules under a DC electric field (Figure 5b,c for +50 and −50 V/mm, respectively). The response time of TiO_2 nanoparticles was approximately 1 s. As another response for electric fields, the ER fluids have been extensively investigated [28]. It has been observed that in contrast to the particle migration of the electrophoretic phenomena, the ER fluids mainly form chains under an applied electric field with minor electrophoresis [29].

In conclusion, microcapsules containing electrophoretic particles and a dielectric medium were prepared using an in situ polymerization. The microcapsule walls polymerized with urea, melamine, and formaldehyde were found to be rigid and smooth. When an electric field (E=±50 V/mm) was applied, the TiO_2 nanoparticles responded rapidly with a 1 s response time.

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