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Microencapsulation of electrophoretic dispersion is one of the key steps in realizing the portable electrophoretic display technique, electronic paper. In this study, electrophoretic TiO_2 nanoparticles were uniformly dispersed in a dielectric medium of halocarbon oil and the TiO_2 based core material was emulsified using a polymeric surfactant of poly(sodium 4-styrene sulfonic acid) (PSSA). After the colloid particles were stabilized, the microencapsulation of the core materials was accomplished by the polycondensation of melamine/urea-formldehyde prepolymer. Average diameter of the microcapsules obtained was about 50 μm and their thermal stability was measured by TGA. The surface morphology of the microcapsule was dependent on the molar ratio of melamine/urea to formaldehyde and the water content.

Keywords: amino prepolymer; electrophoretic ink; microencapsulation; nanoparticle; TiO_2

INTRODUCTION

A flexible and portable thin film electronic display has great potential to be utilized in many applications such as wearable computer screens, electronic newspaper, electronic signs, and smart identity cards, and so

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on [1]. Especially, microcapsule-type electrophoretic display [2,3], using the electromigration phenomena of charged nanoparticles in dielectric medium, shows intrinsic bistability, high contrast and reflectivity as well as low power consumption and can be applied to many display devices. Commercially, E-Ink Corp. developed microcapsule-type electronic inks for high- and low-resolution displays, while SiPix produced electronic papers compatible with all display types. TiO_2 nanoparticles have been most widely used as electrophoretic particles due to their chemical stability and whiteness along with unique optical and electrical properties [4]. The electrophoretic dispersion is usually encapsulated to protect the active particles from environment or to prevent particle clustering, agglomeration and lateral migration [2,5], thereby extending the lifetime of the display device. Various wall materials for microencapsulation were reported such as melamine-formaldehyde, urea-formaldehyde, and gelatin-gum Arabic coacervate [6,7].

In this study, we used rutile TiO_2 nanoparticles as the electrophoretic core material and melamine/urea-formaldehyde resins as the wall material, respectively. TiO_2 nanoparticles dispersed in the dielectric oil droplets were encapsulated by *in-situ* polycondensation [8,9] of prepolymers of methylolated melamine and/or urea. By changing the compositions of melamine/urea-formaldehyde resins, we could control the cross-linking density and transparency of the wall and optimize the mechanical and optical properties of the microcapsules eventually. The effect of the water content during the methylolation on the stability of the final capsule was also investigated.

EXPERIMENTAL

Materials

TiO_2 nanoparticles (R-900) with 250–350 nm in diameter and dielectric medium (halogenated hydrocarbon oil, Halocarbon 0.8) were purchased from DuPont and Halocarbon Products Corp., respectively. As a surfactant, poly (sodium 4-styrenesulfonic acid) (PSSA) was obtained from Alco-Chemical and a charge control agent, polyisobutylene succinimide (OLOA), was purchased from Chevron. Melamine, urea, and formaldehyde (37% of aqueous solution) were purchased from Junsei Chemical and Aldrich. In addition, Oil Red O (Aldrich) was used as a red dye.

Microencapsulation

1.5 g of TiO_2 particles were added to 30 g of Halocarbon containing the red dye and OLOA. The mixture was milled in a ball mill and then

sonicated for 20 min to disperse the TiO_2 particles without aggregation. The prepared core material was emulsified in 200 g of 10 wt% PSSA aqueous solution in a 1 L of reactor with water jacket. When stable and uniform sized oil droplets were formed, melamine/urea-formaldehyde prepolymers were introduced into the reactor and *in-situ* polycondensation was performed on the surface of the droplets to encapsulate the core material at 60°C for 4 hrs in acidic condition (pH 4.5). During the prepolymer preparation, the molar ratio of melamine/urea to formaldehyde or the amount of deionized water to be added was varied to change the characteristics of final microcapsules. After the polycondensation reaction, the product was washed with deionized water several times to remove unreacted chemicals and dried in vacuum oven for further investigation. Wet or dried microcapsules were observed by optical microscopy (BX51, Olympus) and scanning electron microscopy (S-4300, Hitachi). Their chemical structure and thermal stability were investigated by both FT-IR (FTS 40 A, Bio-rad) and TGA (Q 500, TA Instrument).

RESULTS AND DISCUSSION

Chemical structure of the dried microcapsule was analyzed by an FT-IR, as shown in Figure 1. FT-IR spectrum of the microcapsule in Fig 1(a) displayed characteristic peaks from TiO_2, (Ti−O stretching at 400–800 cm^{-1}), halocarbon (C−Cl stretching at 970 cm^{-1}, C−F stretching at 1100 and 1250 cm^{-1}), and melamine/urea-formaldehyde resins (N−H stretching at 3300 cm^{-1}, C−H stretching at 2900–3000 cm^{-1}, C−N absorption at 1330 cm^{-1}, C−O stretching at 1180 cm^{-1}). Therefore, we can confirm that the microcapsule is consisted of TiO_2 particles dispersed in halocarbon as core and amino resins encapsulating the core. The presence of TiO_2 particles in the microcapsules is clearly demonstrated by OM photograph in Figure 2, where the inorganic particles appear darker. The diameter of the microcapsules was from 40 μm to 100 μm and its globular shape is due to the protection of emulsion droplets by PSSA during *in-situ* polycondensation to form wall. The molar ratio of melamine/urea (MU) to formaldehyde (F) was varied and its effect on the surface morphology of the microcapsule was investigated by SEM. In general, melamine-formaldehyde resin is more transparent than urea-formaldehyde, but its higher degree of methylolation (the increase in the cross-linking sites) increases brittleness. Thus, we used both melamine and urea for the fine tuning of the optical and mechanical properties in this study. As the molar ratio of MU to F decreased, the surface of the capsule became smooth (Figure 3(a) and (b)). However, when the

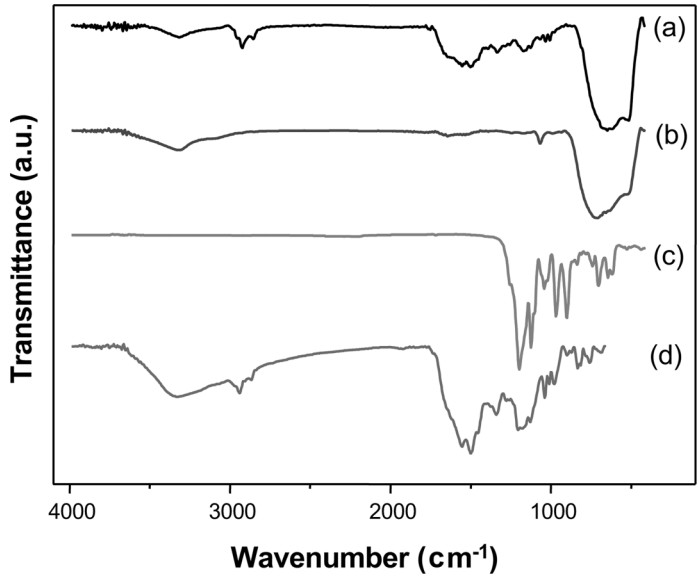

FIGURE 1 FT-IR spectra of (a) dried microcapsule, (b) TiO_2 (c) halocarbon oil, and (d) melamine/urea-formaldehyde resin.

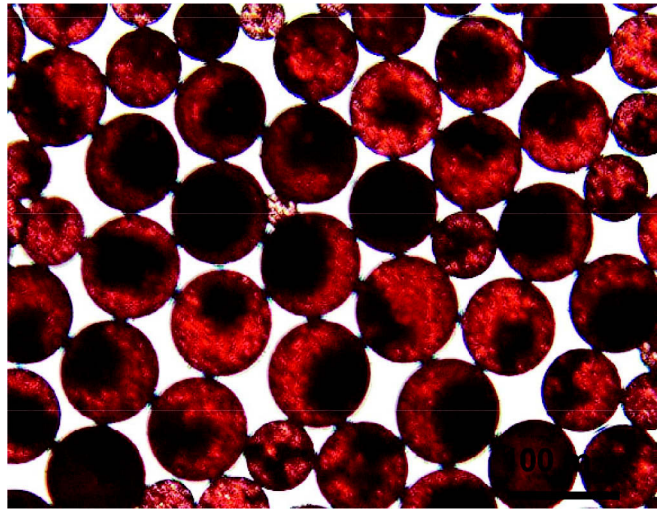

FIGURE 2 OM image of microcapsules of TiO_2 suspensions before drying.

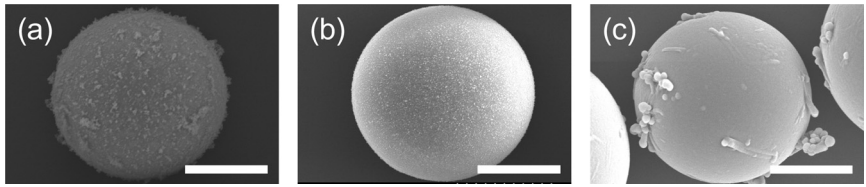

FIGURE 3 SEM images of dried microcapsules with different molar ratio of melamine/urea (MU) to formaldehyde (F): (a) MU/F = 0.50, (b) MU/F = 0.33, (c) MU/F = 0.25 (scale bar = 20 μm).

concentration of F is too high compared to that of MU, some juts were observed on the surface of the capsule, as shown in Figure 3(c). Kim *et al.* [3] reported similar surface morphology when the reaction time for polycondensation became longer than a certain value. We believe juts were formed because there were too much amino resins available to encapsulate oil droplets. Therefore, both the molar ratio of MU to F

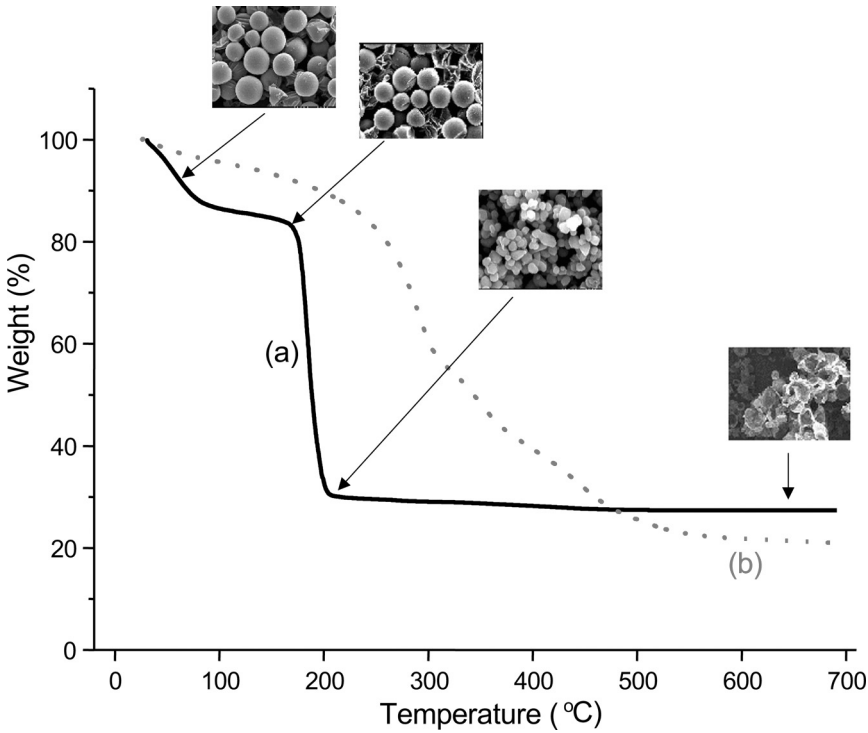

FIGURE 4 TGA thermograms of (a) microcapsule and (b) melamine/urea-formaldehyde resin.

and the reaction time are considered to be important to obtain well-encapsulated particles. Meanwhile, the amount of water was also changed during the preparation of pre-polymer (F/MU = 2, constant). The stability of the microcapsules after drying was dependent on the amount of water. As the concentration of the pre-polymer was increased, polycondensation reaction for wall formation went well and the stability of the microcapsule during drying was also improved. The thermal stability of the microcapsule was monitored by both TGA and SEM in Figure 4. The sample was heated from room temperature to 700°C at the rate of 20°C/min. At the first stage, gradual weight loss was observed due to the evaporation of the residual water. However, most microcapsules were stable at 65°C without breakage and many microcapsules at 170°C. The abrupt weight loss between 170°C and 200°C is because of the collapse of microcapsules and loss of the dielectric medium. Melamine/urea-formaldehyde resin was thermally degraded below 500°C, and TiO_2 nanoparticles remained at 700°C.

CONCLUSION

Electrophoretic TiO_2 nanoparticles dispersed in the dielectric oil droplets were encapsulated by *in-situ* polycondensation of prepolymers of methylolated melamine and/or urea.

The surface morphology and stability of the microcapsules were dependent on the molar ratio of melamine/urea to formaldehyde and the water content during preparation of prepolymers. At adequate concentrations of melamine/urea and formaldehyde (MU/F = 0.33 without water), we obtained stable microcapsules with smooth surface. The electrical response of the microcapsules containing modified TiO_2 nanoparticles under electric field is being studied.

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