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Investigation of a Light-Thermal Sensitive Imaging System Based on the Microcapsule Technique

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Abstract. *A silver-free photothermal sensitive imaging system which captures a photo image with microcapsules and can be thermal processed has been investigated. The photosensitive functional compounds are encapsulated with the interface polymerization method. Scanning Electron Micrographs show that the shape and diameter of the resulting microcapsules are comparable with silver halide grains under the condition of a shear velocity at 7000 rpm and a protecting colloidal concentration of 4.5% polyvinyl alcohol. Microcapsules with size smaller than 1 μm have been synthesized, which can act as basic imaging cells with excellent resolution compared with silver halide materials. The infrared spectra indicate that the wall of the microcapsule is composed of polyurea. The thermal response of the wall material detected with the thermal gravimetric and differential scanning calorimetry technique show that the optimal thermal development temperature is about 135 °C. Image density research confirms that the mechanism of image formation may be ascribed to the penetrability variety of the microcapsule under given thermal condition after exposure.* © *2007 Society for Imaging Science and Technology.*
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INTRODUCTION

Microcapsules are a kind of function-controllable material in which liquid droplets, solid particles, or gas bubbles are coated with a continuous film of synthetic or natural polymers. For years, microcapsules have been receiving much attention for both fundamental scientific and practical reasons.[1–5] Scientific interest is based on the possibilities for designing and manipulating novel functional compounds, while practical interest arises from possible applications in materials separation, controlled release, etc.[6–8] Recent research activities directed towards image recording materials here also focused on the microcapsule recording system.[9] A microcapsule image recording system may be cheap and friendly to the environment compared with the traditional silver recording films. There already are some patents covering microcapsule materials and direct-thermal image recording products have appeared in the market.[10,11] However, the technique for synthesis of information recording microcapsules has not been thoroughly investigated and the microcapsules size, usually 10–100 μm, is not comparable with that of the silver halide microcrystal which is about 1 μm. In addition, a further problem is the design of photosensitive microcapsule systems.

In this article, a light-thermal sensitive microcapsule system which can record a light image is introduced and the synthesis technique is investigated. In addition, the mechanism of image production is also discussed.

EXPERIMENT

The colorless dye precursors comprised of ODB-2 (Yamamoto Chemicals, Inc., 15 g) and CK-16 (Longsheng Co., 10 g) were put into a beaker, then mixed with ethyl acetate 20 g as solvent, with UV7600 (Aliphatic urethane acrylate, Nippon Synthetic Co., Ltd., 10 g) and TMPTA (trimethylolpropane triacrylate, 8 g) as photocuring compounds. The mixture was heated to dissolve. When the solution was cooled to room temperature, D110N (Mitsui Takeda Chemical Co., Ltd., 60 g) as one of the microcapsules wall forming materials, as well as the photoinitiator was added under safelight. The oil phase or the photosensitive core of the microcapsule was thus obtained.

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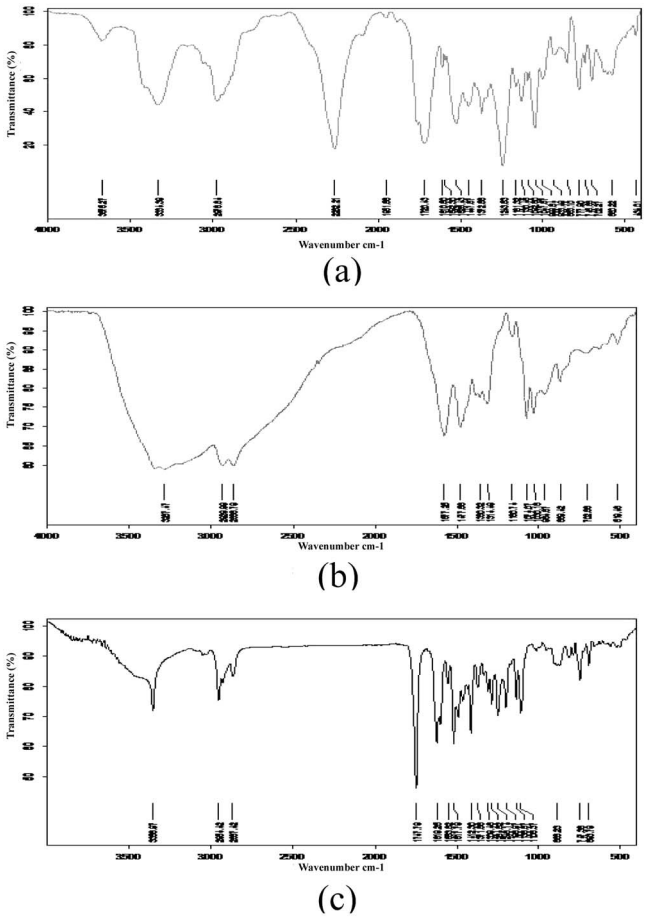

Figure 1. IR spectra of (a) D110, (b) microcapsule sample, and (c) the dye precursors of ODB-2.

To encapsulate the core compound, the oil phase was put into aqueous solution comprising 400 ml polyvinyl alcohol (PVA) 224 and 20 g 7# (3-[N-Dodecyl-N,N-dimethyl-aminium]-2-Hydroxyl-propylsulfonate), (80 g/l) surfactant at 25 °C. The mixture was emulsified with a high velocity shear mixer at 3000–9000 rpm. Diethylentriamine, 8.0 g in 500 g water, was added. The emulsion was heated to 60 °C, and emulsified for another 30 min, then stirred at 700 rpm using an overhead stirrer for 3 h at 60 °C. It was finally deposited overnight at room temperature to complete capsule formation. At the same time, the developer dispersion include HBB (hydroxybenzyl benzoate), TGSA (bis(3-allyl-4-hydroxyphenyl)sulfone) prepared by a similar method was obtained. During the interface-polymerization process, the high velocity shear is a significant step to control the diameter distribution of the microcapsules.

To obtain a solid mixture, the microcapsules (12% solid, 22 g) HBB developer dispersion (14% solid, 24 g) 12# (Sodium 1,2-di-(octyloxycarbonyl)ethane sulphonate, 80 g/l) surfactant 1 g), and 0.5 g glycerin were mixed thoroughly. The *p*H was adjusted to 8.0. The mixture was coated onto a 175 μm blue polyethylene terephthalate film with a no. 250 bar and dried at 50 °C to obtain the light-thermal sensitive recording material. The dry thickness was measured as ~21 μm.

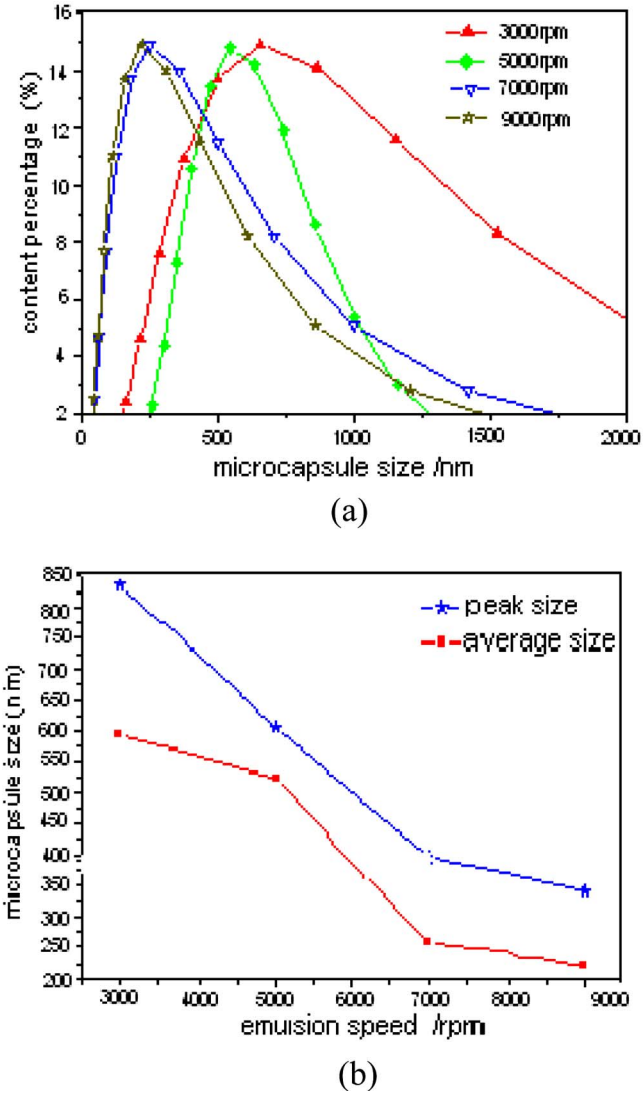

Figure 2. Relationship between particle diameter distribution and the shear velocity. (a) The diameter distribution of microcapsules. (b) The peak size and average size of the microcapsule distribution at 3000, 5000, 7000, and 9000 rpm.

The mean diameter and the particle size distribution were determined using a Coulter counter. The IR spectra were obtained with a Nicolet impact 400D infrared spectrometer. Differential scanning calorimetry (DSC) was performed using a SSC 5200H instrument in which samples of approximately 5 mg each were heated at the rate of 10 °C/min up to 350 °C. Thermal gravimetric (TG) analysis for microcapsules were performed by using a TG-DTA 2000S instrument. Samples of approximately 6.0 mg each were heated to 670 °C at a rate of 10 °C/min. Scanning electron microscopy (SEM) was performed by using a Hitachi S-4200 electron microscope.

The light-thermal sensitive recording material was exposed by mercury-arc lamp at 43 cm distance; the exposure times were 10, 30, 50, 70, 90, and 110 s, respectively. The recording material samples after exposure were heated at 100 and 110 °C for 3 s and the resulting transmission optical densities were measured by densitometer.

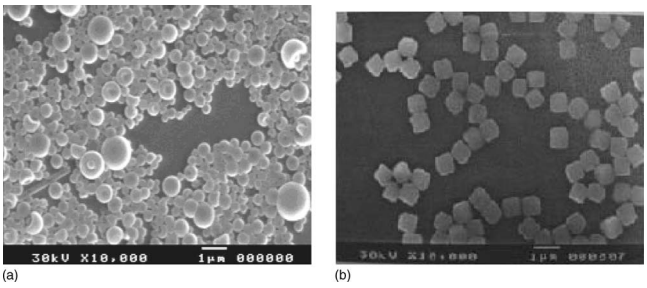

Figure 3. Comparison between the SEM of (a) microcapsules synthesized in our experiment and (b) the traditional silver halide cubic microcrystals.

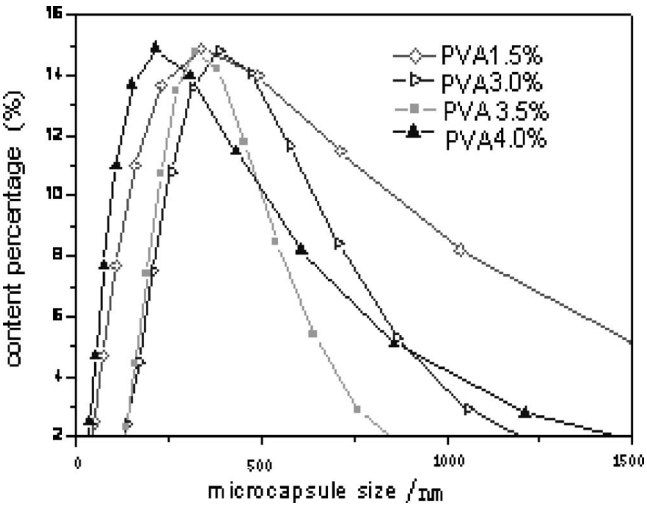

Figure 4. Relationship between particle diameter distribution and the concentration of PVA.

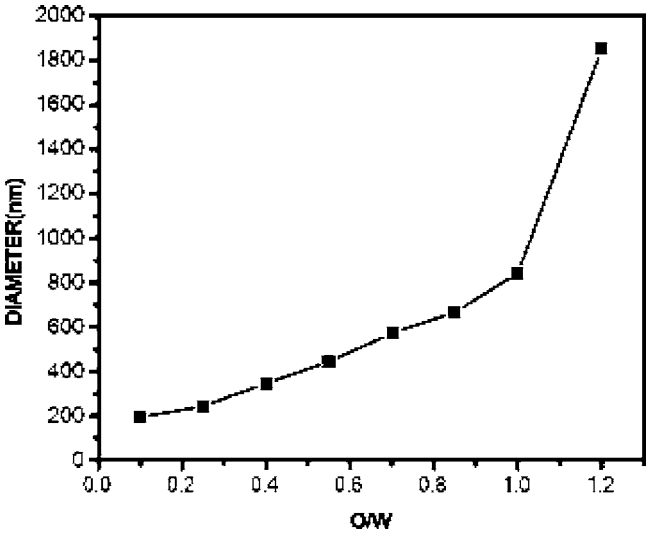

Figure 5. Average particle diameter against the O/W ratio.

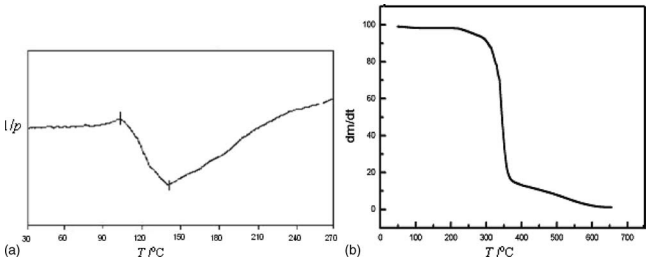

Figure 6. Thermal analysis of the microcapsule synthesized in our experiment: (a) the DSC plot and (b) the TG plot.

RESULTS AND DISCUSSION

Microcapsules Structure

Compared with the spectra of D110 in Fig. 1(a), the IR spectra of the microcapsule in Fig. 1(b) shows an increase in the intensity of the absorption bands at 1647–1540 cm^{-1} for the CO stretch of urethane and at 3322 cm^{-1} for the N-H stretch. At 2276 cm^{-1}, there has been a decrease in the NCO absorption band. The N-H stretching vibrations at 3322 cm^{-1} indicate the formation of strong hydrogen bonds on the wall membranes. All the spectra indicated the completion of wall polymerization from the decrease of the NCO absorption band and an increase in the N-H and CO absorption bands. When compared with the IR spectra of ODB-2 in Fig. 1(c), it shows that a similar absorption band structure of ODB-2 has appeared after polymerization. These comparisons confirm that wall membranes of the microcapsules are polyurethanes into which ODB-2 of the dye precursors has been encapsulated.

Effect of Shear Velocity and Protecting Colloidal Concentration on the Particle Size Distribution

Figure 2 shows the relationship between particle size distribution of microcapsules and the shear velocity during polymerization process. The diameter of the microcapsules may be in the range of a few hundred nanometers, owing to adequate vigorous agitation. When sheared at 3000 rpm, the microcapsule size shows the widest distribution. Its plot has a peak at 837 nm are an average size of 595 nm. With the increase of dispersion energy at higher shear velocity, the average size decreases, and the uniformity increases. As seen in the plot for 7000 rpm shear, the peak size and average size change to 384 and 250 nm, respectively, which is similar to the result at 9000 rpm. Small particles form much larger specific surface areas than larger ones, and the small particles can also produce highly controlled and sustained release profiles of the core material. Therefore, the particle size distribution can be a very important factor with respect to the penetrability of the microcapsule wall, because a narrow distribution indicates the formation of many small particles, which create a larger surface area than do large particles. Surface morphologies of the microcapsules are shown in Fig. 3, and the average particle size comparison between microcapsules obtained with our technique and traditional cubic silver halide microcrystals are presented. The particles in Fig. 3(a) were prepared by stirring emulsions vigorously at 7000 rpm. Over 60% of all the microcapsules are in the size range of 0.3–1.1 μm. The diameter of the microcapsule obtained at 7000 rpm is comparable with that of the silver

Table I. Image density at different exposure times and thermal developing temperatures.

T (°C)	t (s)						
	0	10	30	50	70	90	110
100	1.29	1.01	1.15	1.06	1.1	1.04	0.71
110	1.6	1.3	1.44	1.36	1.38	1.3	1.12

halide crystals. So when the microcapsules are controlled to be of uniform size during polymerization, a high resolution comparable to that of traditional silver salt films can be obtained for information recording.

In Fig. 3(a), the particle dispersion is relatively good in that over 85% of the particles were below 1.1 μm. However, agglomerate formation is also seen in the samples. To increase the lubricity of the particle, the protecting colloidal plays an important role. Figure 4 presents the relationship between protecting colloidal concentration and microcapsule size distribution when sheared at 7000 rpm. As PVA concentration increases, the peak size firstly increases and then decreases. With PVA at 4.5%, the particle size has a uniform distribution and its peak is at 340 nm. PVA can act not only as protecting colloidal but also as surfactant. The trend in particle size distribution can be attributed to the interplay between the two functions of PVA during microcapsule formation. In our experiment, the concentration of 4.5% is used to obtain uniform and well-lubricated particles.

In addition, the ratio of oil and water phases in the synthesis process can also affect the particle size distribution. We have monitored the relation between O/W ratio and the particle average diameter when sheared at 7000 rpm and PVA 4.5%. From Fig. 5, it can be concluded that the larger the O/W, the bigger the particle diameter is. Before the ratio reaches to 1.0, the particle diameter increases nearly linearly, but as the ratio approaches 1.2, the diameter increases more rapidly. We infer that when the O/W ratio is larger than 1.0, we obtain water in oil rather than oil in water microcapsules.

Thermal Properties of the Microcapsules

To act as information recording media, the thermal properties of microcapsules prepared in our experiment are important. In Fig. 6(a), the permeability coefficient, P, of the microcapsules is analyzed as a function of temperature by DSC. As is clearly observed, the permeability coefficient changes in value between 100 and 200 °C. The values of P were highest below 135 °C, considered to be the melting temperature of the microcapsules, although they change rapidly depending on temperature between 90 and 140 °C. On the other hand, above 135 °C, the value of P is low and the values change slowly depending on temperature between 135 and 200 °C. This result shows that the release character of microcapsule can be controlled thermally.

TG diagrams of these microcapsules are shown in Fig. 6(b). Weight loss of each sample also verifies the formation

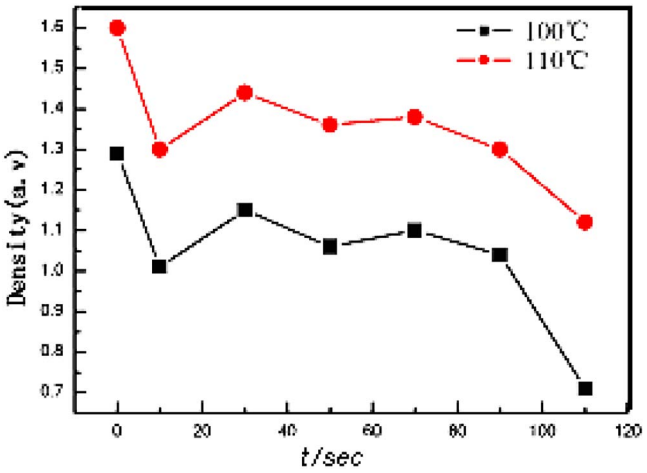

Figure 7. Image density of the light-thermal microcapsule media vs exposure time for thermal processing at 100 and 110 °C.

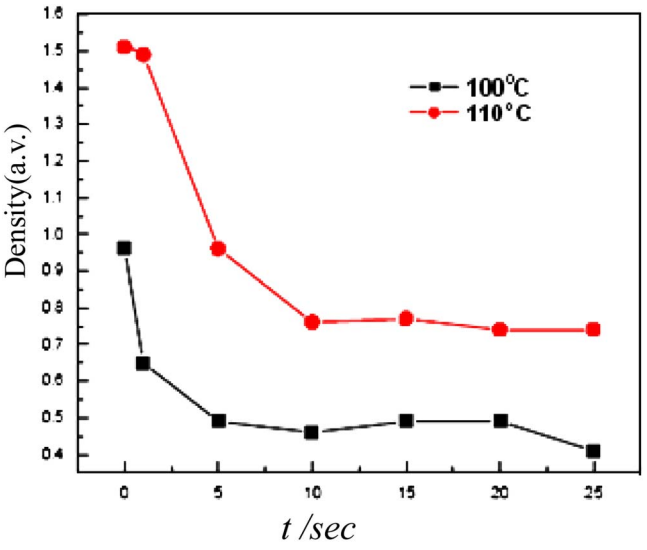

Figure 8. Image density of the oxygen-scavenged microcapsules vs exposure time when thermal processed at 100 and 110 °C.

of microcapsules with high thermal stability. The microcapsule sample undergoes a sudden and dramatic change above 350 °C. From the TG result, we conclude that the thermal properties of the polymer wall membrane are stable at room temperature and throughout the melting temperature range from 100 to 200 °C. This result defines the regime of practical usage of the microcapsules for light information recording.

Light-Thermal Information Recording Properties

The light-thermal recording material prepared in our experiment was exposed and processed. The optimal density of the unexposed area is higher than that of the exposed area, which is proof of successful recording of light-thermal information by our technique. Accordingly our microcapsule media the relationship between exposure time and image density of the recording material is shown in Table I and Fig. 7.

From Table I and Fig. 7, we can conclude that the density of the exposed area decreases compared with the unexposed area. The reason is that when the recording material is exposed by mercury-arc lamp, the photocurable compounds in the microcapsule solidify and the penetrability of the microcapsule decreases, so it becomes more difficult for the developer outside the microcapsule to penetrate the microcapsule wall and next with the dye precursor in the cured core after exposure. In the unexposed area, the penetrability of the microcapsules is unaltered and they react according to the principles inferred from DSC and TG analysis. The developer can transfer into the unexposed microcapsule and react with the core to form image at given development temperature. Figure 7, also shows that the density of unexposed or exposed areas developed at 110 °C is higher than that at the lower temperature (100 °C), which implies a higher penetrability of the microcapsule wall at the higher temperature, consistent with the DSC analysis result.

From Fig. 7, we also find that the density does not change with a monotonic trend as the exposure time increases, and there is even a density increase when exposure time changes from 10 to 30 s, while a density fluctuations occur with exposures from 50 to 110 s. When it comes to the practical information recording, the microcapsule material with such a behavior pattern cannot be used directly, as the increase from 10 to 30 s would significantly impact the practical use. The density variance is attributed to the quenching effect of oxygen molecules, which exist in the microcapsule during microcapsule synthesis, on the initiating agent excited by UV light. To scavenge oxygen, triethanolamine (6.5 g) is put into the oil phase, and microcapsules are synthesized by the same technique. The relationship between exposure time and image density of the oxygen scavenged microcapsule are shown in Fig. 8. For exposure times of 1, 5, 10, 15, 20, and 25 s.

In this case, the image density versus exposure time shows a monotonic variance trend, and the densities from 5 to 25 s are almost the same. This result implies that the light information recording properties of the oxygen-scavenged microcapsules are consistent and they can be used in practice.

CONCLUSIONS

The polyurea microcapsules containing light hardenable compounds are prepared by interfacial polymerization. The size distribution of the resulting microcapsules has been analyzed under different conditions of shear velocity, protecting colloid concentration of PVA, and O/W ratio. Some optimal parameters are obtained and the microcapsules with diameter smaller than 1 μm synthesized. From DSC and TG results, we conclude that polyurea microcapsules had higher thermal stability and the release character can be thermally controlled. Based on these properties, an individual light-thermal microcapsule acts as a basic imaging cell to record light information in our media. The image density as a function of exposure time and developing temperature confirms that the light-image reproduction may be ascribed to the variability of penetrability of the developer material through the microcapsule wall under given thermal conditions after exposure. Oxygen-scavenged microcapsule material is required for practical use. As the size of the microcapsules can match that of silver halide crystals in the commercial films, the resolution character of the image system should be excellent. At the same time, a film employing this microcapsule technology should be cheap and friendly to the environment.

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