Thermal Stability and Decolorization Property of Cationic Photoinitiated Color Forming Microcapsule Material

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Core-shell structured microcapsule with 0.44 µm diameter had been prepared by encapsulating the cationic photoinitiator and fluorane dye as photo-sensitive color-forming ingredients. The encapsulation ratio was detected as about 61.6%. The shell was thermal stable below 270 °C. After UV exposure for 20 s, the color-forming image density had been increased from 0.1 to 0.75. Decolorization property had been observed that the higher the temperature was, the more decrement the image density decolorized. The density decayed from 0.74 to 0.23 in just 5 min at 180 °C. It was proposed that the higher temperature influenced the decolorization process through competitive procedures. One procedure was the thermal decomposition of cationic photoinitiator to heighten color image density, and the other was to destroy the carboxy bonds in the color-formed fluorane dyes after thermal energy transmitted through phase-changed microcapsule shell. It was concluded that the latter one played a more significant role under higher temperature above 140 °C, and performed the decolorization property.

Keyword: decolorization, thermal stability, cationic photoinitiator, microcapsule

1. Introduction

Photoimaging technique such as photolithography, computer driven pattern formation, 3D machining, and so on, have played more and more important roles in modern manufacturing industries. The photoimaging procedure can be manipulated with high accuracy, which is determined by the resolution of the exposure source including laser and conventional lamps. The basic feature in such technique is involved with the photoinitiator and photosensitizer, which can be excited for chain reaction to form photopolymer. H. Ito et al. had reported that the acid could be amplified by combining acidolysis polymer and cationic photoinitiator which generated acid upon radiolysis [1]. Such reports had been rapidly noticed and widely accepted as key point for photo-polymerizing negative or positive tone [2-3]. Novel photoinitiators including free-radical and cationic types have widely been investigated in order to acquire higher initiating efficiency [4-5]. Besides of the photoimaging application, photo-initiation and photo-polymerization operated in small volume scale had the advantages for synthesizing multi-stimuli responding functional materials with high spatial resolution in three dimensions. Beebe et al. introduced novel approach by combining lithography, photopolymerization and microfluidics to create functional components, and PH-sensitive hydrogels of different shapes and sizes was simultaneously integrated into microfluidic channel after UV-exposure through masks [6]. B. Cumpston et al. reported a class of À-conjugated new
initiators that enhanced two-photon sensitivity in small volume with the ultra-limit of order $\lambda^3$ [7]. Encapsulating cells within hydrogels for biomedical applications was obtained by repeatedly photo-crosslinkage using pulses of UV light defined through a transparency mask, when prepolymer solution containing cells was flowed through a microfluidic device [8]. Micro-encapsulation technique can also be applied under such processing procedure. By UV irradiation, Choi et al. triggered polymerization of NIPAM monomer in the thin microcapsule shell membrane, and thermal sensitive function obtained [9]. Optical-responding function had been authorized by photoinitiators. Since microcapsule can be used as reactors in small scale, the cationic photoinitiator was encapsulated to utilize its acid-photolysis capacity, and color-formation function was obtained in this paper. The thermal stability and decolorization property had been observed and focused to discuss.

2. Experimental

2.1. Optical-sensitive Microcapsule Core Material

The photosensitive color-forming composite was consisting of IHT-PI 430, which was a type of colourless liquid triarylsulfonium hexafluorophosphate cationic photoinitiator mixed with propylene carbonate at the ratio of 50 wt%, and ODB-2 with color-forming group of lactone ring. The molecular structure was shown in Fig. 1.

The ODB-2 of 2 g solved in acetic ether with weight ratio of 10 wt%. After that, the IHT-PI 430 of 20 mL or 15 mL was mixed, respectively.

2.2. Microcapsule Shell Material

To achieve enough mechanical stability, the microcapsule shell should be compact polymer. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), which had two isocyanate groups at different molecular terminals, was selected to form 3-dimentional polymer. The polycondensation was reacted between the tetraethylenepentamine (TEPA) and IPDI, with weight ratio of 5 g to 20g. The polymerization scheme is present as followed.

2.3. Microcapsule Preparation

The interfacial polymerization technique was utilized to form microcapsule. The optical-sensitive core material and IPDI were mixed together as oil phase, and then dispersed into 7 wt% PVA deionized water solution. The mixture was stirred simultaneously at 2,000 rpm. After mixing procedure, the shearing velocity was held at 7,000 rpm for 10 min. The shearing instrument had emulsified the oil phase from continuous form to small droplets. Betaine of 7 mL (80 g/L in deionized water) was injected as surface active agent to reduce the potential energy in the oil/water interface. The shell polycondensation reaction was controlled at the condition of 6,000 rpm and 60°C for 4 h.

The obtained emulsion was centrifuged, and then the isolated microcapsules were

![Figure 1. (a)IHT-PI 432 (CAS NO: 104558-95-4). (b)ODB-2 (C$_3$H$_6$N$_2$O$_3$, CAS NO: 89331-94-2).](image-url)
washed by vacuum filtration. Dried sample was stored in darkroom at room temperature for further investigation.

2.4. Measurement of Cationic Photoinitiator Color Forming Microcapsule

The granularity of microcapsule was determined by Malvern Mastersizer 2000 instrument. Its morphology and structure was observed by TEM (Transmission Electron Microscope, JOEL, JEM2010). The differential scanning calorimetry was performed by NETZSCH DSC200-F3 instrument with heating rate of 10 °C/min.

The microcapsules, dispersed in 10 wt% PVA solution, had been coated on acetate film with the thickness of about 12 µm. Light source was high pressure mercury lamp. X-Rite 504 spectrodensitometer was operated to detect the reflection spectra intensity, and quantitatively computed the color-forming property as image density.

3. Results and Discussion

3.1. Microcapsule Structure

The microcapsule had uniform size around 0.44 µm, as shown in Fig. 3. The long trailing edge in the distribution curve higher than the 0.44 µm peak was ascribed to the Ostwald pipening process. The previously indicated oil droplets had aggregating trend to compose bigger oil particles, in order to lessen the interfacial potential energy.

Core-shell structure was micrographic detected in Fig. 4. The internal-external surface of the shell was regularly smooth. Also, it should be noticed that the thickness of the shell was isotropic. This implied that the emulsified oil droplet had been kept as sphere shape during shell forming process, and the IPDI molecules isotropic diffused from droplet inner to the oil/water interface. The polyurea polycondensation reaction was uniformly progressed. The shell thickness was about 32 nm, and the ratio of the effective core volume to the whole microcapsule was calculated as about 61.6%. Functional ingredients could be efficiently encapsulated.

3.2. Microcapsule Thermal Character

As composite material, the thermal response was determined jointly by the shell and the core of the microcapsules. DSC curve was present in Fig. 5.

Figure 3. Microcapsule diameter distribution curve.

Figure 4. TEM micrograph of the synthesized core-shell structured microcapsule.

Figure 5. DSC curve of the microcapsule material.
The transition point of the microcapsule shell was at 129 °C, and the decomposition process started from 270 °C correlated to the heat release peak at 270, 316, 383, 531 °C respectively. When thermally developed lower than 270 °C, the absorbed heat energy had been converted to the deformation of the molecular bonds in the shell polymer. The shell was thermal stable below 270 °C.

3.3. Color-forming Evaluation of Cationic Photoinitiator Microcapsule

The color-forming property of the coated microcapsule film was displayed in Fig. 6 (a). After exposed for 20 s, the image density had been 0.75 for 25 mL photoinitiator encapsulated, and been 0.69 for 15 mL in Fig. 6(b). Lower photoinitiator containment caused lesser image density increment.

When it comes to the photochromic mechanism, the color-formation is based on the reaction between the protons H+ photolysis of the IHT-PI 430 photoinitiator molecule and the lactone ring of the ODB-2. The energy level of the ODB-2 had been modified and the absorption range was transferred, so the color of the microcapsule changed from white to pitchy as shown in Fig. 6(a).

The initial image forming process was similar for the two encapsulating concentration, and the difference occurred after exposure of 15 s. Rising trend kept further for more photoinitiator encapsulated. This was ascribed to the photoinitiator consumption that the H+ generation in higher photoinitiator concentration sample could react further for color forming than the less one.

3.4. Decolorization Property of the Exposed Microcapsules

The photoinitiated color-formed samples were stored in darkroom at room temperature, and the image density was monitored daily. It was interest that the image density was unstable, and decolorization had been presented in Fig. 7(a). The more the photoinitiator concentration was, the higher the decolorization extent appeared.

The reason of such a variance was evaluated and estimated that it was relied on such a pathway, that the unstable structure of the carboxylic group, formed by the reaction between proton H+ photolysis of photoinitiator and lactone ring in fluorine dyes, would be reversible to be decolorized as shown as Fig. 7(b).

![Image](image_url)

Figure 6. (a) The color-forming pattern on the coating film after sufficient exposure. (b) Relationship between image density and exposure time of microcapsule contained with different concentration of cationic photoinitiator.

![Image](image_url)

Figure 7. (a) The decolorization property of the cationic photoinitiator microcapsule, presented as the relationship between image density and time under room temperature after exposure. (b) Reversible color-forming and decoloring scheme.

Such a decoloration process was affected by thermal environment. Higher temperature had accelerated the decolorization reaction, and the image density decayed from 0.72 to
0.23 in just 5 min at 180 °C. But the trend was contrary at lower temperature, and there had even rising image density variance when thermal developed at 60, 80, 100 °C.

This was ascribed to the competition that the photoinitiator appeared further decomposition under thermal temperature of 60-100 °C, but did not access the decolorization energy to destroy the carboxy bonds in the color-formed fluorine dyes.

3.5. Thermal Stability of the Unexposed Microcapsules

As seen above, the cationic photoinitiator could be decomposed to generate H⁺ proton by thermal processing at certain temperature. Then, a question had to be put forward about the thermal stability at room temperature for the unexposed microcapsules.

The unexposed microcapsule film was stored in darkroom at room temperature. Fig. 9(a) gave the image density variance in a period of 35 days. There had no remarkable increase of image density. But when higher temperature thermally developed at 120 °C for 4 h, the image density had increased from 0.1 to 0.24, and at 180 °C to 0.27. The thermally decomposition of photoinitiator had affected the image density in an extent of maximum increment only 0.17.
4. Conclusion

Core-shell structured microcapsule with 0.44 μm diameter had been prepared with interfacial polycondensation technique, in which cationic photoinitiator and fluorane dye was encapsulated. The polycondensation reaction to form polyurea shell was isotropic operated in the oil/water interface. The encapsulation ratio was detected as about 61.6%. The shell was thermally stable below 270 °C. Image density results, obtained by evaluating the color-formation and decolorization property of the microcapsules, confirmed that the thermal processing influenced the decolorization process through competitive procedures. One procedure was the thermal decomposition of cationic photoinitiator to heighten color image density, and the other was to destroy the carboxy bonds in the color-formed fluorane dyes after thermal energy transmitted through phase changed microcapsule shell. It was concluded that the latter procedure played a more significant role to perform decolorization property at higher temperature especially above 140 °C.

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