Photochromic Characteristic of Cationic Photoinitiator and Fluorane Dye System Microencapsulated in Sub-micrometre Scale

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Photochromic microcapsule had been synthesized by the interfacial polymerization technique. Polyurea polymer shell was polycondensed between –NCO isocyanate group of IPDI and –NH₂ group of TEPA. The cationic photoinitiator and fluorane dye system was encapsulated in core-shell structured microcapsule with the average size of sub-micrometer. The microcapsule was thermally stable, and showed a high optical-sensitivity to achieve color-forming reaction between the H⁺ proton photo-dissociated from cationic photoinitiator and the lactone ring inside the fluorane dye. Exposure for 15 s had heightened the image density from 0.1 to 0.8. By comparing the different exposing effect on photochromic image density, the color-forming reactions presented the superposition principle of exposure energy.

Keyword: cationic photoinitiator, photochromic, microcapsule, fluorane dye

1. Introduction

Photoinitiators are the essential ingredient for photocurable coating, by converting absorbed irradiation energy to generate free radicals or cations for initiating subsequent polymerization [1]. Other than free-radical photoinitiators, cationic kind has been extensively applied in the fields of optical lithography, 3D printing, Computer-To-Plate processing, and so on [2-3]. Strong proton acids or Lewis acids, photo-decomposed from cationic photoinitiator, have been acted as reactive species to open the epoxide/oxetane rings and to initiate chain growth in such photoimaging applications, with the advantages of post-curing, low shrinkage and outstanding adhesion [4]. To promote the initiating efficiency, modification of the sensitive absorption spectra were focused as key point. Polyaromatic structures of truxene derivatives and tris(aza)pentacene were presented by Tehfe et al. as novel metal-free photocatalysts, to promote ring-opening polymerization even upon visible light exposure [5]. Novel visible light sensitive photoinitiator system had been designed by J. Crivello based on a two-step process: free radicals firstly generated by absorption of visible light, and the radicals assisted the decomposition of diaryliodonium salt to derive strong acid subsequently [6]. Visible light sensitive photoinitiator system for cationic polymerization had been synthesized using highly conjugated thiophene derivatives, with exciplex formed after absorption of light in first step and excited electron transfer to iodonium ion to yield cations of the thiophene derivatives subsequently [7]. Novel cationic photoinitiator carrying two photo-chromophoric groups was synthesized by J. Kreutzer et al. [8].

Since the proton H⁺ produced from cationic photoinitiator were high reactive to participate in further reactions, a new
viewpoint is proposed to perform photochromic reaction for extending the cationic photoinitiator application. It is also meaningful to confine the photochromic process in a given volume scale. Therefore, the cationic photoinitiator and fluorane dye system is encapsulated in sub-micrometer sized scale, and the photochromic characteristic shown as color-forming image density has been investigated and discussed in this article.

2. Experimental

2.1. Materials

Triarylsulfonium hexafluorophosphate cationic photoinitiator salt IHT-PI 432, obtained from Yinli Corp., was solved in 50 wt% propylene carbonate. Other reagents including 2-Anilino-3-methyl-6-dibutyl-aminofluorane (ODB-2) and 3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI) were obtained commercially and used as received.

![Scheme 1. Reagents used in the experiment.](image)

2.2. Synthesis of Cationic Photoinitiator Microcapsule

The interfacial polymerization technique was applied to synthesize core-shell structured microcapsule. To composing the photosensitive material, solution of IHT-PI 432 (20 mL) was added in the liquid mixture of ODB-2 (2 g) and acetic ether (18 g). After IPDI of 20 g addition, the oil phase solution was obtained, which furthermore was stirred at 60°C for 20 min. The water phase was consisting of 150 mL PVA solution (5 wt% in deionized water) and 7 mL betaine solution (80 g/L).

Stirred at 2,000 rpm, the oil mixture was slowly injected into the water phase. By shearing with 5,000 rpm for 10 min, the oil-water emulsion was obtained. The oil phase would be sheared as droplets dispersed in water phase. After tetraethylenepentamine (TEPA) of 15 mL (250 g/L) added, the shell structure was polymerized in the oil/water interface. The reaction temperature was held at 60°C for 4 h. The synthesized emulsion was washed, and microcapsules were centrifuged out and dried for further usage.

2.3. Photochromic Property

The microcapsules, dispersed uniformly in 6 wt% PVA solution, were coated on cellulose acetate film with thickness of 12 μm. After dried in room temperature, the film was exposed by high pressure mercury lamp, 40 W fluorescent lamp or even the sunlight. The photochromic property was presented as image density, which could be detected by X-Rite 504 spectrodensitometer.

2.4. Measurement

The characteristic absorption during shell polymerization was monitored by BRUKER Tensor27 Fourier transform infrared spectrometer. Microcapsule morphology and particle size distribution were detected by SEM (JEOL, JSM6510) and Particle size analyzer (MALVERN, Mastersizer 2000), respectively. Thermogravimetric (TG) analysis was performed on a NETZSCH TG209-F3 thermal analyzer with heating rate of 10 °C/min.

3. Results and Discussion

3.1. Synthesis of Microcapsule

During emulsification process, the shearing
mechanical energy had been transferred to form the interface of the oil droplets. The acuter the shearing process did, the more energy the interface could be obtained. After shearing, the TEPA could inter-joint the IPDI molecule. Such a shell-forming process of microcapsule was monitored as IR spectra series, as shown in Fig. 1(a).

With time increasing, the spectra intensity at 2,252 cm\(^{-1}\), which corresponds to the characteristic absorption of \(-\text{NCO}\) bond in IPDI molecule, has been obviously reduced. After 120 min, the \(-\text{NCO}\) absorption disappeared. Such a variance indicated that the isocyanate groups in IPDI had been intermolecular condensed with \(-\text{NH}_2\) bond of TEPA, with the \((-\text{NHCONH}-)\) bond formed as shown in Fig. 1(b). Since the condensation reaction could be occurred at the two direction of IPDI with the \(-\text{NH}_2\) in TEPA acted as bridging groups, the shell structure was confirmed as polyurea polymer. The polyurea shell formation process was quantitatively present in Fig. 1(c) by calculating and normalizing the absorption area around 2252 cm\(^{-1}\). The shell formation had been performed 90% percentage before 60 min, and perfectly finished after 120 min.

Granularity distribution of the microcapsules was present in Fig. 2. Oil droplets with high interfacial energy had been confined in the solid shell. The microcapsule distribution had a peak size at 0.83 \(\mu\)m. Half-width of the curve was 1.1\(\mu\)m. It indicated that the synthesized microcapsules had regular size distribution.

Morphology of the microcapsule was displayed in Fig. 3. Spherical capsules had smooth surface. With the average size of sub-micrometer, such core-shell structured small-scale reactors could be authorized with...
novel functions by manipulating the core component. In this article, the photosensitive behavior had been achieved by encapsulating the mixture of cationic photoinitiator and fluorane dye system.

Figure 3. SEM micrograph of the synthesized microcapsules.

3.2. Thermal stability of the Microcapsule

For practical application, thermal stability of microcapsules was essential. TG curve of microcapsules was given in Fig. 4.

![Figure 4. TG curve of the synthesized microcapsules.](image)

Below 126.6 °C, there had negligible weight loss. After the cut-off point, the loss rapidly increased, and with a slowly-varying step followed from 202.8 °C. This phenomenon should be attributed to the phase change of the microcapsule shell in such temperature range, and the glass transition temperature \( (T_g) \) was about 126.6 °C. The permeability of microcapsule shell had been heightened, which brought fast release of core ingredients and performed as the fast weight loss from 126.6 °C. After 306.0 °C, the shell was decomposed, corresponding to the remarkable weight loss until 606 °C.

Thus, the microcapsule was thermally stable below 306 °C. The microcapsules could be photo-sensitively functionalized at room temperature.

3.3. Photochromic Evaluation

After high-pressure mercury lamp exposing, the color-change presented as image density variance in Fig. 5. The initial density was about 0.1 without exposure, while color formed as image density of 0.37 by exposed for 1 s. The longer the exposure time was, the higher the image density obtained. After 15 s, there had no further color density variance. The optical response had been initiated by cationic photoinitiator in microcapsule core, and it should be explained based on the generally accepted viewpoint that \( H^+ \) acid had been produced from cationic photoinitiators under UV irradiation [9].

![Figure 5. Relationship between image density and exposure time when exposed by high-pressure mercury lamp.](image)

The characteristic absorption band of the cationic photoinitiator IHT-PI 432 was appeared around 296 nm reported by the producer, which corresponding to the emission peak of high pressure mercury lamp.
around 245 and 304 nm in Fig. 6. The absorbed UV photon had efficiently excited to generate H⁺ acid and other active radicals decomposed from photoinitiator.

![Figure 6. Normalized luminescence spectra of the high-pressure mercury lamp.](image1)

When it comes to the photochromic mechanism, the ODB-2 used in this article had lactone structure. H⁺ proton reacted with lactone ring to form –COOH carboxyl group, which was shown in Fig. 5. Then the absorption of microcapsule had been modified, and the reflective spectra of microcapsules formed a variable color.

At 15 s after color-forming process, the image density was about 0.8, and did not change further though exposure time raised. It may be due to the exhaust of generated H⁺ protons.

Such photosensitive results indicated that the photochromic microcapsule consisting of cationic photoinitiator and fluorane dye had been achieved. The optical-responding efficiency was directly manipulated by the exposure technique.

3.4 Exposure Effect on Photochromic Density

The irradiation spectra to excite microcapsule had distinctively effect on the photochromic density. A 40 W mercury fluorescent lamp was used as another exposure source. Compared with 10 s of exposure time to access density 0.7 and 15 s for maximum density 0.8 exposed by high pressure mercury lamp in Fig. 5, the stable density of only 0.7 was appeared after 10 day exposed by such a lamp in Fig. 7.

![Figure 7. Relationship between image density and time when exposed by a 40 W fluorescent lamp.](image2)

The H⁺ proton was slowly generated in day-scale due to so low exposure energy of the 40 W lamp. But it could be also noticed that the photochromic was solely determined by the cationic photoinitiator, and the color-forming reaction was complied with the principle of energy superposition. The maximum density in Fig. 7 was smaller with the extent of only 0.1 than that exposed by high pressure mercury lamp. This was ascribed to the decreased penetrating thickness into microcapsule core for the low energy irradiation, which caused the insufficient consumption of the inner photoinitiators in microcapsules.

![Figure 8. Relationship between image density and time when exposed by sunlight.](image3)
An interesting phenomenon had also been observed that sunlight exposure could more efficiently utilize the photoinitiators. Image density of 0.84 had been obtained after exposed for 13 s. The continuous emission spectrum of sunlight was more suitable to excite photoinitiator molecules used in this paper at its maximum absorption wavelength, while the line spectrum of high energy mercury lamp did not be sufficiently absorbed by the photoinitiators, though the latter had higher total emission energy than the sunlight.

4. Conclusion
This article proposed photochromic viewpoint for the cationic photoinitiator application. Photochromic microcapsule had been successfully synthesized by the interfacial polycondensation of IPDI to form polyurea polymer shell. The cationic photoinitiator and fluorane dye system was encapsulated in the sub-micrometer sized scale. The microcapsule was thermally stable, and showed a high optical-sensitivity to achieve color-forming reaction between the H\(^+\) proton isolated from cationic photoinitiator and the lactone ring inside the fluorane dye. Exposure for 15 s had obtained the image density of about 0.8. The color-forming reactions presented the superposition principle of exposure energy. Sunlight, with its continuous emission spectrum, had the advantage of including the suitable sensitive wavelength of the photoinitiator used in this article, and had efficiently utilized the photoinitiators for color-forming.

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