Image-formation Property Based on Thermosensitive Color-reaction and Photo-sensitive Polymerization in Sub-micrometer Microcapsules

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The thermal sensitive dye precursor ODB-2 and photosensitive resin TMPTA as well as photoinitiators TPO are encapsulated in sub-micrometer sized microcapsules. After heating processed, the color-forming reaction is produced in microcapsule cell, which presents that the encapsulated ODB-2 has achieved color-forming reaction with the D-8 transmitted through the thermal phase-changed shell. Based on UV irradiation, the thermal image density decrease rapidly with increase of exposure time, then take stable status after exposed for 30s. FT-IR and TG analysis verifies that the C=C cleavage and photo-crosslinking process has been produced in microcapsules, and the stable C=C conversion rate is 20.4% exposed for 30s. By encapsulating the ODB-2 monomers in the photo-solidified polymer network, the thermal color-reacting extent in microcapsules is manipulated by the photopolymerization extent under different exposure time, though the mixed ODB-2 has reduced the photopolymerization efficiency by competitive absorption to the UV irradiation.

Keyword: microcapsule, photopolymerization, thermal-sensitive color-forming, interfacial polycondensation

1. Introduction

Microcapsules, as core-shell structured composites, can achieve functions to mimic the stimuli-responding systems and fabricate nano- or micrometer-scale components [1-3]. In information recording researches, the image formation functions have been achieved by pressure-sensitive microcapsules [4], which used as carbonless paper, based on shell-cracked method to initiate the color-forming reaction between inner ingredients and outer reagents. The thermo-sensitive color-forming reaction in TA paper is also ascribed to the shell phase change through heating process, and the diffusion efficiency of outer or inner ingredients across the microcapsule shell is adjusted [5-6]. Also, electrically charged granules have been encapsulated to transform reflected color of microcapsules by electrophoresis in electronic field [7].

Compared with the abundant investigations of pressure-, thermo- or even electrical-sensitive microcapsules, the photosensitive microcapsules, based on the inner ingredients spectral response, have not been paid enough attentions, though some patents about photo-stimuli responding microcapsule materials have been issued [8-10], and Arney reports the oxidation kinetics of TMPTA in microcapsules [11].

In this paper, the core-shell microcapsule is synthesized by interfacial polycondensation technique. The thermal color-forming extent is measured as image density after UV-exposure. Based on TG and DTG analysis, the microcapsule core status, changed from liquid status to some extent of photo-initiated solidification after UV irradiation, is outlined. The FT-IR absorption is detected during
exposure to indicate the photopolymerization process in the microcapsules. The factors influenced the photopolymerization efficiency is discussed.

2. Experimental
2.1 Microcapsule Preparation

The photosensitive core ingredients are comprised of photoinitiator TPO (2, 4, 6-trimethylbenzoyldiphenyl phosphine oxide) 1.0 g mixed with TMPTA (trimethylolpropane triacrylate) resin 20 g, as well as the colorless dye precursor ODB-2(C_{13}H_{36}N_{2}O_{3}, melting point at 182°C) 2.0 g as color-forming material. D-110N (tri-isocyanate in ETAC) 20 g as shell-forming reagent are dissolved with the photosensitive solution to form the oil phase (O). The PVA224 (4.5 mass%) 150 ml forms water phase (W), acted as protective colloid and surfactant.

The O/W mixture is sheared at 5000 rpm for 9 min. After TEPA (tetraethylpentamine, 25 mass%) 20 ml are added to initiate polycondensation reaction in O/W interface, the emulsification process is kept at 800 rpm for 4 h under 60°C.

Obtained microcapsule emulsion are washed and deposited at 25°C for 24 h. Based on FT-IR investigation, the polyurea microcapsule shell has been formed to encapsulate the liquid photosensitive material and the dissolved dye precursor ODB-2.

The grinded D-8 dispersion (C_{13}H_{36}O_{3}, melting point at 130°C) is mixed with the obtained microcapsule emulsion at the mass ratio of 1.5:1 to perform color-forming reaction. The mixture is coated onto paper base and dried to obtain thermal-optical sensitive material.

All reagents above stated, except D-110N have been diluted by ETAC, are used without further purification.

2.2. Experiment Methods

The microcapsule size distribution is detected by Malvern Mastersizer 2000E instrument. TGA is obtained by DTU-2C system (Boyuang Jingzhun). FT-IR analysis is used to inspect the photopolymerization extent in microcapsules by Bruker Tensor27 FT-IR spectrometer. The thermal color-reaction in microcapsules is observed by Leica DM2500P microscope. After exposed with high-pressure mercury lamp at the distance of 10 cm and heating developed, the color-forming image density of the film is detected by X-rite 504 spectrodensitometer. The initial image density of the coated film on paper base is 0.08.

3. Results and Discussion
3.1. Diameter Distribution Detection

Diameter distribution of the synthesized microcapsules and the grinded D-8 aggregates are shown in Fig. 1.

![Particle diameter distribution of (a) the synthesized microcapsules and (b) the D-8 dispersed aggregates.](image)

With distribution peaks at 1.4 μm, the half width of the microcapsules is about 1.37 μm. Since larger total surface areas can be created by narrower diameter distribution, the synthesized microcapsules can be manipulated by thermo- or photo- stimuli through microcapsule shell with higher efficiency. The D-8 aggregates, acted as color-forming developers, are dispersed with 2.86 μm diameter to heighten the touching area with the 1.37 μm sized microcapsules.

The core-shell structure of the microcapsules is observed as shown in Fig. 2. The shell-core thickness ratio is about 1:16, and the shell has some mini-structure as accidened morphology on the inner and outer surface, which is due to the interfacial effect between different kinds of substances.
Fig. 2 TEM micrograph of the synthesized microcapsules.

3.2. Thermo-sensitive Color-Forming Process in Microcapsules

The thermo-sensitive function of the microcapsules is controlled by heating process. Thermal property of the microcapsule shell is the key factor to affect the thermal reaction efficiency of the encapsulated ingredients ODB-2 with the outside D-8 aggregates. TG analysis of the microcapsules is present in Fig. 3.

The remarkable weight loss appears at 190°C, which means that the photo-thermal sensitive microcapsules are stable at room temperature and can be thermally controlled in the temperature range between 40°C to 190°C. After 190°C, the microcapsule shell start to decompose and the core ingredients diffuse until 260°C, which has shown a nearly linear weight loss trend. After 310°C, there has a following linear decrease trend and ended at 620°C based on the further decompose of the remnant composites. TG result presents that the microcapsule can be controlled by thermal technique, which is the basis to control the diffusive effectiveness of the D-8 developer aggregates for traversing through the microcapsule shell and reacting with encapsulated ODB-2 molecules to form color-image.

Before heating process, the inner of microcapsules are colorless as shown in Fig. 4a, while after heated at 150 °C for 20s, the microcapsule micrograph is shown in Fig. 4b.

According to Fig. 4b, the microcapsule inner color has been obviously changed after heating process. It means that the color-forming reaction is processed in the microcapsules. The microcapsule has been acted as basic pixel cell in imaging formation.

When it comes to the color-forming process, it implies that the D-8 substance with melting point at 130 °C can be melted and penetrate into the microcapsules when microcapsule shell has been heated to its thermal phase-change status at 150 °C, and reacted with the ODB-2 molecules to form color.

In conclusion, the thermo-sensitive color-forming approach is ascribed to the manipulation of the microcapsule shell thermal-change property.

3.3. UV Photopolymerization Influence on the Thermal Color-forming Process

The microcapsules can also respond to UV exposure based on the encapsulated UV
photocrosslinkable reagents. After exposure, the color-forming variance is detected as image density and shown in Fig. 5. The heating process of the exposed microcapsule material is produced at 130°C or 150°C, respectively.

From Fig. 5, it indicates that after exposing and heating process, the color-forming density increase remarkably compared to initial image density 0.08 of the unheated area, with the image density 0.78 at 150°C and 0.58 at 130°C. Such results verify that the colorless dye precursors ODB-2 in the microcapsule has color-reacted with the D-8 penetrated through the microcapsule shell, according to the principle presented by TG and microscopy analysis. In Fig. 5, the color density processed at 150°C is higher than that at 130°C. This implies that the thermal penetrability efficiency of microcapsule shell is affected by the heating temperature. The higher the temperature is, which should below 190°C to hold the stable status of the microcapsule, the more efficient the penetrability of the shell is.

As for the UV response, with exposure time increase, the image density decreases rapidly and achieves stable density after 30s. The UV response has affected the thermal color-forming extent in microcapsules.

The photo-polymerization process in microcapsules is detected by calculated the relative variance of the FTIR absorption area around 1635cm⁻¹, which is the characteristic absorption of C=C bonds of TMPTA. In Fig. 6, the photo-polymerization rate in microcapsules is present.

With exposure time increased, the C=C cleavage rate rises rapidly at first, and then to stable conversion rate of 20.4% at 30s. It means that the photopolymer network has been formed in microcapsules.

The TG and DTG analysis in Fig. 7 also present that there has structure change for the UV-exposed microcapsule. The weight loss process of the exposed microcapsules decreases at lower velocity in the temperature range from 190°C to 495°C, compared with the unexposed sample.

The DTG also present that the weight loss of exposed microcapsules has different change rate, which means that the exposed microcapsule core material has been solidified and the thermal
decomposition process has been decreased at lower weight loss velocity.

Also, TG and DTG analysis has shown that the shell thermal property has not been affected by the inner photopolymers, and the weight loss from 40 to 190°C is nearly unchanged after exposure.

In order to analyze the photopolymer structure formed in the microcapsules, the core mixture is directly UV exposed. The solidified composite structure is detected by FT-IR technique. In Fig. 8, the characteristic absorption at 1519, 1554 and 1604 cm\(^{-1}\) of ODB-2 molecules appears in the extracted and dried photopolymers.

Fig. 8. FT-IR spectra of (a) the extracted photopolymer, (b) TMPTA resin and (c) ODB-2 monomer.

The ODB-2 monomers have been encapsulated in the photopolymer network. It implies that the network would constrain the reaction efficiency of ODB-2 monomers to form color density with the penetrated D-8 molecules in microcapsules, which is the basis for the optical manipulated function of the microcapsules.

Since the color-formation process is thermally produced, the stability of the photopolymer network is important to affect the color reaction. TG analysis of the photopolymer substance with or without ODB-2 mixed is shown in Fig. 9. The photopolymer without ODB-2 encapsulated has higher thermal stability and the remarkable decomposing point is started at 297°C, while for the ODB-2 mixed system, the decomposing point has been decreased to 195°C. Results imply that the solidified composite in microcapsules is thermal stable during the color-forming process when heating developed below 180°C. From Fig. 9, it can also be concluded that with ODB-2 mixed, the photocrosslinking extent of the photo-responding system has been reduced, and the network structure is relatively fragile compared with the photopolymers without ODB-2 mixed.

According to the absorption spectra of ODB-2 monomer and photoinitiator TPO shown in Fig. 10, the reduced photopolymerization is ascribed to the competitive absorption between ODB-2 and TPO.

Fig. 9. TG analysis of the photopolymer. (a) Without ODB-2 encapsulated and (b) with ODB-2 mixed.

Fig. 10. UV-Visible absorption spectrum of (a) ODB-2 and (b) photoinitiator TPO.
During the competitive absorption process between photoinitiator TPO and the dye precursor ODB-2, the effective irradiation energy is reduced for exciting TPO molecules, which cause the decrease of the free-radical yield. As a result, the crosslinking extent is lower for the ODB-2 mixed photosensitive system.

In addition, the ODB-2 molecules may weaken or quench the C=C bonds crosslinking reaction during photopolymerization process in the microcapsules.

4. Conclusion

Microcapsule materials have potential application in information recording regions. In this article, the thermal sensitive color-forming reaction has been achieved in the core-shell structured microcapsules with the shell penetrability adjusted by thermal processing. The microcapsules are acted as pixel at sub-micrometre resolution. To manipulate the color-forming density, the photocrosslinking function of the microcapsules is realized under UV irradiation. The core status variance from liquid to solidified form is verified by TG and microscopy analysis after exposure. The color-forming efficiency in microcapsules has been controlled based on the constraining effect of solidified core polymer network on the encapsulated dye precursor ODB-2. As UV-exposure time increases, the color-forming image density has shown sequentially decrease trend with the photopolymerization rate increase in microcapsules. When it comes to the thermal stability of the constraining effect during thermal developing process, the photopolymer are thermal stable below 195°C, though the thermal stability has been remarkably decreased by ODB-2 mixed. Such phenomenon is laid on the competitive absorption between ODB-2 molecules and the photoinitiators TPO. The thermal-optical sensitive microcapsule can be applied as information recording medium to realize thermal image density contrast by adjusting UV-exposing conditions.

Results also indicate that the photopolymerization reaction in microcapsules is not efficient enough as the conversion rate is only 20.4%. To heighten the photopolymerization rate, the dual-shell structured microcapsules can be considered, with the photosensitive system in first layer and the thermal sensitive dye-precursor in the second layer. The dual-shell structure can heighten the photocrosslinking efficiency of the photosensitive system by competitive absorption avoided, and the image density variance would be increased to form practical image density contrast under different exposure conditions.

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References