Thermal-optical response property of the core-shell structured microcapsule material

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Polyurea core-shell structured microcapsules with shell thickness of 80nm are synthesized by interfacial polycondensation method. Thermal sensitive function of the microcapsules is presented as image density rise with heating time increase, and optimal thermal condition is 5s at 150℃ to obtain maximum image density 0.72. Optical function is achieve by C=C bonds cleavage of TMPTA monomers to form polymer network in microcapsules. The color-forming reaction of core ingredients is constrained by the cross-linked network polymers and obtains maximum image density decrease variance 0.26 after UV exposure for 20s. Such microcapsules can act as functional cells responding to thermal and photo stimuli at micrometre scale.

Keywords: Microcapsule, Image density, Thermal and optical sensitive, Photo-crosslink, Core-shell structure
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1. Introduction

Core-shell structured microcapsules with high stability are of both scientific and technological importance [1-5]. The microcapsules usually act as smart polymer composites to achieve various functions such as slow-release of core ingredients, energy-storage by core phase-change material, structure crack self-healing based on microcapsule shell rupture, artificial organ to encapsulate insulin etc [6-7]. The driving-forces for microcapsule applied so far are mostly ascribed to the similitude between natural macromolecule and such artificial core-shell structured microsphere. Both have continuous and semipermeable films or coatings, and applied as micro-carriers or micro-reactors to manipulate physical, chemical or biological response in confined space, based on external stimuli of PH, temperature, or pressure etc [8-11]. For example, J. Park et. al. has proposed micro-biomedical diagnostic system for endoscopic microcapsule [12], to integrate micro cell lysis, micro bead affinity chromatograph, micro-needle and micro-fluidic devices into microcapsule to enhance separation efficiency of the target proteins and reduce the purification time, consumption of samples.

In last decade, the temperature sensitive microcapsules have been intensively investigated [13-15], and the most distinct achievement is the negative temperature sensitive microcapsule based on plasma grafting of PNIPAM (poly N-isopropylacrylamide) chains into microcapsule surface pores [16-17]. When it comes to optical response, Sawada et. al realized photoacid generation in microcapsules [18], while Lu et. al. photo-crosslinked the acrylamide derivatives in layer-by-layer (LBL) assembled microcapsules to form medical slow-release core composites [19]. Since highly selective regulation can be conveniently achieved by selecting the exposure wavelength and photo-reactive core compounds, the optical functional microcapsules have potential application in pharmacy, cosmetic, or in environment protection. But compared with the fast development of temperature-sensitive microcapsules, the optical-sensitive microcapsules have drawn few attentions which are restrained by lack of information about synthesis technique and behavior of such materials when irradiation exposure is applied.

In this paper, interfacial polycondensation method combined with O/W (oil/water phase) emulsification is applied to encapsulate the optical sensitive compounds. The shape and diameter of the microcapsules are investigated and microcapsules with micrometre size have been synthesized, which can act as basic functional cell to respond the outside thermal and optical

stimuli. Thermal phase change character is discussed. By image density detection, the thermal and optical functions are outlined based on the color-forming reactions in microcapsules. Such microcapsules can be directly applied as biomedical material to response temperature or optical signals in medical-image processing region.

2. Experimental

2.1 Oil/water emulsion preparation

TMPTA (Trimethylol propane triacrylate, $(CH_2=CHCOOCH_2)_3$-CCH_2CH_3, Sanmu Group) 20g are mixed with photoinitiators of TPO (2, 4, 6-trimethylbenzoyldiphenyl phosphine oxide, $C_{22}H_{21}PO_2$, absorption wavelength range from 273 to 370nm, Sanmu) 0.6g and ITX (2-Isopropyl Thioxanthone, $C_{16}H_{14}OS$, absorption wavelength range from 258 to 382nm, Sanmu) 0.4 g to obtain the optical response reagents. The solution mixes with colorless dye precursor ODB-2($C_{35}H_{36}N_2O_3$, melting point at 182□, Yamamoto Chemicals) of 2g as microcapsule core material. After the mixture is heated to dissolve and cooled to room temperature, D-110N (75% tri-isocyanate in ethyl acetate, Mitsui Takeda Chemical) 20g as microcapsule wall forming material is added. The oil phase is obtained.

To encapsulate the core compounds, the oil phase is put into water phase comprising of 135ml PVA224 (Polyvinyl Alcohol ,4.5 mass%, Kuraray) and surfactant (3-[N-Dodecyl-N,N-dimethyl- aminium]-2-Hydroxyl-propylsulfonate, 8 mass%) 7ml. The O/W (oil/water) emulsion is prepared.

2.2 Microcapsule preparation

The O/W mixture is emulsified at shear velocity of 5000rpm for 9min. After TEPA (Tetraethylenepentamine, 25 mass%,) 20ml are added to initiate polycondensation reaction within O/W interface, the emulsion is stirred by an overhead stirrer at 800rpm for another 3h under 60□. Finally deposit overnight at room temperature to complete microcapsule formation.

The obtained microcapsules are mixed thoroughly with D-8 (4-Hydroxy-4'-Isopropoxydiphenylsulfone, $C_{15}H_{16}O_4S$, melting point at 130℃) dispersion, which can react with the ODB-2 molecules to perform color-forming reaction. The mass ratio between microcapsule emulsion and D-8 dispersion is 1:1.5. The mixture is coated onto PET film and dried at 40℃ to obtain thermal and optical sensitive material. The dry thickness of the film is measured as about 21μm.

2.3 Analysis methods

The microcapsule size distribution is determined by Mastersizer2000 Counter (Malvern). FT-IR spectra are obtained with Bruker Tensor27 spectrometer. Thermal Gravimetric (TG) and Differential Thermal Analysis (DTA) for microcapsules are performed by DTU-2C analyzer (Boyuan Jingzhun Co.) with samples of 10.0 mg heated to 700□ at a rate of 10℃/min. Transmitting electron microscopy (TEM) is performed by using Hitachi-800 instrument. After exposed with high-pressure mercury lamp and heating developed by hot-plate (EH-35B, Suzhou Hope-team Co.), the color-forming density of the film is detected by X-rite 504 spectrodensitometer.

3. Results and discussion

3.1 Microcapsule morphology

The diameter distribution of the oil droplets in O/W emulsion before TEPA added is shown in Fig. 1a. With dispersion time increase from 1min to 4min, the distribution width is narrowed remarkably, while the distribution peak is unchanged around 0.8μm. External dispersion energy has transformed as surface energy of the oil droplets to create smaller size. When increase the

O/W emulsification time to 9min, the particle size distribution only narrowed slightly, which means the total surface energy of the oil droplets have held balance with the mechanical energy.

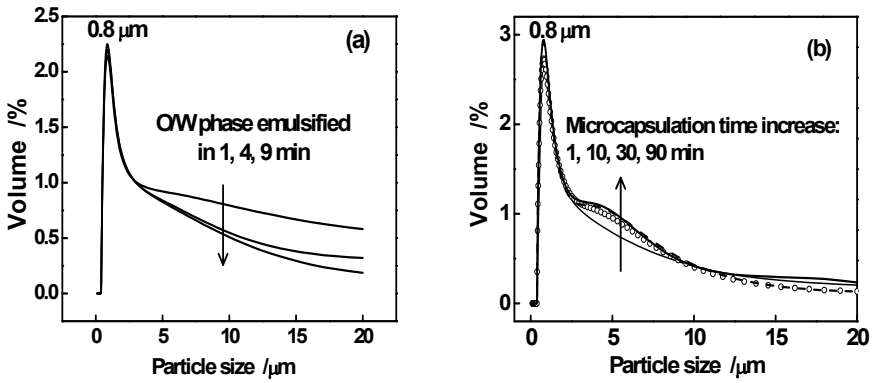

Fig. 1. (a) Diameter distribution of oil droplets during O/W emulsification; (b) Diameter distribution of microcapsules during interfacial polycondensation reaction.

After TEPA added, the peak of the particle size distribution is nearly unchanged at 0.8μm, and with microencapsulating time increase after 10min there has a shoulder form distribution around 5μm, which is presented in Fig. 1b. This may be due to the microcapsule agglomeration during shell formation process.

The morphology of the functional microcapsules is shown in Fig. 2. Most of the microcapsules are regular core-shell structured microsphere. The shell thickness is approximately 80nm. Part of the microcapsules are agglomerated together with the shell adhered to form interconnecting structure, which is accorded with the microcapsule size distribution variance in Fig. 1b. It implies that in interfacial polycondensation reaction the microcapsule shell has been formed after TEPA is added.

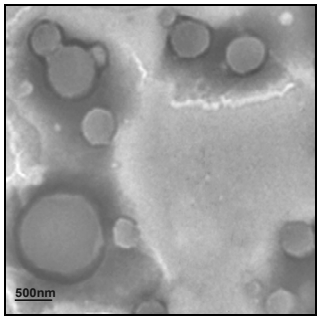

Fig. 2. TEM micrograph of the microcapsules.

3.2 Microcapsule shell formation detection

To investigate the microcapsule shell formation process, the FT-IR spectra is obtained at different time after addition of TEPA. In Fig. 3, the absorbance at 2263cm^{-1} decrease obviously at 10min; while at 30min, the absorption at 2263cm^{-1} is only slightly shown. After 40min, this absorption peak disappears. Since 2263cm^{-1} is the characteristic absorption of —N=C=O bonds in isocyanate molecules, it suggests that polyurea capsule shell are synthesized by polycondensation reaction between -NCO bonds of D-110N and -NH_2 end-groups of TEPA. This confirms that the shell formation process starts after TEPA addition and takes completion after 40min.

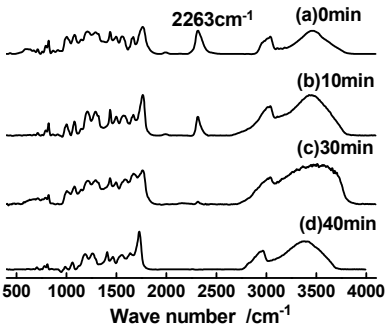

Figure 3. Microcapsule shell formation detection: FT-IR spectra of the microcapsule emulsion at different time.

The microcapsule shell formation reaction between tri-isocyanate molecules and TEPA during the interfacial polycondensation process is shown in Fig. 4.

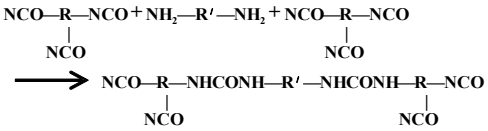

Figure 4. Microcapsule shell formation reaction between tri-isocyanate molecules and TEPA during the interfacial polycondensation process.

3.3 Thermal response property

To apply as micro-reactors, the microcapsule thermal property is important. In Fig. 5a, the thermal decomposability (TG) of microcapsules is analyzed as a function of temperature. The microcapsule presents linear decomposing trend before 115□, and a sudden increase until 135□, then an obvious precipice appears above 135□. Before complete decomposition, there also has remarkable mass loss variance at 230, 335, 370, 520□ as presented in DTG curve in Fig. 5b. These may be ascribed to the diffusion of core reagents and weight loss of wall material. Above 520℃, the residual materials are decomposed further with a slowdown trend and ended at 610℃. From the TG result, it can be concluded that the microcapsule shell membrane are thermal stable in room temperature and the phase change point is started from 115℃, which is confirmed as heat release process by DTA analysis in Fig. 5c. Such a result shows that the microcapsule can be controlled by thermal technique, which is the basis for practical usage of the microcapsules when stimulated by thermal variety.

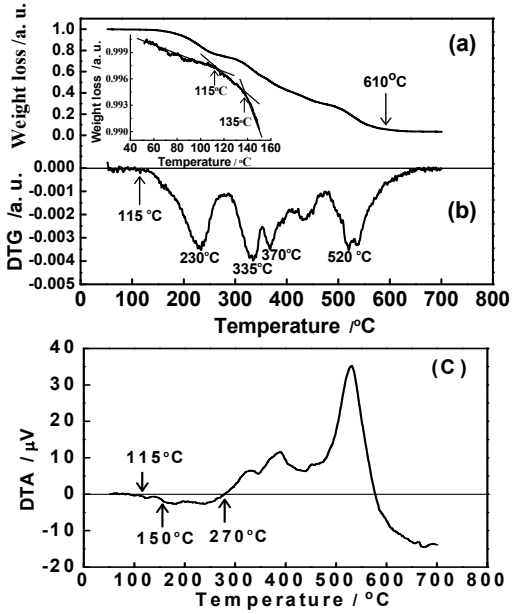

Figure 5. (a)TG, (b) DTG and (c) DTA analysis of the microcapsules at heating rate of 10□/min.

The thermal image density is detected with the microcapsule samples heated at 150 □, which is the phase transition temperature according to TG and DTA analysis. In Fig. 6, the image density increase to 0.2 at 0.5s; during heating time rise, an increasing trend presents with the maximum density 0.72 achieved at 5s. It implies that the D-8 dispersion have been melted at 150□, then traversed the microcapsule shell and reacted with the ODB-2 molecules in the microcapsule core to form color image. After 5s, the image density is almost unchanged, which is ascribed to the completion of the color-forming reaction. The color-forming degree is decided by the reacting time when heating developed under shell phase transition temperature. The core-shell structured microcapsule is applied as micro-reactors to respond the external temperature stimuli by manipulating the shell thermal state.

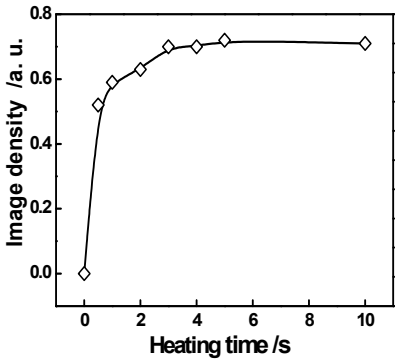

Figure 6. Thermal response of the microcapsules: relationship between image density and heating time when developed at 150℃.

3.4 UV irradiation response of microcapsule

On the basis of high thermal stability at room temperature, the microcapsules are exposed with UV irradiation at different time. To detect optical reaction in the microcapsules, the image density variance when heating developed at 150℃ for 10s is obtained as shown in Fig. 7. With exposure time increase, image density has a fast decrease trend before 20s; after 20s, the image

density is almost unchanged with further exposure. The maximum decrease variance of image density is 0.26, compared between 0.72 at 0s and 0.46 after exposed for 20s. UV irradiation has changed the microcapsule core state and affects the image-forming reaction between the D-8 and ODB-2 molecules.

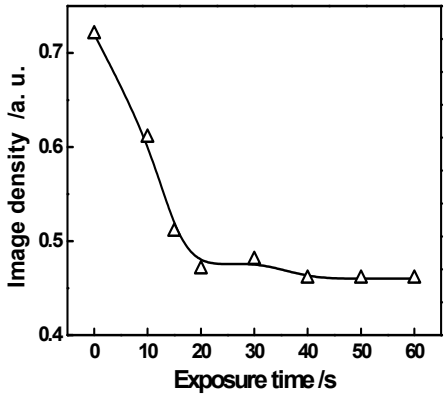

Figure 7 Optical response of the microcapsules: relationship between image density and exposure time when heating developed at 150℃ for 10s.

To illustrate the optical-response generated in microcapsules, FT-IR spectra are detected as shown in Fig. 8.

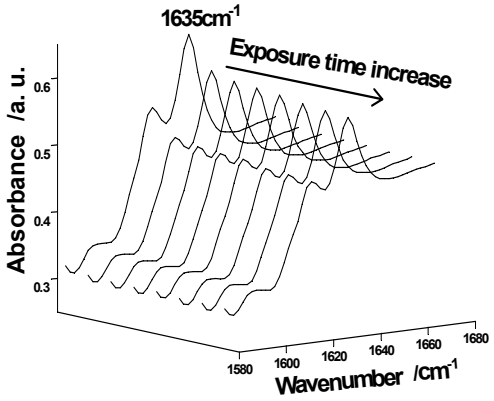

Figure 8. The FT-IR absorption spectra around 1635cm^{-1} at different exposure time.

With exposure time increase, the absorbance at 1635 cm^{-1} decreases. Since absorption peak at 1635 cm^{-1} is the characteristic absorbance of C=C bonds, it implies the TMPTA monomers have performed C=C bond cleavage reaction initiated by the ITX and TPO free-radicals, and cross-linking polymer network are formed in microcapsules when exposed by UV irradiation. Since the optical sensitive reagents in microcapsules have been mixed with ODB-2 molecules as blending solution, ODB-2 molecules are confined in the polymer networks. As a result, the color-forming process is constrained by decreasing ODB-2 concentration in the reaction.

The C=C bonds cleavage rate of TMPTA monomer in microcapsules shown in Fig. 9b is compared with the relative decrease rate of image density in Fig. 9a. The maximum conversion rate of C=C bonds cleavage and image density variance appear at 20s. It suggests that the cross-linking polymer network in microcapsules is the decisive factor to affect the color-forming degree. When it comes to the difference of conversion rate between 9.5% for C=C bonds cleavage and 33% for image density variance at 20s, the photo-crosslinked polymers have encapsulated ODB-2 blending solution by network structure to decrease ODB-2 concentration in the color-forming reaction with higher efficiency. The image-forming functions of the core

ingredients have directly manipulated by UV response function of the microcapsules.

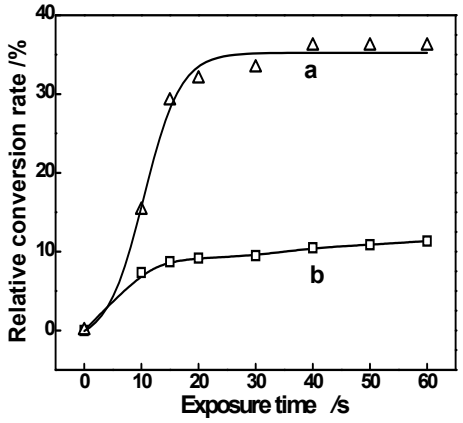

Figure 9. Relative conversion rate of (a) image density and (b) absorbance at 1635cm^{-1} versus exposure time.

4. Conclusions

The core-shell structured microcapsules with micrometre size are synthesized by interfacial polycondensation method. The interfacial polycondensation reaction takes completion after TEPA added for 40min, and the microcapsule shell membranes are polyurea structure with thickness of about 80nm. With high thermal stability at room temperature, the microcapsules are optically active due to C=C bonds cleavage of TMPTA monomers to form network polymers in microcapsule core. According to image density detection, the optical function of the microcapsules is presented based on the decreasing variance of color-forming image density in the microcapsules after UV irradiation. In microcapsules, the C=C cross-linked polymer network have encapsulated ODB-2 blending solution with higher efficiency to decrease reaction concentration of ODB-2 in color-forming process. In this paper, the thermal sensitive function of the obtained microcapsules is also discussed as the rising color-forming density with increase of heating time under shell phase change temperature (150°C). The core-shell structured microcapsule can be applied as micro-reactors to respond the external optical and temperature stimuli by manipulating the core and shell property.

New efforts are currently devoted to enhance the efficiency of C=C bonds cleavage and polymer network formation by encapsulating novel photo-responding ingredients in the microcapsules, with the aim to heighten the optical response function of the microcapsules.

Acknowledgements

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