A Novel Method to Control Microcapsule Release Behavior Via Photo-Crosslink Polyurethane Acrylate Shells

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ABSTRACT: A microcapsule system with polyurethane acrylate (PUA) shell is prepared by interfacial polymerization between acrylic polyurethane diisocyanate and water to achieve controlled release via UV irradiation. The size of the microcapsule is influenced by the concentration of protecting colloid and property of acrylic polyurethane diisocyanate. When concentration of polyvinyl alcohol (PVA) is 5% and molar ratio of TDI and acrylic ethoxylated pentaerythritol (acrylic PP50) rises to 1.50, average diameter of the microcapsule is only 3.3223 μm. Delivery of 4-hydroxy-4′-isopropoxydiphenylsulfone (D-8) encapsuled by PUA microcapsule in solution can be prevented effectively by 30-min UV irradiation. Lightness (L*) is used to measure color changes of reaction between D-8 in PUA microcapsule and 2-anilino-6-dibutylamino-3-methylfluoran (ODB-2) under thermal treatment. In dry state, irradiated PUA microcapsules are much harder to release D-8 than those not irradiated. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1008–1016, 2009

Key words: microencapsulation; irradiation; photopolymerization; dyes and pigments

INTRODUCTION

At present, microcapsule is typically used in noncarbon paper and thermosensitive paper.[1–3] In this case, microcapsules containing a developer or a color-producing material are fasten on the fibrous cells of paper. When external stimulation is added, such as stress and heating, microcapsules are destructed and the development is achieved by coupling of color-producing dye and its developer.

To achieve higher record speed and resolution, ultraviolet (UV) is used and the image is obtained from the difference between cured and uncured areas. For example, photosensitive esters can be added into microcapsule cores and be cured under UV irradiation to retard dye's release from core to outside as being heated or pressed, whereas microcapsules with uncured ore can release dye freely under the same condition.[4] Based on this principle, many newly reported microcapsule systems have great potential to be applied as image record materials. Lei et al. prepared a reversible photoresponsive microcapsule containing cis-trans transition of azobenzene moieties. The microcapsule can be used for controlled releasing and it is especially suitable for very small encapsulated substrates through phosphate bilayer membranes.[5] Polyelectrolyte microcapsule shells are prepared via layer-by-layer self-assembly method, in which the weak interaction between diazo resin/poly(styrene sulfonate) could be converted into covalent bonds by UV radiation.[6] Photodimerization can also be used in the controlled release microcapsules: polyorganosiloxane nanoparticles esterified by photoactive dyes can convert into shells in water/oil/water emulsion under UV irradiation and the shells can be cleaved by UV light as well to release their aqueous cores.[7] Takao prepared gelatin gel microcapsule and theoretically proved that the melting and releasing temperature of gelatin gel microcapsules can be dramatically increased by UV irradiation,[8] which enable irradiated microcapsules release more quickly than the nonirradiated under thermal treatment.

However, all these controlled releasing microcapsules are built by delicate biomaterials or crystal. The changes of their release function can only show in liquid medium. Hence, microcapsules with steady properties in common condition and show image at dry state are significant to image record materials.

Acrylic ester is a kind of photosensitive material with low cost, satisfying thermostability and mechanical strength. Chai-Hoon et al. used acrylic copolymer to enhance mechanical strength of collagen microcapsules by photo-crosslink reaction.[9] Image record material based on microcapsule has acrylic

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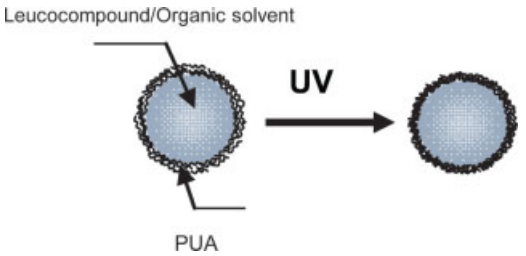

Figure 1 Principle of photosensitive PUA microcapsule. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ester as core substance to control release property under high temperature.[5] In this article, polyurethane acrylate (PUA) microcapsules containing leuco compound are prepared by interfacial polymerization. As is shown in Figure 1, the photo-crosslink reaction is expected to retard the penetration of leuco compound and prevent the color changes in uncured areas. Such microcapsules show effective photo-controlled release behavior in organic solvent or at dry state and will have a promising application as image record materials.

EXPERIMENT

Materials

Ethoxylated pentaerythritol (trade mane: PP50, Perstorp Chemical Trading Co., Ltd, Shanghai, China) to be esterified by 1 mol acrylic acid and polymerized with diisocyanate as shell phase was purchased from Perstorp. Acrylic acid together with *p*-toluenesulfonic as catalyst and 4 methoxyphenol as crosslink retarder were supplied by Beijing Chemical Reagent, Beijing, China. Tolylene-2,4-diisocyanate (trade name: TDI) and dibutyl tin dilaurate (trade name: DBTDL) as catalyst of reaction between TDI and acrylic PP50 were supplied by Beijing Chemical Reagent. Leuco 4-hydroxy-4′-isopropoxydiphenylsulfone (trade name: D-8) and its coupler 2-anilino-6-dibutylamino -3-methylfluoran (trade name: ODB-2) were kindly supplied by Lucky, (China Lucky Film Co., Baoding, Hebei, China). 2-Hydroxy-2-methylpropiophenone (trade name: 1173) used to initiate photopolymerization in shell phase was obtained from Ciba, (Shanghai Ciba Gao-Qiao Chemical Co. Ltd., Shanghai, China). Protecting colloid, polyvinyl alcohol (trade name: PVA) was purchased from Beijing Organic Chemical Factory, China. Organic solvents such as ethyl acetate, cyclohexanone, toluene were all supplied by Beijing Chemical Reagent. All the materials are used as received without any further purification.

Synthesis of acrylic polyurethane diisocyanate

Acrylic PP50, the photosensitive oligomer, is prepared by the reaction between ester PP50 and acrylic acid, as is shown in the Reaction a, Figure 2. PP50 (0.5 mol) and 1 mol acrylic acid were added into the flask and then mixed with 0.5 wt % catalyst *p*-toluenesulfonic, 0.5 wt % 4 methoxyphenol as crosslink retarder, and 20 wt % toluene as extracting medium to remove water. The reaction is carried out at 97°C for around 8 h and ended when the acid number reached the value of 10 mg KOH/g. The acid number is determined by the titration method.[10]

The production is filtered to remove *p*-toluenesulfonic and 4-methoxyphenol, and then the product (acrylic PP50) is obtained by evaporating toluene under low pressure. TDI (1.25 g; 7.2×10^{-3} mol) , 6 g cyclohexanone, and two drops of DBTDL are added into a round-bottomed flask and stirred slightly at room temperature. Acrylic PP50 (4.75 g; 9.6×10^{-3} mol) is dissolved in 6 g cyclohexanone, and then the obtained solution is added dropwise into flask. The whole reaction lasted for 4 h, and the final production (acrylic polyurethane diisocyanate/cyclohexanone solution) can be directly used to prepare microcapsule without any further purification. The structure of acrylic polyurethane diisocyanate is shown in Reaction b, Figure 2. To obtain a final product with higher disocyante concentration, 2.5 g of TDI is used, and all other materials and procedures are the same as previous description during synthesis.

Fourier transform infrared spectrometer (FTIR, Nicolet 5700) is used to characterize the synthesized polymer/oligomers. The measurement is performed by using a drop of acrylic PP50 or synthesized acrylic polyurethane diisocyanate on KBr windows. Uncured or cured PUA microcapsule is grinded with KBr powder, and then pressing them into crystal pieces for FTIR measurement.

Preparation of acrylic PUA microcapsules

Acrylic PUA microcapsule is obtained by using interfacial polymerization method. The detail procedure is as follows: solution with 18 g acrylic polyurethane diisocyanate/cyclohexanone solution (synthesized by 1.25 g TDI and 4.75 g acrylic PP50) is mixed together with 0.2 g 1173 and 2 g leuco D-8. O/w emulsion is formed by pouring 20 g of the organic solution into l00 mL 1 wt % PVA aqueous solution. The resulting emulsion is stirred under atmospheric pressure at 25°C for 8 h and forms PUA microcapsules containing cyclohexanone, 1173 and D-8 as core materials. The structure of PUA microcapsule wall is shown in Reaction c, Figure 2. The microcapsule slurry is decanted and washed with 30% ethanol aqueous solution to remove unreacted acrylic polyurethane diisocyanate and other organic solvent on their surfaces. The filtered microcapsules are dried at room temperature for 48 h. For convenience of description, the microcapsule is called Microcapsule A. Microcapsule B is

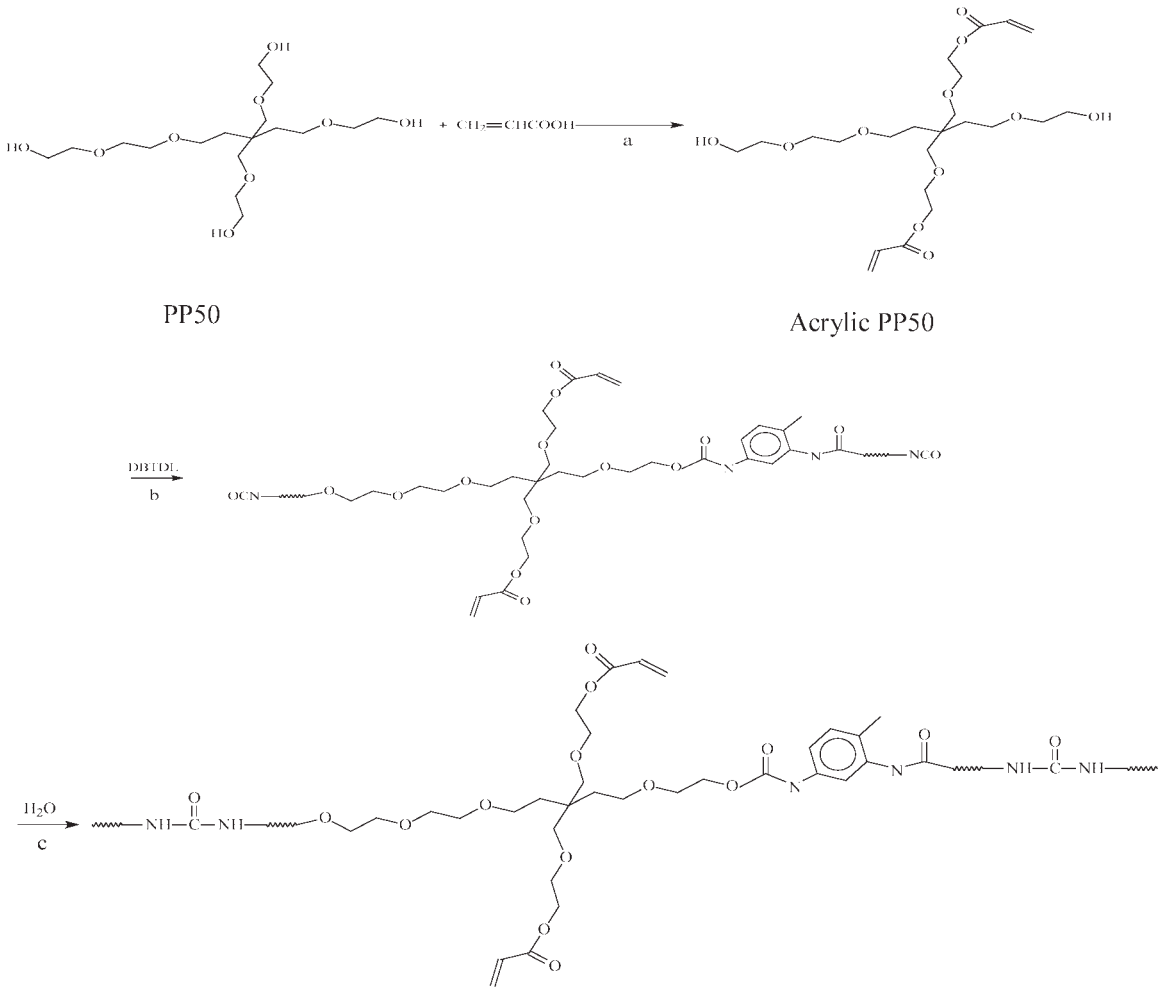

Figure 2 Three reactions in the preparation of PUA microcapsule shell.

prepared by 7.25 g acrylic polyurethane diisocyanate (synthesized by 2.5 g TDI and 4.75 g acrylic PP50), and the amounts of other components are the same with Microcapsule A. Microcapsule C is prepared in 5 wt % PVA aqueous solution and the other amounts are the same with Microcapsule B.

PUA microcapsules (Microcapsule D) containing ethyl acetate and D-8 are prepared for studying release behavior in organic solvent. The detail procedure is the same as that of Microcapsule A except that ethyl acetate is used instead of cyclohexanone and 1173 is not added.

Morphology of microcapsule is observed by using electron scanning microscope (SEM, Hitachi S-4700) and optical microscope (Olympus MM6-LS22). The microcapsule diameters can be measured from SEM images, and the size distribution is calculated based on 300 particles.

Release behavior in organic solvent

According to the studies on drug delivery,[10,11] we design the following experiment on PUA microcapsule's release behavior. Microcapsule D (0.25 g) is examined in 100 mL ethyl acetate as extraction medium, with light stirring and kept at 20°C. One milliliter of solution is drawn from the releasing system and added into volumetric flask to dilute into 25 mL solution. To ensure the volume of extracting medium unchanged, another 1 mL pure ethyl acetate is added into releasing system at the same time. The concentration of D-8 solution from the volumetric flask can be evaluated by UV/visible spectrophotometer and the corresponding concentration in releasing system can be calculated. The release profile measured in this way is indicated as uncured microcapsule release profile.

To investigate the effects of UV curing of the microcapsules on the release profile, UV radiation produced by UV dot lamp house (RW-UVA200U, RUN WING, China) is applied to the system for 30 min. The release behavior of cured microcapsules is measured in the same procedures as the uncured release profile.

Color-producing procedure under thermal treatment

Microcapsule suspension is coated on a piece of white Paper By LUG-S coating machine (Yuanda

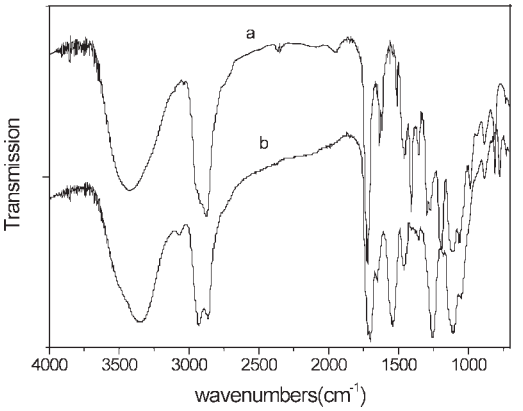

Figure 3 FTIR curves of (a) acrylic PP50 and (b) acrylic polyurethane diisocyanate.

Company, China), which is named Paper A. Another piece of white paper, named Paper B is immersed into 5 wt % D-8/cyclohexanone solution for about 5 min. Both Paper A and Paper B are dried in room temperature and are cut into pieces with dimension of 3 cm × 3 cm. A piece of Paper A is put on a piece of Paper B with the coating side face together, and then put the two pieces of paper in thermotransfer machine at certain temperature. The color changes of Paper B at different time can be measured by using UV/visible spectrophotometer assistant with integrating sphere.

Release behavior of acrylic PUA microcapsules exposed on UV radiation for 200 s on Paper A can also be determined by the color variations of Paper B. In practical application, Paper A works as image record materials, whereas Paper B is used to read the recorded image.

RESULTS AND DISCUSSION

Chemical characterization

FTIR spectra of compounds from Reactions a and b are presented in Figure 3, and their molecular structures are shown in Figure 2. As seen in Figure 3(a), the spectrum shows C=O stretching of ester at 1724 cm^{-1}, C=C stretching at 1636 cm^{-1}, and C=C bending at 987 cm^{-1}, which depicts the esterification between PP50 and acrylic acid has been achieved. In Figure 3(b), transmissions at 1710 and 1255 cm^{-1} correspond to the stretching of C=O and O=C—O—C in urethane structure, respectively, and transmission at 1541 cm^{-1} is bending of N—H in urethane, which is demonstrated by Reaction b in Figure 2.

Curves in Figure 4 are obtained by grinding uncured or cured PUA microcapsule with KBr powder, and then pressing them into crystal pieces for FTIR measurement. According to Reaction c in Figure 2, acrylic polyurethane diisocyanate can form urea and urethane structure by its reaction with water. In Figure 4(a), 3550–3166 cm^{-1} is a broad transmission band for N—H in both urea and urethane. Affected by phenyl, C=O stretching in urea has the same transmission peak at 1640 cm^{-1} as C=C in acrylic ester group. Hence, the FTIR curve in Figure 4(a) is similar to that in Figure 3(b). In Figure 4(b), having been cured by UV, the disappearance of peak at 992 cm^{-1} demonstrates crosslink reaction of acrylic double bonds.

Size distribution and morphology

Control of size distribution of microcapsule is usually affected by small changes of circumstance in interfacial encapsulation.[12] As the size of the droplets decreases, the quality of the protective polymer membrane formed around the droplets deteriorates and the extent of microcapsules agglomeration increases.[13] It has been proved that increasing agitation rate reduces size and narrows size distribution.[10] Here, we lay emphasis on influences from the concentration of protective colloid and amount of TDI used to prepare acrylic polyurethane diisocyanate.

The methods to prepare Microcapsules A, B, and C have been mentioned in section "Preparation of acrylic PUA microcapsules" and their differences are shown in Table I. Comparing Curves b and c in Figure 5, we can find that increasing concentration of protective colloid can decrease size and narrow size distribution dramatically and the direct view of this phenomenon is shown in Figure 6(b,c). Formation of microcapsule is a dynamic equilibration. Mechanical stir cuts oil phase into small pieces, and these pieces

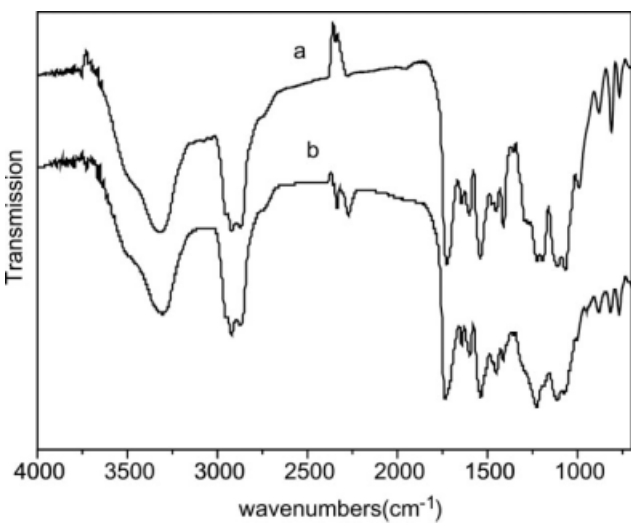

Figure 4 FTIR curves of (a) uncured PUA microcapsule and (b) PUA microcapsule cured for 300 s.

TABLE I
Statistcs of Particle Size Distribution

Microcapsule	Preparation PVA%	Preparation TDI/acrylic PP50 (mol/mol)	Statistics of particle size Mean (μm)	Statistics of particle size SD (μm)
A	1%	0.75	41.5108	26.4687
B	1%	1.50	14.5255	9.1928
C	5%	1.50	3.3223	1.0567

tend to agglomerate into bigger ones to decrease interfacial energy before the formation of microcapsule. Increasing PVA concentration leads to higher viscosity of water phase, which prevents agglomeration of oil phase and facilitate formation of microcapsules with smaller size.

Amount of TDI used to synthesize acrylic polyurethane diisocyanate is another significant factor to size control. In Table I and Figure 5, when the ratio of TDI/acrylic PP50 doubled, there also exist obvious decrease in size and narrowing in size distribution. The direct view is shown in Figure 6(a,b). According to Reaction b in Figure 2, TDI can form hard segment in polyurethane and increase amount of TDI in Reaction b can increase percentage of hard segment and lead to higer elastic modulus[14] in acrylic polyurethane diisocyanate. As is shown in Figure 7(a), microcapsule's shell seem to be soft and vulnerable to outside forces. Microcapsule's shell in Figure 7(b) possess more hard segments in molecular structure and stick to its smooth surface.

Changes of TDI amount can control size distribution through changes of acrylic polyurethane diisocyanate's property. The particular process of how size distribution is controlled deserves further study.

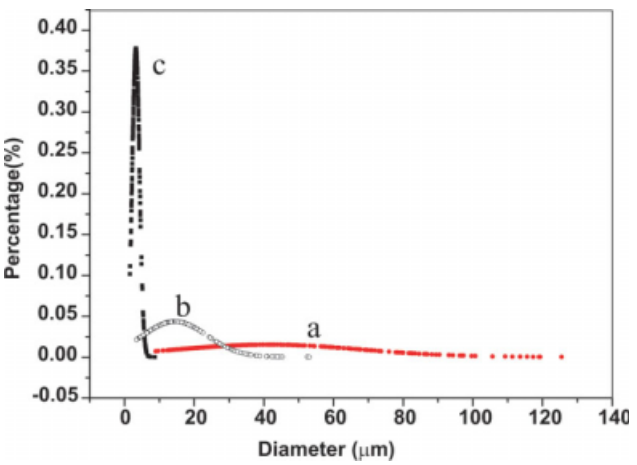

Figure 5 Size distribution of PUA microcapsules: (a) Microcapsule A; (b) Microcapsule B; (c) Microcapsule C, with stirring speed of 2000 rad/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UV irradiation can change the appearance of PUA microcapsule. Microcapsule D is prepared in the same procedure as Microcapsule A and they have the same appearance before UV irradiation. UV irradiation can shrink microcapsule shells and make

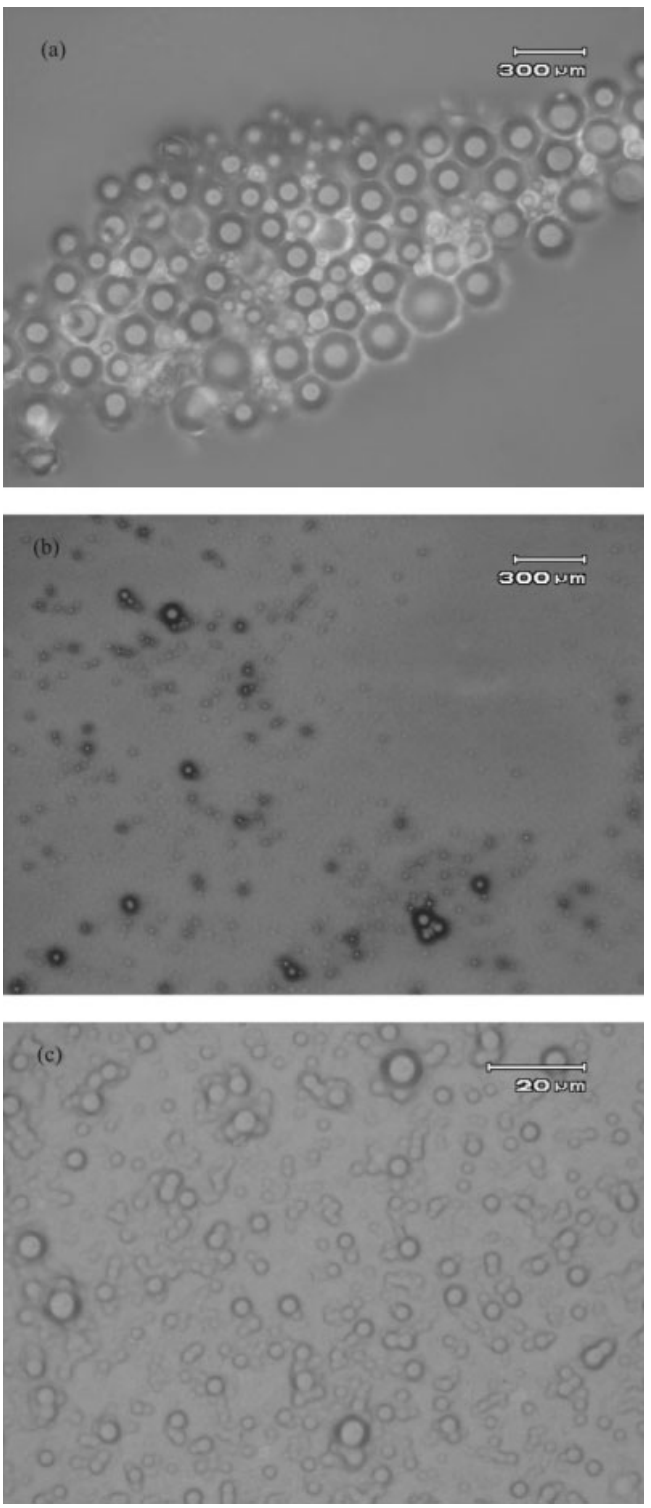

Figure 6 Optical microscopic photographs of (a) Microcapsule A, (b) Microcapsule B, and (c) Microcapsule C.

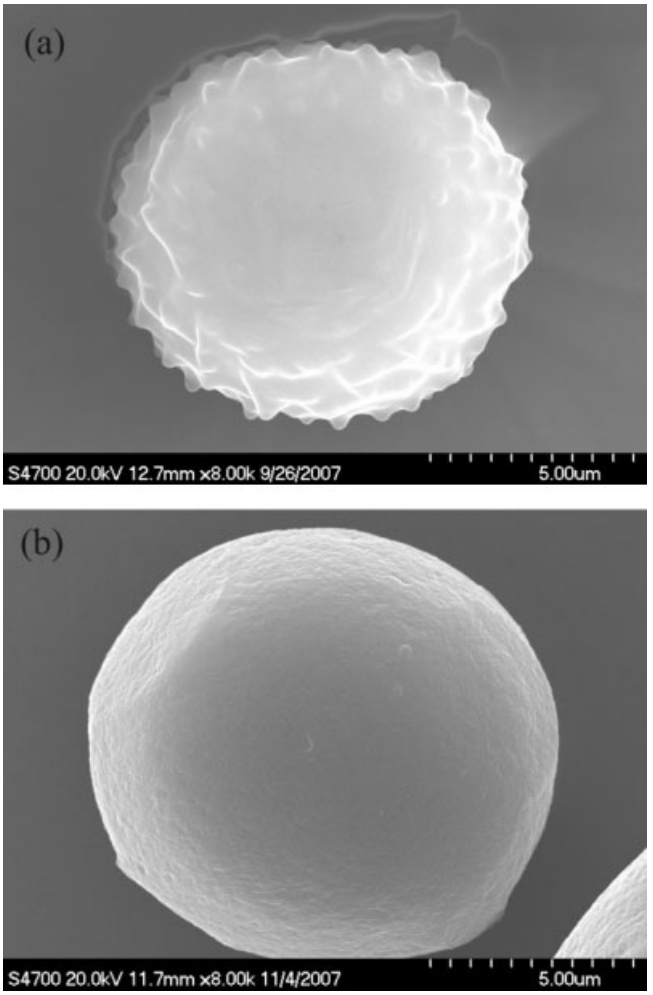

Figure 7 SEM photographs of (a) Microcapsule A and (b) Microcapsule B.

them compact. However, if the core is composed of low-boiling point solvent, such as ethyl acetate and having been irradiated by high-pressure mercury lamp, ethyl acetate with 77°C boiling point evaporates and leaves porous shells, which is shown in Figure 8(a). In Figure 8(b), the cross section of another Microcapsule D, there exist many shrunk tiny pores, because acrylic double bonds lead to shrink of whole shell under UV irradiation. Moreover, the hollow core demonstrates that photo-crosslink reaction occurs only in shells. The evaporation of organic solvent destroys the shell's quarantine and make photo-crosslink useless to release control. To avoid it, we can select UV lamp producing little heat or organic solvent with high boiling point as core.

Release property in solvent

In this study, leucocompound D-8 works as penetrator and UV/visible spectrophotometer is used to measure variations of D-8 concentration in extractor. To minimize influences, we tend to use the same solvent as extracting medium with that in microcapsule's core. Although cyclohexanone is a good solvent of D-8 and has high boiling point (155°C), it can not work as medium in UV/visible spectrophotometer. Finally, we choose ethyl acetate as extracting medium. It is hard to remove PVA on the outside surface of microcapsules prepared in 5% PVA solution and the left PVA may affect microcapsule's release property. Hence, Microcapsule D (mentioned in section Preparation of acrylic PUA microcapsules) prepared in 1% PVA is adopted.

Usually, the study on release property is carried out with microcapsules having narrow size distribution.[12,15] However, as the discussion in section "Size distribution and morphology," microcapsules prepared in 1 wt % PVA aqueous solution have wide size distributions. Takao proposed an equation to solve this problem.[16] With the help of integral, a wide size distributing microcapsule group is regarded as cooperation of various narrow size

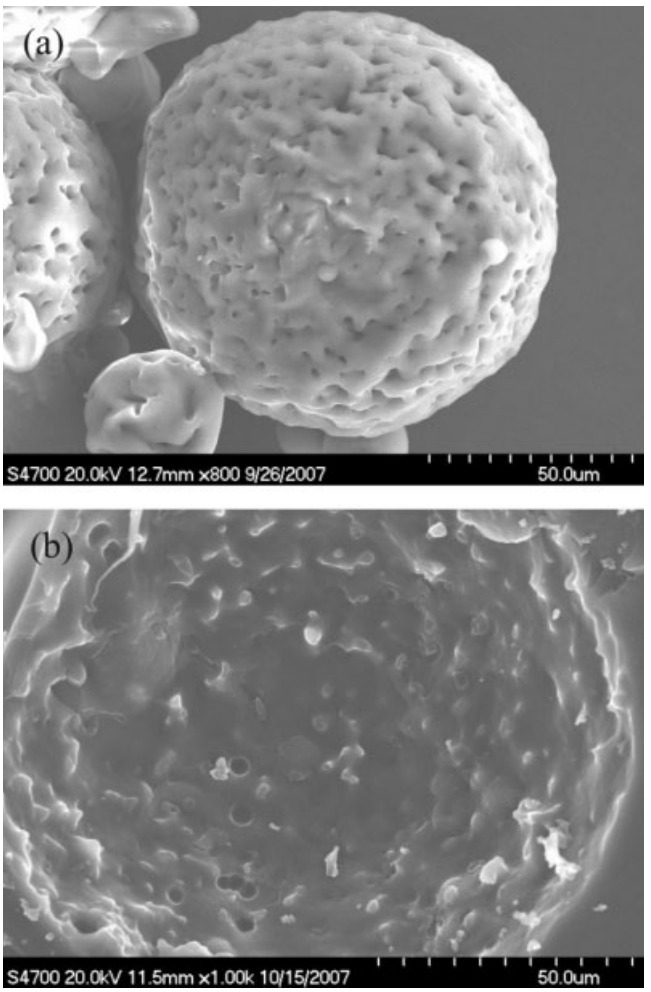

Figure 8 SEM photographs of (a) cured Microcapsule D and (b) cross section of (a).

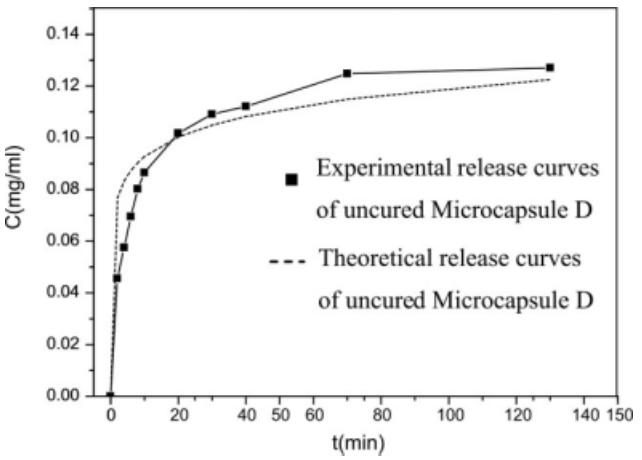

Figure 9 Experimental and theoretical release curves of uncured Microcapsule D.

distributing microcapsule groups. The final equation is as follows:

$$\ln^{\ln}\left(1-\frac{C}{C^{\mathrm{eq}}}\right)^{-1}=\alpha\ln\ t-\alpha\ln\ \tau_{\mathrm{eff}} \qquad (1)$$

In which, C means concentration of penetrator in extracting medium at a given time. C^{eq} is concentration of penetrator in extracting medium at equilibrium state. α reflects size distribution of microcapsule, and the narrower size distribution, the nearer α to 1. τ_{eff} means effective time for release, in which 63.2% penetrator is released.

Based on the experimental data in Figure 9, two parameters can be calculated, $\alpha = 0.33448$, $\tau_{\mathrm{eff}} = 27.06534$, which are got by the least square method. With these parameters, a theoretical release curve is drawn in Figure 9, which can describe the release property of uncured PUA microcapsule properly.

Curves in Figure 10 dedicate that uncured microcapsules release D-8 quickly during the first 20 min and then the release rate decrease dramatically. Having been irradiated by UV dot lamp house for 30 min, D-8 can only be detected more than 1 h later. The result confirms that PUA microcapsule has satisfying photo-controlled release property in organic solvent.

Thermo-release property

To assess released amount of dye in dry state, reaction between leuco and its coupler is helpful. In heated circumstance, thermosensitive leuco obtains color through reaction with its coupler. Dense of color increases with the development of reaction. Hence, changes of photodensity can be used to describe thermo-release property of microcapsules.[16] Light reflectance spectrophotometer has the same function.[17] K/S value is another common method to evaluate color depth and can build direct relationship with dye's concentration.[18] However, its application is limited to simple colors, such as blue, yellow,[18] which possess one obvious $\lambda_{\max}$.

In this study, thermosensitive dye used is black without any obvious $\lambda_{\max}$ in UV/visible spectra. To make accurate description on color changes, we select UV/visible spectrophotometer assisted by integrating sphere for color measurement. According to International Commission on Illumination (CIE) color space,[19] lightness (L*) calculated from tristimulus values, is an important property of color. It can change from 0 (total black) to 100 (total white) and the higher, the brighter. Since the reaction between the leuco and its coupler is changed from colorless to black, L* is suitable to our study. L* has been applied in many fields successfully, such as in medicine to assess teeth health[20] and skin bruise,[21] in geology to determine concentration of hematite[22] or water in soil.[23] Because many physical or chemical changes bring color changes, it is feasible to relate those changes in lightness. In a given thermosensitive dye system, development of reaction decreases L* correspondingly.

In Figure 11, point blank means the lightness of blank white paper. Coated with microcapsule suspension colloid, lightness of paper decreases because the paper's surface changes from smooth to coarse and the coat is not as white as paper. Three curves under different thermo treatment depict PUA microcapsule can release core substance at dry state and the release speed increases with ascent of temperature.

Curves in Figure 12 show the similar trend to those in Figure 11. However, UV irradiation can retard release of core substance and change of the

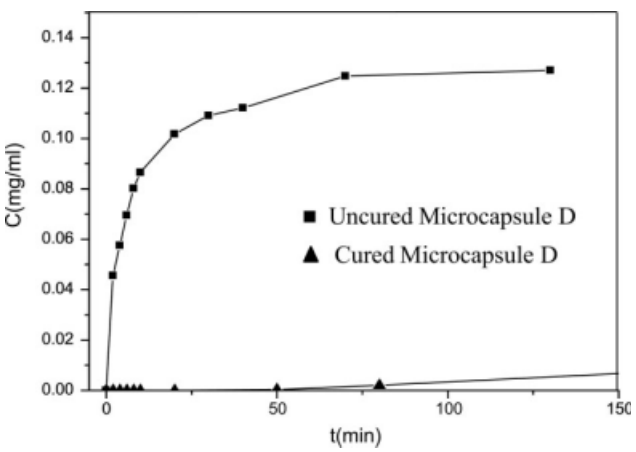

Figure 10 Release curves of both uncured and cured Microcapsule D.

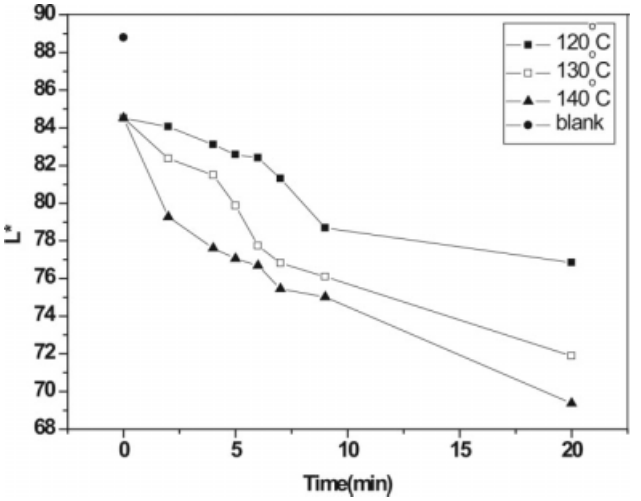

Figure 11 Release curves of uncured PUA microcapsule by different heat treatments.

curves is much smaller than their counter partners in Figure 11.

ΔL* means difference of lightness between uncured and cured microcapsule. Here, a conclusion can be drawn that to maximize the difference of lightness between uncured and cured areas, prolonging time for thermo-treatment and increasing temperature are effective ways. However, it is noteworthy that the trend of 140°C is different from the other two in each figure. The thermo-release property may be changed nearing boiling point of core (155°C). High temperature may cause unsteady release of microcapsule. Hence, to PUA microcapsule, 130°C is an appropriate temperature for steady and quick release and 10 min is an acceptable time period.

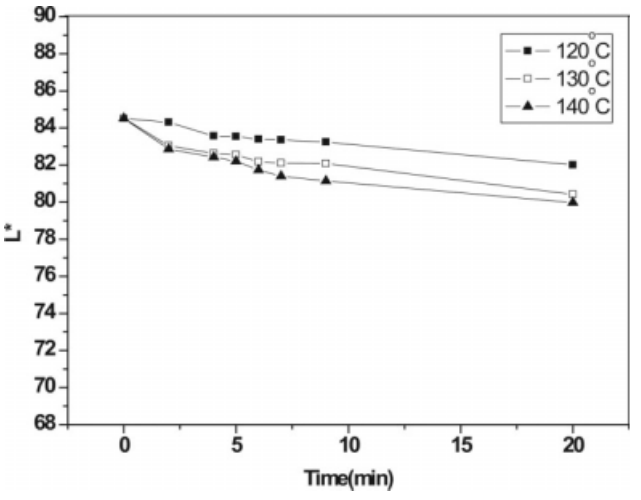

Figure 12 Release curves of cured PUA microcapsule by different heat treatments.

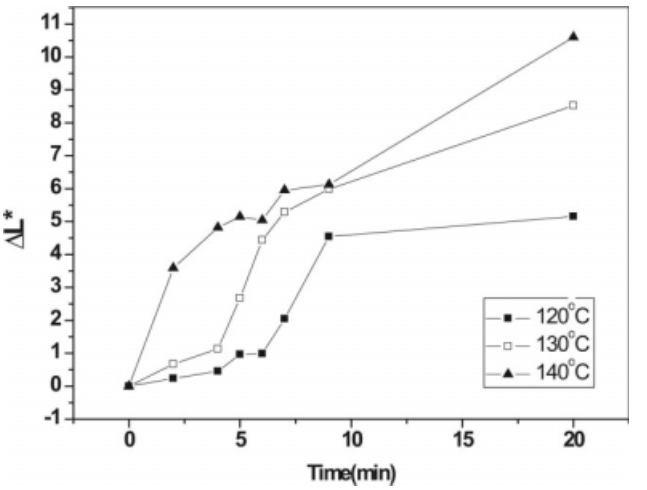

Figure 13 The difference of lightness between uncured and cured PUA microcapsule by different heat treatments.

CONCLUSION

A new method to control behavior of microcapsules is proposed on the basis of photosensitive PUA shells prepared by interfacial polymerization. During the formation of microcapsules, the size distribution and morphology are influenced dramatically by concentration of protecting colloid and mol ratio of TDI/acrylic PP50 in the synthesis of acrylic polyurethane diisocyanate. 5 wt % PVA solution ensures relatively uniform size and small diameter. Increasing amount of TDI in the synthesis of acrylic polyurethane diisocyanate can decrease average size of microcapsules.

UV irradiation can vary shells' permeability effectively by photopolymerization of acrylic double bond. The 30-min irradiation from UV dot lamp house can prevent dye release of microcapsule in organic solvent at room temperature. SEM photograph of Microcapsule D's cross-section confirm that the crosslink occurs only in shells. Even at high temperature (120–150°C), the release behavior of microcapsules in dry state is varied definitely by UV irradiation. The great difference between uncured microcapsules and those cured ensure them a promising information-recording material.

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