Microencapsulation of energy conversion photochromic materials with epoxy resin shell by interfacial polymerization

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Abstract. In this study, a novel type of photochromic spirooxazine microcapsule was prepared by interfacial polymerization between epoxy resin and polyamine compound. The effects of different process parameters on the formation, microstructure and performance of microcapsules, such as curing reaction temperature, emulsification shear rate and the addition of silica nanoparticles were studied in this paper. The morphology, microstructure, diameter and distribution, as well as the thermal stability of microencapsulated photochromic spirooxazine were also investigated by field emission scanning electron microscope, laser particle size analyzer and thermogravimetric analysis systematically. In addition, the photochromic performance of microcapsule was studied as well.

1. Introduction

Photochromic material refers to a kind of smart material that can undergo color change after stimulated by a light source, it has been widely used in smart anti-counterfeiting, information storage, textile and apparel, daily necessities and other fields [1-5]. When exposured directly to external oxygen, pH, light, heat and other occasions, the chemical structure of photochromic dyes would change inevitably, and then probably result in the attenuation or instability about discoloration performance [3]. Encapsulation of photochromic materials can achieve permanent solidification to core material and protect it from the external environment effectively [6-7], then facilitate its application and increase its weather ability.

Zhou et al. [2] encapsulated a variety of photochromic materials via in-situ polymerization, they prepared microcapsules with melamine-formaldehyde (MF) as shell. The absorbance test showed that it would reach an absorbance maximum value when the mass concentration of the photochromic materials was 2 wt%, and the value would vary with the different photochromic material. The lifetime of photochromic microcapsules could extend from 6~7h to 69~75h under continuous UV, meanwhile the performance of water resistance, acid/alkali resistance, soaping resistance, light resistance and fatigue resistance have improved. Photochromic materials can also be encapsulated through physical mechanical methods. Valh et al. [8] dissolved different amounts of photochromic materials and ethyl cellulose in dichloromethane to obtain a homogeneous oil phase, then the mixture of oil phase and water phase was emulsified to obtain nano-sized emulsion droplets, finally the photochromic

nanocapsules were prepared by solvent evaporation method. There exist residual formaldehyde when select amino resin (such as melamine formaldehyde resin, urea formaldehyde resin, phenolic resin, or their copolymers) as shell of microcapsules [9-11], which is irreconcilable with the current concept of green sustainable development, and organic solvents generated during this microencapsulation could also destroy our environment and health, all of these limited the popularization and application of photochromic microcapsules. Epoxy resin have a variety of types, these characteristics such as low viscosity, low shrinkage, high bond strength, good electrical insulation properties and chemical stability, make it be researched extensively in aerospace, automotive manufacturing, electronic technology, textiles and other fields[12-14].

Though there were some reports about epoxy resin microcapsules prepared by interfacial polymerization [14], photochromic microcapsules with epoxy resin shell have not been almost studied. In this paper, E-51 epoxy resin was selected as shell-forming prepolymer, and ethylenediamine as curing agent to form the shell, photochromic spirooxazine dissolved in dioctyl phthalate and subsequently microencapsulated through interfacial polymerization. The morphology, microstructure, diameter distribution, thermal stability and photochromic performance of microencapsulated photochromic spirooxazine were investigated systematically.

2. Experiment

2.1. Materials

Epoxy resin (E-51, 65wt%) purchased from Jining Baiyi Chemical Co. Ltd. and ethylenediamine from Tianjin Guangfu Fine Chemical Research Institute were used to synthesize the shell of microcapsule; Spirooxazine, a photochromic material was kindly supplied by Tianjin UVOS Tech Co. Ltd.; Dioctyl phthalate (DOP, Tianjin Weichen Chemical Reagents Co. Ltd) was employed as solvent; an aqueous solution of the sodium salt of styrene-maleic anhydride copolymer solution (SMA, 19 wt%) was kindly supplied by institute of functional fiber (Tianjin Polytechnic University), and employed as dispersant. Nanosilica (solid content 27.47 wt%), purchased from Xuancheng Jingrui New Material Co. Ltd. All chemicals were of reagent quality and used as received without further purification.

2.2. Fabrication of photochromic microcapsules

Photochromic microcapsules with epoxy resin shell were fabricated as follows: 54g E-51 epoxy resin, 54g spirooxazine and dioctyl phthalate solution were mixed to obtain oil phase, 60g SMA and 200g distilled water formed aqueous phase, the mixture of oil phase and aqueous phase was homogenized using a homogenizer at 5000 rpm for 30 min to obtain stable oil-in-water emulsion. The emulsion was then transferred to three-necked flask under stirring at 300 rpm and a certain temperature. 6g ethylenediamine was added dropwise to flask with speed of 3 g/h. After 2 hours, the interfacial reaction of epoxy resin and curing agent ethylenediamine completed, photochromic microcapsules were finally obtained after centrifuged, washed and dried.

2.3. Characterization

The surface morphology of microcapsules were observed and analyzed using field emission scanning electron microscope (FE-SEM, S-4800). The particle size and distribution of microcapsules were gauged by laser scattering particle size distribution analyzer (LA-300). TGA (thermogravimetric analyzer, Netzsch, STA449F3) was used to investigate the thermal stability of microcapsules, the temperature range was 20~800oC and scanning rate was 10 oC•min-1 under nitrogen atmosphere. In addition, camera was used to photograph and compare the microcapsule samples before and after exposured by ultraviolet light.

3. Results and discussions

3.1. Effect of temperature on epoxy resin curing

Ethylenediamine containing an active hydrogen atom could interact with the epoxy resin, which make epoxy group ring-open and form hydroxyl group, then the etherification reaction happened between resulting hydroxyl and epoxy group, after underwent liquid and gel stage, a net or body polymer finally generated. The Influence of different temperature on curing process between epoxy resin and ethanediamine was investigated and results were shown in Figure. 1. By contrast, it could be clearly seen that the E-51 epoxy resin still remain flowing liquid state as shown in Figure. 1(f) and (g), which was mainly resulted from that epoxy and ethylenediamine didn't start to react substantially at 20°C and 30°C. When temperature increased to 40°C, there appeared some gel-like materials, and epoxy cured completely at 60°C, the cured polymer had strong mechanical properties as Figure. 1(e) and (j) shown. So we concluded that suitable curing temperature of E-51 epoxy resin and ethylenediamine was 40 °C~60 °C, and further confirmation of accurate temperature should be explored by other experiments below.

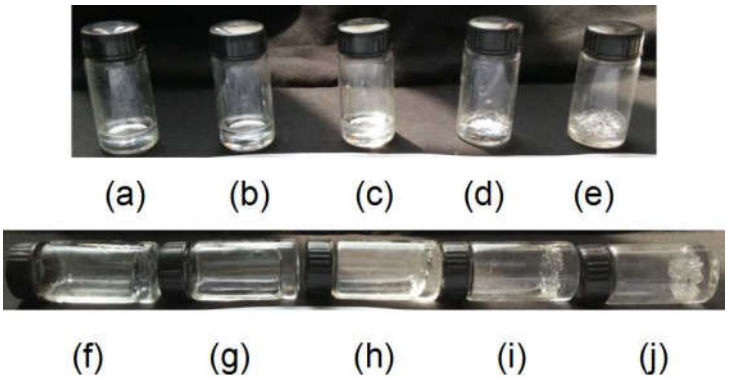

Figure 1. Influence of different temperature on curing reaction between epoxy resin and ethanediamine: (a) (f): 20°C; (b) (g): 30°C; (c) (h): 40°C; (d) (i): 50°C; (e) (j): 60°C.

3.2. Effect of curing temperature on the morphology of microcapsules

The morphology of microcapsules prepared with different temperature were characterized by FE-SEM shown in Figure. 2. As presented in Figure. 2(a) and (d), microcapsules still didn't form fully at 40°C, this might due to the curing reaction between epoxy resin and ethylene diamine have not carried out completely at this temperature. When temperature was raised to 60°C, it could be observed that most microcapsules with irregular shape glued together, which attributed to the reaction was too rapid at 60°C, microcapsules have shaped before they had not formed spherical, this also caused serious adhesion to each other. By contrast, microcapsules prepared at 50°C were uniform and dispersed well as shown in (b) and (e), however, the product was not plump, this depressions were likely to because the thin shell didn't have sufficient mechanical strength to support the original spherical shape, resulting in the evaporation of liquid core material during sample processing.

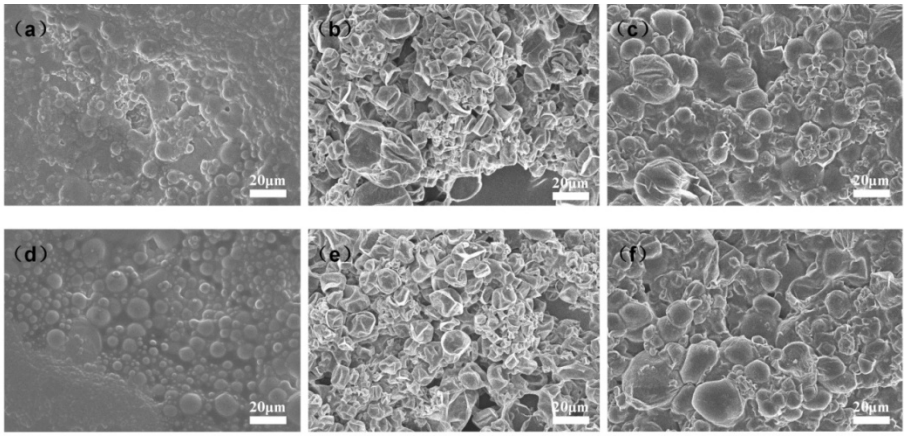

Figure 2. Influence of different curing temperature on the structure and morphology of microcapsules: (a) (d): 40°C; (b) (e): 50°C; (c) (f): 60°C.

3.3. Effect of emulsifying rotation speed on morphology

The micrographs in Figure. 3 displayed the morphology of microcapsules fabricated with different emulsifying emulsification rate, and Figure. 4 showed the particle size and distribution of corresponding microcapsules. As presented in Figure. 3, the microcapsules size decreased with an increase in emulsification speed. When emulsified with 3000 rpm, microcapsules with diameter ranging from 10 to 40 μm were fabricated, the distribution curve in Figure. 4(a) also shown that the particle size distribution was wide, the particle size of the microcapsules in 11~30 μm was about 94%, and the average particle size was calculated to be 21.88 μm. Besides, we could find broken microcapsules in Figure. 3(a), this because it was difficult to encapsulate these large size drops, the large diameter capsules were also limited their applications in fiber spinning, coating, plastics processing and other fields. When emulsification speed enhanced to 6000rmp, the average particle size was reduced to 18.67 μm accordingly, the size distribution became narrow as Figure. 4(c) and (d) displayed. When emulsifying speed increased to 9000 rpm, the particle size of microcapsules were 15.65 μm. This decrease was not obvious, which might own to the high viscosity of epoxy resin in the oil phase limited its emulsification efficiency to some extent. However, the addition of co-emulsifier or lower viscosity epoxy resin could be selected to produce microcapsules with optimal diameter and broaden its application.

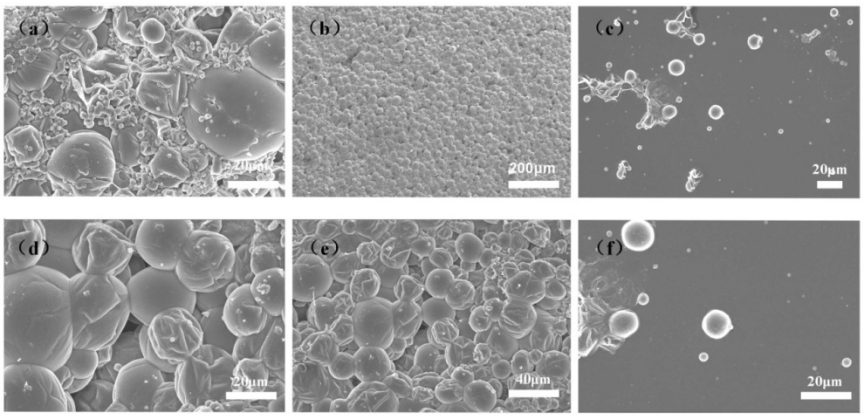

Figure 3. Structure and morphology of microcapsules under different emulsifying emulsification speed (a) (d): 3000rpm; (b) (e): 6000rpm; (c) (f): 9000rpm.

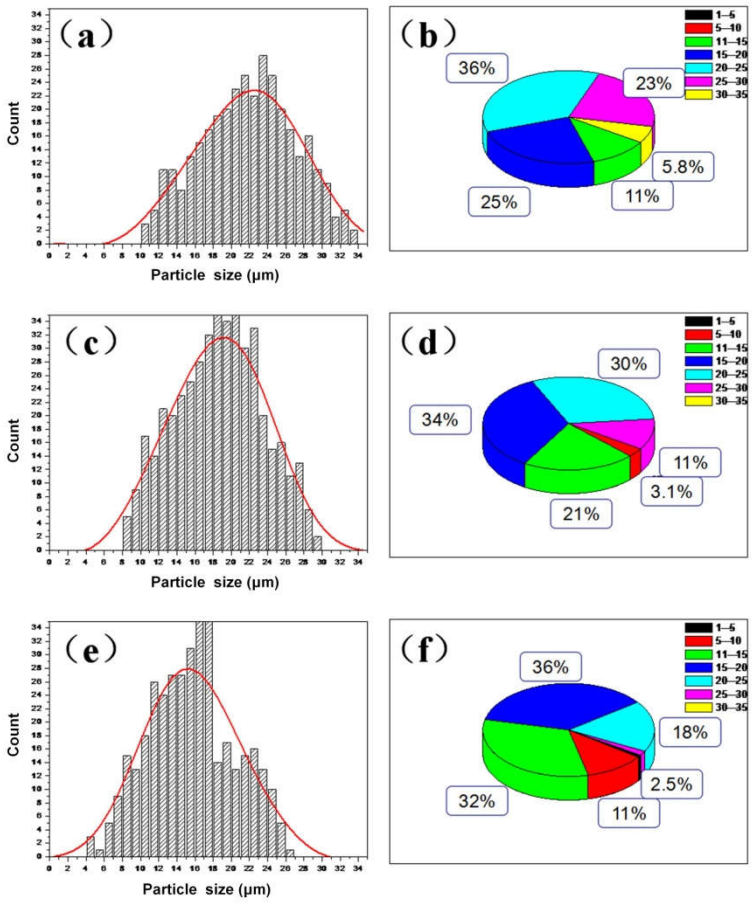

Figure 4. Particle size and distribution of microcapsules under different shear emulsification speed

(a) (d) 3000rpm; (b) (e) 6000rpm; (c) (f) 9000rpm.

3.4. Effect of silica nanoparticles addition on morphology of microcapsules

In order to reduce the adhesion between microcapsules and enhance the dispersibility and mechanical properties of product, we added silica nanoparticles suspension during the microcapsule preparation process. The morphology comparison of microcapsules with or without nano-silica were shown in Figure. 5. As can be seen, after modification with silica nanospheres, the dispersibility of microcapsules has been improved significantly, and the adhesion situation was also controlled. Besides, it could find that microcapsules show plump spherical shape after adding silica nanospheres, which also proved that mechanical properties of microcapsules had little improvement. At the same time, there were some silica nanospheres on the surface of microcapsules, and only little fell out after undergoing multiple centrifugation, this demonstrated the silica nanospheres have bound well on the microcapsules shell, so that the mechanical property of microcapsules could be enhanced.

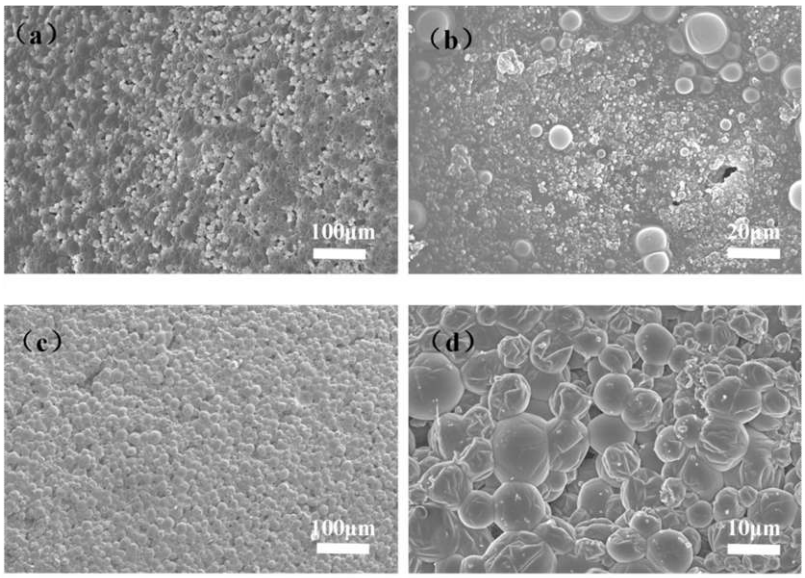

Figure 5. Influence of silica nanoparticles on microcapsules (a), (b) microcapsules adding silica nanospheres (c), (d) microcapsules without silica nanospheres

3.5. The discoloration properties of photochromic microcapsules

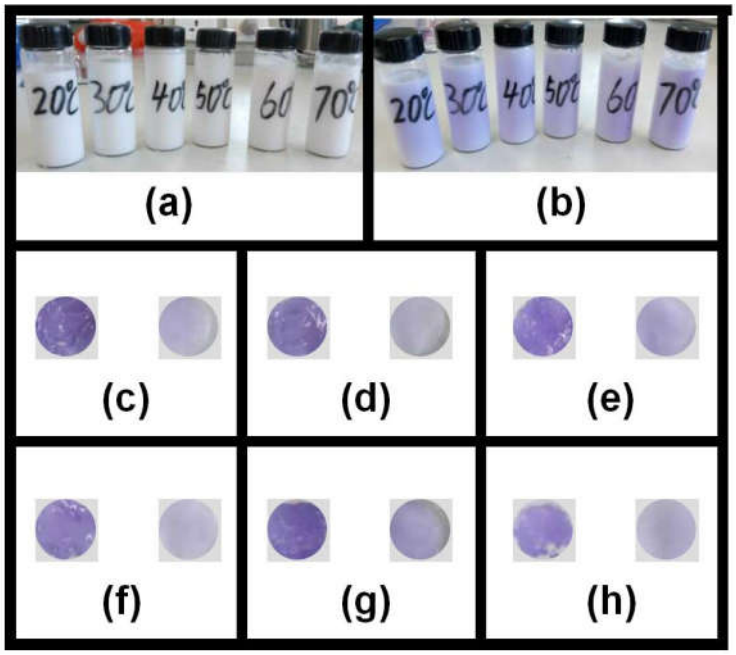

Figure 6. Images of (a) photochromic microcapsules before UV-irradiation and (b)after UV-irradiation; the discoloration of centrifugal supernatant liquid and precipitate with different temperature treated (c) 20°C (d) 30°C (e) 40°C (f) 50°C (g) 60°C (h) 70°C.

It could be seen clearly from Figure. 6(a) and (b) that after irradiation of UV light, the color of the microcapsule suspension changed from colorless to violet and remained for a while. After centrifugal separation, the supernatant liquid and precipitate were obtained respectively, as Figure. 6 (c-h) shown, the supernatant liquid had little color transform, and in comparison, the precipitate in lower layer was discolored obviously after irradiation. Besides, optical microscope and SEM were used to further

confirmed that there were no microcapsules found in supernatant liquid, and microcapsules in lower sediments were packed densely, which could due to the fully cured epoxy resin product had higher density than water, this also verified encapsulation efficiency was high. In addition, heat treatment at a temperature from 20° C to 70° C had little effect on the discoloration properties of photochromic microcapsules.

3.6. Thermo gravimetric analysis of photochromic microcapsules

The thermal stability of photochromic microcapsule is considered as a key parameter for its practical application, therefore, TGA measurements of photochromic and microencapsulated photochromic were performed as shown in Figure. 7 As can be found, photochromic material began to lose weight at about 226°C, and the temperature of maximum weight loss rate was 270°C, after encapsulated by the epoxy resin, the photochromic microcapsule began to loss weight at 239°C, this illustrated that epoxy resin shell provided a thermal resistance for photochromic core, which could protect it from permeation firmly, and the maximum weight loss temperature of microcapsules rose to 368°C, which improved about 128 °C compared to core material, this improvement of thermal stability extend its application in many fields. More importantly, microencapsulation can also block the oxygen, light, and pH of external environment to prolong its weather ability.

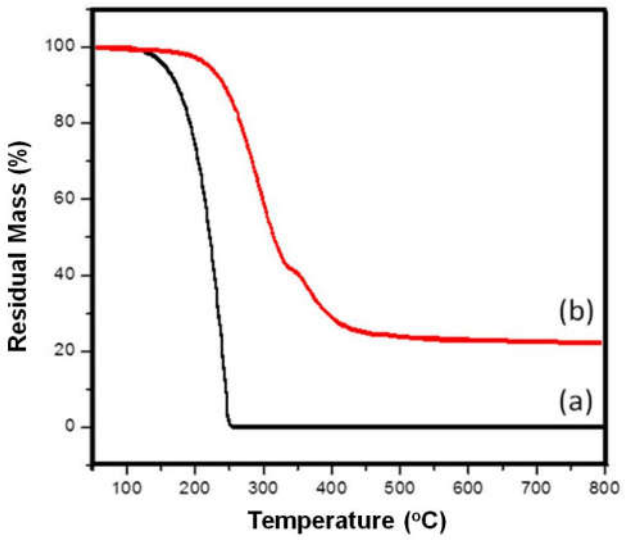

Figure 7. TGA curve of epoxy resin photochromic microcapsule: (a) photochromic material; (b) photochromic microcapsule.

4. Conclusion

In this work, photochromic spirooxazine was encapsulated by interfacial polymerization using epoxy resin E-51 and ethylenediamine successfully. The measurement results showed that suitable curing temperature of epoxy and ethylenediamine was 50°C, spherical microcapsules with uniform particle size were fabricated. With emulsification rates gradually increasing, the particle size of photochromic microcapsules reduced from 21.88 μm to 15.65 μm, the distribution of particle size turned narrower. Besides, the addition of silica nanospheres during microcapsule preparation could improve its dispersibility and mechanical property effectively, and microcapsule exhibited excellent discoloration property under UV irradiation. Furthermore, compared to core material, the initial and maximum weight loss temperature of microcapsule improved 44 °C and 128°C respectively. Owing to its thermal stability, photochromic microcapsules would also offer tremendous potential applications in intelligent textiles, fibers, solar energy storage and other fields.

Acknowledgments
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