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Preparation and heat sensitive color-developing behaviour of poly (MMA-*co*-St) nanocapsules

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Abstract

The heat sensitive color-developing poly(methylmethacrylate-*co*-styrene) (P(MMA-*co*-St)) nanocapsules were prepared by emulsion polymerization with leucocompound as a core material and P(MMA-*co*-St) as a wall material. The nanocapsules were characterized by scanning electron microscopy(SEM), Fourier transform infrared spectrophotometry (FTIR) and densitometry. The effects of St Content on the heat sensitive color-developing behaviours of nanocapsules were discussed in detail. The FTIR analysis of leucocompound-containing nanocapsules demonstrated that leucocompound was successfully encapsulated in the nanocapsules. The resultant nanocapsules at St content being 20wt% had smooth surface. The nanocapsules with different St content showed different heat sensitive color-developing behaviour.

Keywords: Poly(MMA-*co*-St) nanocapsule, emulsion polymerization, heat-sensitive color-developing behaviour

1. Introduction

At present, stimuli-sensitive nanocapsules have attracted more and more attention due to their potential applications in widespread fields such as phase change material, controlled drug delivery system, magnetic nanocarrier, food and so on[1-4]. Heat sensitive color-developing nanocapsules encapsulating a leuco compound have been widely employed in the heat-sensitive recording material, including medicinal images, printers, labels and facsimiles, etc. [5]. The leucocompound is an electron-donating dye precursor, which reacts with the electron-accepting compound (developer) to develop a color. However, because of very strong activity of leuco compound it is hoped to coat leucocompound with a protective matrix or wall of synthetic or natural polymers by nanoencapsulation technique [6, 7]. In other words, the sensitive leucocompound is first isolated from the external medium in order to avoid the adverse reaction at ambient temperature. And then when the wall of the nanocapsule is heated above its glass transition temperature, the material transmittance of the wall increases and the leucocompound contained in the core of the nanocapsule and the developer outside of the nanocapsule transmits the wall of the nanocapsule to develop a color, in which the nanocapsule is not broken by heat and has the heat-sensibility control ability [5, 8].

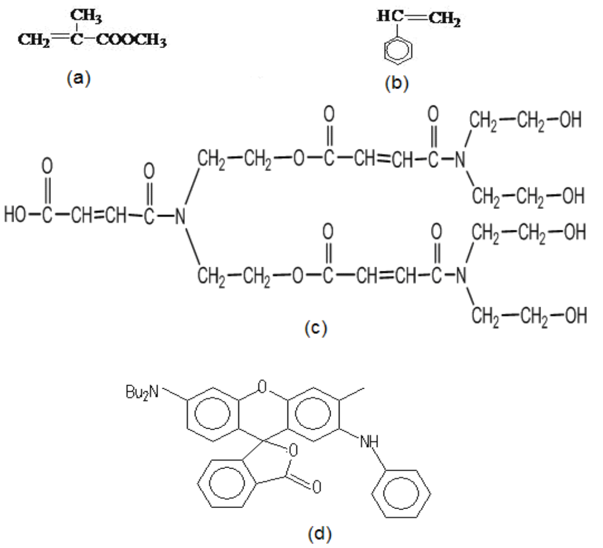
Herein we synthesize the nanocapsules by conventional emulsion polymerization of methylmethacrylate (MMA) using St as a comonomer and unsaturated hyperbranched poly (amide-ester) as a cross-linking agent to obtained the nanocapsules with different heat sensitive color-developing behaviour. The nanocapsules are characterized by SEM, FTIR and densitometry. The effects of St content on the heat sensitive color-developing behaviours of nanocapsules are discussed in detail.

2. Experimental

2.1 Materials

Methyl methacrylate (MMA, distilled under vacuum prior to use) was purchased from Tianjin Huadong Reagent Factory. Styrene (St, distilled under vacuum prior to use) was purchased from Tianjin Huadong Reagent Factory. Ammonium persulfate (APS) was purchased from Beijing the Third Chemical Reagent Factory. Triton X-100 was purchased from Shanghai Tianlian Fine Chemical Reagent Co. Poly(vinyl alcohol) 224 (PVA 224) was purchased from Junsei Chemical. Ethyl acetoacetate was obtained from Tianjin Damao Chemical Reagent Factory. Ethyl acetate was obtained from Tianjin Meilin Chemical Co.. The leucocompound was 2-Phenylamino-3-methyl-6-(di-*n*-butylamino) fluorane and was obtained from Jiangsu Longsheng Co. Benzyl *p*-hydroxybenzoate was obtained from Jiangsu Longsheng Co.

All the purchased reagents were in analytical grade. Hyperbranched unsaturated poly(amide-ester) (UHBP) ($\overline{M}_w$, 3775) was produced according to the literature[9]. Scheme1 shows the chemical structure of the aforementioned wall-forming materials and core material.



Scheme 1: Chemical structure of wall-forming materials and core material used: MMA (a), St (b), UHBP (c), and leucocompound (d)

2.2 Preparation of nanocapsules

In a typical synthesis, 1.2 g of the leuco compound was previously dissolved in 1.2 g of ethyl acetoacetate and 5.6 g of ethyl acetate. The prepared solution that became an oil component in the system was poured into 32.0 g of aqueous solutions containing 1.8 g of PVA224 and 0.24 g of Triton X-100. The mixture was then vigorously agitated at 6500 r/min for 12 min with a homogenizer (BME100L, Shanghai Weiyu Co.) to obtain o/w emulsion. The o/w emulsion was poured into a four-necked flask equipped with a magnetic stirrer (Tokyo Rikakikai Co., Ltd.), a thermometer, and a nitrogen gas inlet and outlet. Then the flask was immersed into a 70 °C oil bath and the nitrogen gas was bubbled through the solution for deoxygenation. The stirring speed was fixed at 500 r/min. After 20 min, the mixture of the desired amount of MMA and St and 0.6 g of the cross-linking agent (UHBP) were poured into the reaction flask and stirred for 15 min. Then 0.06 g APS was added into the reactor. The polymerization was carried out at 70 °C for 5 h. The obtained nanocapsule slurry was first washed with distilled water and centrifuged three times at 16000 r/min for 20 min, and then washed with ethyl acetate to remove free leucocompound on their surfaces and dried for at least 24 h under reduced pressure at ambient temperature.

2.3 Characterizations of nanocapsules

The morphology of the nanocapsules were observed by scanning electron microscopy (SEM, JSM-5400, JEOL, Japan). The nanocapsules were sprinkled onto a double-sided tape, sputter-coated with gold and examined in the microscope using the accelerated voltage of 30 kV. The IR spectra were recorded with a Fourier transform infrared spectrophotometer (Vector22, Bruker Co., Germany). The sample were ground with dried KBr powder, and compressed into a plate. The KBr plate was scanned by a FTIR spectrophotometer.

2.4 Heat sensitive color-developing behaviours

The heat sensitive color-developing behaviour measurement was performed by a conventional method [10]. The mixture containing 1.0g of nanocapsule and 0.5g of developer suspension was dipped on a polyethylene terephthalate (PET) film, spread homogeneously with a wire bar and dried completely by a dryer. The protective colloid, PVA, played the role of a binder between the PET sheet and the nanocapsule thin layer. The thickness of the coating layer was ca. 15 μm, which was evaluated by a thickness analyzer (Carl Zeiss Jena Co., Germany). The color yield of color-produced nanocapsules was evaluated as the transmission density. And then the transmission density by using a thermal printer with changing heat energy applied to a thermal head was measured using an X-Rite-310 densitometer (Michigan Co., USA).

3. Results and discussion

3.1 Morphology of nanocapsules

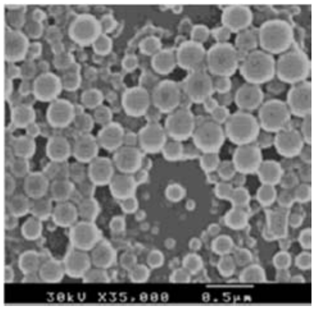


Fig 1: SEM photograph of nanocapsules

Fig1 illustrates the scanning electron microphotograph of the nanocapsules at the St content being 20wt%. As displayed in Fig1, the nanocapsules exhibit smooth surface and spherical shape and good dispersibility. The particle sizes mostly concentrate between 50 nm and 450 nm. The morphology of nanocapsules will affect other properties of nanocapsules[11].

3.2 Chemical structure of nanocapsules

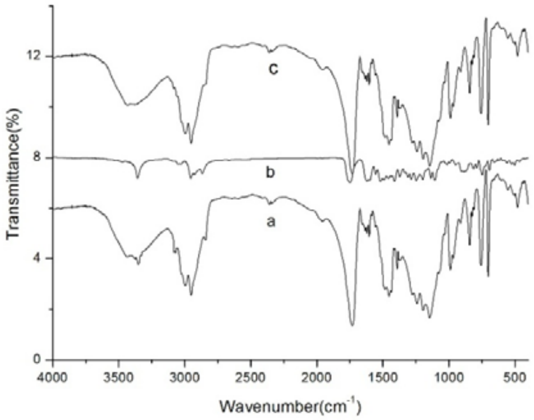


Fig2: FTIR spectra of **a** leucocompound-containing nanocapsules, **b** leucocompound and **c** the shells made from crosslinked P (MMA-*co*-St)

FTIR spectroscopy results for the samples are shown in Fig2. Fig2a corresponds to leucocompound-containing nanocapsules, and Fig2b and Fig2c to leucocompound and the shells that were prepared in the same way as the hybrid systems without the addition of leucocompound, respectively.

In the spectrum of Fig2c, =C-H stretching in the phenyl ring at 3040 cm^{-1}, C=C stretching and =C-H out-plane rocking vibration in the phenyl ring at 1550 cm^{-1}, 1520 cm^{-1} and 750 cm^{-1}, 690 cm^{-1} are observed[12]. Furthermore, the peaks at 1390 cm^{-1} and 1440 cm^{-1} are attributed to the $-CH_3$ vibration and CH_3-O vibration of MMA, respectively. The peak with wavenumber of 1640 cm^{-1} corresponds to the amide bond stretching of UHBP[9]. The results confirm that the shells of the nanocapsules are composed of crosslinked P(MMA-*co*-St) as expected. In addition, as shown in the spectrum of Fig2a, N-H stretching appears at 3350 cm^{-1}, indicating that leuco-compound is encapsulated in the nanocapsules. Moreover, the characteristic peaks of the shells as described above (Fig2c) are observed. Thus we could say that the nanocapsules with leucocompound as a core material and crosslinked P(MMA-*co*-St) as a wall material can be prepared by this method.

3.3 Heat sensitive color-developing behaviours

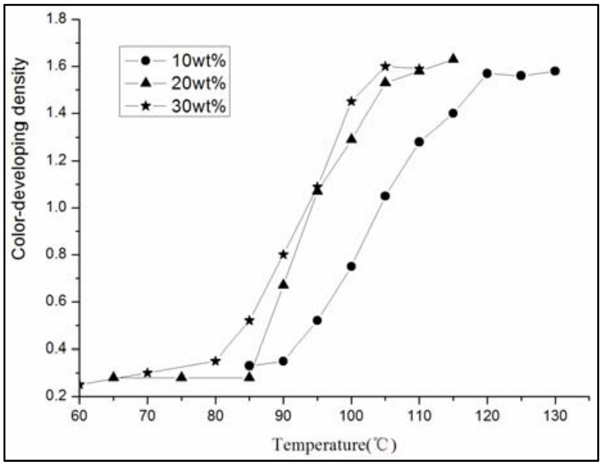


Fig3: Heat sensitive color-developing density of nanocapsules prepared at different St content

Fig3 exhibits the heat sensitive color-developing density of the resultant nanocapsules at different St content, in which all values of density have no change below glass transition temperatures of nanocapsules prepared at different St content, confirming that the walls of resultant nanocapsules are compact. And when the nanocapsules prepared at different St content were heated above its glass transition temperatures, the color-developing density values increased with increasing the temperature. Our previous work reported that glass transition temperatures of the nanocapsules for 10wt%, 20wt% and 30wt% of St were 112.0, 107.7, and 103.6°C, respectively[13]. For example, the value of density has no change below 85 °C at the St content being 20wt%. And when the nanocapsule was heated above 85 °C, the color-developing density value increased with increasing the temperature. This is due to when the wall of the nanocapsule is heated above its glass transition temperature, the transmittance of the wall material increases and a color-developing component contained in the core and outside of the nanocapsule transmits the wall of the nanocapsule to develop a color. In other words, the glass transition temperature changes with different St content, resulting in different heat sensitive color-developing density. In addition, the color-developing density value of the nanocapsules increases with increasing St content at the same temperature. The reason should be that the average hydrodynamic diameter of resultant nanocapsule becomes smaller with increasing St content, and smaller particle size nanocapsules would have larger total specific surface area, therefore causing the density to be higher than that of larger particle size nanocapsules at the same temperature. This outcome is consistent with the research of the relation between particle size and sustained release rate by Yamamoto *et al.* [14].

4. Conclusion

The Poly (MMA-*co*-St) heat sensitive color-developing nanocapsules have been synthesized by emulsion polymerization, in which leucocompound is used as core material and MMA and St as wall-forming materials. The FTIR analysis of leucocompound-containing nanocapsules demonstrates that the leucocompound is successfully encapsulated in the P(MMA-*co*-St) matrix. The resultant nanocapsules at the St content being 20wt% had smooth surface. The nanocapsules with different St content showed different heat sensitive color-developing behaviour.

5. Acknowledgment

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