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Research Article

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Synthesis and characterization of poly (MMA-*co*-St) heat sensitive color-developing nanocapsules

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Abstract

A series of poly(methylmethacrylate-*co*-styrene) (P(MMA-*co*-St)) heat sensitive color-developing nanocapsules were synthesized by emulsion polymerization with leucocompound as a core material and P(MMA-*co*-St) as a wall material. The nanocapsules with different glass-transition temperatures (T_gs) were obtained through adjusting the percentage weight of St. The nanocapsules were characterized by Malvern particle size analyzer, scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that nanocapsules with smooth surface and spherical shape were prepared at different percentage weight of St. The mean particle size of the prepared nanocapsules decreased with the increase of the percentage weight of St. The nanocapsules showed higher thermal stabilities. T_gs of the nanocapsules were 112.0, 107.7 and 103.6°C with the percentage weight of St being 10 wt%, 20 wt% and 30 wt%, respectively.

Keywords: heat sensitive color-developing systems, glass-transition temperature, Poly(MMA-*co*-St), nanocapsules, emulsion polymerization.

Introduction

Nanoencapsulation technique is one of the important techniques by which the chemical agents such as phase change material, drug, food, dye, pigment, etc. as the core materials are surrounded by a coating wall or embedded in a homogeneous or heterogeneous matrix [1-5]. These core materials are first isolated from the external medium in order to avoid the adverse reaction or loss and then released into the outer phase of nanocapsule by a controlling process [6, 7]. Heat sensitive color-developing nanocapsules encapsulating a leucocompound have been widely employed in the heat-sensitive recording material, including medicinal images, facsimiles, printers and labels [8], etc. 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 leucocompound it is hoped to coat leucocompound with a protective matrix or wall of synthetic or natural polymers by nanoencapsulation technique [9, 10]. 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 [8, 11]. Because the heat sensitive color-developing property of nanocapsules depends upon its T_g, It is necessary to synthesis of nanocapsules with different T_g. Copolymerization is one of the main ways to adjust the T_g of polymer. The T_g of copolymer is between the T_g of homopolymer which is made up of the copolymerization

monomer. And it exhibits the linear or nonlinear diversification along with the variation in composition of the copolymers[12, 13].

In this paper, to obtained the nanocapsules with different T_g, the nanocapsules were prepared by conventional emulsion polymerization of MMA using St as a comonomer and unsaturated hyperbranched poly(amide-ester) as a cross-linking agent. The nanocapsules with different T_g can easily be prepared through adjusting the percentage weight of St.

A series of P(MMA-co-St) heat sensitive color-developing nanocapsules were synthesized by emulsion polymerization. The effects of St content on the particle size distribution, morphology and T_g of nanocapsules were discussed in detail. The nanocapsules were characterized by particle size analyzer, SEM, TGA and DSC. The goal of the work is to lay the foundation for further studies of P(MMA-co-St) nanocapsule such as its application to the heat-sensitive recording material, which is important from an academic as well as an industrial point of view.

Experimental

Materials

Methyl methacrylate (MMA, distilled under vacuum prior to use) purchased from Tianjin Huadong Reagent Factory was used as a wall-forming material. Styrene (St, distilled under vacuum prior to use) purchased from Tianjin Huadong Reagent Factory was used as a comonomer. Ammonium persulfate (APS) purchased from Beijing the Third Chemical Reagent Factory was used as an initiator. Triton X-100 purchased from Shanghai Tianlian Fine Chemical Reagent Co. was used as an emulsifier. Poly(vinyl alcohol) 224 (PVA 224) purchased from Junsei Chemical was used as the protective colloid[14]. Ethyl acetoacetate obtained from Tianjing Damao Chemical Reagent Factory and ethyl acetate obtained from Tianjin Meilin Chemical Co. were used as the high and low boiling point solvents for the leucocompound, respectively. The leucocompound used as a core material was 2-Phenylamino-3-methyl-6-(di-*n*-butylamino)fluorane and was obtained from Jiangsu Longsheng Co.. All the purchased reagents were in analytical grade. Hyperbranched unsaturated poly(amide-ester) (UHBP) ($\overline{M}_w$, 3775) produced according to the literature was used as the cross-linking agent[15].

Methods

Preparation of nanocapsules

In a typical synthesis, 1.2 g of the leucocompound 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 (see Table1) 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 recentrifuged 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.

Table 1 Recipe for preparing crosslinked P(MMA-*co*-St) nanocapsules by emulsion polymerization

Sample no.	Continuous phase (g)	Dispersed phase (g)	MMA (g)	St (g)	Percentage weight of St (wt%)	UHBP (g)	APS (g)
1	32	8	8.64	0.96	10	0.6	0.06
2	32	8	7.68	1.92	20	0.6	0.06
3	32	8	6.72	2.88	30	0.6	0.06

Characterizations of nanocapsules

The average hydrodynamic diameter (d) and size distribution were measured by zeta potential and particle size analyzer (Zetasizer 3000HS, Malvern Instruments, UK). Before measurement, the samples were diluted with deionized water at 1:5000 volume ratio. The morphology and cross section 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 thermo-gravimetric analysis was determined by

thermo-gravimetric analysis (TGA, Perkin Elmer Co., USA). About 5 mg of sample was put into a crucible for thermo-gravimetric analysis. The heating rate was 20 °C /min in a stream of nitrogen with a flow rate of 20 mL/min. The recorded temperature range was from 50 ºC to 850 ºC. The glass transition temperatures (T_g) of dried samples were investigated by differential scanning calorimetry (Diamond DSC, Perkin Elmer Co., USA). Each sample of about 5 mg was primarily heated from 25ºC to 160ºC at 20°C/min heating rate and then were cooled to 25°C. Second, the samples were reheated to 160°C. The T_g of the sample was determined from the second cycle where the highest point of the inflection was taken as the T_g. All operations were carried out in a stream of nitrogen with a flow rate of 20 mL/min.

Results and Discussion

Particle size distribution of nanocapsules

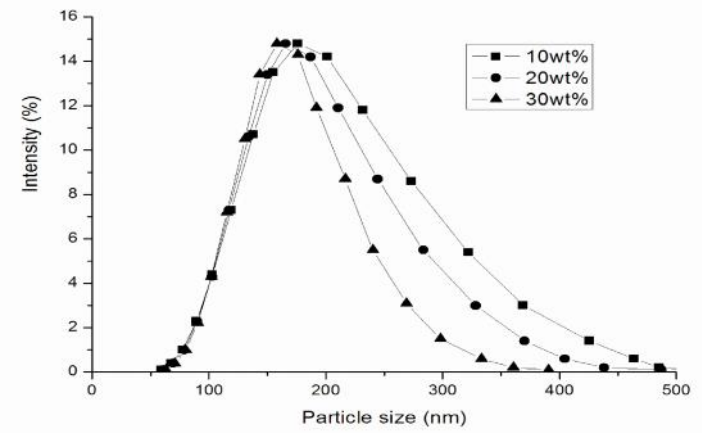
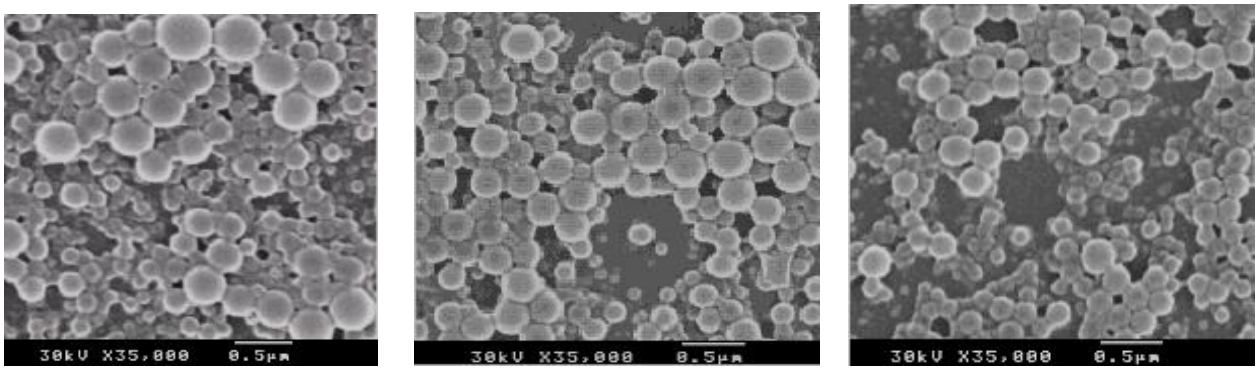


Fig. 1 Particle size distribution of nanocapsules prepared at different St content

Fig. 1 illustrates the particle size distribution of the nanocapsules at different St content. In the experiment, the other reaction conditions do not change and only the St content increase in the reaction system. The average hydrodynamic diameters of the nanocapsules for 10wt%, 20wt% and 30wt% of St content are 181.2, 170.4 and 163.1 nm, respectively. The average hydrodynamic diameter of resultant nanocapsule becomes smaller and size distribution becomes narrower with increasing St concentration. The decrease of the average particle size may be because the St is more insoluble in the reaction medium than MMA, resulting in smaller average particle size.

Morphology of nanocapsules



(a) 10wt% **(b) 20wt%** **(c) 30wt%**

Fig. 2 SEM photographs of nanocapsules prepared at different St content

Fig. 2 shows SEM photographs of the nanocapsules with different St content. All the nanocapsules reveal smooth surface and spherical shape and good dispersibility. The average particle size decreases with the increase of the percentage weight of St. The results of SEM photographs are basically consistent with those of the particle distribution measurement.

Glass Transition Temperature Analysis

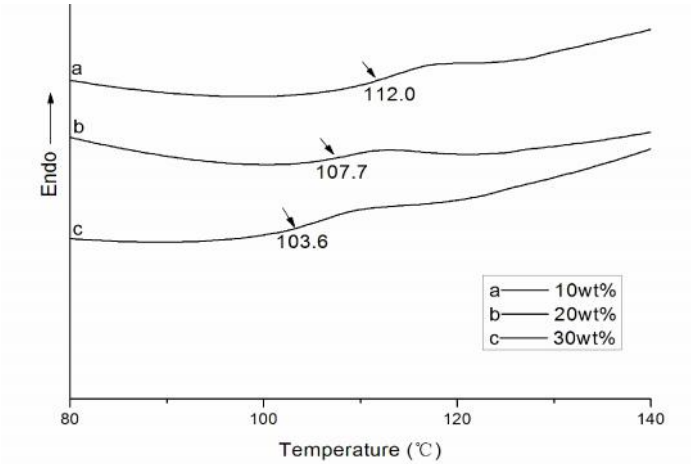


Fig. 3 DSC curves of nanocapsules prepared at different St content

To prepare the nanocapsules with different T_g, the St contents change from 10wt% to 30wt%. The nanocapsules with different T_g can easily be prepared through adjusting the percentage weight of St. Fig. 3 depicts DSC thermograms of the nanocapsules prepared at different St content. The T_gs of the nanocapsules for 10wt%, 20wt% and 30wt% of St content are 112.0, 107.7 and 103.6°C, respectively. The results show that T_g of the nanocapsules decreases as the St concentration in feed increases. This indicates that the St provides a plasticizing effect to the copolymer particles. A previous work on the synthesis of P(St-*co*-MMA) also reported the similar result that incorporation of St in the copolymer gave rise to the decrease of T_g [16]. The T_g would have an effect on the heat-sensitive color-developing property of the resultant nanocapsules [8].

Thermal stability of nanocapsules

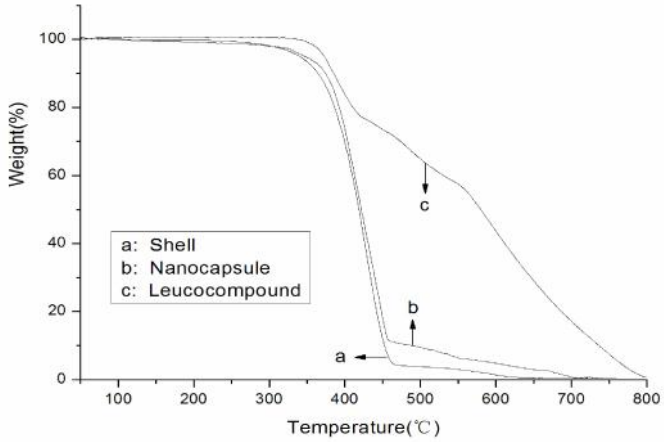


Fig. 4 TG curves of leucocompound, leucocompound-containing nanocapsules and the shells made from crosslinked P(MMA-*co*-St)

Fig. 4 illustrates the TG curves of leucocompound, No.3 leucocompound-containing nanocapsules and the No.4 shells that were prepared in the same way as the hybrid systems without the addition of leucocompound. As shown in Fig. 4, the onset temperatures of the thermal decomposition process for the leucocompound, leucocompound-containing nanocapsules and the shells are 360, 347 and 340 °C. The onset temperature of the thermal decomposition process for the leucocompound-containing nanocapsules is slightly higher than that for the shells. This result seems to be caused by the thermally stable leucocompound itself. In addition, the onset temperatures of the thermal decomposition process for the leucocompound, leucocompound-containing nanocapsules and the shells are higher than the T_g of the leucocompound-containing nanocapsules, which is especially fit for the application of the heat sensitive nanocapsules.

Conclusion

A series of P(MMA-*co*-St) heat sensitive color-developing nanocapsules were prepared by emulsion polymerization, in which leucocompound is used as a core material and crosslinked P(MMA-*co*-St) as a wall material. The nanocapsules with different T_gs were obtained through adjusting the percentage weight of St. TGA results show that the resultant nanocapsules had good thermal stabilities. The nanocapsules with smooth surface and spherical shape and core/shell structure were prepared at different percentage weight of St. The mean particle size of the prepared nanocapsules decreased with the increasing St content. T_gs of the nanocapsules were 112.0, 107.7 and 103.6°C with the percentage weight of St being 10wt%, 20wt% and 30wt%, respectively..

Acknowledgments

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