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Preparation and characterization of crosslinked poly(methylmethacrylate) heat sensitive color-developing microcapsules

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ABSTRACT

The crosslinked poly(methylmethacrylate) (PMMA) heat sensitive color-developing microcapsules were prepared by emulsion polymerization, in which leucocompound was used as core material and methyl methacrylate and unsaturated hyperbranched poly(amide-ester) as wall-forming materials. The microcapsules were characterized by Malvern particle size analysis, scanning electron microscopy, Fourier transform infrared spectrophotometry (FTIR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) and densitometry. Triton X-100 was used as the emulsifier of emulsion polymerization. The effects of the emulsifier content on the particle size distribution and morphology of microcapsules were discussed in detail. The FTIR analysis of leucocompound-containing microcapsules demonstrated that leucocompound was successfully encapsulated in the crosslinked PMMA matrix. TGA results showed that the prepared microcapsules had good thermal stabilities. The DSC analysis of the resultant microcapsules indicated that the glass transition temperature of the microcapsules was 123.8 °C. The resultant microcapsules had narrower particle size distribution, smoother surface and higher heat sensitive color- developing density when emulsifier mass fraction was 0.6%.

KEYWORDS

Heat sensitive color-developing microcapsule;
Emulsion polymerization;
Crosslinked poly(methylmethacrylate);
Leucocompound.

INTRODUCTION

The heat-sensitive recording material is a novel digital image recording material. Due to its unique fast recording speed, good imaging quality, simple and inexpensive recording device and low noise as recording, the heat-sensitive recording material has been widely employed in a series of fields including facsimiles, printers and labels[1], etc. The color-developing in the heat-sensitive recording material lies in the reaction between leucocompound and the developer. 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 microencapsulation technique and to control the release as the occasion demands[2]. In other words, the sensitive leucocompound is first isolated from the external medium in order to avoid the adverse reaction and then

released into the outer phase of microcapsule by controlling process according to the characteristic of polymeric wall[3-5].

Many methods have been developed for microencapsulation technique. Among these microencapsulation approachees, the emulsion polymerization is one of the most feasible methods[6,7]. The key for the microcapsule preparation by emulsion polymerization is that the organic phase containing core material is dispersed into fine droplets. And then polymerization is initiated on the surface of core material to form microcapsules. Hence it is essential to select the adequate emulsifier[8]. And MMA is a monomer which is in common use by emulsion polymerization. PMMA is a thermoplastic resin with excellent physical and chemical properties such as abrasion resistance, water repellency, high degree of transparency, etc., and wide applications containing adhesives, paints, drugs and so on[9]. Moreover, the attention to hyperbranched polymers (HBP) is rapidly growing due to their unique physical and chemical properties such as low viscosity, high solubility and possessing high density of functional terminal groups to be accessible for chemical modification[10-12]. Therefore, HBPs are attractive for some applications such as adhesive, cross-linking agents and viscosity modifiers[13,14]. As a result, crosslinked PMMA with unsaturated hyperbranched poly(amide-ester) (UHBP) as cross-linking agent has many advantages such as non-toxicity, high degree of transparency, compact property.

In this work, heat sensitive color-developing microcapsules with the crosslinked poly(methyl methacrylate)(PMMA) as wall-forming material was prepared by emulsion polymerization, in which unsaturated hyperbranched poly(amide-ester) was used as the cross-linking agent and Triton X-100 was used as the emulsifier. The effects of the emulsifier content on the particle size distribution and morphology of microcapsules were discussed in detail. The aim of the study is to gain a better understanding of the fundamentals of crosslinked PMMA with unsaturated hyperbranched poly (amide-ester) as the cross-linking agent applied to preparation of heat sensitive color-developing microcapsules, which lays the foundation for further studies of crosslinked PMMA microcapsule such as its application to the heat-sensitive recording material.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, distilled under vacuum prior to use) purchased from Tianjin Huadong Reagent Factory was used as a wall-forming material. 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. 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.. Benzyl p-hydroxybenzoate obtained from Jiangsu Longsheng Co. was used as a developer. 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].

Preparation of microcapsules

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 the desired amount of Triton X-100 (see TABLE 1). 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, 9.6 g of freshly distilled MMA and 0.6 g of the cross-linking agent (UHBP) was 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 microcapsule 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 : Recipes of aqueous phase for the o/w emulsion[a] preparation

Sample No.	PVA (g)	w(emulsifier)[b] (%)	Aqueous phase (g)
1	1.8	0.1	32.0
2	1.8	0.3	32.0
3	1.8	0.6	32.0
4	1.8	0.9	32.0

[a]o/w emulsion: 40.0g. [b]based on o/w emulsion

Characterizations of microcapsules

The particle size and its 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 of the microcapsules was observed by scanning electron microscopy (SEM, JSM-5400, JEOL, Japan). The microcapsules 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. The thermo-gravimetric analysis was determined by thermo-gravimetric analyzer (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). All samples of each about 5 mg were 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 Tg of the sample was determined from the second cycle where the highest point of the inflection was taken as the Tg. All operations were carried out in a stream of nitrogen with a flow rate of 20 mL/min.

Heat sensitive color-developing properties

The heat sensitive color-developing property measurement was performed by a conventional method[16]. The mixture containing 1.0g of microcapsule 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 microcapsule thin layer. The thickness of the coating layer was ca. 15 μm. The color yield of color-produced microcapsules 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).

RESULTS AND DISCUSSION

Effects of the emulsifier content on the particle size distribution and morphology of microcapsules

To study the effects of the emulsifier content on the particle size distribution and morphology of microcapsules, the emulsifier content was changed from 0.1% to 0.9%. In the experiment, the other reaction conditions do not change and only the emulsifier content increase in the reaction system. Figure 1 illustrates the particle size distribution of the microcapsules at different emulsifier contents. As shown in Figure 1, the mean sizes of the microcapsules for 0.1%, 0.3%, 0.6% and 0.9% of emulsifier contents are 250.6, 222.0, 189.7 and 200.5 nm, respectively. As the emulsifier content increase from 0.1% to 0.6%, the mean size of resultant microcapsule becomes smaller and size distribution becomes narrower. During the emulsification process, the emulsifier can decrease the interfacial tension of the system, which the organic phase is easily dispersed into finer droplets. Moreover, the emulsifier can enwrap the surface of dispersed droplets to prevent dispersed

droplets from coalescing[17]. And during the emulsion polymerization process, the emulsifier molecules form emulsifier micelles containing core material and wall-forming materials. Polymerization was initiated on the surface of core material to form microcapsules. As a result, the mean size of resultant microcapsule becomes smaller and size distribution becomes narrower with an appropriate increase in emulsifier content. As the emulsifier content increase from 0.6 to 0.9%, the mean size of resultant microcapsule becomes bigger and size distribution becomes broader. This can be explained by that excessive emulsifier micelles contain excessive monomers. Therefore excessive monomers can be reacted rapidly on the surface of the cores to cause coalescence among the particles.

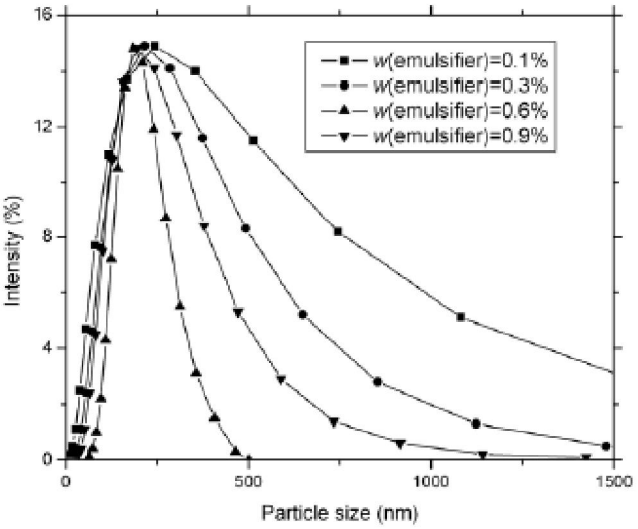
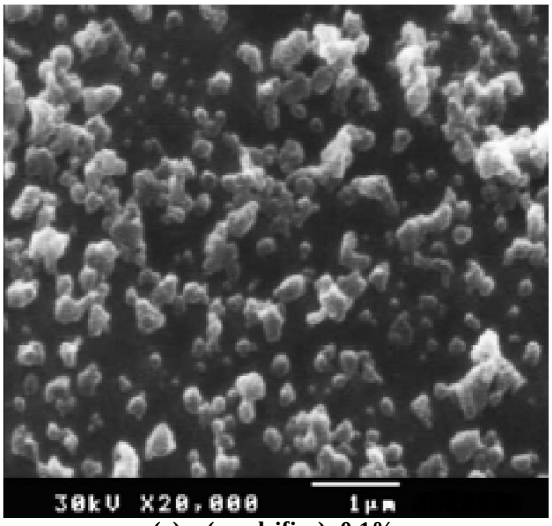
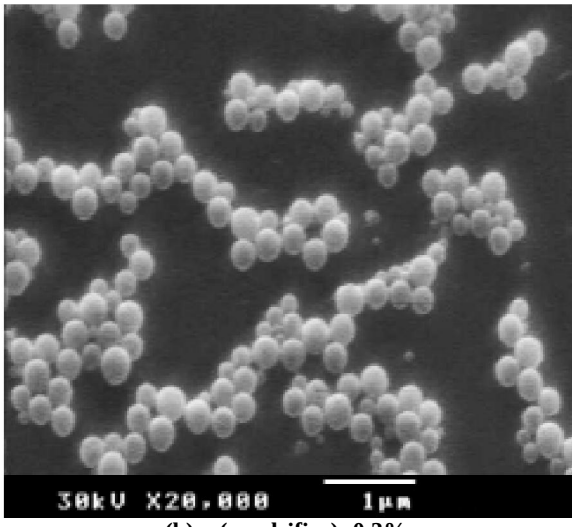


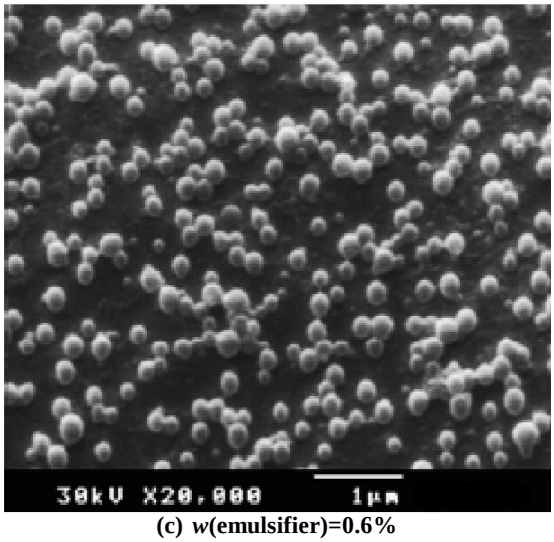
Figure 1 : Particle size distribution of microcapsules prepared at different emulsifier contents



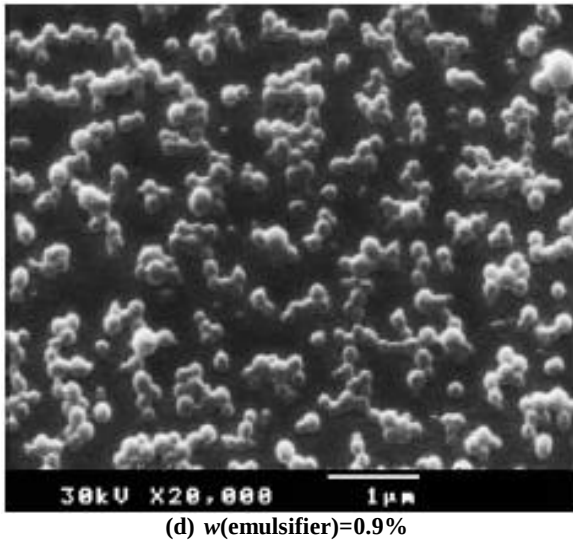
(a) *w*(emulsifier)=0.1%



(b) *w*(emulsifier)=0.3%



(c) *w*(emulsifier)=0.6%



(d) *w*(emulsifier)=0.9%

Figure 2 : SEM photographs of microcapsules prepared at different emulsifier contents

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Figure 2 shows the scanning electron microphotographs of the microcapsules prepared at different emulsifier contents. The SEM image of the emulsifier content of 0.1% was shown in Figure 2a. Such particles exhibited an irregular shape with evidence of particle aggregation. Figure 2b and Figure 2c showed the image of the microcapsules prepared with the emulsifier contents being 0.3 and 0.6%. The microcapsules revealed smooth surface and spherical shape and good dispersibility. Figure 3d showed the image of the microcapsules prepared with the emulsifier content being 0.9%. A rough surface and the coagulation among the particles had been observed. The results of scanning electron photographs were basically consistent with those of the particle distribution measurement.

Structure of microcapsules

FTIR Spectroscopy results for the samples are shown in Figure 3. Figure 3a corresponds to No.3 leucocompound-containing microcapsules, and Figure 3b and Figure 3c to leucocompound and the No.3 polymer shells, respectively. In the spectrum of Figure 1a and Figure 1b, N-H stretching at 3350 cm^{-1}, =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, indicating that the leucocompound is encapsulated in the microcapsules[18]. In addition, as shown in the spectrum of Figure 3a and Figure 3c, 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[15]. The results confirm that the shells of the microcapsules are composed of MMA and UHBP as expected.

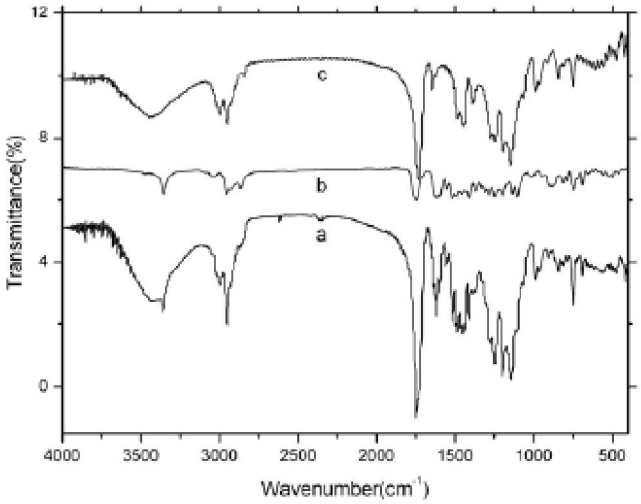

Figure 3 : FTIR spectra of (a) leucocompound-containing microcapsules, (b) leucocompound and (c) the polymer shells.

Glass transition temperature analysis

The DSC thermograms of No.3 leucocompound-containing microcapsules and the No.3 polymer shells are depicted in Figure 4. As it is shown in Figure 4, the glass-transition temperature (T_g) of the microcapsules and shells is 123.8 and 132.6°C, respectively. Evidently, the T_g of the leucocompound-containing microcapsules is lower than that of the shells. This is due to a plasticization effect of core materials. The core molecule is much smaller than shell polymer molecule, which would increase the movement of polymer segment and result into a decreased T_g. The T_g would have an effect on the heat-sensitive color-developing property of the resultant microcapsules[1].

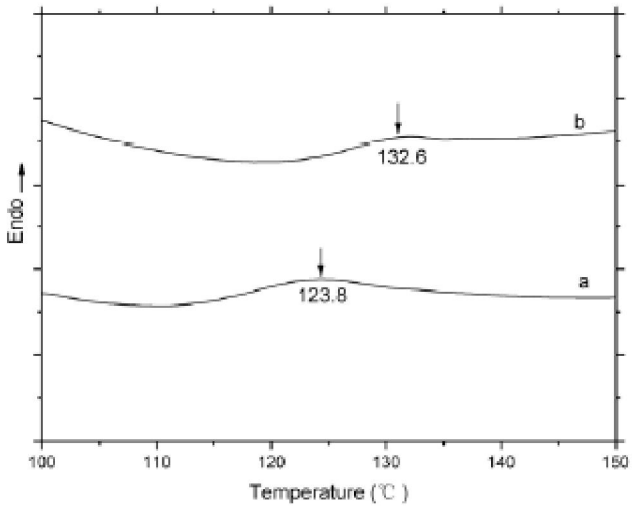

Figure 4 : DSC thermograms of (a) Leucocompound-containing microcapsules and (b) The polymer shells

Thermal stability of microcapsules

Figure 5 shows the TG curves of the leucocompound, No.3 leucocompound-containing microcapsules and the No.3 polymer shells. As shown in Figure 5 and TABLE 2, the onset temperatures of the thermal decomposition process for the leucocompound, leucocompound-containing

microcapsules and the shells are 360, 308 and 293°C. The onset temperature of the thermal decomposition process for the leucocompound-containing microcapsules 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 microcapsules and the shells are higher than the T_g of the leucocompound-containing microcapsules, which is especially fit for the application of the heat sensitive microcapsules.

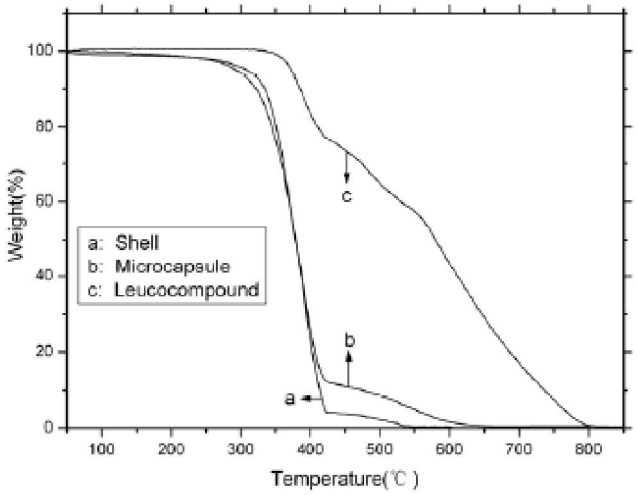

Figure 5 : TG curves of leucocompound, leucocompound-containing microcapsules and the polymer shells

TABLE 2 : Pyrolytic characteristics of leucocompound, leucocompound-containing microcapsules and the polymer shells

Material	First pyrolytic stage		Second pyrolytic stage	
	$T_{1,onset}$[a] (°C)	$T_{1,end}$[b] (°C)	$T_{2,onset}$[a] (°C)	$T_{2,end}$[b] (°C)
leucocompound	360	422	549	796
microcapsule	308	426	426	643
Shell	293	426	426	536

[a] $T_{1,onset}$, $T_{2,onset}$: Onset temperatures of the first and second pyrolytic stages, respectively.

[b] $T_{1,end}$, $T_{2,end}$: End temperatures of the first and second pyrolytic stages, respectively.

Heat sensitive color-developing properties

Figure 6 illustrates the heat sensitive color-developing density of the resultant microcapsules at different emulsifier contents. As shown in Figure 6, the values of density have no change below 95 °C at the emulsifier contents being 0.3% and 0.6%. This is confirmed that the walls of resultant microcapsules are compact. And when the microcapsules prepared at both 0.3% and 0.6% are heated above 95 °C, the color-developing density values increase with the increase of the temperature. This is due to when the wall of the microcapsule is heated above its glass transition temperature (112.1~123.8 °C, see Figure 4a), the transmittance of the wall material increases and a color-developing component contained in the core and outside of the microcapsule transmits the wall of the microcapsule to develop a color. In addition, the color-developing density value from the microcapsules at the emulsifier content being 0.6% is higher than that from the microcapsules at the emulsifier content being 0.3% 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.[19]. The reason should be that the mean size from the microcapsules at the emulsifier content being 0.6% is smaller than that from the microcapsules at the emulsifier content being 0.3%, and smaller particle size microcapsules would have larger total specific surface area, therefore causes its density to be higher than that of larger particle size microcapsules at the same temperature.

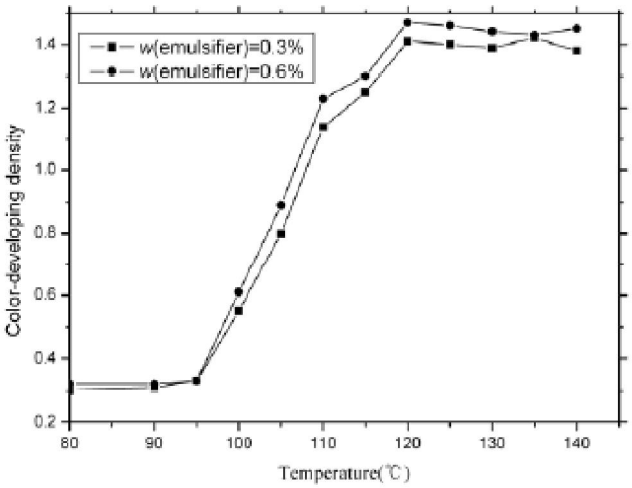

Figure 6 : Heat sensitive color-developing density of microcapsules prepared at different emulsifier contents

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CONCLUSIONS

The crosslinked poly(methylmethacrylate) heat sensitive color-developing microcapsules have been synthesized by emulsion polymerization£¬in which the leucocompound is used as core material and methyl methacrylate and unsaturated hyperbranched poly(amide-ester) as wall-forming materials. The FTIR analysis of leucocompound-containing microcapsules demonstrates that the leucocompound is successfully encapsulated in the crosslinked PMMA matrix. TGA results show that the prepared microcapsules had good thermal stabilities. The DSC analysis of the resultant microcapsules indicates that the glass transition temperature of the microcapsules was 123.8 °C. The resultant microcapsules have narrower particle size distribution, smoother surface and higher heat sensitive color-developing density when emulsifier mass fraction was 0.6%.

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