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Preparation of polyacrylate/paraffin microcapsules and its application in prolonged release of fragrance

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ABSTRACT: The purpose of the present work was to develop a fragrance encapsulation system using polyacrylate/paraffin microcapsules. The polyacrylate/paraffin microcapsules were fabricated by the method of suspension polymerization in Pickering emulsion. Morphology, size distribution, and thermal resistance of polyacrylate/paraffin microcapsules were investigated by scanning electron microscopy, light scattering particle size analyzer, and thermogravimetric analyzer. Results indicated that the crosslinked PMMA/paraffin microcapsules and P(MMA-co-BMA)/paraffin microcapsules prepared under optimal conditions presented regular spherical shape and similar size distribution. The crosslinked P(MMA-co-BMA)/paraffin microcapsules exhibited better thermal stability, with a thermal resistance temperature up to 184 °C. Fragrance microcapsules were prepared by encapsulating fragrance into crosslinked P(MMA-co-BMA)/paraffin microcapsules. The prolonged release performance of fragrance microcapsules was measured by ultraviolet-visible near-infrared spectrophotometer. 63.9% fragrance was retained after exposing fragrance microcapsules in air for 3 months, and the fragrance continued to release over 96 h in surfactant solution (sodium lauryl sulfonate, 20 wt %). © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44136.

KEYWORDS: applications; copolymers; crosslinking; properties and characterization; synthesis and processing

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INTRODUCTION

Fragrance is one of the main ingredients in food, cosmetics, pharmaceuticals, and other daily necessities.[1–3] Pleasant aroma always makes people happy. However, the poor stability and volatile nature of fragrance molecules have made them hard to guarantee the quality of the products.[4,5] The encapsulation technology used for fragrance storage provided an effective solution to avoid the deterioration and volatilization of fragrance.[5–7]

The current publications on encapsulated fragrance reported that various organic supporters like sunflower oil,[8] hexadecane,[9] and diethyl phthalate[5] were used to encapsulate the oily fragrance into coating materials. Paraffin, a commercial hydrocarbon compound, was used as a preferred supporter in our work for its advantages such as excellent compatibility with oily fragrance, good chemical stability, no corrosion, and ecological harmlessness.[10,11] Considering the large proportion of the supporter in oil phase, the first step of this study was focused on enveloping bulk paraffin into micro-sized capsules.

So far, various techniques have been developed for the synthesis of paraffin or other *n*-alkanes microcapsules. The common methods described in the literatures including emulsion polymerization,[12] suspension-like polymerization,[13,14] *in situ* polymerization,[15] and interfacial polymerization.[16] The methods mentioned above revealed that the interfacial phenomenon in the processes was a key factor for microcapsulation. The Pickering emulsions were formed from the irreversibly adsorption of solid colloid particles in high-energy oil-water interface.[17] The enhanced interfacial stability of Pickering emulsions were superior to the classical emulsions stabilized by traditional emulsifiers (i.e., surfactants and polymers). A robust colloidal layer generated by the adsorption of solid colloid particles at oil-water interface tended to endow a good protection against droplets aggregation.[18] Moreover, the structural properties of Pickering emulsion made it a good template for forming microcapsules.[19]

Current studies reported that the progresses have been designed for the successfully encapsulation of paraffin and other *n*-alkanes using different types of polymers or inorganic matters, that is, melamine-formaldehyde (MF),[20,21] urea-formaldehyde (UF),[22] polyurethane (PU),[23] gelatin/Arabic gum,[24] poly(methyl methacrylate) (PMMA),[25] silicon dioxide (SiO_2),[26] titanium dioxide (TiO_2)[27], and calcium carbonate ($CaCO_3$).[28] The latest literature indicated that PMMA used as shell materials have attracted more attentions for its advantages like easy handing and processing,

Table I. Formulas of Polyacrylate/Paraffin Microcapsules

Sample	35°Paraffin (g)	MMA (g)	BMA (g)	LMA (g)	PETRA (g)	Water (g)	Emulsifier (g)
1	10.00	10.00	—	—	—	95.00	5.00
2	10.00	10.00	—	—	2.00	95.00	5.00
3	10.00	10.00	—	—	2.50	95.00	5.00
4	10.00	10.00	—	—	2.50	80.00	5.00
5	10.00	10.00	—	—	2.50	65.00	5.00
6	10.00	10.00	2.00	—	3.00	65.00	5.00
7	10.00	10.00	—	2.00	3.00	65.00	5.00

good chemical resistance, relatively high impact strength and nontoxicity.[13] Al-Shannaq *et al.*[29] microencapsulated paraffin with PMMA by means of suspension polymerization. Pentaerythritol tetraacrylate (PETRA) was selected as crosslinking agent. The addition of PETRA improved the surface morphology and produced microcapsules with much higher paraffin content. Sari *et al.*[12] utilized emulsion polymerization to encapsulate *n*-nonadecane with PMMA and obtained the capsules with various *n*-nonadecane encapsulation ratios by altering the weight ratios of MMA/*n*-nonadecane. Chang *et al.*[30] fabricated *n*-octadecane containing microcapsules using PMMA network-silica hybrid shell via sol-gel process. The introduction of SiO_2 to PMMA network shell improved the density of polymer shell, and promoted the increase of *n*-octadecane content. Besides, the copolymerization of MMA with other monomer as copolymer shells was also widely investigated for the properties of microcapsules could be modified by varying the macromolecular composition of copolymer shells. Tumirah *et al.*[15] studied the encapsulation of *n*-octadecane with styrene (St)-methyl methacrylate (MMA) copolymer shell by miniemulsion in-situ polymerization method, and found that the P(St-co-MMA)/*n*-octadecane capsules for St/MMA mass ratio of 4 had relatively uniform size, smooth, and compact surface with spherical shape. Sanchez-Silva *et al.*[31] utilized suspension-like homopolymerization to microencapsulate PRS paraffin with PMMA, P(MMA-co-MA), and P(MMA-co-MA-co-MAA) shells, respectively, and the biggest paraffin load amount was achieved for a P(MMA-co-MA-co-MAA) shell. Tang *et al.*[32] fabricated the microcapsules containing *n*-alkanes (*n*-hexadecane, *n*-octadecane, and *n*-eicosane) with *n*-octadecyl acrylate (ODA)-MMA copolymer shell through suspension-like polymerization, and discovered the degree of supercooling of *n*-alkanes decreased progressively with the increase of molar ratios of ODA in the synthesis.

The aim of the present work was to develop a fragrance encapsulation system using polyacrylate/paraffin microcapsules. Firstly, polyacrylate/paraffin microcapsules were fabricated by suspension polymerization in Pickering emulsion. The formation of well encapsulated paraffin microcapsules was a challenging issue because several crucial factors had great effects on the properties of microcapsules, such as the addition amount of crosslinking agent, the mass concentration of deionized water, and the type of comonomer. Subsequently, oily fragrance was encapsulated into polyacrylate/paraffin microcapsules and the release behaviors of fragrance in air and in surfactant solution were measured, respectively.

EXPERIMENTAL

Materials

Paraffin with melting point of 34–36 °C (35° paraffin) and 60–62 °C (61° paraffin) were purchased from Zhenjiang Runzhou Zezhong Special Wax Factory. β-cyclodextrin (β-CD) and MMA (CP) were provided by Sinopharm Chemical Reagent Co., Ltd. Butyl methacrylate (BMA, CP) was supplied by Guangdong Guanghua Chemical Factory Co., Ltd. Lauryl methacrylate (LMA, 99 wt %) and sodium lauryl sulfonate (SDS, AR) were purchased from Aladdin Chemistry Co., Ltd. PETRA (99 wt %) was provided by Liyang Puxin New Material Develop Co., Ltd. Benzoyl peroxide (BPO, CP) was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. 406026 flower garland (fragrance) was supplied by Symrise. Ethanol (AR) was purchased from Wuxi Yasheng Chemical Co., Ltd.

Fabrication of Pickering Emulsifier

β-CD/paraffin microparticles were simply prepared as follows: β-CD and 61° paraffin with mass ratio 8:1 were added into a 250 mL round bottomed flask. Then deionized water was dropped slowly under vigorous stirring at 70 °C, and the stirring was continued for 1 h to make paraffin embed into β-CD thoroughly. Afterwards, the obtained solution was slowly cooled to room temperature and the formed precipitated complex was used to stabilize O/W Pickering emulsion. The whole system was used as a water phase for the further suspension emulsion polymerization.

Fabrication of Polyacrylate/Paraffin Microcapsules

Polyacrylate/paraffin microcapsules were fabricated using suspension emulsion polymerization in Pickering emulsion. The preparation of polyacrylate/paraffin microcapsules was conducted in a 250 mL three-neck round bottomed flask equipped with a mechanical agitator, a reflux condenser, and an inlet tube for nitrogen gas. The temperature was adjusted by a water bath. Besides the water phase mentioned above, the acrylate monomer (MMA, BMA, LMA, etc.), core material 35° paraffin, crosslinking agent PETRA and initiator BPO constituted the oil phase, and the basic formulas of different constituents were listed in Table I. The desired amounts of MMA, BMA, LMA, 35° paraffin, PETRA, and BPO were mixed together in the glass reactor with medium agitation at 40 °C for 15 min. Next, the as-prepared water phase was added drop-wise into the mixture solution with vigorous stirring and then the constant stirring was maintained for another 1 h to form a stable O/W emulsion system. Subsequently, the polymerization process was carried out for 8 h with mild agitation at 60 °C. To avoid the oxidation of MMA, BMA, LMA, and PETRA, the

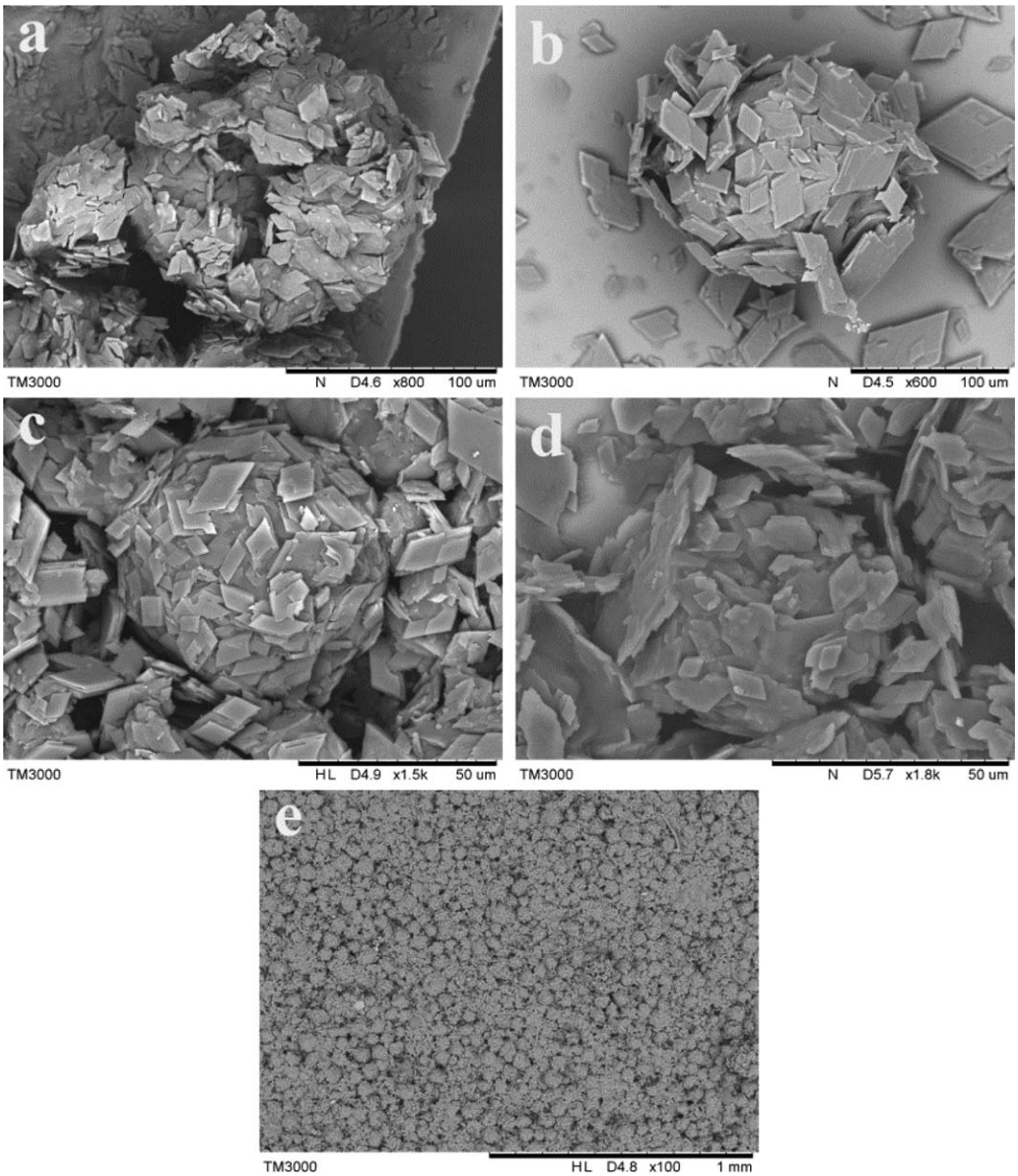

Figure 1. SEM micrographs of polyacrylate/paraffin microcapsules with various polymer shells: (a) sample 1 (microcapsules with uncrosslinked PMMA shell); (b) sample 3 (microcapsules with crosslinked PMMA shell); (c) and (e): sample 6 [microcapsules with crosslinked P(MMA-co-BMA) shell]; (d) sample 7 [microcapsules with crosslinked P(MMA-co-LMA) shell].

reactor was purged with nitrogen gas during the experiment. The resultant hybrids were slowly cooled to room temperature and were filtrated and washed twice with 50 °C deionized water to remove unencapsulated paraffin. The purified products were then dried at room temperature.

Fabrication of Microcapsules Containing Fragrance

A certain amount of fragrance was first mixed well with 35° paraffin, MMA, BMA, PETRA, and BPO as oil phase, and then, water phase was added drop-wise into oil phase followed by homogenizing to form Pickering emulsion. The Pickering emulsion was then heated up to 60 °C to run the reaction of polymerization. The specific experimental operation could refer to fabrication of polyacrylate/paraffin microcapsules.

Characterization of Polyacrylate/Paraffin Microcapsules

The surface morphologies and structure features of fabricated polyacrylate/paraffin microcapsules were characterized through a scanning electronic microscope (SEM, Hitachi TM3000). All samples were coated with a layer of gold prior to the observation.

The thermal stability properties of the dried polyacrylate/paraffin microcapsules were assessed using a thermogravimetric analyzer (TGA, Shimadzu DTG 60H) at a heating rate of 10 °C/min from 35 °C to 500 °C under nitrogen atmosphere.

The particle size distribution of polyacrylate/paraffin microcapsules was carried out on a particle size analyzer (Microtrac S3500). All samples were diluted to proper concentration before analysis.

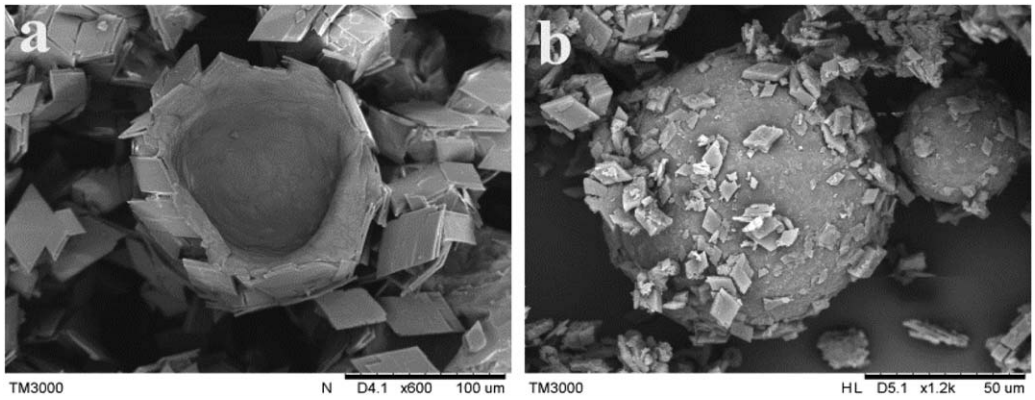

Figure 2. SEM micrographs of sample 3 (microcapsules with crosslinked PMMA shell): (a) a crack-open hollow microcapsule hemisphere; (b) an intact microcapsule after the peel of paraffin/β-CD microparticles.

The prolonged release performance of fragrance in fragrance microcapsules was monitored using ultraviolet-visible near-infrared spectrophotometer (UV-VIS-NIR spectrophotometer, PerkinElmer Lambda 950) at the characteristic absorption peak of fragrance at λ_{max} of 286 nm. The extraction agent used in this work was absolute ethanol.

RESULTS AND DISCUSSION

Morphology of Polyacrylate/Paraffin Microcapsules

SEM micrographs of as-prepared dried uncrosslinked and crosslinked polyacrylate/paraffin microcapsules were showed in Figure 1(a–e). All microcapsules presented rough surfaces due to the dense coverage of β-CD/paraffin microparticles. However, the surface profiles of these microcapsules exhibited apparently distinction. There were several distinct concaves on the surface of the uncrosslinked microcapsules while no significant concaves were found on the surface of the crosslinked microcapsules except microcapsules with crosslinked P(MMA-co-LMA) copolymer shell. This indicated that crosslinked polymer shell afforded microcapsules better mechanical strength than uncrosslinked polymer shell, which could effectively resist the shell concaves caused by the volume change of paraffin from melting phase to crystal state in the cooling process, as well as the density variation between acrylate monomers and polymer. In addition, the serious concaves on the surface of crosslinked P(MMA-co-LMA)/paraffin microcapsules might be attributed to the tremendous decline of mechanical strength caused by excessive long flexible alkyl chain of LMA.

SEM micrographs of the fine structures of crosslinked PMMA/paraffin microcapsules were shown in Figure 2. The crack-open hollow microcapsule hemisphere and the intact microcapsule without the adhesion of β-CD/paraffin microparticles ascertained the formation of microcapsules with core-shell structure. It was noticeable that the internal and external surfaces of microcapsule were smooth and compact, and the cavity structure provided the valuable room for the encapsulation of paraffin.

Size Distribution of Polyacrylate/Paraffin Microcapsules

The size distribution curves of crosslinked PMMA/paraffin microcapsules based on different mass concentrations of deionized water were shown in Figure 3. It was observed that the diameters of microcapsules showed a decreasing trend, and the size distribution was more uniform by varying the mass concentration of deionized water from 78 to 70%. It was well known that during the formation of microcapsules, some β-CD/paraffin microparticles absorbed irreversibly to the surface of oil droplets, while the others formed an entangled network structure in the continuous phase.[17] With the decrease of the mass concentration of deionized water, the amount of microparticles dispersed in the water reduced, and more microparticles would adsorb on the surface of oil droplets, which consequently made the diameter of the formed microcapsules decrease.

Figure 4 showed the size distribution curves of microcapsules with various polymer shells. The results indicated that the size distribution of microcapsules with crosslinked P(MMA-co-BMA) shell was similar to that of microcapsules with crosslinked PMMA shell. However, the size distribution of microcapsules with crosslinked P(MMA-co-LMA) shell was more nonuniform than that of microcapsules with crosslinked PMMA shell or crosslinked P(MMA-co-BMA) shell. The addition of

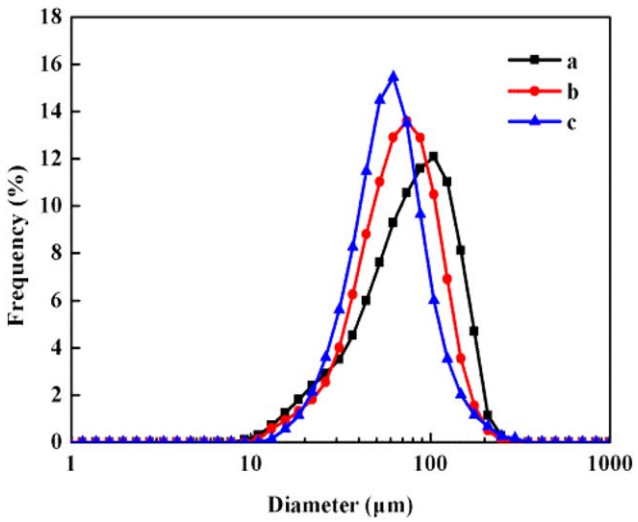

Figure 3. Size distribution curves of crosslinked PMMA/paraffin microcapsules with different mass concentrations of deionized water, C_w: (a) sample 3 (at C_w =78%); (b) sample 4 (at C_w =74%); (c) sample 5 (at C_w =70%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

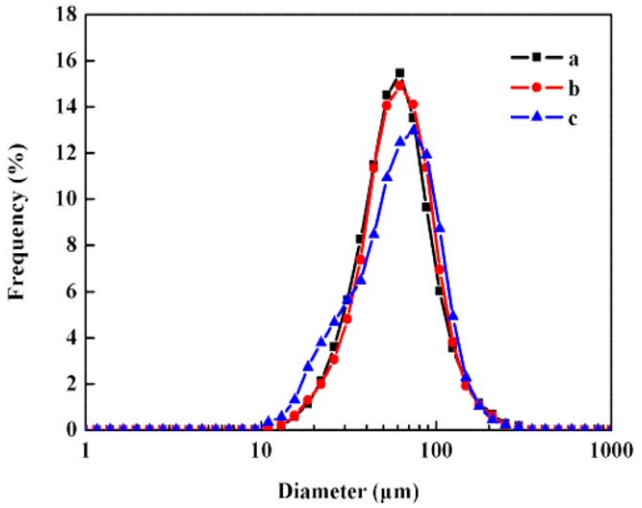

Figure 4. Size distribution curves of crosslinked polyacrylate/paraffin micrcapsules with various polymer shells: sample 5 (microcapsules with crosslinked PMMA shell); (b) sample 6 [microcapsules with crosslinked P(MMA-co-BMA) shell]; (c) sample 7 [microcapsules with crosslinked P(MMA-co-LMA) shell]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

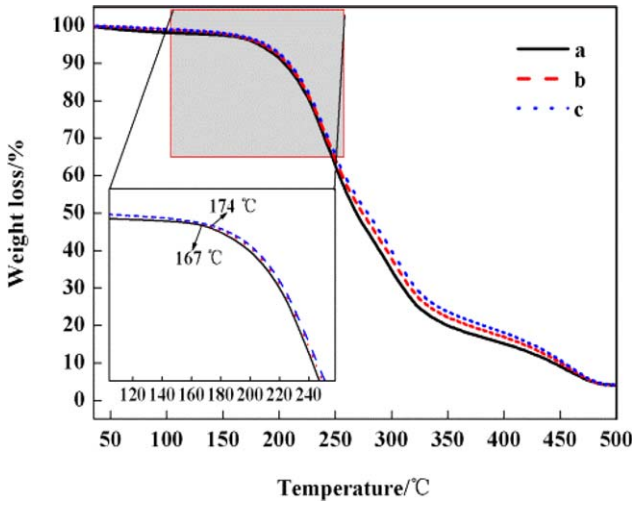

Figure 6. TGA thermograms of crosslinked PMMA/paraffin microcapsules with different mass concentrations of deionized water, C_w: (a) sample 3 (at $C_w = 78\%$); (b) sample 4 (at $C_w = 74\%$); (c) sample 5 (at $C_w = 70\%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

LMA might lead to the severe reduction in the mechanical strength of shell, and some microcapsules were broken during the posttreatment, thus causing the increase in the number of small paticles.

Thermal Stability of Polyacrylate/Paraffin Microcapsules

TGA thermograms of paraffin, PMMA/paraffin microcapsules with different dosage of crosslinking agent were represented in Figure 5. Paraffin started to lose weight at approximately 148 °C, and it completely lost weight at 285 °C. The TGA curve of paraffin

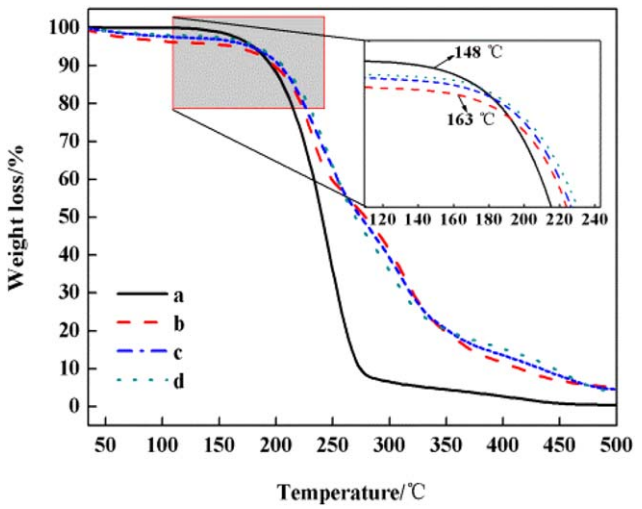

Figure 5. TGA thermograms of paraffin, PMMA/paraffin microcapsules with different dosage of crosslinking agent: (a) paraffin; (b) sample 1 (microcapsules with uncrosslinked PMMA shell, m_{MMA}:m_{PETRA} = 1:0); (c) sample 2 (microcapsules with crosslinked PMMA shell, m_{MMA}:m_{PETRA} = 5:1); (d) sample 3 (microcapsules with crosslinked PMMA shell, m_{MMA}:m_{PETRA} = 4:1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was steep, which was ascribed to the rapid evaporation and decomposition of linear alkyl molecules. By comparision, the TGA curves of uncrosslinked and crosslinked PMMA/paraffin microcapsules were mild. This implied that polymer shells could protect paraffin from the rapid weight loss. The initial weight loss temperature of uncrosslinked PMMA/paraffin microcapsules was 163 °C, which was 15 °C higher than bulk paraffin. The weight loss process of crosslinked PMMA/paraffin microcapsules showed a delay to some extent with the introduction of more crosslinking agent to polymer shells. The phenomenon indicated that the increase of the crosslinking agent dosage could provide more crosslinking sites for the polymerization of acrylate monomer. It could benefit the formation of dense three-dimensional network, and lead to the improvement for the thermal stability of microcapsules.

The effects of the mass concentration of deionized water on the thermal stability of crosslinked PMMA/paraffin microcapsules were presented in Figure 6. It was clear that the decrease in the mass concentration of deionezed water would result in the increase in the thermal stability of microcapsules. When the mass concentration of deionized water was 70%, the initial weight loss temperature of microcapsules delayed to 174 °C. It was known that the use of less mass concentration of deionized water allowed obtaining smaller size microcapsules. This suggested that small size microcapsules were easier to achieve finer encapsulation, and imparted the microcapsules better thermal stability.

Figure 7 compared the thermal stability of crosslinked polyacrylate/paraffin microcapsules with various polymer shells. It was found that the initial weight loss temperature of microcapsules with crosslinked P(MMA-co-BMA) shell delayed about 10 °C compared to that of microcapsules with crosslinked PMMA shell. It might be ascribed to that the appropriate improvement in shell Young's modulus caused by the butyl group chain in BMA would lead to the increase on the thermal stability of

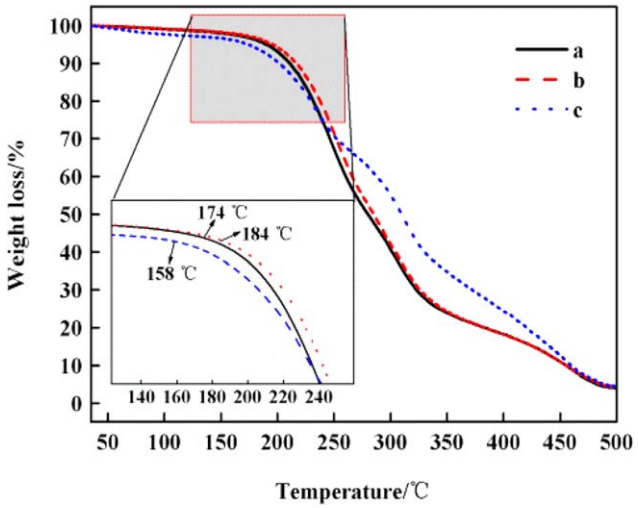

Figure 7. TGA thermograms of crosslinked polyacrylate/paraffin microcapsules with various polymers shells: (a) sample 5 (microcapsules with crosslinked PMMA shell); (b) sample 6 [microcapsules with crosslinked P(MMA-co-BMA) shell]; (c) sample 7 [microcapsules with crosslinked P(MMA-co-LMA) shell]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microcapsules. In addition, there was a decrease about 16 °C at the initial weight loss temperature of microcapsules with crosslinked P(MMA-co-LMA) shell compared to that of the microcapsules with crosslinked PMMA shell. It could be attributed to that the increase of shell Young's modulus could not compensate the influence of the decrease in shell mechanical strength caused by the dodecyl group in LMA. Therefore, the thermal stability of microcapsules with crosslinked P(MMA-co-LMA) shell decreased greatly.

The Prolonged Release Performance of Fragrance Microcapsules

Functionalization of crosslinked P(MMA-co-BMA)/paraffin microcapsules was performed by encapsulating fragrance into paraffin at the fragrance/paraffin ratio of 10 wt %. The release behavior of fragrance microcapsules in air and in surfactant solution (SDS, 20 wt %) was investigated as follows.

The cumulative release of fragrance from fragrance microcapsules against time in air was showed in Figure 8. It was observed that in air the release of fragrance from fragrance microcapsules was very fast during the first month. After that, fragrance kept a steady release over time. At the time of three months, 63.9% fragrance was still reserved in the microcapsules. In addition, the smell experience of fragrance indicated that strong scent could be smelled in one month, and the smell became lighter and lighter in the later months. Nevertheless, intense scent reappeared by rubbing the microcapsules into fragment. From these results, it could be considered that the encapsulation of fragrance into fragrance microcapsules would effectively delay the release of fragrance toward the air. Besides, the small quantity of fragrance trapped by β-CD/paraffin microparticles might explained the fast release mechanism of fragrance in the initial stage.

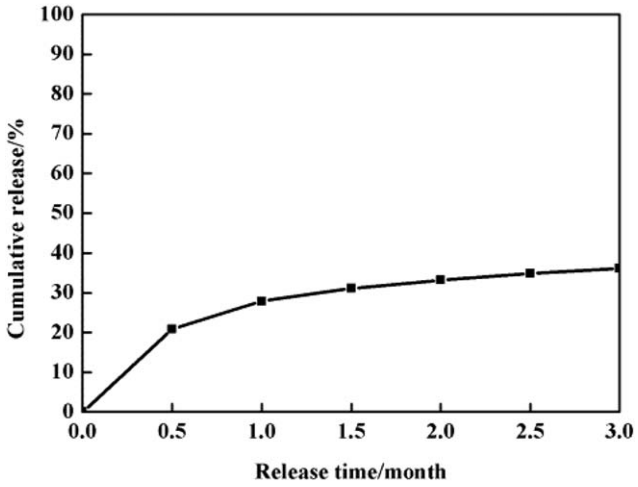

Figure 8. Release of fragrance from fragrance microcapsules in air.

Two gram of fragrance microcapsules was added into 160 mL surfactant solution (SDS, 20 wt %) and stirred at 400 r/min, the effect of temperature factor on the release of fragrance was showed in Figure 9. As observed in Figure 9, the three curves had similar kinetics. Fragrance rapidly released during the first 8 h. Then, from 8 to 96 h, although fragrance continued to release from microcapsules, the release rate was very slow. In addition, the quantity of fragrance released at 40 °C was markedly higher than that at 30 °C while only a slight increase could be found when the temperature changed from 40 °C to 50 °C. This was mainly because that the temperature changes from 30 °C to 40 °C could influence the phase of paraffin, which would further affect the prolonged release performance of fragrance microcapsules. Compared to solid paraffin (at 30 °C), melt paraffin (at 40 °C) facilitated the release for it tended to remove fragrance from the inside of microcapsules into release medium. Furthermore, the temperature shifted from 40 °C to 50 °C could accelerate the movement of fragrance molecules, promoting the release of fragrance to some extent.

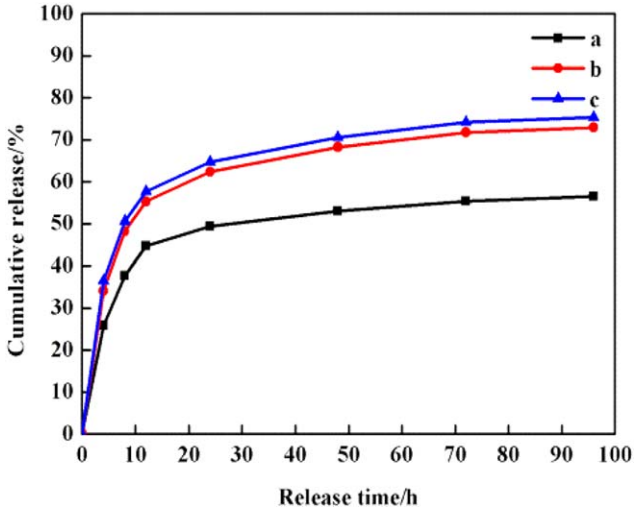

Figure 9. Release of fragrance from fragrance microcapsules in surfactant solution (SDS, 20 wt %) under different storage temperatures: (a) at 30 °C; (b) at 40 °C; (c) at 50 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Microcapsules containing paraffin with different polyacrylate shells were successfully fabricated via suspension emulsion polymerization in Pickering emulsion. β-cyclodextrin/paraffin microparticles were selected as Pickering emulsifier. BMA and LMA were used as comonomers to copolymerize with MMA. PETRA was applied as a crosslinking agent. SEM results ascertained that the synthesized microcapsules were core-shell structure. The surface defects of microcapsules with both crosslinked PMMA and P(MMA-co-BMA) shells were dramatically less than those of microcapsules with uncrosslinked PMMA and crosslinked P(MMA-co-LMA) shell. Particle size of microcapsules with crosslinked PMMA polymer shell decreased with the decrease of mass concentrations of deionized water. The microcapsules with crosslinked P(MMA-co-BMA) shell showed similar size distribution to that of corresponding microcapsules with crosslinked PMMA polymer shell. Thermal stability of microcapsules with crosslinked PMMA polymer shell was improved by increasing the dosage of crosslinking agent and decreasing the mass concentration of deionized water, and it was further enhanced by adding BMA comonomer. Hence, the microcapsules with crosslinked P(MMA-co-BMA) shell exhibited the best thermal stability. The thermal resistant temperature was up to 184 °C. Release experiment of fragrance microcapsules revealed that the encapsulation of fragrance into crosslinked P(MMA-co-BMA)/paraffin microcapsules showed excellent potential for the prolonged release of fragrance. It was found that most fragrance was still reserved in the microcapsules after exposing them in air for 3 months. The release of fragrance in surfactant solution was quick, especially when the temperature was higher than the melting point of paraffin. However, the total release time was still over 96 h.

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