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High Performance Poly(methyl methacrylate-acrylic acid-divinylbenzene) Microcapsule Encapsulated Heat Storage Material for Thermoregulating Textiles

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Abstract: The preparation of high performance poly(methyl methacrylate-acrylic acid-divinylbenzene) (P(MMA-AA-DVB)) microcapsule encapsulating octadecane (OD) having carboxyl groups on the surface for textile application was studied. The P(MMA-methyl acrylate (MA)-DVB) microcapsule was previously prepared by microsuspension iodine transfer polymerization prior to hydrolysis of MA segment to obtain AA in the P(MMA-AA-DVB) shell. Using 30 wt% of MA and 20 wt% of DVB, the latent heats of melting and crystallization of the encapsulated OD were close to those of original OD (245 and 251 J/g-OD, respectively). After hydrolysis, the zeta potential value of the obtained P(MMA-AA-DVB) microcapsule surface was -33 mV representing the formation of carboxyl groups of PAA derived from PMA. The influences of nucleating agent amount and type on the reduction of supercooling were then investigated. Using 1-octadecanol at 10 wt% of OD provided the best result. T_c of the encapsulated OD increased and reached to that of original OD while the latent heats were maintained. The hydrolyzed P(MMA-AA-DVB) presented higher efficiency than P(MMA-MA-DVB) microcapsules for fabric coating without external binder which may due to the interaction of microcapsule surface functional group with fabric.

Keywords: Thermal properties, Microcapsule, Heat storage material, Microsuspension iodine transfer polymerization, Supercooling

Introduction

The utilization of a latent heat storage system using heat storage or phase change materials (PCMs) is an efficient method of advanced energy technology. PCMs are materials which able to change their status with temperature [1-5]. They are attractive for many industrial applications such as energy storage, building conditioning and textiles [6-11]. Paraffin wax is one of the most famous PCMs having outstanding properties such as moderate heat capacity, nontoxic and low cost. However, it is low thermal conductivity which limits the applications. To improve this disadvantage, the encapsulation is used to increase heat transfer area. Among various encapsulation techniques, microsuspension polymerization using internal phase separation mechanism is one the most famous technique [12]. Many kinds of polymer shell have formed for the encapsulation of paraffin wax by microsuspension conventional radical polymerization (*ms* CRP). For example, poly(divinyl benzene) (PDVB) was prepared for the encapsulation of octadecane (OD) [13-16], hexadecane (HD) [17,18] and Rubitherm®27 (RT 27) [19, 20]. Methyl methacrylate (MMA) copolymer with DVB [19, 21], and polystyrene (PS) [22-25] were used as microcapsule shells for the encapsulation of RT 27 as a commercialized PCM. In those cases, the latent heats (heats of melting (ΔH_m) and crystallization (ΔH_c)) of encapsulated PCMs were decreased depended on the kind of polymer shell. It was found that the reduction of latent heats of the encapsulated HD in PDVB shell from those of bulk HD were improved by copolymerization with hydrophilic monomers such as methyl acrylate (MA), ethyl acrylate and butyl acrylate as functions of their copolymerized contents [17,18]. Recently, we found that the latent heats were same as those of original RT27 using PMMA shell prepared by *ms* CRP [20]. However, a large amount of free PMMA particles (~40 wt% of monomer) were formed in an aqueous medium resulting in the formation of microcapsules with multiple dents because of low shell strength. To overcome this drawback, microsuspension iodine transfer polymerization (*ms* ITP) was applied [26]. ITP is one of well-known controlled/living radical polymerization (CLRP) techniques [27,28]. It is an environmental friendly method without the utilization of heavy metal, using iodine compounds such as iodoform (CHI_3) as control agent. The iodoform used as control agent efficiently reduces radical exited during polymerization. It greatly reduced the formation of PMMA free particles via emulsion polymerization in aqueous medium. As a result, the spherical PMMA microcapsules having high shell strength were obtained. However, the reduction of crystallization temperature (T_c) of the encapsulated PCM called supercooling was still observed. One of the efficient methods to reduce supercooling is the addition of appropriate nucleating agent

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in the system [29-31].

PCM microcapsules can be incorporated into polymer solutions, melt during fiber spinning [32-34] as hollow fibers or applied to fabrics during finishing processes by conventional pad-dry-cure or coating methods for thermo-regulating textiles [35,36]. The adsorption via intermolecular force as H-bonding and electrostatic interaction or covalent bonding via esterification is one of important issues for application of PCMs microcapsule to some fabrics having special functional group or electric charge such as amino and hydroxyl groups outer surface. It was reported that the microcapsule having acrylic group on their surfaces were prepared for thermal comfort textiles [37,38].

Therefore, in this study, the preparation of functional P(MMA-acrylic acid (AA)-DVB)/OD microcapsules without the formation of free particles were carried out by *ms* ITP. The influence of monomer ratio on the formation and properties of microcapsules was investigated. Moreover, the effects of the amount and type of nucleating agents (chloroacetic acid, Rubitherm 58 (RT 58) and 1-octadecanol) on the reduction of supercooling and morphology were studied as well. The obtained microcapsules were expected to effectively adsorb onto textiles via covalent bonding.

Experimental

Materials

MMA (Aldrich, Wisconsin, USA; purity, 99 %) and MA (Aldrich, Wisconsin, USA; purity, 99 %) were purified by passing through a column packed with basic aluminum oxide. DVB (Aldrich, Wisconsin, USA; purity, 80 %) was washed with 1 M sodium hydroxide (NaOH; BDH Prolabo, Leuven, Belgium) solution to remove the polymerization inhibitors before use. OD as a core material (Merck, Munich, Germany; 99.5 %) was used as received. Reagent-grade benzoyl peroxide (BPO; Merck, Munich, Germany) was purified by recrystallization. CHI_3 (Aldrich, Wisconsin, USA; purify, 99 %) and poly(vinyl alcohol) (PVA; Aldrich, Wisconsin, USA; degree of saponification 87-90 %, molecular weight 3-7×10^4 g/mol) were used as received. 1-Octadecanol (Aldrich, ReagentPlus®, purity, 99 %), RT 58 (Rubitherm Technologies GmbH, Berlin, Germany; Commercial grade) and chloroacetic acid (Sigma aldrich, Germany; Analytical reagent, purity, 99 %) were used as the nucleating agents as received.

Microcapsule Preparation

The Preparation of P(MMA-AA-DVB)/OD Microcapsule

The P(MMA-AA-DVB)/OD microcapsules were prepared for textiles application in two steps. Firstly, P(MMA-MA-DVB)/OD microcapsules were prepared by *ms* ITP under the conditions listed in Table 1. The monomers as MMA, MA and DVB were homogeneously mixed with OD, BPO and CHI_3 as an oil phase. The homogeneous oil phase was poured into a PVA aqueous solution (1 wt%) and homogenized at 5,000 rpm for 5 min to form an oil in water (o/w) emulsion. Thereafter, the o/w emulsion was transferred to a round bottom flask, sealed with silicone rubber septum and purged with five vacuum/N_2 cycles. It was finally then polymerized at 80 °C for 3 h and followed by 90 °C for 5 h at a stirring rate of 200 rpm. In the second step, the obtained P(MMA-MA-DVB)/OD microcapsules were subsequently hydrolyzed with 0.05 M potassium hydroxide (KOH) solution for 24 h with stirring to form P(MMA-AA-DVB)/OD microcapsules.

The Influence of Nucleating Agent on the Reduction of Supercooling

The polymer microcapsules containing nucleating agent were prepared by *ms* ITP under the recipes listed in Table 2. The monomers, OD, BPO, nucleating agent, and CHI_3 were homogeneously mixed as an oil phase. It was then polymerized with the same procedure of the preparation of P(MMA-AA-DVB)/OD microcapsule as described above. The obtained polymer microcapsules containing nucleating

Table 1. Reagent amounts for the preparation of P(MMA-MA-DVB)/OD by *ms* ITP[a] of monomer/OD droplets[b] (monomer/OD=50/50, w/w) with various monomer ratios

MMA:MA:DVB (wt%)	MMA (g)	MA (g)	DVB (g)	OD (g)	BPO (g)	CHI_3 (g)	PVA solution (1 wt%) (g)
85:10:5	2.12	0.25	0.12	2.50	0.12	0.02	45.0
75:20:5	1.88	0.50	0.12	2.50	0.12	0.02	45.0
65:30:5	0.62	0.75	0.12	2.50	0.12	0.02	45.0
80:10:10	2.00	0.25	0.25	2.50	0.12	0.02	45.0
70:20:10	1.75	0.50	0.25	2.50	0.12	0.02	45.0
60:30:10	1.50	0.75	0.25	2.50	0.12	0.02	45.0
70:10:20	1.75	0.25	0.50	2.50	0.12	0.02	45.0
60:20:20	1.50	0.50	0.50	2.50	0.12	0.02	45.0
50:30:20	1.25	0.75	0.50	2.50	0.12	0.02	45.0

[a] N_2, 80 °C for 1-3 h, following by 90 °C for 4-8 h and [b] prepared by homogenized at 5,000 rpm for 5 min.

Table 2. Reagent amounts for the preparation of polymer microcapsules by *ms* ITP[a] of monomer/OD droplets[b] (monomer/OD=50/50, w/w) with various amounts of nucleating agent[c]

Ingredients	Nucleating agent (%wt of OD)		
	5	10	15
MMA (g)	1.25	1.25	1.25
MA (g)	0.75	0.75	0.75
DVB (g)	0.50	0.50	0.50
OD (g)	2.37	2.25	2.12
Nucleating agent[c] (g)	0.12	0.25	0.37
BPO (g)	0.12	0.12	0.12
CHI_3 (g)	0.02	0.02	0.02
PVA aqueous solution (1 wt%) (g)	45.0	45.0	45.0

[a)] N_2, 80 °C for 1-3 h, following by 90 °C for 4-8 h, [b)]prepared by homogenized at 5,000 rpm for 5 min, and [c)]chloroacetic acid, 1-octadecanol, RT 58.

agent were hydrolyzed with 0.05 M KOH solution for 24 h with stirring to form P(MMA-AA-DVB)/OD microcapsules.

Fabric Coating with Polymer Microcapsules

The prepared microcapsule before [P(MMA-MA-DVB)/OD] and after [P(MMA-AA-DVB)/OD] hydrolysis were coated on fabric by pad-dry-cure method (%pickup > 80 %). The 20×20 cm cotton fabric was soaked in the microcapsule suspension (2.5 wt% in water) about 1 minute. It was then padded, dried and cured at 130 °C for 5 minutes. The coating amount in term of add on efficiency (%) was measured by gravimetry.

Characterization

The inner structure and morphology of microcapsules surface were observed with an optical microscope (OM, SK-100EB & SK-100 ET, Seek Inter Co. Ltd., Thailand) and a scanning electron microscope (SEM, JSM-6510, JEOL, JEOL Ltd., Japan), respectively. Monomer conversion was measured by gravimetry at 70 °C. For the measurement of the thermal properties, free polymer particles in an aqueous medium were firstly removed from each suspension. The OD content in the dried washed microcapsules was determined by thermogravimetric analyzer (TGA, TGA 4000, Perkin-Elmer, USA) at a heating rate of 10 °C/min in N_2 atmosphere. The ΔH_m and ΔH_c (J/g-capsule) and melting temperature (T_m) and T_c of the encapsulated OD in dried microcapsules after washing with 2-propanol for 1 minute [26] were measured with a differential scanning calorimeter (DSC, DSC 4000, Perkin-Elmer, USA) under a N_2 flow in a scanning temperature range of 0 to 40 °C and at a heating/cooling rate of 5 °C/min for three times. ΔH_m and ΔH_c (J/g-OD) values were obtained using the following equation (1) from the heating/cooling peak areas of the DSC thermogram and OD content (% loading experiment) in the washed microcapsules obtained from the TGA analysis.

$$A = [B/C] \times 100 \tag{1}$$

where, A: ΔH_m and ΔH_c of the encapsulated OD in unit of joules per 1 g of encapsulated OD (J/g-OD)

B: ΔH_m and ΔH_c of the encapsulated OD in unit of joules per 1 g of microcapsule (J/g-capsule) measured with DSC

C: % loading (experiment) of OD in the washed microcapsules measured with TGA

The % theoretical loading of OD in the washed microcapsules was calculated by equation (2) using % conversion and % free polymer particles.

$$\%\ \text{Loading (theory)} = \left(\frac{W_{\text{wax}}}{\left(W_{\text{wax}} + W_{\text{m}}\left(\frac{\%\ \text{Conversion} - \%\ \text{Free polymer particle}}{100}\right)\right)}\right) \times 100 \tag{2}$$

where, W_m and W_wax are weights of monomers and OD (with/without nucleating agent), respectively, in the polymerization recipes shown in Tables 1 and 2.

The encapsulation efficiency (%) of OD was calculated using equation (3).

$$\%\ \text{Encapsulation efficiency} = \left(\frac{\%\ \text{Loading experiment}}{\%\ \text{Loading theory}}\right) \times 100 \tag{3}$$

The surface charge of microcapsules was measured with dynamic light scattering instrument (DLS, Delsa Nano C, Beckman Coulter, USA) by zeta potential mode at room temperature.

The add on efficiency (%) of polymer microcapsules coated fabric was calculated using the following equation (4).

$$\%\ \text{Add on} = [W_\text{Cap}/W_\text{Cap} + W_\text{Fab}] \times 100 \tag{4}$$

where, W_Cap: Weight of the polymer microcapsules coated on the fabric (g)

W_Fab: Weight of fabric before coated with microcapsules (g)

Results and Discussion

The Preparation of P(MMA-AA-DVB)/OD Microcapsules

The Preparation of P(MMA-MA-DVB)/OD Microcapsules with Various MA and DVB Contents

In general, secondary nucleation in aqueous medium always initiate during microsuspension polymerization of hydrophilic polymer capsules or particles [19-21]. The new particles are actually formed by self-assembling of polymer chains in aqueous medium initiated by the oligomeric radical exited from the monomer droplets or polymerizing particles. To depress this issue, in our previous work, the hydrophobic chain transfer agent as CHI_3 was introduced in the oil phase before monomer droplet generation in *ms* ITP. The oligomeric radicals generated in monomer droplet were then end-capped with the water insoluble chain transfer radical as iodine radical derived from the existed CHI_3. As a result, the radicals exited from the polymerizing particle are significantly decreased which is named "Radical Exit Depressing (RED) effect" [26,39]. Therefore, in this work, the preparation of hydrophilic polymer microcapsule of P(MMA-MA-DVB)/OD was carried out by *ms* ITP. The

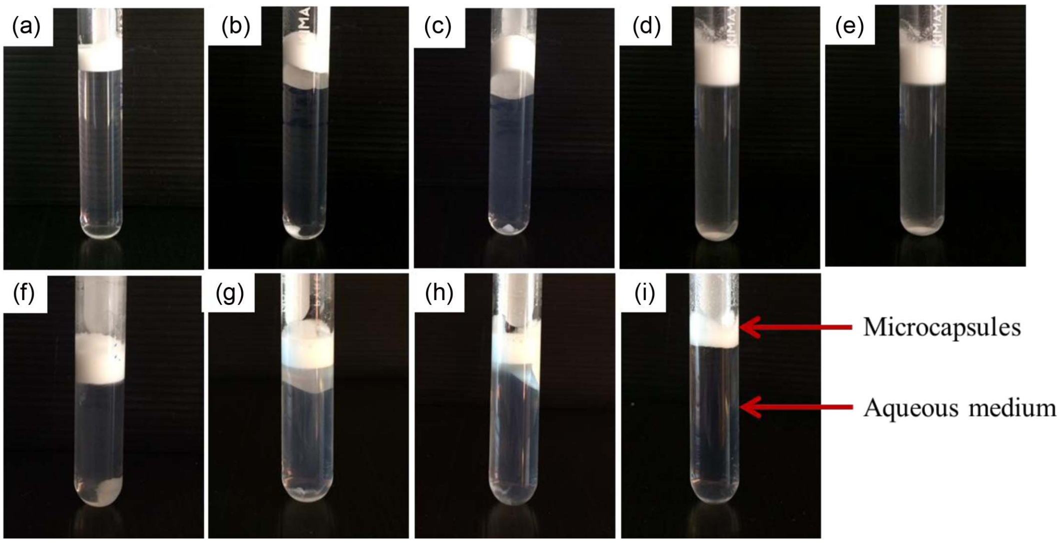

Figure 1. Photos of aqueous suspension of P(MMA-MA-DVB)/OD microcapsules prepared by *ms* ITP at various ratios of MMA:MA:DVB (wt%); 85:10:5 (a), 75:20:5 (b), 65:30:5 (c), 80:10:10 (d), 70:20:10 (e), 60:30:10 (f), 70:10:20 (g), 60:20:20 (h), and 50:30:20 (i).

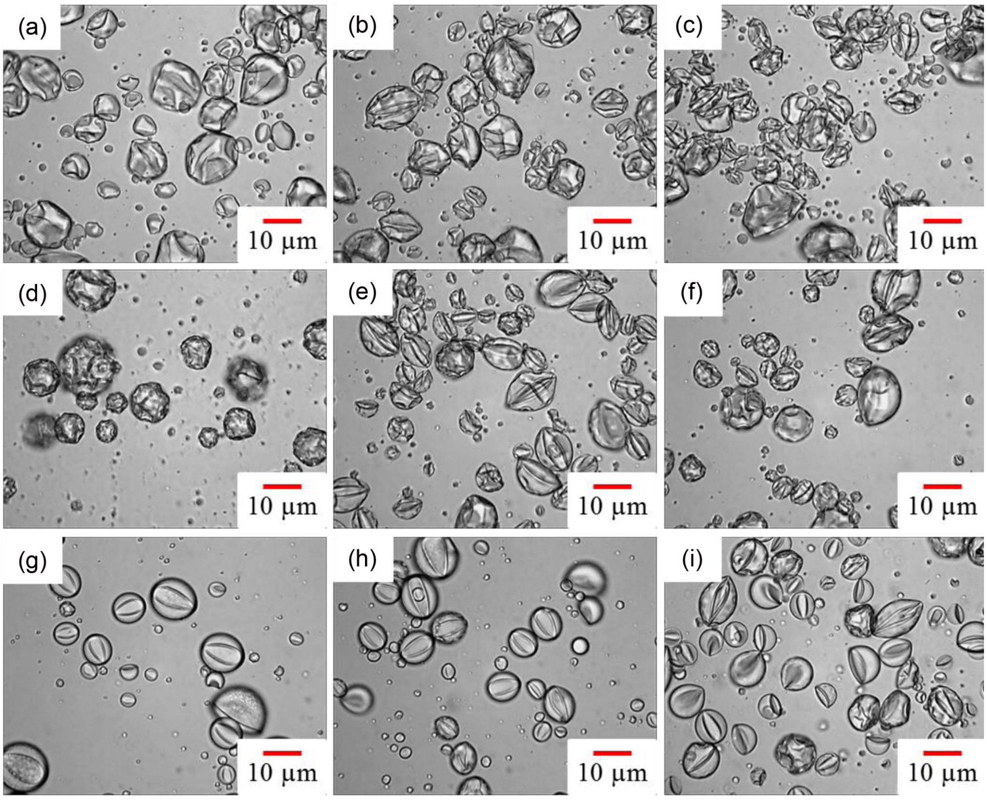

Figure 2. Optical micrographs of P(MMA-MA-DVB)/OD microcapsules prepared by *ms* ITP at various ratios of MMA:MA:DVB (wt%); 85:10:5 (a), 75:20:5 (b), 65:30:5 (c), 80:10:10 (d), 70:20:10 (e), 60:30:10 (f), 70:10:20 (g), 60:20:20 (h), and 50:30:20 (i).

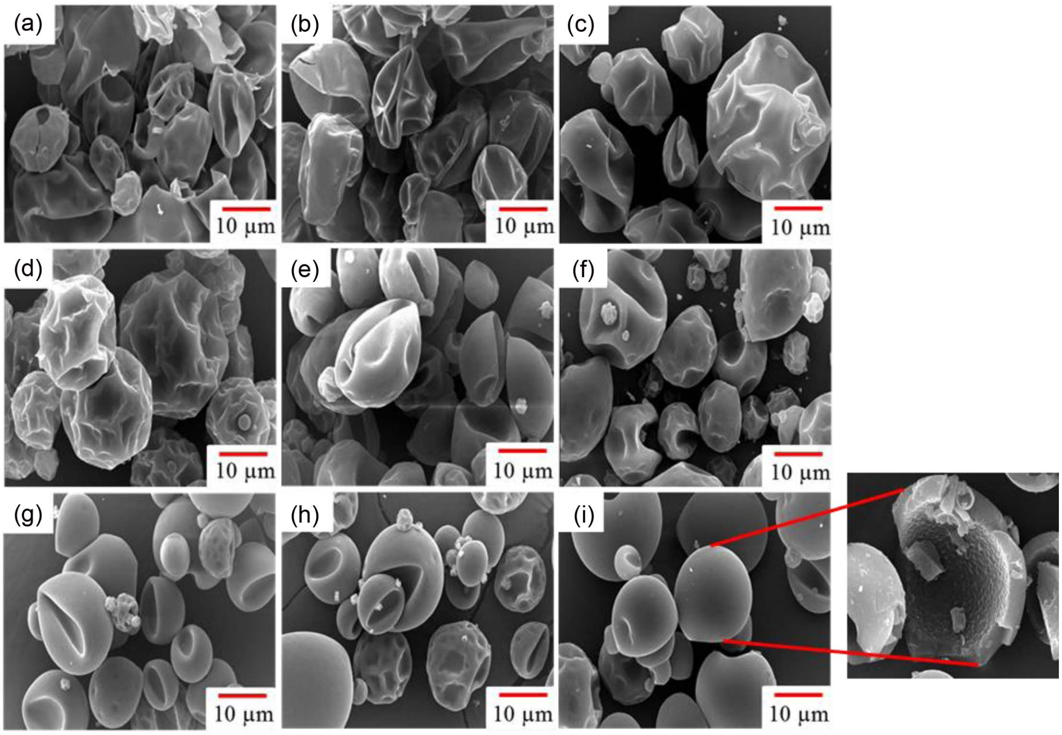

Figure 3. SEM micrographs of P(MMA-MA-DVB)/OD microcapsules prepared by *ms* ITP at various ratios of MMA:MA:DVB (wt%); 85:10:5 (a), 75:20:5 (b), 65:30:5 (c), 80:10:10 (d), 70:20:10 (e), 60:30:10 (f), (d), 70:10:20 (g), 60:20:20 (h) and 50:30:20 (i).

suspension photos of P(MMA-MA-DVB)/OD microcapsules after centrifugation at 5,000 rpm were shown in Figure 1. The microcapsules were floated on the upper layer because the total density of the microcapsules was lower than that of water [20] while the lower layer (aqueous medium) was quite transparent. This indicates that only small amount of secondary or free polymer particles were formed in the system [26] due to the RED effect as previously described. It accorded with low amount of secondary particles (<5 wt%) of all conditions measured with gravimetry. The obtained microcapsule yields were approximately 100 %.

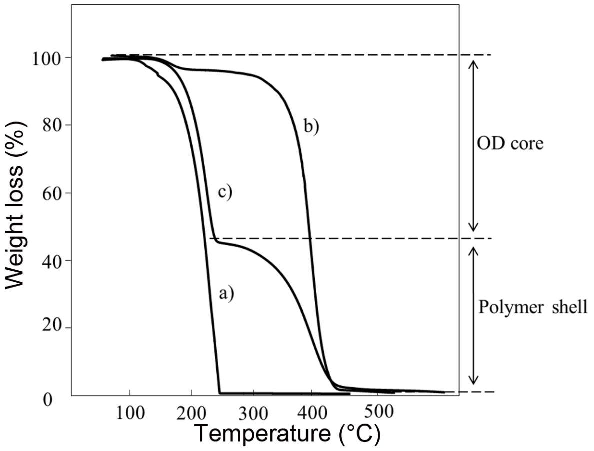

Figure 4. TGA thermograms of original OD (a), P(MMA-MA-DVB) (b) and P(MMA-MA-DVB)/OD microcapsules (c) at the MMA:MA:DVB (wt%) ratio of 50:30:20.

The optical and SEM micrographs of the obtained P(MMA-MA-DVB) microcapsules at various monomer ratios were shown in Figures 2 and 3, respectively. The shell strength of P(MMA-MA-DVB) microcapsules obtained in this work was lower than that of PDVB [13-15] and P(MMA-DVB) [19,21] microcapsules of previous works as shown in the form of nonspherical shape in all conditions. In addition, it is clearly seen that the shell strength decreased (as increasing of dented size) with increasing of MA content at various crosslinking agent contents as 5 wt% (Figures 2 and 3(a)-(c)), 10 wt% (Figures 2 and 3(d)-(f)) and 20 wt% (Figures 2 and 3(g)-(i)). It is due to the presence of low glass transition temperature (T_g) polymer segment as PMA in the polymer shell resulting in the reduction of T_g of the terpolymer shell. However, the shell strength was then improved with increasing of DVB content from 5 to 20 wt%. At the highest content of DVB (Figures 2 and 3(g), (h) and (i)), the shell strength seems mainly depend on the crosslinking content as the microcapsule shape were not different with various MA contents. In addition, after grinding the obtained microcapsule at the MMA:MA:DVB ratio of 50:30:20 and washing with 2-propanol (Figure 3(i)), the broken microcapsule clearly represented the core-shell structure containing an OD core (washed out) and a

P(MMA-MA-DVB) shell. This result accords with the previous work where RT27 core was encapsulated inside the PMMA shell produced by *ms* ITP [26].

The TGA thermogram of P(MMA-MA-DVB)/OD microcapsule (Figure 4(c)) as a representative of the other compositions was compared with original OD (Figure 4(a)) and P(MMA-MA-DVB) (Figure 4(b)) in which the microcapsules were washed with 2-propanol to remove the unencapsulated OD on their surfaces before measurement based on previous work [20]. The degradation temperature of original OD was 100-220 °C, whereas it was 250-450 °C for P(MMA-MA-DVB). In the case of the P(MMA-MA-DVB)/OD microcapsule, the degradation temperature was two steps at 110-250 °C and 260-550 °C which corresponded to those of the encapsulated OD and P(MMA-MA-DVB) shell, respectively. These TGA results indicate that OD was encapsulated inside P(MMA-MA-DVB) shell. In addition, % loading of the encapsulated OD at various MA and DVB contents was approximately 50 wt%, which was almost the same as the theoretical % loading obtained from equation (2) shown in Table 3. From these results and based on equation 3, it can be concluded that OD was encapsulated inside P(MMA-MA-DVB) shell with high encapsulation efficiency (100 %).

Table 3. % Loading and % encapsulation of OD in P(MMA-MA-DVB)/OD microcapsules (after washing with 2-propanol)

MMA:MA: DVB (wt%)	Loading (wt%)		Encapsulation (wt%)
	Experiment (±SD)*	Calculation	
85:10:5	69±0.31	64	100
75:20:5	61±0.12	56	100
65:30:5	63±0.36	60	100
80:10:10	51±0.33	51	100
70:20:10	53±0.20	54	100
60:30:10	55±0.06	51	100
70:10:20	54±0.25	51	100
60:20:20	55±0.19	51	100
50:30:20	54±0.32	51	100

*n=3.

The thermal properties of encapsulated OD in the P(MMA-MA-DVB)/OD microcapsules at various MA and DVB contents comparing to those of the original OD were shown in Table 4. The ΔH_m and ΔH_c of encapsulated OD calculated from equation (1) were almost the same as those of original OD (237±7.0 and 246±7.0 (J/g) for ΔH_m and ΔH_c, respectively). These indicate that the encapsulated OD is completely separated from the polymer shell according to our works proposed in the previous articles [20,26]. In addition, T_m of all conditions were about 24-25 °C which were almost the same as that of original OD (25 °C). In contrast, T_c values were greatly shifted from the original one to lower temperature (13-15 °C). It is general phenomenon of the encapsulated paraffin wax obviously observed in the micro- and nano-capsules which is called “supercooling”. It is well-known that the crystallization of waxes is normally nucleated by impurities named heterogeneous nucleation [31]. In the bulk waxes where impurities are homogeneously distributed therein, such supercooling phenomenon is not found. In contrast, in confine space as the microcapsule containing the different amounts of impurities, the nucleation efficiency of encapsulated waxes would different [29]. This drawback will be further improved in the next step.

The Hydrolysis of P(MMA-MA-DVB)/OD Microcapsules

To apply microcapsule in textile application with coating process, the presented carboxyl group on the microcapsule

Table 4. The latent heats (ΔH_m and ΔH_c) and transition temperatures of the encapsulated OD in P(MMA-MA-DVB)/OD microcapsules (after washing with 2-propanol)

MMA:MA:DVB (%wt)	Thermal properties					Zeta potential (mV) (±SD)*
	ΔH_m (J/g-OD) (±SD)*	ΔH_c (J/g-OD) (±SD)*	T_m (°C)	T_c (°C)		
				T_{c1}	T_{c2}	
Original OD	237±7.0	246±7.0	25	25	-	-
85:10:5	241±2.1	248±2.1	24	23	15	-
75:20:5	225±5.0	229±3.6	24	23	15	-
65:30:5	230±5.6	227±5.8	25	23	14	-
80:10:10	225±5.5	226±6.1	25	23	14	-19±2.4
70:20:10	232±5.8	234±7.1	25	23	14	-29±3.7
60:30:10	219±11.3	217±10.6	25	22	14	-37±3.0
70:10:20	226±3.5	228±4.6	25	21	13	-21±4.3
60:20:20	222±4.7	222±4.6	25	22	13	-31±3.9
50:30:20	224±7.8	226±7.8	25	22	13	-33±1.3

*n=3.

surface would effectively increase the percent add on. Therefore, the obtained P(MMA-MA-DVB)/OD microcapsules were then hydrolyzed by 0.05 M KOH solution. The infrared absorption spectra of original OD, the unhydrolyzed P(MMA-MA-DVB)/OD and the hydrolyzed P(MMA-AA-DVB)/OD microcapsules were presented in Figure 5. In the case of original OD (Figure 5(a)), the characteristic absorption peaks at about 700, 1400 and 2,900 cm^{-1} correspond to the in-plane rocking, C-H stretching and C-H bending vibrations of the methylene group, respectively. In the case of P(MMA-MA-DVB)/OD spectrum (Figure 5(b)), the strong characteristic absorption peaks at about 1,100 and 1,700 cm^{-1} are C-O and C=O stretching vibrations of MMA and MA segments. In addition, all the above characteristic peaks of original OD are able to observe in the spectrum of the P(MMA-MA-DVB)/OD (Figure 5(b)). These results indicate that OD is incorporated in the microcapsules. All characteristic absorption peaks of P(MMA-AA-DVB)/OD (Figure 5(c)) microcapsules were similar as those of P(MMA-MA-DVB)/OD microcapsule. However, the O-H stretching peak at about 3500 cm^{-1} was clearly observed in the case of P(MMA-AA-DVB)/OD microcapsule (Figure 5(c)) which indicated that PMA segment of P(MMA-MA-DVB) shell was successfully hydrolyzed to be PAA of P(MMA-AA-DVB) shell. In addition, the zeta potential of the microcapsule was measured to confirm the formation of PAA in terpolymer microcapsule shell. The zeta potential values of P(MMA-AA-DVB)/OD microcapsules were negative in the range of -19 to -37 mV (Table 5) due to the present of carboxyl groups at microcapsule surface which accords with the FTIR results. Furthermore, the negative charge increased with the increase of MA content. The existence of these carboxyl groups at microcapsule surface would benefit for further fabric coating. Based on microcapsule shell strength, thermal properties and zeta potential, P(MMA-AA-DVB)/OD microcapsule using MMA:MA:DVB at 50:30:20 was selected as the optimum condition for the next study.

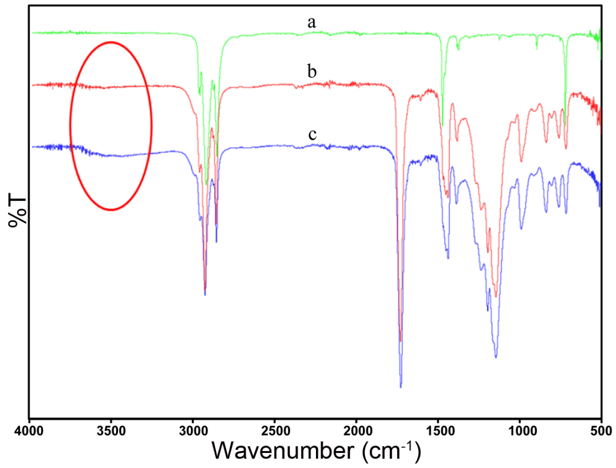

Figure 5. ATR-FTIR spectra of original OD (a), P(MMA-MA-DVB)/OD (b) and P(MMA-AA-DVB)/OD (c) microcapsules.

The Influence of Nucleating Agent on the Reduction of Supercooling

To decrease the degree of supercooling of the encapsulated

Table 5. The latent heats and transition temperatures of the encapsulated OD in P(MMA-MA-DVB) microcapsules with various types and amounts of nucleating agent

Sample	Thermal properties					Zeta potential (mV) (±SD)*
	ΔH_m (J/g-OD) (±SD)*	ΔH_c (J/g-OD) (±SD)*	T_m (°C)	T_c (°C)		
				T_{c1}	T_{c2}	
Original OD	245±7.00	251±7.00	25	25	-	-
Chloroacetic acid	147±4.72	151±6.31	56	57	-	-
RT 58	264±5.60	277±2.80	56	56	-	-
1-octadecanol	244±5.60	241±5.60	57	56	-	-
0	224±7.80	246±7.00	25	22	17	-33±1.3
5 wt% chloroacetic acid	221±0.71	222±0.35	25	23	15	-48±2.0
10 wt% chloroacetic acid	251±9.24	252±8.72	25	22	14	-50±2.6
15 wt% chloroacetic acid	220±8.39	221±7.57	25	21	16	-53±1.7
5 wt% RT 58	240±7.40	248±8.30	25	25	17	-30±2.2
10 wt% RT 58	248±8.30	247±10.6	25	25	17	-32±5.8
15 wt% RT 58	237±2.90	237±9.70	25	25	19	-28±3.3
5 wt% 1-octadecanol	243±2.80	246±3.50	26	24	-	-30±1.8
10 wt% 1-octadecanol	262±5.60	262±5.60	26	26	-	-29±2.2
15 wt% 1-octadecanol	234±11.4	234±11.4	26	26	-	-31±3.7

*n=3.

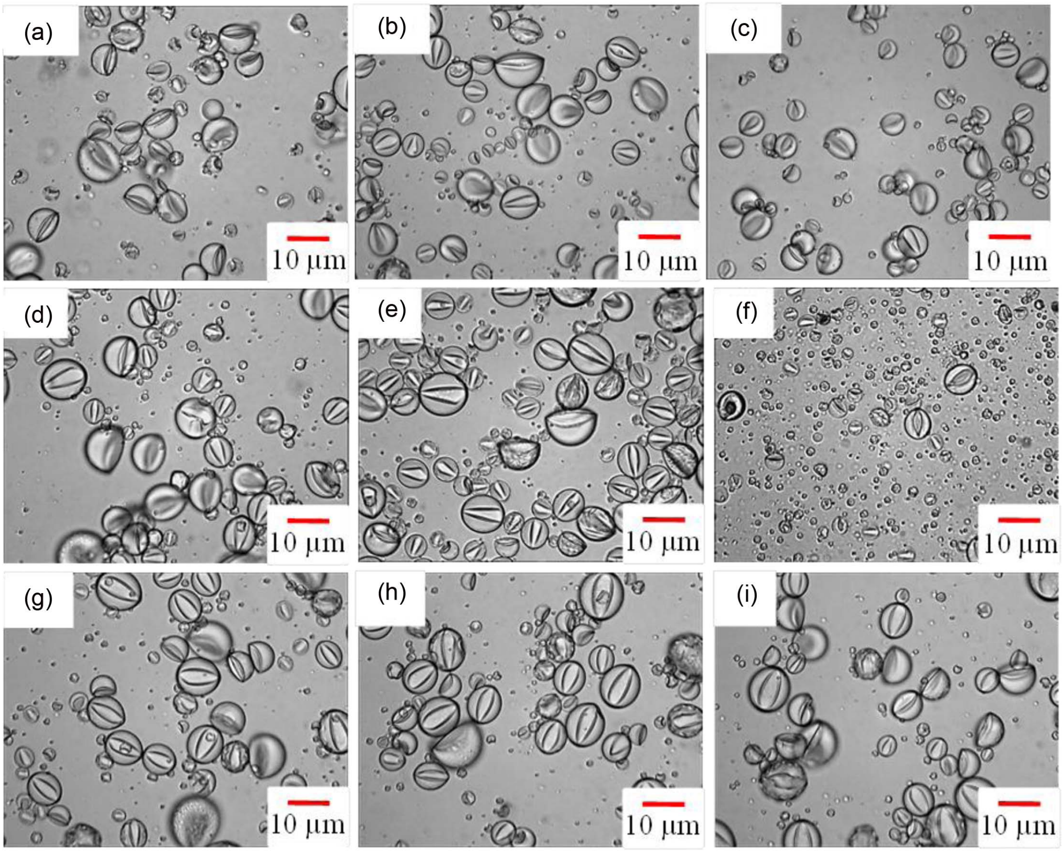

Figure 6. Optical micrographs of microcapsules using various nucleating agents: chloroacetic acid: (a-c); RT 58 (d-f) and 1-octadecanol (g-i) at various amounts (wt%): 5 (a, d and g), 10 (b, e and h) and 15 (c, f and i').

OD, various types and amounts of nucleating agent were added in the microcapsules. Figure 6 shows the optical micrographs of microcapsules containing nucleating agents. They were nonspherical in shape with a dent on the outer surface similar to those of P(MMA-AA-DVB)/OD microcapsules without nucleating agent. It indicated that the addition of nucleating agent did not effect on the formation of microcapsule. In addition, the degradation temperatures measured by TGA of the obtained microcapsules at various nucleating agent types and amounts presented two steps (an example of TGA thermogram of microcapsule containing 1-octadecanol shown in Figure 7(c)) according to capsule core and polymer shell similar to that obtained from microcapsule without nucleating agent. One step degradation of capsule core due to the degradation temperatures of original OD (110-240 °C; Figure 7(a)), chloroacetic acid (100-150 °C), RT 58 (100-240 °C) and 1-octadecanol (110-240 °C; Figure 7(b)) were not different. The accurate encapsulated OD amount then cannot be measured by TGA. The % loading of encapsulated OD containing various types and amounts of nucleating agent were approximately 50 wt% closed to the theoretical % loading (51-56 wt%) obtained from equation (2) based on 100 % conversion with ≤ 4 wt% P(MMA-MA-DVB) free particles. This result indicated that high encapsulation efficiency was then obtained. Based on the incorporation of nucleating agents, the latent heats of the encapsulated OD and nucleating agent were then presented in the unit of J/g-core.

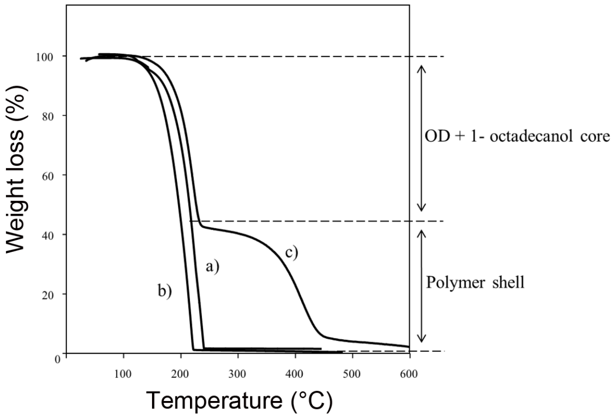

Figure 7. TGA thermograms of original OD (a), 1-octadecanol (b) and P(MMA-MA-DVB)/OD microcapsule using 5 wt% of 1-octadecanol (c) as a nucleating agent.

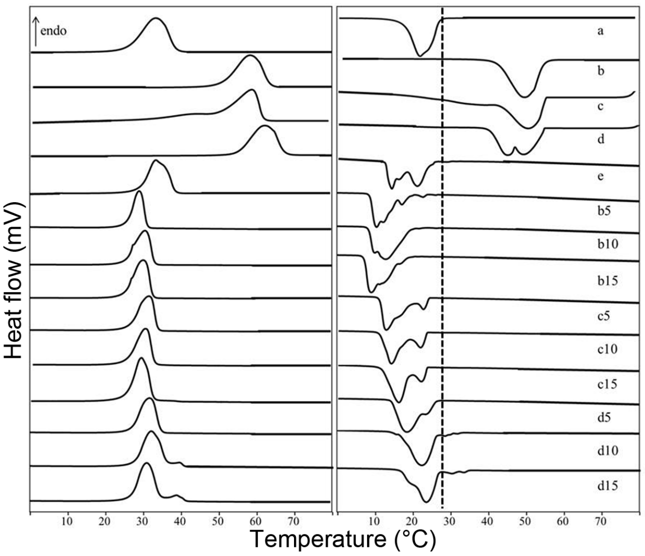

Figure 8. DSC thermograms of OD (a), chloroacetic acid (b), RT 58 (c), 1-octadecanol (d) and the encapsulated OD in P(MMA-MA-DVB)/OD microcapsules (e) using chloroacetic acid (wt%): 5 (b5), 10 (b10) and 15 (b15); RT 58 (wt%): 5 (c5), 10 (c10) and 15 (c15) and 1-octadecanol (wt%): 5 (d5), 10 (d10) and 15 (d15).

The DSC thermograms of original OD, chloroacetic acid, RT 58, 1-octadecanol and P(MMA-MA-DVB)/OD microcapsules with the addition of various nucleating agents after removing of free polymer particles and washed with 2-propanol were presented in Figure 8. In all conditions, ΔH_m and ΔH_c of the encapsulated OD containing nucleating agent obtained from equation (1) were almost the same as those of original OD (Table 5) indicating that the addition of these nucleating agents did not reduce the latent heats of the encapsulated wax as reported in the other works [29,31].

The T_c (56-57 ^{o}C) and T_m (56-57 ^{o}C) of all nucleating agents are not different and much higher than that (25 ^{o}C) of the original OD which may effectively induce the crystallization of encapsulated OD at the normal temperature. T_m values of the encapsulated OD were also similar to that of the original OD. However, the influence of nucleating agent was clearly observed on T_c value. In the case of chloroacetic acid and RT 58 at 5 (Figure 8(b5), (c5)), 10 (Figure 8(b10), (c10)) and 15 (Figure 8(b15), (c15)) wt%, T_c values were still lower than those of the original OD (25 ^{o}C). Supercooling and broad multiple peaks of the encapsulated OD were still observed. Although T_c was increased in the case of 5 wt% 1-octadecanol (Figure 8(d5)), main crystallization peak (the larger shoulder) was still lower than normal T_c. In contrast, T_c of encapsulated OD was shifted significantly from 17 to 24 ^{o}C and almost the same as that of original OD when 10 wt% of 1-octadecanol (Figure 8(d10)) was incorporated. The improvement of supercooling with 1-octadecanol may be due to the similar chemical structure of 1-octadecanol with OD which more homogeneously distributed in the microcapsule core than the other nucleating agents. The crystal of 1-octadecanol solidified at higher temperature induced the crystallization of the encapsulated OD at the normal temperature via heterogeneous nucleation. The supercooling of OD in P(MMA-MA-DVB) shell then was effectively reduced.

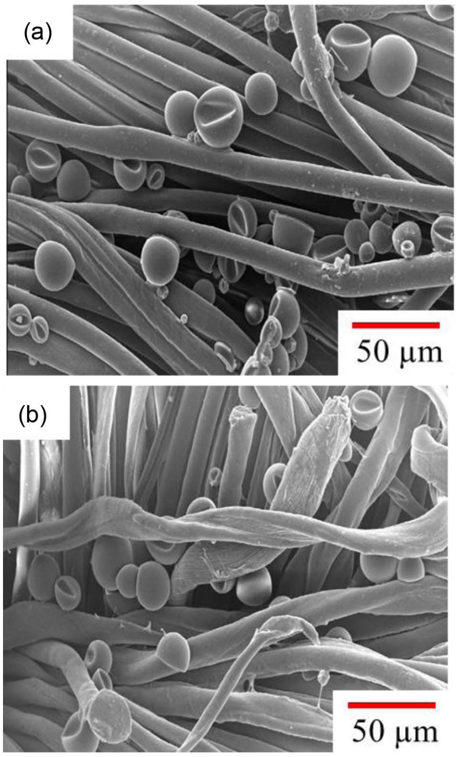

Figure 9. SEM micrographs of cotton fabric coated with P(MMA-AA-DVB)/OD (a) and P(MMA-MA-DVB)/OD (b) microcapsules by Pad-Dry-Cure method without external binder.

Fabric Coating with Polymer Microcapsules

The coating of the unhydrolyzed P(MMA-MA-DVB)/OD and hydrolyzed P(MMA-AA-DVB)/OD microcapsules on cotton fabric was carried out by Pad-Dry-Cure method without binder. The polymer microcapsules were distributed on the fibers in both conditions as shown in Figure 9. In addition, the % add on was twice as high in the hydrolyzed P(MMA-AA-DVB)/OD microcapsules (4.67 %) as it was in the unhydrolyzed P(MMA-MA-DVB)/OD microcapsules (2.78 %). The P(MMA-AA-DVB)/OD microcapsule having carboxylic groups on their surfaces would reinforce the coating due to the covalent bonding via esterification with hydroxyl group of cotton.

Conclusion

P(MMA-AA-DVB)/OD microcapsules were successfully prepared by *ms* ITP following by a simple hydrolysis. The microcapsule shell strength increased with increasing of DVB content. After hydrolysis, the zeta potential values of P(MMA-AA-DVB) microcapsules increased with the increasing of MA content due to the presence of PAA units derived from PMA at microcapsule surface. The latent heats of the encapsulated OD were closed to those of the original OD. The addition of 10 wt% 1-octadecanol nucleating agent was found to effectively prevent the supercooling of OD in the microcapsules. The existence of carboxylic group of PAA would enhance the coating of microcapsules on fabric via covalent bonding.

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