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β-Cyclodextrin을 피커링 유화제로 이용한 열팽창 Poly(acrylonitrile-*co*-methacrylonitrile) 마이크로캡슐의 제조

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Preparation of Thermally Expandable Poly(acrylonitrile-*co*-methacrylonitrile) Microcapsules Using β-Cyclodextrin as Pickering Emulsifier

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초록: 피커링 현탁 중합법을 통하여 열팽창성 poly(acrylonitrile-*co*-methacrylonitrile) 마이크로 캡슐을 제조하였다. 피커링 유화제로서 β-cyclodextrin(β-CD)과 polyvinylpyrrolidone(PVP)의 조합이 최초로 사용되었다. β-CD는 독성이 낮으며 경제적이며 상대적으로 좁은 입자 크기 분포도를 제조하는 것이 가능하다고 알려져 있다. Acrylonitrile(AN)과 methacrylonitrile(MAN)이 단량체로 사용되었으며, β-CD 함량, β-CD/PVP의 단량체에 대한 비율, AN/MAN 비율, 다양한 발포제의 효과에 대하여 입자의 제조 특성 및 마이크로캡슐의 물성에 대하여 조사하였다. 약 125 μm 입경의 캡슐이 제조되었으며, 2 : 1 β-CD : PVP 비율, 3.5 wt%의 피커링 분산제의 함량에서 제조된 캡슐이 가장 우수한 열팽창 성능을 보였다. TGA 분석 결과 약 35%의 발포제가 캡슐화되었다. 결과적으로 본 연구에서 사용된 β-CD는 현탁중합에 있어 우수한 피커링 유화제로서의 성능을 보였다.

Abstract: Thermally expandable poly(acrylonitrile-*co*-methacrylonitrile) microcapsules were prepared by Pickering suspension polymerization. β-Cyclodextrin (β-CD) and polyvinylpyrrolidone (PVP) pair as the Pickering emulsifier was used as picking emulsifiers for the first time. β-CD is low in toxicity, cheap, and can produce particles with a relatively narrow particle size distribution. Acrylonitrile (AN) and methacrylonitrile (MAN) were used as monomers. The effects of β-CD content, the ratio of β-CD/PVP relative to the amount of monomer, AN/MAN ratio, and the various blowing agents were investigated for the preparation and properties of microcapsules. Thermally expandable microcapsules having a size of about 125 μm were produced. When β-CD : PVP was 2 : 1 at a total dispersant content of 3.5 wt%, the microcapsules had the best expansion performance. TGA analysis confirmed that about 35% of the hydrocarbons were encapsulated in the microcapsules. Finally, it was found that β-CD serves as a good Pickering emulsifier in suspension polymerization.

Keywords: thermally expandable microcapsule, β-cyclodextrin, pickering emulsifier, suspension polymerization, poly(acrylonitrile-*co*-methacrylonitrile).

Introduction

Microencapsulation is a procedure in which solids, liquids, or gasses are surrounded by a layer of natural or synthetic polymers to provide microcapsules.[1] It is principally used to preserve unsettled or sensitive functional materials, segregate a core from its surroundings, impede leaching or volatilization risks of a volatile core, and enhance the handling properties of an adhesive material.[2-5] When the blowing agent is encapsulated through in this process, the resulting product is called thermally expandable microcapsule.[6] When the temperature exceeds the glass-transition temperature (T_g) of the shell composed of a polymer, the shell is softened and the hydrocarbon is vaporized, causing the microcapsule to expand.[7,8] Thermally expandable microspheres are used for the printing ink industries to improve the surface texture of textile and wallpaper, and they are used in the automobile industry in underbody coating, tires, gap filler, and adhesive debonding applications.[9]

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In various heterogenous polymerizations such as emulsion and suspension polymerization, Pickering emulsions are more stable opposed to coalescence than conventional surfactants or protective colloids and can gain many useful properties. The existence of Pickering emulsifiers at the interface between the oil and aqueous phases affects not only the preparation of microcapsules, but also the properties of resulting microcapsules, affording superior stability, low toxicity, and stimuli-responsiveness compared to classical emulsions stabilized by surfactants.[10] Various inorganic and organic colloidal particles with different sizes, shapes and surface chemistry have been studied to prepare Pickering emulsions, including silica, clays, wax, layered double hydroxides particles, carbon nanotubes, magnetic particles, and thermosensitive particles like poly(*N*-isopropylacrylamide).[11-18]

Cyclodextrins (CDs), which can make surface active compositions at oil-water interfaces, are attractive alternative emulsion stabilizers due to the capability to form a host-guest inclusion complex.[19-21] It was suggested that such emulsions are a type of Pickering emulsion stabilized by the self-assembled insertion complexes of CD–oil.[22] CDs can be tempting alternative emulsion stabilizers with probable use in food, pharmaceutical and skin care due to their host-guest inclusion complex ability.[23] CDs are biocompatible and nontoxic and previous studies have shown that CDs can form surface active complexes at the o/w interfaces that can stabilize emulsions.[24]

In this study, thermally expandable microcapsules were prepared by suspension polymerization using β-CD as a Pickering emulsifier to stabilize o/w emulsions for the first time. This study reports the preparation and properties of thermally expandable microcapsules with a poly(acrylonitrile-*co*-methacrylonitrile) (poly(AN-*co*-MAN)) using β-CD as a Pickering emulsifier. The effects of β-CD ratio, stabilizer concentration, AN/MAN ratio, and several liquid hydrocarbons were investigated for the preparation of the microcapsules.

Experimental

Materials. Acrylonitrile (AN, Aldrich, USA) and methacrylonitrile (MAN, TCI, Japan) were used as monomers. 1,4-Butanediol dimethacrylate (BDDMA, Aldrich, USA) was used as a crosslinking agent. β-Cyclodextrin hydrate (β-CD; 99%, Samchun Chemicals, Korea) was used as Pickering emulsifier. Polyvinylpyrrolidone (PVP K-30, Junsei, Japan) was obtained. *n*-Octane, *iso*-octane, *n*-pentane, *iso*-hexane from Daejung Chemicals (Korea) were used as blowing agents. Azobisisobutyronitrile (AIBN) was purchased from Junsei Chemical (Japan). Sodium chloride (NaCl; 99.5%) and sodium nitrite ($NaNO_2$; 98.5%) were purchased from Samchun Chemicals (Korea).

Polymerization. To prepare the continues phase, the β-CD powder was dissolved in deionized water with vigorous agitating at 80 °C. Subsequently, 0.5 g NaCl and 0.5 g $NaNO_2$ were added to this mixture. The dispersion phase was prepared with monomers consisting of AN and MAN, which was followed by the addition of hydrocarbon. The dispersion phase mixture was added to the continuous phase and homogenized with IKA Ultra Turrax T25 Basic Instruments at 9500 rpm for 2 min. The homogenized mixture was polymerized in a high pressure reactor made of stainless steel under agitation and nitrogen purging. The pressure was regulated to the proper value and the reaction was carried out for 8 h. After finishing polymerization, the particles produced were filtered and rinsed, and then dried in a vacuum oven at ambient temperature for 24 h.

Characterization. The particle morphology was observed by scanning electron microscopy (SEM, Hitachi, S-4300, Japan). The particle size and particle size distribution were investigated using a laser scattering particle size analyzer (PSA, Mastersizer2000, Malvern Panalytical, USA). Prior to analysis, the particles were sonicated with distilled water in small bottles for 5 min. Thermogravimetric analysis (TGA, TA Q50, TA instruments, USA) was used to measure the encapsulated content of the blowing agent. The samples were heated from 30 to 600 °C with 10 °C/min under a nitrogen atmosphere. Thermomechanical analysis (TMA, TMA 800 system, Instrument Specialists Incorporated, USA) was performed to monitor the expansion properties such as the temperature of maximum expansion (T_{max}) and the displacement of microspheres volume upon heating. The samples were heated from 25 to 250 °C with 10 °C/min under nitrogen.

Results and Discussion

Table 1 shows the composition of thermally expandable microcapsules prepared via Pickering suspension polymerization. To distinctly observe the change of morphology and confirm the influence of β-CD/PVP ratio relative to monomer on the microcapsules, the β-CD/PVP ratio relative to monomers was investigated first (Table 1, sample 1-5). Then, the effects of the stabilizer content were investigated at fixed β-CD/PVP ratio relative to monomers (Table 1, sample 6-11).

Table 1. Composition of Thermally Expandable Microcapsules via Pickering Suspension Polymerization

Run No.	Water (mL)	β-CD (g)	PVP (g)	NaCl (g)	$NaNO_2$ (g)	AN (g)	MAN (g)	AIBN (g)	*n*-Octane (g)	BDDMA (g)
1	100	1.0	0	0.5	0.5	20.3	8.7	0.2	10	0.06
2		0.5	0.5							
3		0.67	0.33							
4		0.75	0.25							
5		0.80	0.20							
6	100	0.185	0.093	0.5	0.5	20.3	8.7	0.2	10	0.06
7		0.56	0.28							
8		0.67	0.33							
9		1.11	0.56							
10		1.67	0.834							
11		2.32	1.16							
12	100	0.67	0.33	0.5	0.5	23.2	5.8	0.2	10	0.06
13						20.3	8.7			
14						17.4	11.6			
15						14.5	14.5			
16						11.6	17.4			
17						8.7	20.3			
18	100	0.67	0.33	0.5	0.5	20.3	8.7	0.2	8.7	0.06
19									10	
20									11.6	
21									13.05	
22									14.50	
	Water (mL)	β-CD (g)	PVP (g)	NaCl (g)	$NaNO_2$ (g)	AN (g)	MAN (g)	AIBN (g)	Blowing agent (10 g)	BDDMA (g)
23	100	0.67	0.33	0.5	0.5	20.3	8.7	0.2	*n*-Octane	0.06
24									*iso*-Octane	
25									*n*-Pentane	
26									*iso*-Hexane	

MAN was used as co-monomer since it has a high coefficient of thermal expansion.[9] To enhance the expansion performance of the microcapsules, AN/MAN ratio was investigated at a fixed stabilizer concentration (Table 1, sample 12-17). After investigating the optimal amount of blowing agent using *n*-octane (Table 1, sample 18-22), four hydrocarbons were used to obtain thermally expandable microcapsules with optimal expansion performance (Table 1, sample 23-26).

SEM morphology of thermally expandable microcapsule particles with different β-CD and PVP concentrations is shown in Figure 1. After 8 h polymerization, microcapsules are formed by using β-CD and PVP. The size of the particles becomes smaller and tends to aggregate together as the β-CD content increases. Above 2:1 wt% of β-CD/PVP relative to the amount of monomer, capsules begin to clump (Figure 1(c) and 1(d)). Figure 2 shows the particle size distribution of expandable microcapsules prepared at different ratios of β-CD/PVP. It indicates that the particle size of microcapsule decreases with increasing β-CD contents. In this experiment, Pickering emulsion droplets are used as reaction receptacle during suspension polymerization. Therefore, the initial emulsion droplet leads to thermally expandable microcapsule particles.[25] Figure 3 shows the TGA thermograms of the microcapsules prepared with a different ratio of β-CD/PVP. Thermally expandable micro-

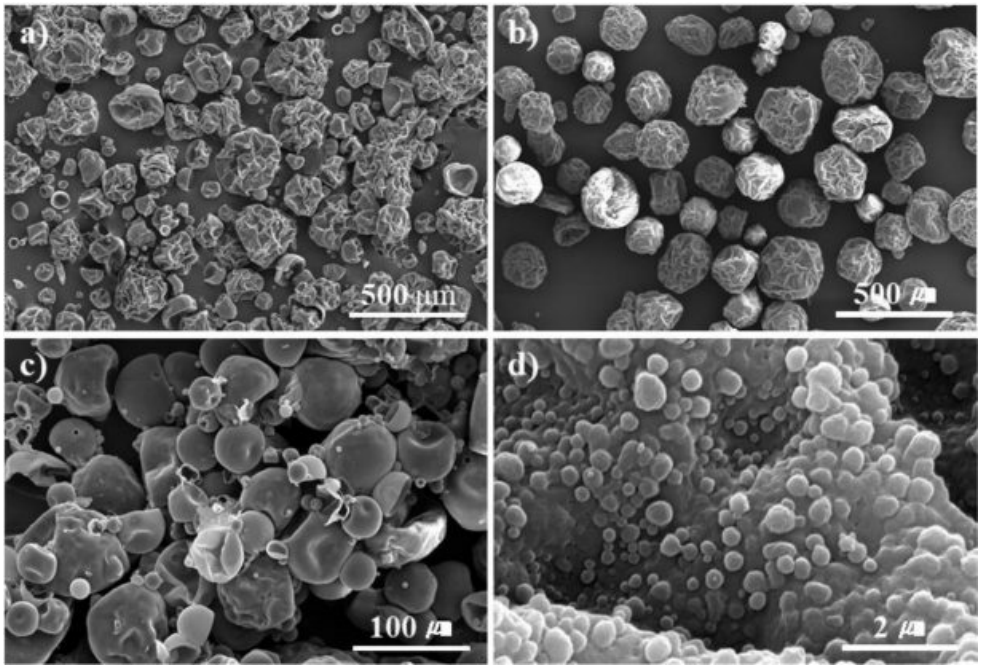

Figure 1. SEM microphotographs of expandable microcapsules prepared at different β-CD/PVP ratios: (a) 1:1; (b) 2:1; (c) 3:1; (d) 4:1 w/w.

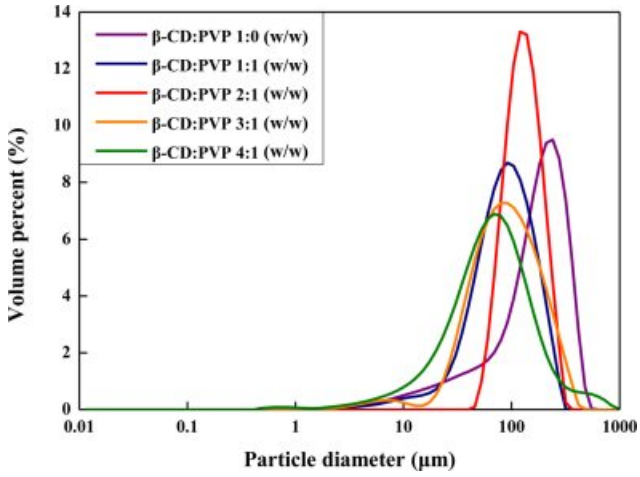

Figure 2. Particle size analysis of the expandable microcapsules prepared at different β-CD/PVP ratios.

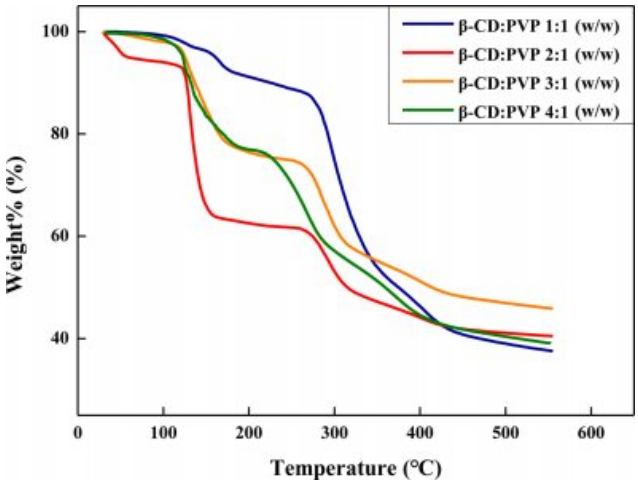

Figure 3. TGA thermograms of expandable microcapsules prepared at different β-CD/PVP ratios.

capsules have two-step decompositions process. The first weight loss at around 125 ℃ is due to the vaporization of the hydrocarbon blowing agent. And second weight loss is ascribed to the thermal decomposition of the polymeric shell. When the microcapsules are heated above the boiling point of *n*-octane, 125 ℃, the polymeric shell starts to expand and finally blows up because the polymeric shell cannot endure the internal pressure by vaporization of the hydrocarbon.[26] When the ratio of β-CD/PVP was 2:1 wt/wt%, the largest amounts of hydrocarbons was encapsulated. At low β-CD concentrations, the o/w emulsions were so precarious that the droplets can be broken easily, and high β-CD concentration resulted in the low encapsulation of the blowing agents. It seems that as great amount of stabilizers cover the surface of the emulsion droplets, they prevent the hydrocarbon from entering the core of the particles.

TMA thermograms indicate the expansion properties of microcapsules prepared with different ratio of β-CD/PVP rel-

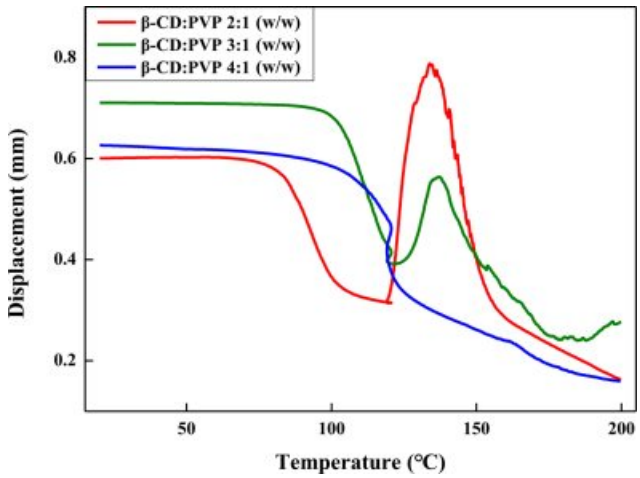

Figure 4. TMA thermograms of the expandable microcapsules prepared at different β-CD/PVP ratios.

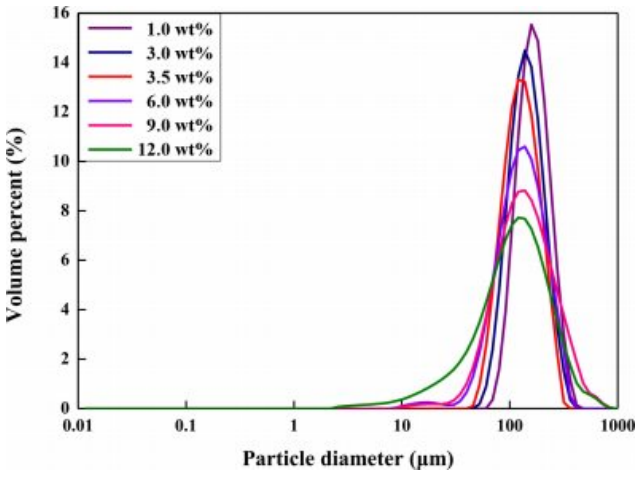

Figure 6. Particle size analysis of the expandable microcapsules prepared with different contents of stabilizer.

ative to the amount of monomer, which show the individual characteristic for thermally expandable microcapsules as the expansion performance. During heating the microcapsules, the polymeric shells should endure the pressure of vaporized hydrocarbons. The start point of expansion temperatures is between 100 °C and 150 °C, which is associated with the degradation starting temperatures obtained from TGA. As shown in Figure 4, the TMA results have good expansion performance with microcapsules composed of 2:1 β-CD/PVP. Therefore, subsequent experiments were studied with a fixed 2:1 ratio of β-CD/PVP relative to the amount of monomer.

The effects of the stabilizer contents on thermally expandable microcapsules were investigated at a 2:1 β-CD/PVP ratio. Different recipes for this set of experiment are shown in Table 1 (sample 6-11). The morphology of the particles in Figure 5 was not completely spherical in structure. As seen in Figure 6, the range of particle diameters becomes broad. Also, the particle size distribution peaks were shifted to the left with increasing amounts of stabilizers, indicating that the decrease in particle sizes of microcapsules. Figure 7 shows the TGA thermograms of the microcapsules prepared at different contents of the stabilizer. When the contents of stabilizer were 1 wt%, the amounts of the blowing agent encapsulated in the microcapsules were the highest at about 60%. However, the TMA thermograms shows that the expansion properties of microcapsules were dramatically increased by using 3.5 wt%

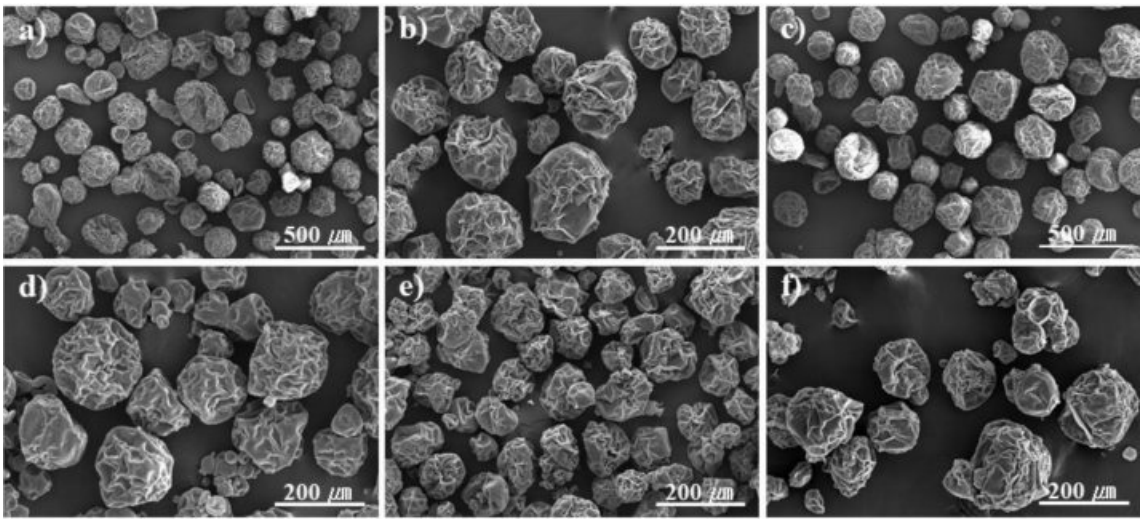

Figure 5. SEM microphotographs of expandable microcapsules prepared at different contents of stabilizer. (a) 1.0; (b) 3.0; (c) 3.5; (d) 6.0; (e) 9.0; (f) 12.0 wt%.

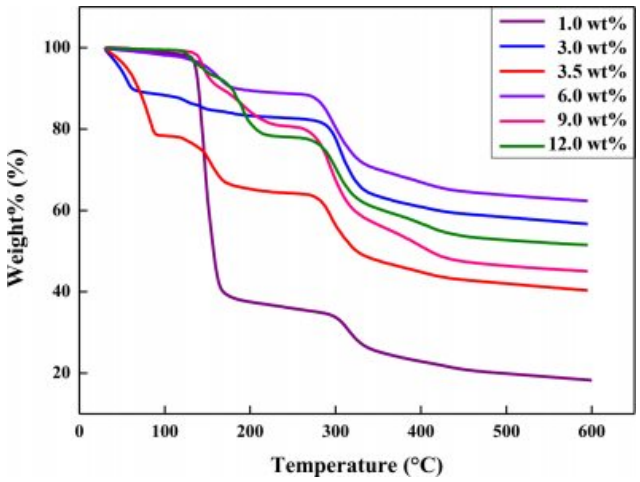

Figure 7. TGA thermograms of expandable microcapsules prepared with different contents of stabilizer.

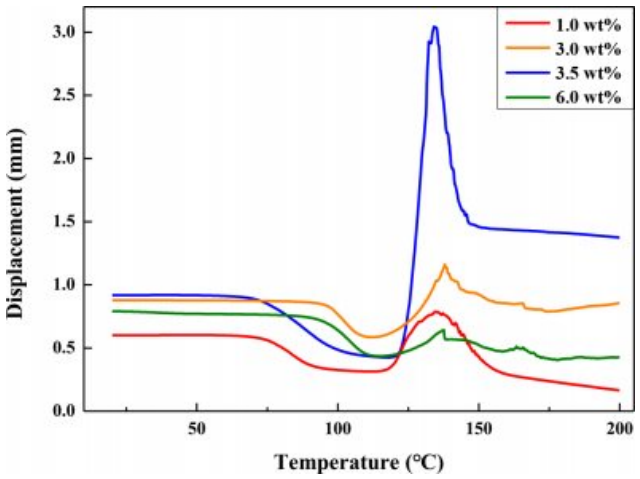

Figure 8. TMA thermograms of the expandable microcapsules prepared with different contents of stabilizer.

of stabilizer relative to the amount of monomer, which indicated the maximum displacement of about 3.1 mm in Figure 8. Therefore, the optimum amount of stabilizer for expansion performance was 3.5 wt%.

The influence of AN/MAN ratio was investigated at a fixed stabilizer concentration, 3.5 wt% relative to the amount of monomer. The various ratios are shown in Table 1 (sample 12-17). As shown in Figure 9, when the ratio of AN is higher, it can be observed that small grains are attached to the surface. This formation of small particles is due to the fact that monomers, such as AN, which has low solubility in water would enter the continuous phase, and secondary particles would form on the droplet surface during polymerization.[26] Methacrylonitrile (MAN) has a high thermal expansion coefficient, and polyacrylonitrile (PAN) is famous for its excellent gas barrier properties.[27] However, adding an excess of MAN will not encapsulate the hydrocarbons (Figure 9(e) and 9(f)). The diameter of the microspheres increased as the AN portion became primary. Figure 10 shows the thermal decomposition phenomena of the microcapsules prepared at various AN/MAN ratios. As the amount of AN decreases, the second decomposition temperature decreases. The blowing agent vaporizes and increases in volume of the microcapsules. The microcapsule expands because it pushes the shell out. The optimum proportion of monomers can be found at AN:MAN 70:30 w/w.

Finally, the microcapsules were compared by changing

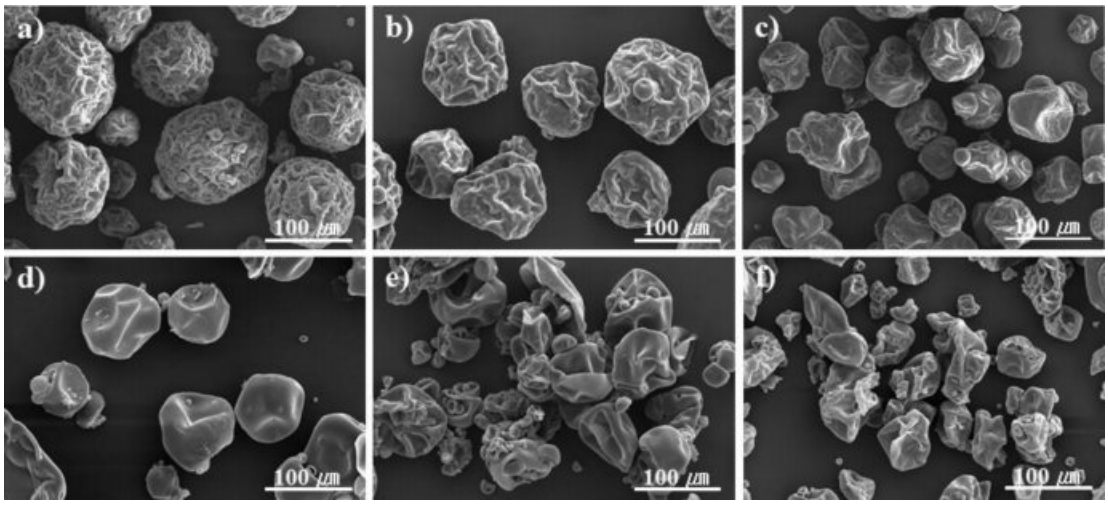

Figure 9. SEM microphotographs of expandable microcapsules prepared at different AN/MAN ratios: (a) 80:20; (b) 70:30; (c) 60:40; (d) 50:50; (e) 40:60; (f) 30:70 w/w.

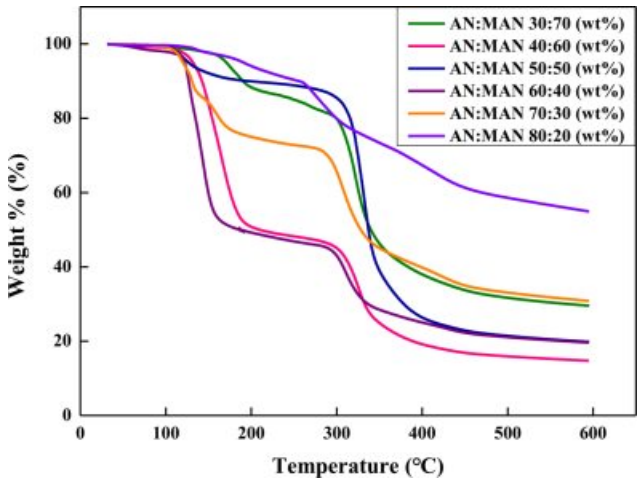

Figure 10. TGA thermograms of expandable microcapsules prepared at different AN/MAN ratios.

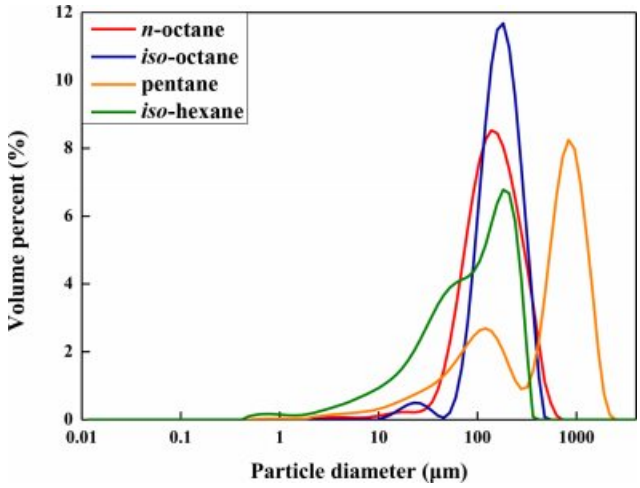

Figure 11. Particle size analysis of the expandable microcapsules prepared at different type of blowing agent.

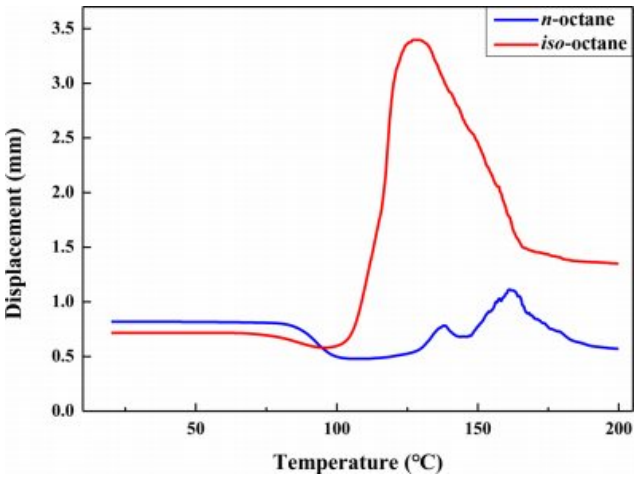

Figure 12. TMA thermograms of the expandable microcapsules prepared with different type of blowing agent.

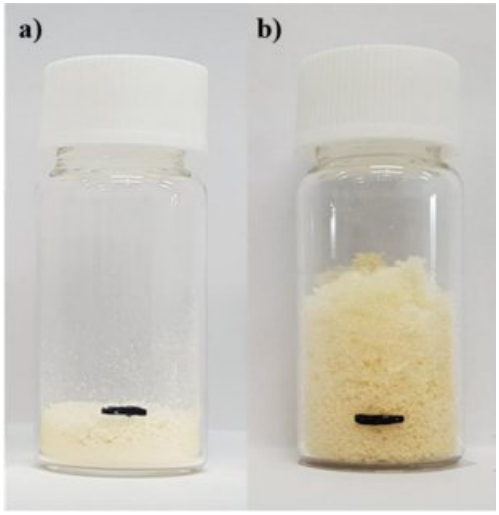

Figure 13. Digital photographs of (a) unexpanded microcapsules; (b) expanded microcapsules (Table 1, sample 24) at 130 °C.

blowing agents. The blowing agents used are *n*-octane, *iso*-octane, *n*-pentane, and *iso*-hexane, respectively. Figure 11 shows the particle size distribution according to the type of blowing agent. When using *n*-pentane and *iso*-hexane, the capsules with unimodal size distribution were not formed. Microcapsules with unimodal particle distribution were prepared using *iso*-octane and *n*-octane. The average particle size of the microcapsules with *n*-octane and *iso*-octane was about 125 and 156 μm, respectively. It is thought that the different solubilities of core hydrocarbons into water and monomer phases would cause the difference in particle size distribution. Figure 12 shows the maximum expansion temperature (T_{max}) of the microcapsules and the size after heating using *iso*-octane and *n*-octane. As shown in Figure 12, the expansion performance of microcapsules using *iso*-octane was the best. Figure 13 visually shows the expansion of the microcapsules before and after expansion at 130 °C in which the microcapsules were prepared using 2 : 1 (β-CD : PVP) ratio and total dispersant content of 3.5 wt% (Table 1, sample 24). The microcapsules have the best expansion performance and the volume of the microcapsule after expansion is about 4 times greater than that before expansion.

Conclusions

In this study, we have succeeded in manufacturing thermally

expandable microcapsules of core-shell structure using Pickering suspension polymerization. β-CD was used as Pickering emulsifier and PVP was used as an auxiliary dispersant. Since the use of β-CD in the preparation of thermally expandable microcapsules has not been reported to date, various experimental parameters were investigated for the formation of microcapsules, including β-CD : PVP ratio, stabilizer concentration, AN : MAN ratio, and types of blowing agents. As the content of β-CD increased, the particle size decreased. At 2 : 1 (CD: PVP) ratio, the encapsulation was the most successful. When the total dispersant content was 3.5 wt%, the microcapsules showed the best expansion performance. The shape of the particles formed uniformly when the ratio of AN/MAN was 70/30 w/w. The microcapsules were most suitably formed when 35 wt% of the blowing agent was added. The expansion performance also varied depending on the type of blowing agent. Among the various blowing agents, *iso*-octane and *n*-octane showed the excellent expansion properties.

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