Ethoxylated Trimethylolpropane Triacrylate를 가교제로 사용한 열팽창 캡슐 제조

임미정 · 소재일 · 정지영 · 심상은†

인하대학교 화학 및 화학공학 융합대학원

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Synthesis of Thermally Expandable Microspheres Using Ethoxylated Trimethylolpropane Triacrylates as Crosslinking Agents

MiJung Rheem, Jae Il So, Ji Young Jung, and Sang Eun Shim†

Department of Chemistry & Chemical Engineering, Inha University, Incheon 22212, Korea

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초록: 분자량이 다른 세가지의 ethoxylated trimethylolpropane triacrylate를 가교제로 사용한 현탁 중합을 통하여 열팽창 캡슐을 제조하였다. 고분자 쉘은 아크릴로나이트릴과 메타크릴로나이트릴로 구성되었으며 발포제인 아이소옥탄을 캡슐화하였다. 쉘의 가교정도가 증가함에 따라 국부의 가교밀도 차이에 의하여 캡슐의 형태는 구형에서 울퉁불퉁하게 변화하였다. 팽창 특성은 가교제의 종류와 함량에 의해 영향을 받았다. 캡슐의 입경은 가교제의 양이 증가함에 따라 증가하였다. 최적의 가교도를 지닌 ethoxylated (6) trimethylolpropane triacrylate를 사용한 캡슐의 열팽창 특성이 가장 우수하였다.

Abstract: Thermally expandable microspheres are synthesized by suspension polymerization using three ethoxylated trimethylolpropane triacrylates with different molecular weights as crosslinking agents. The polymeric shell is made of acrylonitrile and methacrylonitrile and iso-octane is encapsulated as blowing agent. As the crosslinking of shell increases, the shape of the microspheres changes from spherical to bumpy due to different local crosslinking density. The expansion behavior was influenced by types and amounts of crosslinking agents. Average size and thermal stability of expandable microspheres are increased by increasing the amount of crosslinking agent. The microspheres prepared with ethoxylated (6) trimethylolpropane triacrylate to achieve optimum crosslinking results in an excellent expansion performance.

Keywords: thermally expandable microspheres, suspension polymerization, trimethylolpropane triacrylate, crosslinking agent.

Introduction

Thermally expandable microspheres (TEMs) represent the core-shell polymeric capsules which have an expansion characteristic upon heating.[1] Since the manufacturing method of thermally expandable microspheres was originally developed by Dow Chemical Co., in the early 1970's, the preparation method, composition of the polymer shell, and applications of the microspheres have been widely investigated.[1-3] Thermally expandable microspheres are applied to variety of fields to achieve many industrial purposes such as weight reduction,

bulk increase, and printing ink to improve the surface properties. Specifically, in the automotive industry, they are used to reduce noise and weight by underbody coatings and to improve corrosion resistance to protect metal materials.[4,5]

The thermally expandable core-shell polymeric particles encapsulate volatile liquid hydrocarbons as blowing agents. The thermoplastic shell of expandable microspheres is polymerized using polyethylene, polyamide, and poly(vinyl chloride), etc. and crosslinking agent can be added to improve expansion properties. The synthesized microspheres typically have the diameter of 5-50 μm and the shell thickness of 3-7 μm.[6] The thermoplastic polymer shell is softened at around the glass transition temperature during heating, subsequently the liquid hydrocarbon that was contained inside the capsules is vaporized and erupted by internal pressure. Accordingly, the

thermally treated microspheres expand to 50-100 times larger volume like microballoons and their density is decreased from 1100 to 30 kg/m.[3,7,8] In order to achieve excellent expandable microspheres, the conditions that the balancing of the melt viscosity between the shell polymer and the softening point, the choice of a gas-proof polymeric shell composition, and the boiling point and the molecular structure of the hydrocarbon as a blowing agent should be carefully considered.[9,10] During heating, intensity, durability, and ductility of the polymeric shell are also important factors in mechanical and chemical properties. Suspension polymerization method has been widely selected as the manufacturing technique of expandable microspheres, in which the monomer as a dispersion phase is suspended into water as a continuous phase containing stabilizing agent and monomer-soluble initiator by stirring.[11,12] Polymerization takes place within the monomer droplets and the polymer sediment is separated from the monomer droplets because of the lack of solubility, and finally polymers in shape of microspheres are obtained with high conversion.[13,14]

It has been known that the degree of crosslinking in heterogenous polymerization causes changes in morphology of the resulting particles. For the synthesis of TEMs with good performances, a proper choice of crosslinking agents and degree of crosslinking causes the stability of shell upon heating, onset of the expansion, and morphology of the particles. However, only a few publications reports the importance of crosslinking.[1,2,15] In this study, in order to produce stable microspheres and improve expansion property of polymeric shell, a series of ethoxylated trimethylolpropane triacrylates (TMPTAs) having tri-vinyl groups and different lengths of ethoxy groups was employed. In conclusion, TMPTAs significantly contributed to enhance the formation of stable microspheres and improved thermal expansion property.

Experimental

Materials. Acrylonitrile (AN; 99+%, stabilized with 35-45 ppm hydroquinone monomethyl ether, Aldrich) and methacrylonitrile (MAN; stabilized with MEHQ, TCI, Japan) were purchased as monomers. Polyvinylpyrrolidone (PVP; K-30) as a stabilizer and azobisisobutyronitrile (AIBN) as an initiator were purchased from Junsei Chemical. Isooctane used as a blowing agent was purchased from Samchun Chemicals (Korea). Sodium chloride (NaCl) was obtained by Duksan Chemicals (Korea) and sodium nitrite ($NaNO_2$) was supplied by Daejung Chemical (Korea). Ethoxylated (3) trimethylol-

propane triacrylate (SR 454 NS), ethoxylated (6) trimethylolpropane triacrylate (SR 499 NS), and ethoxylated (9) trimethylolpropane triacrylate (SR 502 NS) as crosslinking agents were purchased from Sartomer.

Polymerization of Thermally Expandable Microspheres. A continuous phase was prepared using 5.0 g PVP as a stabilizer in 100 mL distilled water by adding 0.5 g NaCl and 0.5 g $NaNO_2$ by vigorous stirring. The dispersion phase was prepared with 19.4 g AN and 8.4 of MAN as a monomers, which was followed by the addition of 10 g iso-octane. The dispersion phase mixture was put into the continuous phase mixture and homogenized with IKA Ultra Turrax T25 Basic Instruments at 9500 rpm for 2 min. Polymerization was carried out in a high pressure reactor which was made of stainless steel and equipped with an agitation. The pressure was regulated to 3 bars and the reaction was carried out for 8 h at 60 °C. After polymerization reaction was competed, the resulted particles were rinsed and filtered by distilled water, and then dried in an oven at 60 °C for 24 h.

Characterization. The morphology of particles sputter-coated with platinum was observed by scanning electron microscopy (SEM, Hitachi, S-4300). The particle size and size distribution were investigated using a laser scattering particle size analyzer (LS230®, Beckman Coulter, USA). To investigate the first weight loss temperature (T_{start}) and thermal stability of polymeric shell, thermogravimetric analysis (TGA, TA Q50, TA instruments, USA) was carried out. The samples were heated with 10 °C/min from 40 to 500 °C under a nitrogen atmosphere. The maximum expansion temperature (T_{max}) and the displacement of microspheres volume were analyzed by thermomechanical analysis (TMA, TMA 800 system, Instrument Specialists Inc., USA) during elevated temperature from 25 to 250 °C with 10 °C/min under nitrogen.

Results and Discussion

Three types of TMPTAs as crosslinking agents having triacrylate functional groups with different lengths of ethoxylated space unit are used for polymerization. Table 1 shows the structures of crosslinking agents which have different molecular size from ethoxylated (3) trimethylolpropane triacrylate (SR 454) with the shortest chain length to ethoxylated (9) trimethylolpropane triacrylate (SR 502) of the longest chain length. Although the reactivity of triacrylate functional groups would be identical, the ethoxylated space unit is expected to influence the polymerization characteristics. Table 2 sum-

Table 1. Structure of Ethoxylated Trimethylolpropane Triacrylate Crosslinking Agents

Crosslinking agent	Structure
SR 454 NS (Ethoxylated (3) trimethylolpropane triacrylate)	
SR 499 NS (Ethoxylated (6) trimethylolpropane triacrylate)	
SR 502 NS (Ethoxylated (9) trimethylolpropane triacrylate)	
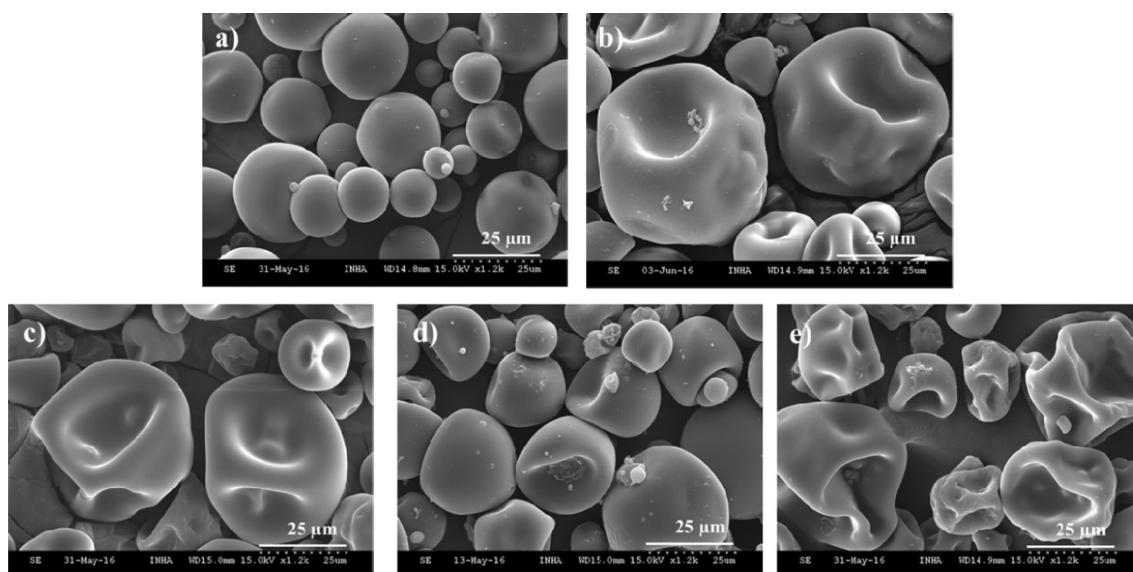
Figure 1. SEM images of microspheres prepared with different amount of SR 454: (a) 0.02; (b) 0.04; (c) 0.06; (d) 0.08; (e) 0.1 g.

marizes the formulation of the polymerization and the properties of the TEMs prepared with three TMPTAs. After the polymerization is completed, it has been confirmed that both the type and concentration of crosslinking agents clearly affect the size, morphology, and expansion properties of the resulting microspheres. Crosslinking agents are used to enhance the strength of synthesized polymeric shell to have the improved performance in thermal expansion of the capsules. Figure 1 shows that the microspheres are formed successfully by using

SR 454 crosslinking agent. Ma *et al*. reported that the monomer having the low solubility in water, such as AN, would diffuse into the continuous phase, and follows forming the secondary nucleation on the droplet surface during the polymerization.[16] All the morphologies of microspheres from Figure 1 have smooth surface without secondary particles due to absence of secondary nucleation by introducing inhibitors such as hydroquinone (HQ). The SR 454 crosslinking agent with 0.02 wt% yields undistorted microspheres while the crumpled

and bumpy shaped microspheres are produced when over 0.04 wt% of crosslinking agent was used. And the degree of distortion of the shape increases with the amount of added crosslinking agent. Our previous paper reported that the synthesized particle morphologies with partially spherical and potato-like shapes were formed at higher reaction pressure with 3 bar. Also, as the amount of crosslinker increases, the degree of crosslinking may become different at molecular scale microstructure. This polymeric shell having different crosslinking degree of microcapsules containing blowing agent can be distorted by the external pressure in the reactor.[17] The robust shell can encapsulate the greater amount of the liquid blowing agent inside which tends to vaporize during polymerization. Therefore, the average diameters of microcapsules are affected by the concentration of a crosslinking agent. As a result, the particles sizes were increased with increasing the amount of crosslinking agent by having size variations from 50.4 μm (0.02 g SR 454) to 75.85 μm (0.1 g SR 454). Kawaguchi *et al*. indicated that the expansion property only depends on the crosslinking density in the polymer shell and the chemical structure and concentration of crosslinking agent give similar expansion performances at optimum condition.[10] Therefore, the concentration of crosslinking agent not only affects the size of microspheres but also improves the expansion characteristic of the particles. It is noted that the increasing crosslinking
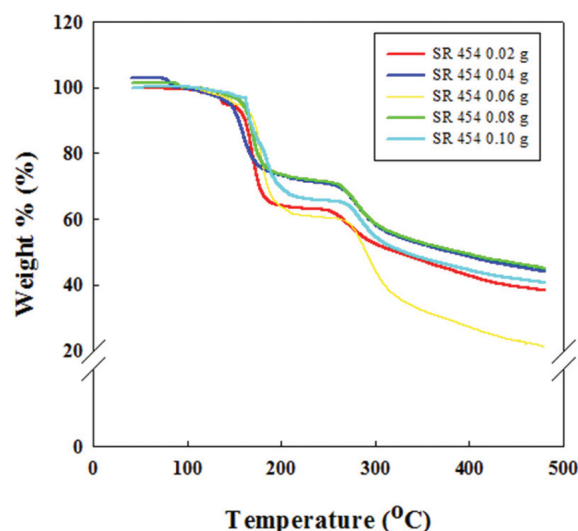

Figure 2. TGA thermograms of the expandable microcapsules prepared with different amounts of SR 454.

agent also improved the first decomposition temperature (T_{start}) as an index of expansion properties as shown in Table 2.

Figure 2 indicates the TGA thermograms of the microspheres synthesized with different amounts of SR 454 crosslinking agent where two-step decompositions are witnessed. The first stage of weight loss originates from the vaporization of hydrocarbon blowing agents and the second stage is

Table 2. Various Uses of Crosslinking Agents *versus* Particle Size and T_{max}

Run	Crosslinking agent			Result	
	SR 454 (g)	SR 499 (g)	SR 502 (g)	Particle size (μm)	First decomposition temperature (°C)
1	0.02	0	0	50.40	141.67
2	0.04	0	0	56.72	147.90
3	0.06	0	0	57.41	160.48
4	0.08	0	0	67.51	161.93
5	0.1	0	0	75.85	163.14
6	0	0.02	0	46.44	140.30
7	0	0.04	0	52.16	147.68
8	0	0.06	0	52.91	155.48
9	0	0.08	0	62.63	159.52
10	0	0.1	0	64.87	163.05
11	0	0	0.02	45.69	135.94
12	0	0	0.04	47.94	145.46
13	0	0	0.06	49.47	152.40
14	0	0	0.08	50.55	155.50
15	0	0	0.1	62.19	162.04

attributed to the thermal decomposition of the polymeric shell. When the microcapsules are heated above the boiling point of iso-octane with 99.3 °C, the polymeric shell starts to expand and finally burst because the polymeric shell could not endure the pressure by vaporization of the hydrocarbon.[17] Increase in crosslinking concentrations leads to increase of the first stage decomposition temperatures, namely vaporization of iso-octane. In fact, the decomposition temperatures of microspheres change from 141.67 to 163.14 °C when the amount of SR 454 crosslinking agent increases from 0.02 to 0.1 g, respectively. Hou *et al.* reported that the weight loss at the first decomposition temperature reached about 7%, and at that temperature the microspheres started to burst.[18] However, in this study, the weight loss at first decomposition temperature, which started from the removal of unreacted monomers and residual water in the microspheres, was confirmed to be about 5%. The second stage decomposition temperatures range from 220 to 230 °C, where there is no significant difference despite of increasing amount of crosslinking agent since the polymeric shell is the copolymer having the same composition with the same monomers.[19] Therefore, the microspheres with higher degree of crosslinking show good thermal properties due to their ability to withstand the vaporization pressure of the blowing agent.[2,20,21]

Figure 3 shows the morphology of microspheres prepared with different amounts of ethoxylated (6) trimethylolpropane triacrylate (SR 499) crosslinking agents from 0.02 to 0.1 g. The resulted average particle size increases from 46.44 m to 64.87 μm. The particle size is also increased with increase of crosslinking agent similar to the previous case of SR 454. This tendency to increase particle size can also be similarly confirmed in the particles prepared using SR 502 crosslinking agent. However, when using different types of crosslinking agent, it can be confirmed that overall the average particle sizes decrease with increase of molecular size of crosslinking agent in order of SR 454, SR 499, and SR 502 as shown in Table 2. From Figure 3, as the amount of SR 499 is increased, the degree of distortion of the microspheres becomes greater having more wrinkles on the shell. These distorted wrinkles enhance the expansion performance. When the blowing agent vaporizes, the internal pressure within the microspheres suddenly increases and collapsed section starts to expand first and the wrinkles support the shell upon the further expansion. As a result, the expandability of microspheres is improved by the higher degree of crosslinking.

Figure 4 shows the particle size distribution of expandable microspheres prepared at different amounts of SR 499. The average size of particles was investigated to understand the relationship between the particle size distribution and amount of crosslinking agent. It was found that the particle distribution became narrower at a higher amount of crosslinking agent. Coats *et al.* reported that the residual stress affects to the particles size distribution. After polymerization reaction, the synthesized particles are generally cooled down and shrinkage takes place during the process of washing and drying of microspheres due to the residual stress. The microspheres prepared
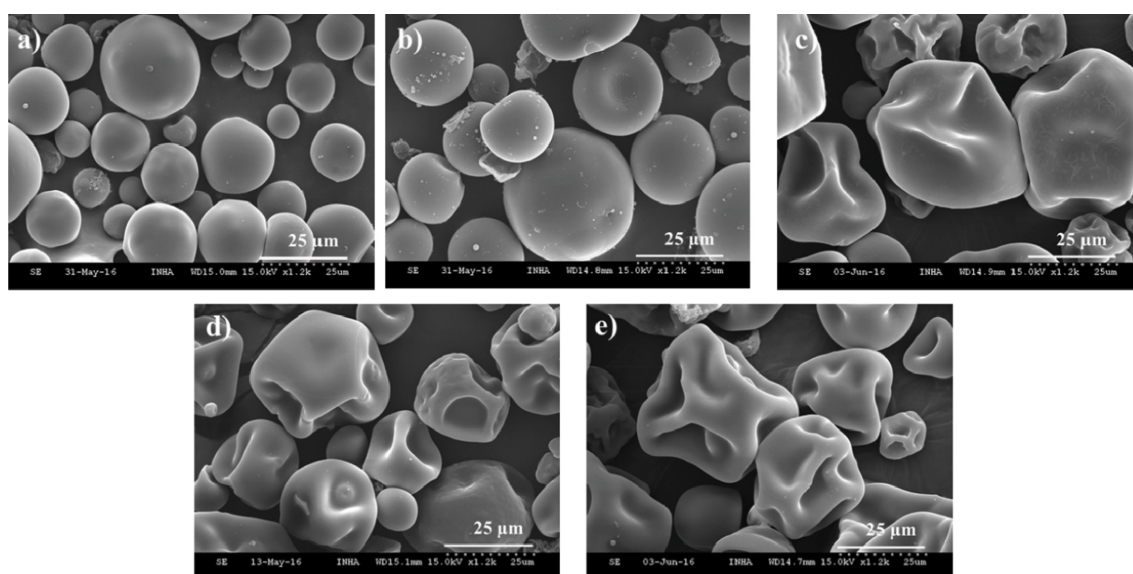

Figure 3. SEM images of microspheres prepared with various amounts of SR 499: (a) 0.02; (b) 0.04; (c) 0.06; (d) 0.08; (e) 0.10 g.
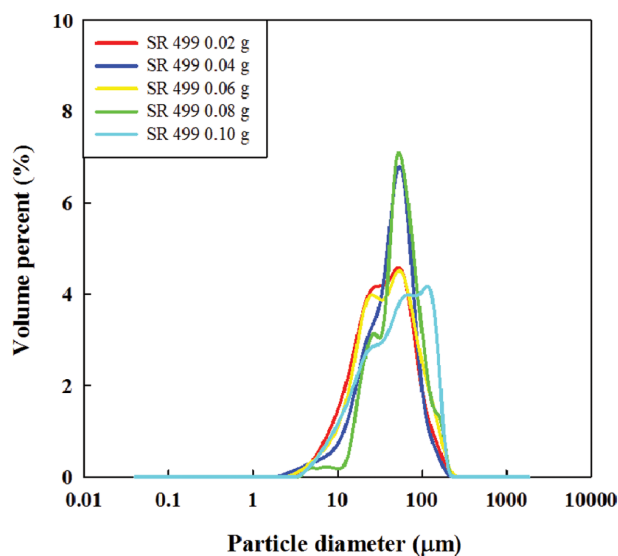
Figure 4. Particle size distribution of expandable microcapsules prepared with different amounts of SR 499.
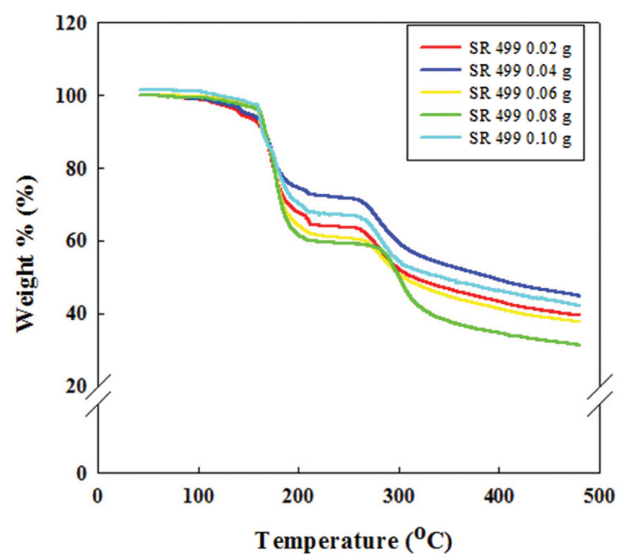

Figure 5. TGA thermograms of the expandable microcapsules prepared with different amounts of SR 499.

with the more amount of crosslinking agent can reduce shrinkage since there exist many crosslinking points which prevent from the shrinkage of shell.[22] Figure 5 shows the thermal degradation of the microspheres prepared at different amount of SR 499. Similar to Figure 2, the first decomposition stage temperatures of the microspheres prepared is elevated with increase of crosslinking agent SR 499 according to run 6-10 as shown in Table 2. The second step decomposition temperatures of the prepared microspheres with SR 499 elevate stepwise from 140.3 to the highest 163.05 °C with increasing

crosslinking agent.

The synthesized microspheres using SR 502 crosslinking agent are shown in Figure 6, which also have the smooth surface of polymeric shell without secondary particles. Well-defined microspheres were obtained below 0.04 g crosslinking agent and the distorted particles were resulted when using over 0.06 g. The lesser degree of distortion of the shape of the microspheres takes place here compared to previous SR 454 and SR 499.

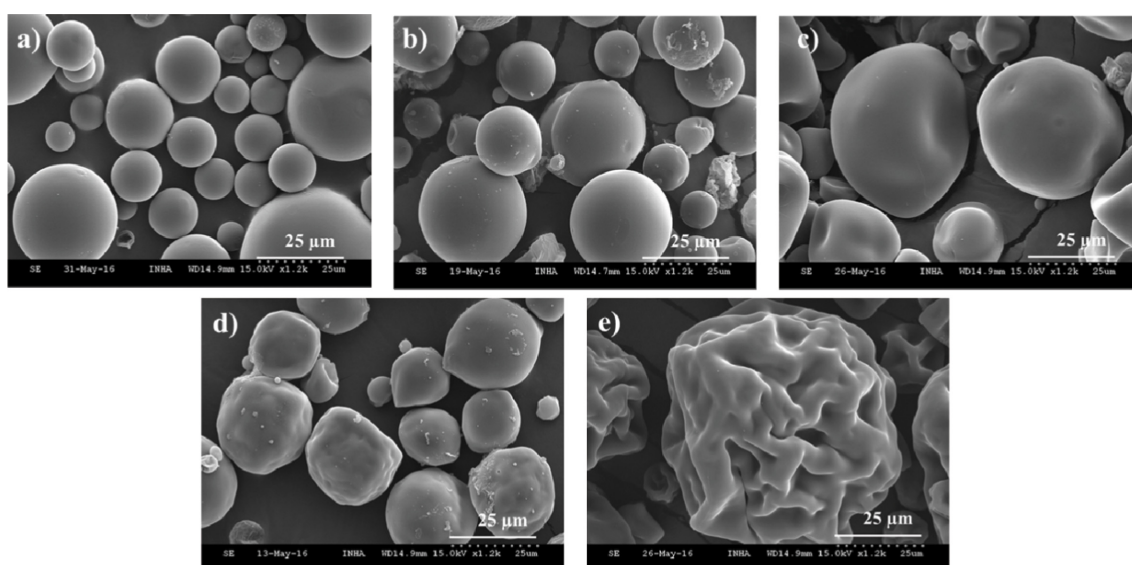Again, the larger sized microspheres are formed with

Figure 6. SEM images of microspheres prepared with various amounts of SR 502: (a) 0.02; (b) 0.04; (c) 0.06; (d) 0.08; (e) 0.10 g.

increase of crosslinking agent amount as like in Figure 6. Average size of microspheres with 0.1 g SR 502 shows the largest with 62.19 μm whereas the smallest diameter is 45.69 μm with 0.02 g SR 502. As mentioned before, when using different types of crosslinking agent, the average particle sizes decrease with increase of molecular size of crosslinking agent in order of SR 454, SR 499, and SR 502. In Table 2, SR 502 crosslinking agent gave the result that particles size decreased with increase of its molecular size due to decrease of crosslinking density when using the same amount of crosslinking agent. Since the chain length of SR 502 is the longest among them, the crosslinking density is lowest, which can make higher the residual stress. Further, the particle size with using SR 502 was smaller than using SR 454 and SR 499.

Figure 7 indicates the thermal stability of the expandable microspheres by TGA analysis. As in Figure 2, the first weight loss temperature of the microspheres elevate with increase of crosslinking agent amount according to Run 11-15 in Table 2. Actually, the microspheres with 0.02 g SR 502 decompose at 135.94 °C while the particles with 0.1 g as a maximum amount of SR 502 decompose at 162.04 °C. In addition, the overall TGA results show that the first decomposition temperatures of microspheres were affected by the type of crosslinking agents for the same amount. Actually, the microspheres with SR 454 have the higher first decomposition temperature compared with SR 499 and SR 502 at same amount. Thus, increase in the crosslinking agent molecular size leads to the decrease in

decomposition temperatures of the microspheres. This phenomenon might be supported from the reason similar to the tendency of increase of the particle size. The larger molecular size of crosslinking agent with longer chain length induces the lower crosslinking density compared to the crosslinking agents with shorter length at the same amount.

In Figure 8, the TMA thermograms show the expansion properties of microspheres with different concentrations of SR 499 crosslinking agents, which show the specific characteristic for thermally expandable microspheres as the expansion performance. While the microspheres are heated, the polymeric shells should endure the pressure of vaporized hydrocarbon. The gasified hydrocarbon molecules interpenetrate the shell due to the inherent gas permeability of the polymer. So the control over the degree of crosslinking and the careful choice of monomer are always important for the TEMs to have a good gas barrier property.[1,2] If the amount of crosslinking agent is low, the ability to maintain good expansion performance is insufficient to overcome the pressure of gasified hydrocarbon. On the other hand, the too high amount of crosslinking agent is also not desired for expansion performance since exorbitant crosslinking may suppress the expansion of TEMs. Thus, the optimum amount of crosslinking agent is required to have good expansion performance. In Figure 8, the expansion properties of microspheres was dramatically improved using 0.08 g SR 499, which presented the maximum displacement about 3.0 mm. Accordingly, Figure 9 compares the expansion fea-
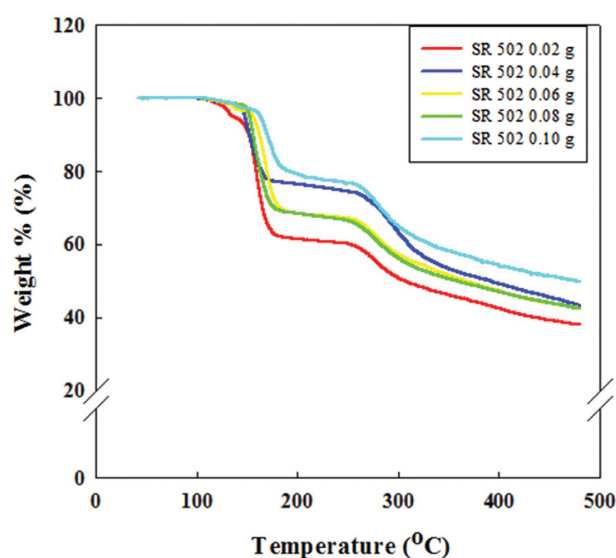

Figure 7. TGA thermograms of the expandable microcapsules prepared with different amounts of SR 502.
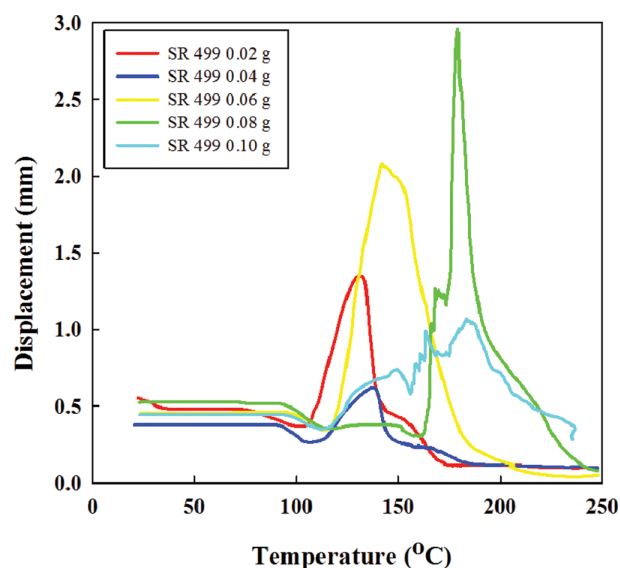

Figure 8. TMA analysis of the expandable microcapsules prepared with different amounts of SR 499.
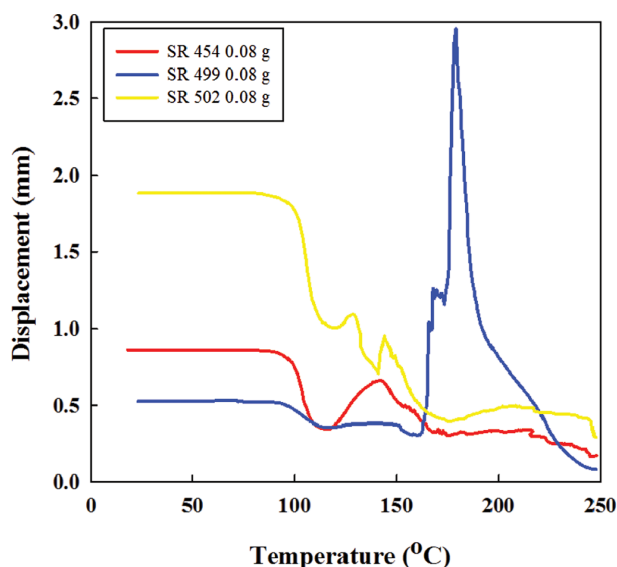
Figure 9. TMA analysis of the expandable microcapsules prepared using different types of crosslinking agents with 0.08 g.
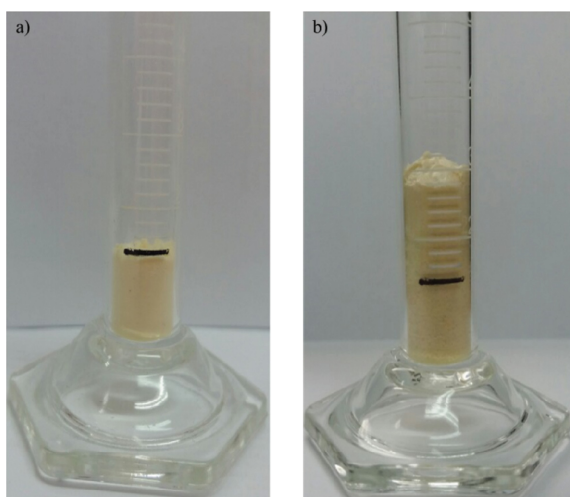

Figure 10. Digital photographs of (a) unexpanded microcapsules; (b) expanded microcapsules with 0.08 g SR 499 by heating at 180 °C.

tures of microspheres prepared with SR 454, 499, and 502 at the same amount. The best expansion performance could be observed with threefold increase in volume at 159.52 °C when the SR 499 was used. The use of crosslinking agent with relatively large molecular size such as SR 502 induces a lower crosslinking density to withstand the vaporization of blowing agent, while the relatively small molecular size such as SR 454 disturbs expansion of microspheres having too high crosslinking density. Finally, Figure 10 displays the digital photographs of TEMs prepared with 0.08 g SR 499 before and

after expansion at 180 °C to confirm the thermal expansion performance. The microspheres containing 0.08 g SR 499 begin to expand at T_{start} and continue to increase in volume to T_{max}, finally expanded particles have the volume over twofold than the original volume.

Conclusions

In this study, thermally expandable microspheres were synthesized by suspension polymerization using a series of ethoxylated trimethylolpropane triacrylates having crosslinkable trivinyl groups and different lengths of ethoxy spacer groups as crosslinking agents. The prepared expandable microspheres sufficiently expanded at high temperature by improving of crosslinking density of polymeric shell. The resulting particles were not perfectly spherical but crumpled and bumpy-shaped. The average particle size increased with increasing amount of crosslinking agent and decreased with increasing molecular size of crosslinking agent. The first decomposition temperature representing the thermal stability was improved with increasing amount and decreasing molecular size of crosslinking agent. The optimum crosslinking density was obtained using 0.08 g SR 499, which achieved excellent expansion performance by reaching a maximum displacement of 3.0 mm through TMA analysis.

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