

Fabrication of thermally expandable core-shell microcapsules using organic and inorganic stabilizers and their application

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ABSTRACT: Thermally expandable core-shell microcapsules (TEM) were fabricated with an organic steric stabilizer and an inorganic Pickering emulsifier. In order to fabricate a TEM, acrylonitrile (AN) and metacrylonitrile (MAN) were used as monomers. Halloysite nanotubes (HNTs) and poly(vinylpyrrolidone) (PVP) were used as the inorganic Pickering emulsifier and the organic stabilizer, respectively. The liquid hydrocarbon content in the core, and the thermal and expansion properties, of TEMs with two different emulsifiers were compared. The mechanical properties of polypropylene (PP) foams containing TEMs prepared with two types of stabilizers were analyzed. The TEMs polymerized with PVP showed a finer expanded cell, while those fabricated with HNTs resulted in a larger expanded cell in the PP matrix. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44247.

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INTRODUCTION

Thermally expandable microcapsules (TEMs) normally have a core/shell structure; the liquid hydrocarbon in the core is encapsulated by a thermoplastic shell.¹ Upon exposure to high temperatures, above the boiling temperature of the liquid hydrocarbon and glass transition temperature (T_g) of the polymeric shell, TEMs expand and increase in volume. Their expanding behaviors are correlation of soften thermoplastic shell above T_g of polymeric shell and increased internal pressure at the core due to encapsulated hydrocarbon gasification.^{1,2} Commercial TEMs are around 15–40 μm in size and can expand up to 150–180 μm upon heating. Because of this property, TEMs can be used as foaming (blowing) agents in the industry.² Expansion behavior of TEMs can be modified by varying the liquid hydrocarbon in the core or the polymeric shell. Monomers such as acrylonitrile (AN) and vinylidene chloride are well-known components of the shell because of their excellent barrier properties.^{3,4} However, the insufficient thermoplasticity of these monomers necessitates the use of alternatives such as methyl methacrylate (MMA), methyl acrylate (MA), and metacrylonitrile (MAN) for the fabrication of thermally expandable capsules.⁵ The barrier properties of a TEM are its key feature as they determine the expansion capacity of a TEM. For example,

if the shell of the TEM is too thin, the encapsulated liquid hydrocarbon cannot be retained by the shell upon heating. On the other hand, a thick shell may not allow the capsule to expand when heated. Shell permeability also affects the expansion of TEMs. The expansion behavior of TEMs can be also controlled by varying the reaction temperature and ratio of monomers in the TEM shell, as well as by the use of blowing agents, crosslinkers, and stabilizers. Since the development of TEMs by Dow Chemical in the early 1970s, considerable research has been pursued in this regard.⁶

Jonsson *et al.* studied influence of the crosslinking density of a TEM. Several functional crosslinkers such as dimethacrylate, diacrylate, and divinylether were used at various concentrations.⁷ Desirable expansion of TEMs was obtained when the polymer shell was crosslinked with 0.05–0.1 mol % 1,4-butanediol dimethacrylate (BDDMA), as opposed to the case where no crosslinker was used. Although most particles having up to 0.2 mol % crosslinker showed similar extents of expansion, the expansion behavior of the capsule differed with the amount and type of crosslinker.

The effects of incorporating various additional monomers into TEMs containing AN and MAN were investigated, in order to study the correlation between the chemical structure and

Table I. List of Abbreviations for Core–Shell Microcapsules

Abbreviation	Continuous phase					Dispersion phase				
	Water (mL)	PVP (g)	HNT (g)	NaCl (g)	NaNO ₂ (g)	AN (g)	MAN (g)	AIBN (g)	n-Octane (g)	BDDMA (g)
TP-2.5	1000	2.5		5	5	194	84	2	100	0.6
TP-5.0		5.0								
TP-7.5		7.5								
TH-2.5			2.5							
TH-5.0			5.0							
TH-7.5			7.5							

expansion properties of the TEMs.⁸ The addition of an acidic monomer into an AN-MAN system resulted in the formation of a heat-resistant microcapsule. Addition of a non-nitrile monomer, methyl methacrylate (MMA), increased the onset temperature of the TEM from 122 °C to 135 °C. EMA also increased the onset temperature of the TEM up to 134 °C.

The influence of the monomer feed ratio and reaction temperature on the TEM was also investigated.¹ A core/shell structure of TEM was obtained for $f(\text{AN})$ (fraction of acrylonitrile in the initial monomer feed) = 0.15–0.90, when the reaction temperature was 62 °C. At 80 °C, the core shell structure of the TEM was polymerized for $f(\text{AN}) = 0.5–0.85$.

Kawaguchi and Oishi studied the expansion properties of TEMs with respect to different concentrations of dipentaerythritol hexaacrylate and showed that the degree of crosslinking plays a crucial role in TEM expansion.⁹ For example, insufficient crosslinking would cause a TEM to collapse and rupture. On the other hand, excessive crosslinking interferes with the TEM expansion. According to their results, a swelling ratio of about 20–25 is needed to achieve optimum expansion without collapse and rupture of the TEM.

Typically, microcapsules are fabricated by emulsion or suspension polymerization. Water-soluble polymers such as poly(vinylalcohol) (PVA), or poly(vinylpyrrolidone) (PVP), are well-known steric stabilizers that stabilize the spherical structure of TEMs, during the initial stage of the polymerizations.^{10,11}

Inorganic particles such as flocculated silica or magnesium hydroxide are often used as surfactants and are commonly used in the polymerization of TEMs.^{12,13} These compounds stabilize the capsules to form the so-called Pickering emulsions, by adsorbing to the capsule interface. Therefore, these particles can prevent coalescence of organic droplets.

Zou *et al.* studied surfactant-free emulsions stabilized by inorganic nanoparticles.¹⁴ Different inorganic particles were used as the surfactant for preparing water/oil/water and oil/water/oil multiple emulsions. The results showed that destabilization due to surfactant diffusion was eliminated and can be applicable for long-term stable multiple emulsions.

In order to utilize TEM for foaming injection molding process, initial particle size, size distribution, and onset expanding temperature of TEM are very important factors since foaming efficiency is strongly depending on these properties.

In this article, we compared the expansion properties of TEMs with an organic steric stabilizer (PVP) and an inorganic particle (halloysite) to figure out the possibility of halloysite as a new steric stabilizer for TEM. The prepared TEMs with two different type of stabilizer were tested for use as blowing agents during injection molding, in order to determine the difference between the final products. It is noted that halloysite nanotubes have not been used as steric stabilizers for TEMs.¹⁵

EXPERIMENTAL

Materials

Acrylonitrile (AN, >99.0%, stabilized with 35–50 ppm hydroquinone monomethyl ether, Daejung, CAS 107-13-1) and methacrylonitrile (MAN, >99.0%, stabilized with MEHQ, TCI, CAS 126-98-7) were used as monomers. Halloysite nanotubes [HNTs: 1:1 aluminosilicate clay material with empirical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Aldrich] and PVP (Samchun, CAS 9003-39-8) were used as the inorganic Pickering emulsifier and organic steric stabilizer, respectively. 1,4-Butanediol dimethacrylate (BDDMA, 95%, stabilized with 100 ppm hydroquinone monomethyl ether, Aldrich CAS 2082-81-7) was used as the crosslinker, and *n*-octane was used as the blowing agent (Aldrich CAS 111-65-9). 2,2-Azo-bis-isobutyronitrile (AIBN) was purchased from Samchun (CAS 78-67-1) and used as the thermal initiator. Sodium nitrite (NaNO_2 CAS 7632-00-0) and sodium chloride (NaCl CAS 7647-14-5) were purchased from Daejung Chemical and Duksan Chemicals, respectively. All chemicals were used as received.

Preparation of Thermally Expandable Microcapsules

For polymerization with the inorganic Pickering emulsifier, an aqueous dispersion of HNTs was prepared by adding the designated amount of HNTs (shown in Table I) to distilled water (1000 mL). NaNO_2 (5 g) and NaCl (5 g) were then added to the mixture. An oil-phase mixture was prepared separately using AN (194 g) and MAN (84 g) as monomers, *n*-octane (100 g) as the blowing agent, AIBN (2 g) as the initiator, and BDDMA (0.6 g). The oil-phase mixture was added into the aqueous phase and homogenized using WiseTis[®] HG-15D at 10,000 rpm for 5 min. In the case of polymerization with the organic steric stabilizer, an aqueous dispersion was prepared with the designated amounts of PVP and NaNO_2 (5 g) and NaCl (5g) in distilled water (1000 mL). The polymerization method for the oil phase mixture was the same as the method used for the

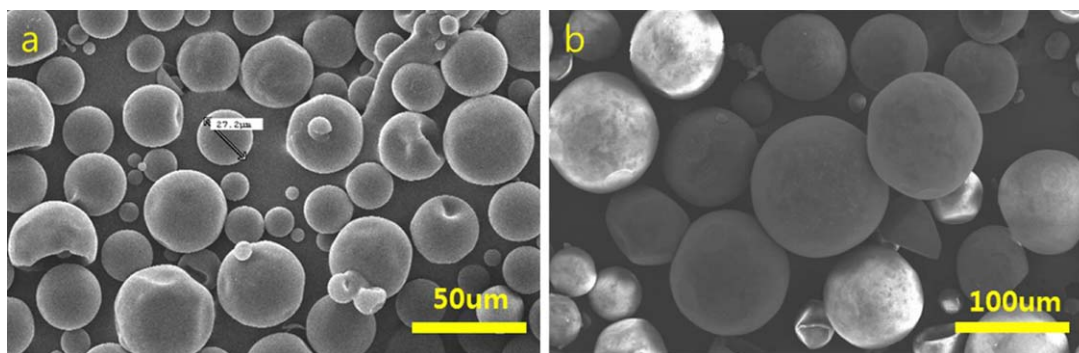


Figure 1. SEM images of (a) TP-0.3 and (b) TH-0.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

inorganic stabilizer. Abbreviations for all polymerizations are listed in Table I.

A 5 L stainless steel reactor was equipped with an agitator and charged with the prepared aqueous- and oil-phase solutions. During polymerization, nitrogen was purged until the pressure of the reactor reached 3 bar. The mixture was polymerized at 60 °C and 1500 rpm for 8 h. After polymerization, the particles were washed with water several times, and the suspending agent was removed from the particles by stirring with acetic acid. Finally, the resultant was filtered and dried at ambient temperature for 48 h.

The dried TEMs (3 wt %) were injection-molded with polypropylene (Lotte Chemical HFJ-371) in order to prepare the test specimens. Core back injection molding conditions (Ube injection molding machine 180 ton) for test specimens were prepared at 190 °C. The mold temperature was set to 50 °C. The cooling time and core back distance were 30 s and 2.0 mm, respectively.

Characterization

The particle morphology was observed by optical microscopy (OM, Metallurgical Microscope, MIC S39A) and scanning electron microscopy (SEM, Hitachi, S-4300). The particle size and size distribution were analyzed by a laser scattering particle size analyzer (Mastersizer 2000, Malvern). The amount of the blowing agent in the TEM was measured by thermogravimetric analysis (TGA 7, Perkin Elmer). TEMs produced with the organic

and inorganic stabilizers were placed in an oven at 180 °C for 10 min, and the degrees of expansion were compared by observations with the naked eye. Thermomechanical analysis (TMA, Scinco M&T, TMA 800) was used to determine the onset temperatures and to measure expansion of the TEMs. The injection-molded test specimens were aged for 1 day and analyzed by universal test machine (UTM, MTDI UT-100F) and Izod (Tinius Olsen IT 406). The cross-section morphology of the specimens was observed by digital optical microscopy (KEYENCE, VHX-700FE).

RESULTS AND DISCUSSION

SEM and OM images of TEM particles with different PVP and HNT concentrations are shown in Figures 1 and 2, respectively. In Figure 2, different brightness between inner side and outer side of the particles are indication for different materials at the core and shell. Therefore, the images can be the evidence that the core-shell structure of the TEM is successfully polymerized. To verify core-shell structure of the particle, they were immersed in liquid nitrogen and crumbled by hammer. Figure 3 showed an image of the broken particles and it clearly showed hollowed inner space and outer shell of the TEM.

Though not shown in Figures 1 and 2, the size and shape of the TEM remained unchanged with the amounts of HNT and PVP. It has previously been reported that when monomers with low solubility, such as AN, are present in the aqueous phase, secondary nucleation can occur and result in the formation of

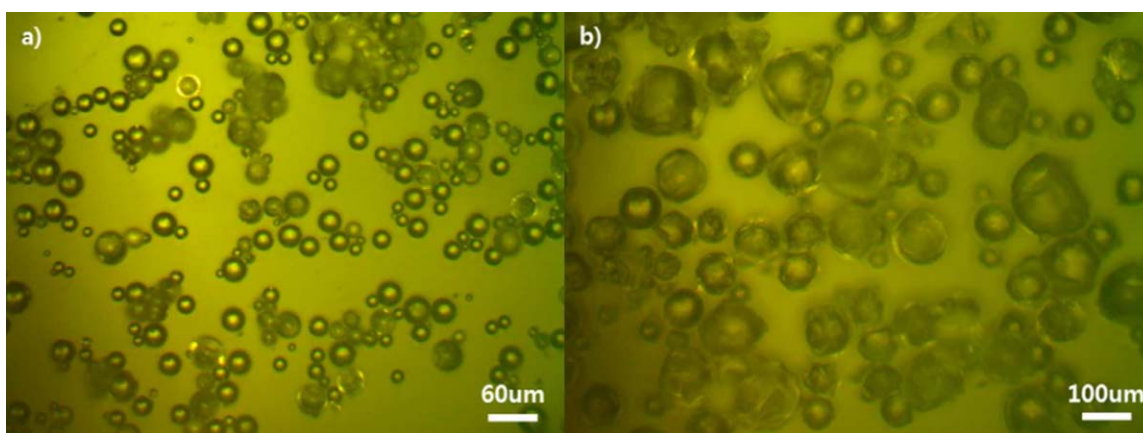


Figure 2. OM images of (a) TP-0.5 and (b) TH-0.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

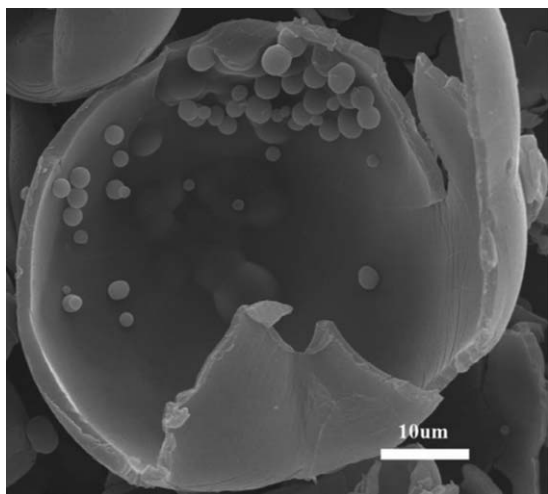


Figure 3. SEM image of broken TP-0.5.

droplets during polymerization.¹⁶ The smaller particles near the capsules in the SEM images are believed to be droplets produced by the secondary nucleation of AN. Kim *et al.* reported that adding a small amount of hydroquinone would minimize this effect.¹⁵ It can be seen from the SEM images that the TEMs were not spherical in shape, probably due to the liquid hydrocarbon in the core. Unlike the polymerized AN-MAN copolymer shell, *n*-octane in the core is a liquid at room temperature. Therefore, if the TEM core is not fully filled by the liquid hydrocarbon, it may not have sufficient strength to support the outer shell. The morphology of the capsules can be changed by selecting different monomer combinations, liquid hydrocarbons, and crosslinkers.^{2,7} According to the SEM and OM results, the diameters of the TEMs fabricated with PVP were between 20 and 50 μm ; on the other hand, the TEMs polymerized with HNT had diameters between 80 and 150 μm .

The average capsule sizes of the TEMs were analyzed by using a particle size analyzer (Figure 4). d0.1, d0.5, and d0.9 indicate TEM sizes below 10, 50, and 90 vol %, respectively. The average particle diameters decreased with increasing HNT content. The calculated average particle sizes of TH-2.5, TH-5.0, and TH-7.5 were 181.7, 157.4, and 55.4 μm , respectively. It has been reported that increasing the HNT content could decrease the formation of emulsion droplets.¹⁷ On the other hand, the average particle diameters of TP-2.5, TP-5.0, and TP-7.5 were 23.6, 28.0, and 33.8 μm , respectively. The TP series showed an increase in the particle size as the PVP concentration increased. Boguslavsky *et al.* reported that increasing the stabilizer concentration may lead to an increase in the viscosity of the continuous phase.¹⁸ Since termination involves the reaction between two chain ends, increase in the viscosity of the polymerization medium may hinder oligo-radical diffusion and thereby lead to deceleration of the termination step of the polymerization. Therefore, under the condition more polymerization can be occurred and particle could have higher chance to grow up.

The amount of encapsulated liquid hydrocarbon was calculated by TGA analysis (Figure 5). In the case of TP-2.5, TP-5.0, and TP-7.5, the hydrocarbon decomposed at around 175 $^{\circ}\text{C}$ and the

polymeric shell decomposed at 370 $^{\circ}\text{C}$. The concentration of PVP barely affected the onset decomposition temperature of the TEMs. However, weight losses observed for different TEMs may reflect the liquid hydrocarbon content. As depicted in Figure 4, TP-2.5 and TP-7.5 showed weight losses of 36 and 45 wt % at 300 $^{\circ}\text{C}$, respectively. The TEMs prepared with HNT showed increasing onset decomposition temperature as the HNT concentration increased. This phenomenon is related to the formation of HNT covered microcapsule. HNT covering the microcapsules hindered thermal transfer from the outside, thus retards the expansion of the capsule. TH-2.5, 5.0, and 7.0 showed approximately 50 wt % loss at 300 $^{\circ}\text{C}$. This indicates that the TH series had a higher amount of liquid hydrocarbon in the core than the TP series.

In order to determine the nature of expansion of the TEMs, the samples were heated in the oven at 200 $^{\circ}\text{C}$ for 5 min. Figure 6 shows the sample after thermal exposure. Although the TGA results indicated that the TH series contained a higher amount of liquid hydrocarbon, the TP series showed a larger expansion of the microcapsules. The stabilizer concentration did not significantly affect the bulk expansion.

Figure 7 shows the TMA results of the TP and TH series. The onset expansion temperatures were between 120 $^{\circ}\text{C}$ and 145 $^{\circ}\text{C}$, which correlated with the onset temperatures obtained from

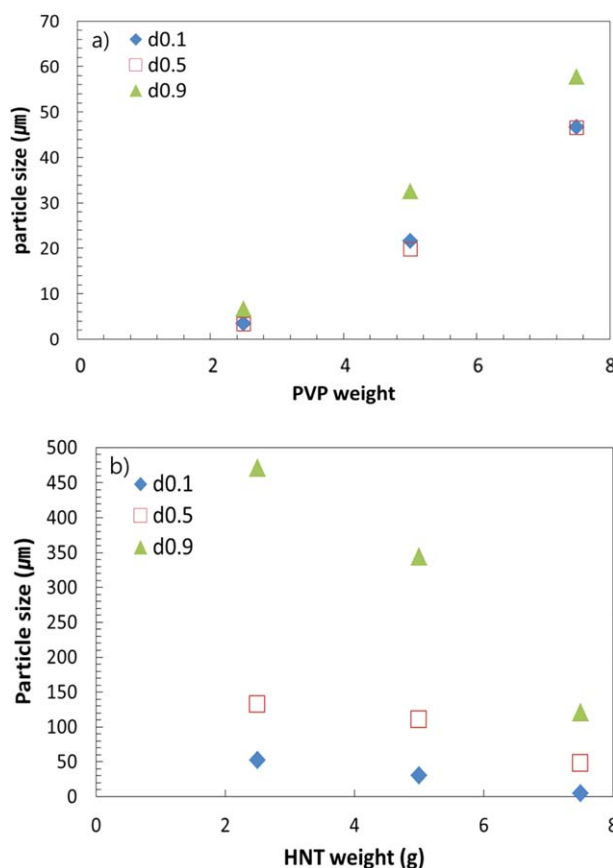


Figure 4. Particle sizes of TEMs fabricated with (a) PVP and (b) HNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

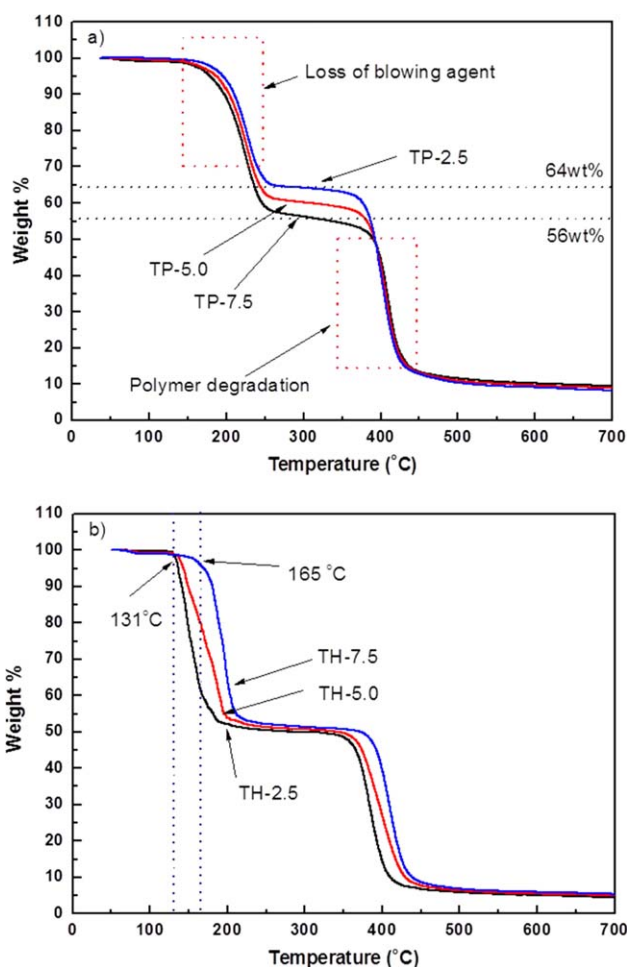


Figure 5. TGA results for TEMs fabricated with (a) PVP and (b) HNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA. The TP series showed much greater expansion than did the TH series. The expansion ability of the TEMs followed the order TP-7.5 > TP-5.0 > TP-2.5 > TH series. This indicates that a higher amount of blowing agent in the core enhances the expansion capacity of the TEMs. However, the TH series, which contained a high amount of liquid hydrocarbon, did not expand

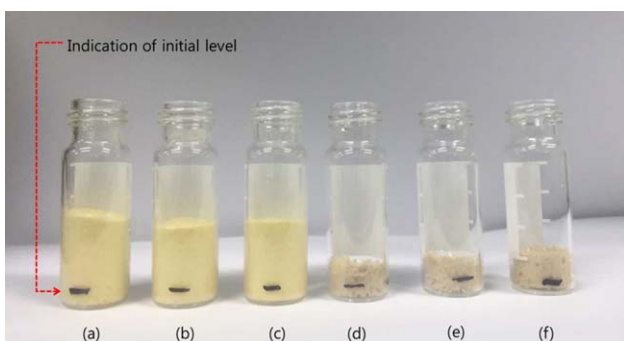


Figure 6. Thermal expansion of (a) TP-2.5, (b) TP-5.0, (c) 7.5, (d) TH-2.5, (e) TH-5.0, and (f) TH-7.0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

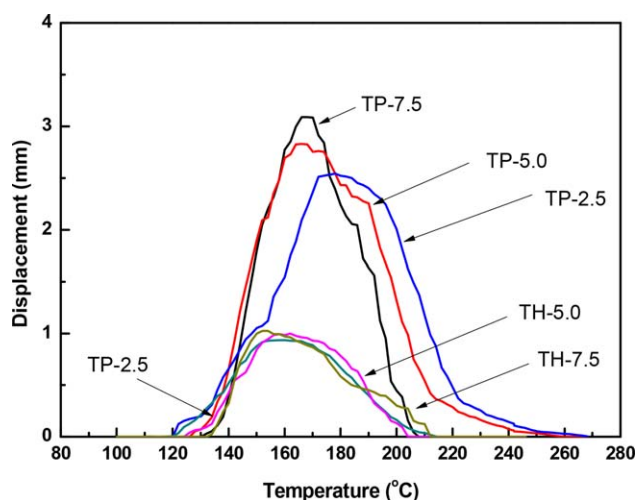


Figure 7. TMA results for TP and TH series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as much as the TP series. This difference may be due to the initial particle size of the capsules. Despite the similar bulk volumes during the test, smaller particles would comprise more microparticles, which in turn would increase the efficiency of expansion. Therefore, it can be concluded that the size of the capsule is an important factor in the expansion of thermally expandable capsules.

The TEMs were injection-molded with polypropylene in order to determine the difference as a blowing agent. Table II shows the tensile strength and impact strength of the PP foams processed with TEMs. It is well known that foaming causes a decrease in the weight of materials and that the mechanical properties degrade as the density decreases.¹⁹ The tensile strength of foamed materials can be predicted by the Power law equation shown below;

$$\frac{M_f}{M_m} = (\rho_r)^n \quad (1)$$

where M_f is the mechanical strength of the foamed material, M_m is the mechanical strength of the original material, and ρ_r is the relative density. n is an experimental constant, whose value is normally between 1 and 3.

$$\rho_r = \frac{\rho_f}{\rho_m} \quad (2)$$

ρ_f and ρ_m are the densities of the foamed material and the original material, respectively.

Table II. Properties of PP Foam Prepared with TEMs

Properties	PP	PP-H	PP-P
Foaming agent	—	TH-5.0	TP-5.0
Density (g/cm ³)	0.99	0.71	0.75
Flexural strength (MPa)	29	21.5	23.3
Flexural modulus (MPa)	1850	1380	1440
Impact strength (J/M)	115	57	69

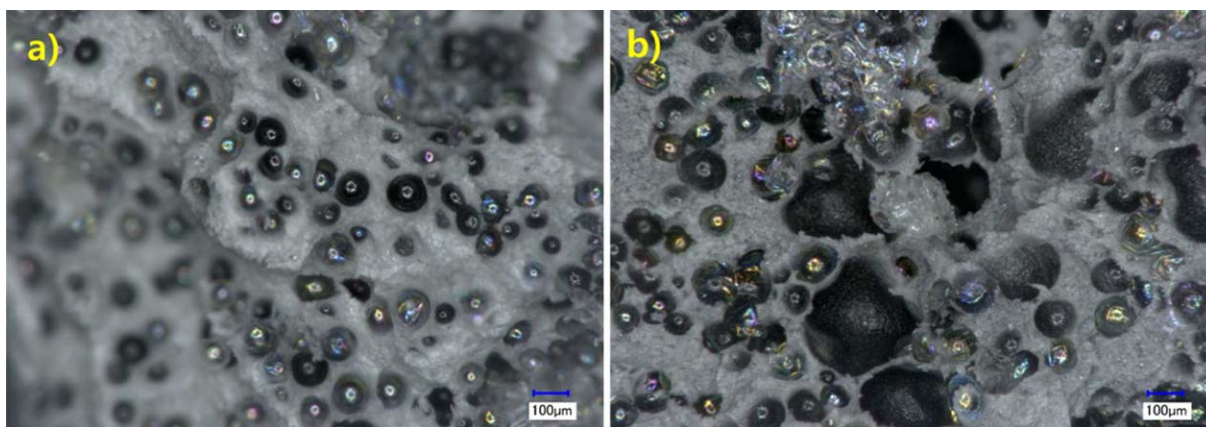


Figure 8. Cross section images of (a) PP-P and (b) PP-H. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 shows the optical microscopic images of the cross section of PP-P and PP-H. Both TEMs were successfully expanded by the injection molding process. TEM-P and TEM-H expanded up to 150 and 300 μm , respectively. The difference in the mechanical properties can also be explained by the morphology of the foamed PP. PP-P shows finer and better dispersed TEMs than does PP-H. TH-0.5 in the PP-H matrix had more expanded cell ruptures. These cell ruptures resulted in larger voids and decreased the area of the continuous PP matrix phase, thereby degrading the mechanical properties.

CONCLUSIONS

Thermally expandable microcapsules with PVP and halloysite nanotubes were successfully fabricated by suspension polymerization. TEMs prepared with PVP had diameters of 20–30 μm , while those with halloysite nanotubes had a diameter of 150–200 μm . TGA results showed that larger TEMs contain higher amounts of liquid hydrocarbon in the core but the expansion properties correlate better to the size of the capsule. The samples in the TP series expanded to almost six times their original size, upon heating in a convection oven (200 $^{\circ}\text{C}$); on the other hand, the TH series showed only three-fold expansion. Since smaller capsules have a higher packing density than do larger capsules, the number of capsules in the TP series occupying a given volume would be greater than that in the TH series. TMA results showed that the TP series has better expansion properties. When used as the blowing agent, both the TEMs successfully reduced the density of PP from 0.99 to 0.71 and 0.75. PP-P showed finer, better dispersed expanded capsules in the matrix, while PP-H showed larger and ruptured cell morphology. The morphology of the foamed PP with the two TEMs was responsible for the difference in the mechanical properties.

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