

# Thermally Expandable Microspheres with Excellent Expansion Characteristics at High Temperature

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**ABSTRACT:** Thermally expandable core/shell particles with a poly(acrylonitrile-co-methacrylonitrile) shell and a hydrocarbon core (blowing agent) have been prepared by suspension polymerization. The objective of this study was to gain a deeper understanding of the parameters determining the expansion properties of these microspheres. It was found that the amount, the boiling point, and the structure of the blowing agent are important parameters for the expansion properties. For example, a higher maximum expansion was reached when using bulkier blowing agents and thus a lower diffusion rate through the polymer shell. Further, the amount and struc-

ture of the crosslinker were also found to be essential for the expansion properties. For this particular system, it was found that a dimethacrylate-functional crosslinker gave significantly better expansion when compared with diacrylate- or divinylether-based crosslinkers. Beside these parameters, it was also observed that the particle-size distribution influence the expansion properties of the microspheres. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 384–392, 2010

**Key words:** core-shell polymers; blowing agents; crosslinking; radical polymerization

## INTRODUCTION

Thermally expandable microspheres are polymeric core/shell particles originally developed by Dow Chemicals Co. in the 1970s<sup>1</sup> and have been further developed by others.<sup>2–5</sup> The microspheres are core/shell particles, typically 5–50  $\mu\text{m}$  in diameter, in which a hydrocarbon is encapsulated by a thermoplastic polymer shell. The particles expand when heated above the glass-transition temperature ( $T_g$ ) of the polymer shell, thereby reducing the density from approximately 1100 to 30  $\text{kg}\cdot\text{m}^{-3}$ . The volume of the particles is retained upon cooling because of the plastic deformation of the polymer shell, and hence, the expansion is not reversible.

A variety of microsphere grades are available and used extensively by the industry.<sup>6,7</sup> Common applications include printing inks, paper and board, extrusion and injection moulding, etc. With the addition of microspheres to printing inks, 3D textures on wall papers and textiles can be created.<sup>1</sup> When used as a lightweight filler in paper board, there is an

improvement of the insulation properties as well as a bulk increase.<sup>8</sup> The automotive industry use microspheres in underbody coatings, tires, composite materials, and for adhesive debonding.<sup>9–12</sup> Interesting new applications of microspheres are as single-use pumps or valves in microfluidic systems<sup>13,14</sup> or as sacrificial templates in the production of foamed ceramics.<sup>15,16</sup>

The expansion temperature, particle size, maximum expansion, and the microsphere surface chemistry are all important parameters when choosing the appropriate microsphere grade. Microspheres expanding at temperatures from approximately 80–220°C are commercially available under the trade name of Expancel<sup>®</sup>.<sup>17</sup> The specific grades are primarily chosen depending on the application process parameters, the process temperature being especially important. Microspheres can be used even when there is no or insufficient heating in the process, by expanding the microspheres before use. The particle size is also important; larger particles generally expand better than smaller ones while the finish of the product surface is generally better with smaller particles. The larger particles (>20  $\mu\text{m}$ ) are usually used when density reduction is a priority, whereas the smaller particles are preferred when the surface finish of the final product is more important as, e.g., in printing inks, putties, and artificial leather. Furthermore, the microsphere's resistance toward shear forces depends on the polymer-shell thickness why

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the maximum possible expansion is not always desirable. The compatibility with the matrix is also important to ensure maximum performance of the microspheres. The surface chemistry of the microspheres differs not only depending on the polymer composition of the shell but also on the stabilization system used during polymerization.<sup>1-3,18-21</sup>

Even though microspheres have been commercially available for nearly 30 years, there are only a limited number of studies published regarding thermally expandable microspheres. In a previous study, we have investigated how the particle morphology is influenced by the monomer composition and the polymerization temperature.<sup>20</sup> It was shown that not only is the particle morphology sensitive to changes in the system but the mechanism of particle formation may differ as well. In another study, we have used controlled radical polymerization to modify the surface of microspheres using hydroxyl groups in the polymer shell as reactive handles.<sup>22</sup> The way the expansion properties are affected by crosslinking of the polymer shell has been investigated by Kawaguchi and Oishi,<sup>18</sup> who found that the degree of crosslinking is very important for the expansion properties. In addition, Oishi and coworkers<sup>19</sup> have studied the correlation between the chemical structure of nonnitrile monomers and the expansion properties in microspheres having a poly(acrylonitrile-*co*-methacrylonitrile) shell. In an extensive study, Huang developed and investigated microspheres expanding at low temperatures (<100°C).<sup>23</sup>

Using thermally expandable microspheres as foaming agent in thermoplastic materials, such as PVC, PE, PP, TPU, etc., has several advantages when compared with other foaming techniques.<sup>24,25</sup> The microspheres are easy to use and handle and creates homogeneous, closed-cell foams with excellent stability. The melt index and barrier properties of the matrix are of less importance when foaming with microspheres when compared with physical and chemical blowing agents since the hydrocarbon is encapsulated within the polymer shell of the microspheres. However, as the maximum processing temperature for using microspheres in injection molding and extrusion is approximately 230°C, potential materials to foam with microspheres are somewhat limited. It is also often beneficial to use microspheres compounded in a carrier because of the ease of handling. However, the present maximum temperature of compounding is approximately 150°C, to avoid premature expansion during the compounding step.

There is an ongoing quest for microspheres expanding at higher temperatures. Increasing the onset temperature of expansion ( $T_{\text{start}}$ ) is interesting as this would enable the compounding of microspheres in a wider range of materials. A higher maximum temperature of expansion ( $T_{\text{max}}$ ) is interesting

as the possibility of a higher processing temperature would enable the foaming of materials with melting temperatures currently too high for microspheres [e.g., engineering thermoplastics (PA, PC, etc.)].

The objective of this study has been to investigate microspheres having an poly(acrylonitrile-*co*-methacrylonitrile) shell to gain a deeper understanding of the parameters determining the expansion properties. On the basis of the findings of Kawaguchi and Oishi,<sup>18</sup> a monomer composition of 70/30 mol/mol acrylonitrile/methacrylonitrile was used throughout the study. The structure, boiling point, and the amount of the blowing agent have been the emphasis of the present study, and the important expansion properties such as the particle size, particle size distribution, and the crosslinking of the polymer shell have also been studied.

## EXPERIMENTAL

### Materials

Acrylonitrile (Alfa Aesar, 99%+, stabilized with 40 ppm 4-methoxy phenol), methacrylonitrile (Acros, 99%, stabilized with 50 ppm 4-methoxy phenol), 1,4-butanediol dimethacrylate (BDDMA, Aldrich, 95%), 1,4-butanediol diacrylate (BDDA, Alfa Aesar, 99%+), 1,4-butanediol divinyl ether (BDDVE, Aldrich, 98%), isopentane (IP, Alfa Aesar, 99%+), isohexane (IH, Aldrich, 99%+), isooctane (IO, Alfa Aesar, 99%), *n*-octane (*n*O, Alfa Aesar, 98%+), *n*-heptane (*n*Hep, Merck, 99.5%), methyl cyclohexane (MCH, Alfa Aesar, 99%+), dilauryl peroxide (AkzoNobel Polymer Chemicals, 99%), sodium hydroxide (Sharlau Chemie, >99%), magnesium chloride (Prelabo, 97%), sodium 2-ethylhexyl sulfate (Fluka, ~ 50% in water). All chemicals were used as received.

### Polymerizations

In a typical experiment, polymerizations were performed according to the general procedure described in Ref. 2. The magnesium hydroxide dispersion was prepared by mixing sodium hydroxide [0.55 g NaOH (s)] with magnesium chloride [1.94 g MgCl<sub>2</sub> × 6 H<sub>2</sub>O (s)] in deionized water (30.0 g) followed by vigorous stirring for 30 min. This dispersion, together with 0.1 g of a 1% solution of sodium 2-ethylhexyl sulfate (aq), was mixed with an organic phase containing acrylonitrile (5.26 g), methacrylonitrile (2.83 g), hydrocarbon (2.03 g), BDDMA (0.064 g), and dilauryl peroxide (0.16 g). The mixture was emulsified using a Silverson high-shear mixer (8000 rpm, 45 s). Polymerizations were performed in 50-mL glass reactors (Tynclave from Büchi) under gentle agitation (62°C, 20 h). The reactions were quenched by cooling to ambient temperature

TABLE I  
Composition and Experimental Data of Microspheres

Entry	Blowing agent		Crosslinker		Particle size <sup>a</sup>		$T_{\text{start}}$ (°C)	$T_{\text{max}}$ (°C)	Probe displacement <sup>b</sup> (μm)
	Name	Weight percent <sup>c</sup>	Name	Molar percent <sup>d</sup>	Micrometer	Span <sup>e</sup>			
1	IP	20	BDDMA	0.2	33.8	0.9	122	188	2100
2	IH	20	BDDMA	0.2	33.3	1.0	138	189	1900
3	IO	20	BDDMA	0.2	37.5	0.8	177	223	1600
4	nO	20	BDDMA	0.2	33.7	1.1	207	213	500
5	IO	10	BDDMA	0.2	36.0	1.6	200	227	200
6	IO	30	BDDMA	0.2	31.1	1.2	176	211	1900
7	IO	40	BDDMA	0.2	31.5	1.1	173	193	500
8	nHep	20	BDDMA	0.2	37.0	1.1	180	211	1100
9	MCH	20	BDDMA	0.2	36.8	1.0	199	208	400
10	IO	20	BDDMA	0.2	40.3	1.1	177	221	1500
11	IO	20	BDDMA	0.2	42.8	0.9	177	214	1400
12	IO	20	BDDMA	0.2	35.2	0.7	178	222	1400
13	IO	20	BDDMA	0.2	30.1	0.7	184	222	1400
14	IO	20	–	–	30.8	1.0	164	178	400
15	IO	20	BDDMA	0.1	31.5	1.0	183	224	2300
16	IO	20	BDDMA	0.3	39.5	0.9	181	205	500
17	IO	20	BDDVE	0.2	30.1	0.7	189	222	700
18	IO	20	BDDA	0.2	30.1	0.7	189	194	500

<sup>a</sup> The volume mean diameter ( $D(0.5)$ ), determined by laser light scattering.

<sup>b</sup> The uncertainty of the expansion is approximately  $\pm 10\%$  because of the complexity of the TMA.

<sup>c</sup> Amount of hydrocarbon charged before polymerization.

<sup>d</sup> Based on the molar amount of monomers and crosslinker in the system.

<sup>e</sup> Particle-size distribution; span =  $(D(0.9) - D(0.1))/D(0.5)$ .

after which the dispersions were passed through a 100 μm sieve to remove any agglomerates and large particles. Finally, the microspheres were collected by filtration and dried at 50°C overnight. The composition and experimental data of the microspheres polymerized in this study are presented in Table I.

### Measurements

Thermal mechanical analysis (TMA) was conducted on a Mettler Toledo TMA/SDTA 841<sup>e</sup>. The samples were heated from 30 to 250°C at 20°C·min<sup>-1</sup> under N<sub>2</sub> atmosphere with a 0.06 N load. Determined expansion parameters are  $T_{\text{start}}$  (the onset temperature of expansion),  $T_{\text{max}}$  (the temperature of maximum expansion), and the maximum expansion (presented as the TMA probe displacement, the values, and thermograms presented are normalized with respect to sample weight to enable comparison).

Thermal gravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA 851<sup>e</sup> to examine the blowing agent loss during expansion. The samples were heated from 30 to 650°C at 20°C·min<sup>-1</sup> under N<sub>2</sub> atmosphere followed by isothermal analysis at 650°C for 8 min in an air atmosphere. The samples contain moisture and residual monomers even though the samples are dried before analysis. Based on experience, the amount of remaining moisture and residual monomers are approximately 1%, respectively. The blowing agent contents presented further are therefore the amount

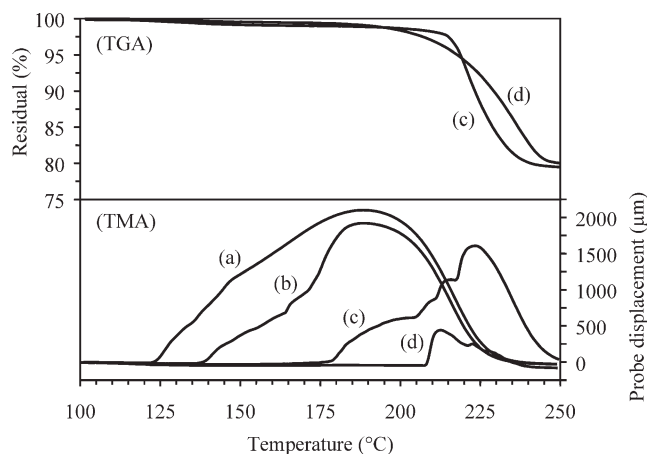
charged before polymerization and may differ from the volatile content as determined by TGA.

Particle size and particle size distribution were determined on a Malvern Mastersizer Hydro 2000 SM light-scattering apparatus and are presented as the volume mean diameter  $D(0.5)$  and span (defined as  $D(0.9) - D(0.1)/D(0.5)$ ). Dilute water dispersions of the microspheres were sonicated for 10 min before analysis to break any agglomerates formed as the microspheres were dried following the polymerization. Our study shows that the particle-size distribution affects the expansion properties of the microspheres. A few samples having a broad span was therefore fractionated using sieves to narrow the particle-size distribution and thereby enable better comparisons of results between experiments.

## RESULTS AND DISCUSSION

### The effect of the blowing agent on the expansion properties

A simple but effective way to tailor the expansion temperatures ( $T_{\text{start}}$  and  $T_{\text{max}}$ ) is to choose the encapsulated hydrocarbon carefully (Fig. 1).  $T_{\text{start}}$  is directly dependent on the boiling point of the encapsulated blowing agent. This is logical as the microspheres expand when the internal pressure is high enough to overcome the modulus of the polymer shell. The glass-transition temperature ( $T_g$ ) for the polymer forming the microsphere shell used in this



**Figure 1** TGA and TMA for microspheres containing 20 wt % of blowing agents with different boiling points (Entries 1–4, Table I): (a) IP, (b) IH, (c) IO, and (d) *n*O.

study is approximately 105°C according to the Fox equation,<sup>26</sup> which correlates well with values determined by DSC for similar polymer compositions in our laboratory.  $T_{\text{start}}$  for microspheres consisting of this polymer shell and IP as the blowing agent is around 120°C (Entry 1, Table 1), while  $T_{\text{start}}$  increases with increasing boiling point of the blowing agent and is approximately 85°C higher when

*n*O is the blowing agent (Entries 2–4, Table I).  $T_{\text{max}}$  is also dependent on the boiling point of the blowing agent. However, the structure of the blowing agent is assumed to be much more important for the  $T_{\text{max}}$  as the polymer-shell thickness is reduced during expansion. This is evident when comparing IO and *n*O as blowing agents.  $T_{\text{max}}$  is significantly higher with IO, even though *n*O has a higher boiling point. Our assumption is that the linear *n*O diffuses through the polymer shell more easily than do the bulky structure of IO (Fig. 1). This not only reduces  $T_{\text{max}}$  but also causes the expansion to be very poor.

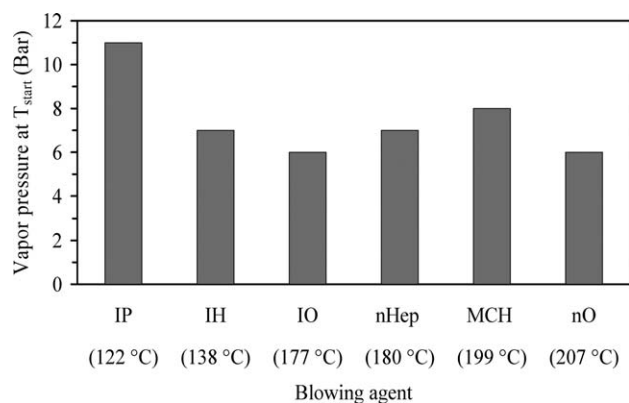
The encapsulated blowing agent can be assumed to approach the behavior of an ideal gas in the microspheres. However, this assumption is only valid when the microspheres are expanded. When unexpanded, the internal pressure in the confined space of the microspheres is limited by the vapor pressure of the blowing agent. The blowing agent is therefore mainly in the condensed state regardless of temperature in the unexpanded microspheres. When the microspheres expand, the condensed blowing agent rapidly evaporates increasing the volume tremendously. Throughout this study, vapor pressures have been calculated using the formula and constants given in Perry's chemical engineers handbook (Table II).<sup>27</sup> These calculations are based on the

**TABLE II**  
Boiling Points and Data Used for Calculating Vapor Pressures<sup>a</sup> of the Hydrocarbons Used as Blowing Agents in This Study<sup>27,28</sup>

Hydrocarbon	Boiling point (°C)	Vapor pressure constants				
		C1	C2	C3	C4	C5
IP 	28	72.35	-5010.9	-7.883	$8.9795 \times 10^{-6}$	2
IH 	60	77.36	-5791.7	-8.4912	$7.7939 \times 10^{-6}$	2
IO 	99	87.868	-6831.7	-9.9783	$7.7729 \times 10^{-6}$	2
<i>n</i> Hep 	99	87.829	-6996.4	-9.8802	$7.2099 \times 10^{-6}$	2
MCH 	101	92.611	-7077.8	-10.684	$8.1239 \times 10^{-6}$	2
<i>n</i> O 	126	96.084	-7900.2	-11.003	$7.1802 \times 10^{-6}$	2

<sup>a</sup> Vapor pressure (in bar) =  $\exp[C1 + (C2/T) + C3 \times \ln(T) + C4 \times T^{C5}] \times 10^{-5}$ ; temperatures are in Kelvin.

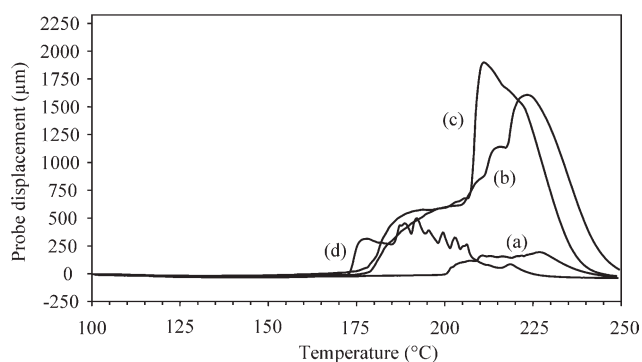




**Figure 2** Calculated vapor pressures of different blowing agents at  $T_{start}$  for microspheres in this study (the temperatures used when calculating the vapor pressures for each blowing agent are given within the brackets).

assumption that the microspheres have a closed cell structure and there is no diffusion of blowing agent through the polymer shell. In addition, no consideration is taken to possible contributions from residual monomers, etc. Depending on the blowing agent, the vapor pressure at  $T_{start}$  varies (Fig. 2). It can be seen that the modulus of the polymer shell is comparatively high near its  $T_g$  as the calculated vapor pressure at  $T_{start}$  is much higher for IP than the other blowing agents in this study. At temperatures well above  $T_g$ , there are less differences in the vapor pressures at  $T_{start}$ , indicating that the modulus of the polymer shell is of less importance in determining the  $T_{start}$ .

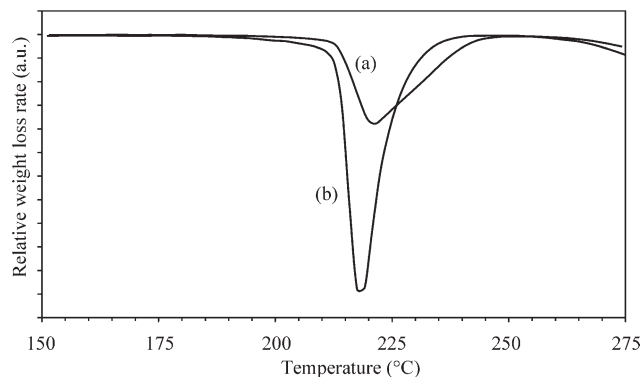
The maximum expansion correlates to the molar amount of blowing agent, if the blowing agent is assumed to approach the behavior of an ideal gas as soon as the microspheres are expanded. Therefore, increasing the blowing agent content is often effective but can have a detrimental effect on the expansion as the polymer-shell thickness is reduced. This can clearly be seen in Figure 3 in which TMA for microspheres with various amounts of IO are presented. When the IO content is 10 wt % (Entry 5, Table I), poor expansion and a relatively high  $T_{start}$



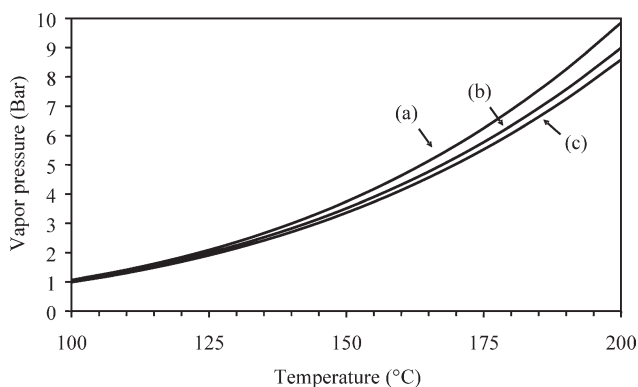
**Figure 3** TMA for microspheres containing various amounts of isooctane as blowing agent (Entries 3, 5–7, Table I): (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, and (d) 40 wt %.

is observed. This behavior arises from a too low blowing agent content, resulting in insufficient pressure in combination with a relatively thick polymer shell. On the other hand, when the IO content is 40 wt % (Entry 7, Table I), the expansion is also poor but with a relatively low  $T_{start}$ . This is because of a too high amount of blowing agent, implying that a relatively thin polymer shell was available, which rapidly becomes unable to withstand the pressure and the microspheres ruptures rather than expands.

There seems to be an optimum amount of IO at around 20–30 wt % depending on the desired properties of the microspheres. Better expansion is achieved with 30 wt % IO (Entry 6, Table I), whereas the thermal resistance is better with 20 wt % (Entry 3, Table I) as shown by the higher  $T_{max}$ . These differences can be explained by taking into account the results of differential TGA (Fig. 4), which show that the sample containing 30 wt % IO not only exhibits faster weight loss than the sample containing 20 wt % IO but also indicate that the blowing agent is lost almost entirely above  $T_{max}$ . The suggested reason is that the occurrence of rapid expansion (Fig. 3) was able to minimize diffusion of the blowing agent and therefore permitting the microspheres to expand until the polymer shell ruptures, which lead to an instantaneous loss of blowing agent. In comparison, the microspheres containing 20 wt % IO shows a very different behavior with nearly 50% of the IO being lost before reaching  $T_{max}$ . The expansion rate is lower in this case since less blowing agent results in lower internal pressure. Furthermore, with lower expansion rates diffusion of the blowing agent must be taken into consideration. The polymer shell becomes thinner during expansion, which increases the diffusion rate. As the blowing agent can be assumed to behave almost as an ideal gas at this stage of expansion, diffusion reduces the internal microsphere pressure, thus reducing the expansion rate even further. Therefore, reducing the blowing agent content from 30 to 20 wt % reduces the



**Figure 4** Differential TGA showing the blowing agent loss of microspheres with different amounts of encapsulated IO (Entries 3, 6, Table I): (a) 20 wt % and (b) 30 wt %.



**Figure 5** Calculated vapor pressures as a function of temperature for hydrocarbons having similar boiling points<sup>27</sup>: (a) *n*Hep, (b) IO, and (c) MCH.

probability of the microspheres expanding to such an extent that their shell ruptures. Instead, the blowing agent is lost mainly through diffusion and  $T_{\max}$  is reached when the internal pressure is no longer sufficient to maintain the expanded volume.

Hydrocarbons of different structures (linear, cyclic, and branched) were compared to further investigate how the expansion is affected by the blowing agent. *n*Hep, IO, and MCH were chosen based on their similar boiling points<sup>28</sup> (99, 99, and 101°C, respectively) and vapor pressures (Fig. 5).<sup>27</sup> The expansion properties of these microspheres are surprisingly different (Fig. 6) considering the initially apparent similarities in the physical properties of the blowing agents.

IO provides excellent expansion at high temperatures because of its bulky structure, which minimizes blowing agent diffusion at temperatures well above  $T_g$  of the polymer shell. Although the microspheres are significantly expanded at 215°C, there is only a limited IO loss [Fig. 6(b)]. However, as the temperature increases, the microspheres are expanded even further. It is then evident from the TGA results that the encapsulated IO is lost, presumably through diffusion as discussed earlier and at approximately 225°C, the internal pressure of the microspheres is insufficient to retain the expanded volume of the sample.

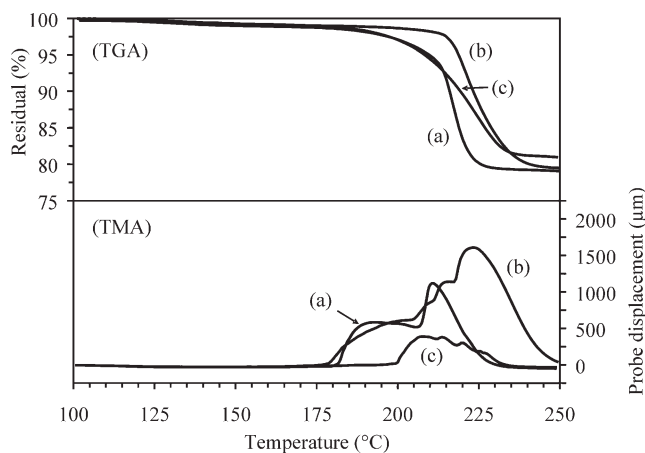
A completely different behavior is seen for the microspheres containing MCH (Entry 9, Table I), as it supposedly diffuses through the polymer shell at temperatures well below  $T_{\text{start}}$  [Fig. 6(c)]. This in combination with the slightly lower vapor pressure of MCH when compared with IO severely affects the expansion of the microspheres resulting in poor volume increase and a relatively high  $T_{\text{start}}$ . It is reasonable to assume that the blowing agent loss is mainly caused by diffusion and not by ruptured polymer shells in this case, since the expansion of the microspheres is poor. Also, as the polymer shell

thickness is relatively unaffected due to the poor expansion, the diffusion of MCH is comparatively slow when compared with the diffusion in microspheres containing *n*Hep.

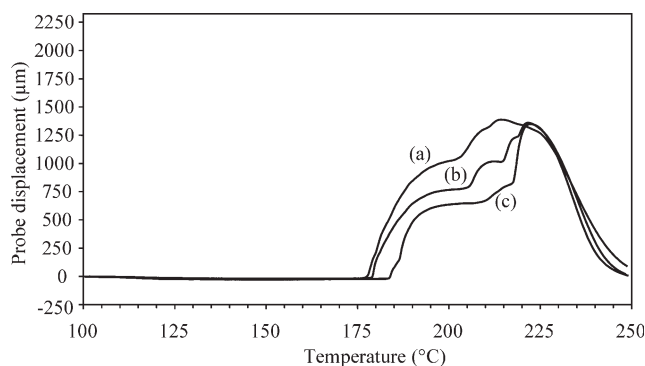
$T_{\text{start}}$  is slightly higher with *n*Hep as blowing agent (Entry 8, Table I) when compared with IO while the expansion ratio and  $T_{\max}$  are considerably lower (Fig. 6). A lower  $T_{\text{start}}$  would be expected for the sample containing *n*Hep, considering that the vapor pressure for *n*Hep is higher than for IO (Fig. 5). In addition, the molar amount of *n*Hep is higher than the amount of IO samples since all three samples contain 20 wt % blowing agent. However, as in the case of MCH, diffusion of the encapsulated *n*Hep presumably affects the expansion properties. Although the samples containing *n*Hep and MCH show a similar behavior in TGA up to 210°C, the vapor pressure of *n*Hep is enough to expand the microspheres. Our assumption is therefore that the diffusion rate of *n*Hep increases when the microspheres expand, thereby limiting  $T_{\max}$  and the maximum expansion.

#### Influence of the particle size on the expansion properties

A sample (Entry 10, Table I) was fractionated with respect to particle size to determine how the expansion properties vary with particle size. Thus, three well-defined fractions (Entries 11–13, Table I) were collected using sieves (20, 32, 45, and 63  $\mu\text{m}$  in pore size). The fraction passing through the 20  $\mu\text{m}$  sieve was too small to allow for the analyses, whereas the fraction collected by the 63  $\mu\text{m}$  sieve was excluded as the particle-size distribution in this fraction was broad (span = 1.4).  $T_{\text{start}}$  and  $T_{\max}$  are clearly dependent on the particle size (Fig. 7). Both  $T_{\text{start}}$  and  $T_{\max}$  are approximately 7°C higher for the fraction for which the mean particle size is 30  $\mu\text{m}$ , when



**Figure 6** TGA and TMA for microspheres containing 20 wt % of blowing agents having different structure but similar boiling point (Entries 3, 8, 9, Table I): (a) *n*Hep, (b) IO, and (c) MCH.



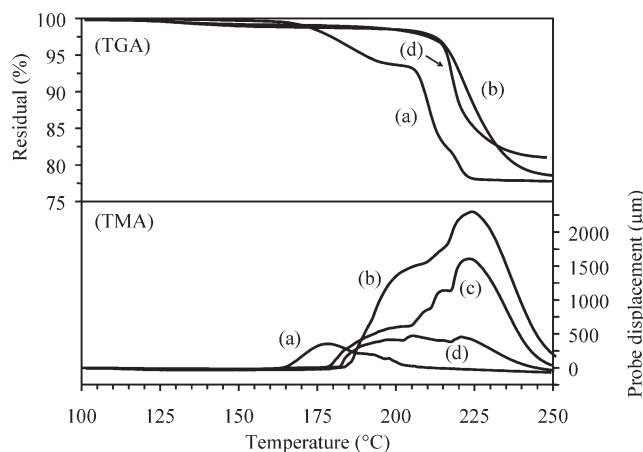
**Figure 7** TMA of microspheres from a sample fractionated with respect to particle size (Entries 11–13, Table I): (a)  $D(0.5) = 42.8 \mu\text{m}$ , (b)  $D(0.5) = 35.2 \mu\text{m}$ , and (c)  $D(0.5) = 30.1 \mu\text{m}$ .

compared with the fraction being  $43 \mu\text{m}$  in size. In these fractions, there seems to be no differences in the maximum expansion. However, it appears that the larger fractions have a wider window of expansion, which is valuable in many applications. At  $200^\circ\text{C}$ , for example, there is a significant difference in expansion between the different fractions indicating that larger microspheres are more readily expanded at lower temperatures.

These differences in expansion properties depending on the particle size are important to take into consideration when evaluating the results of different experiments. It is also obvious that a narrow particle-size distribution is desirable to get well-defined expansion properties, whereas a broader particle-size distribution implies more robust expansion systems.

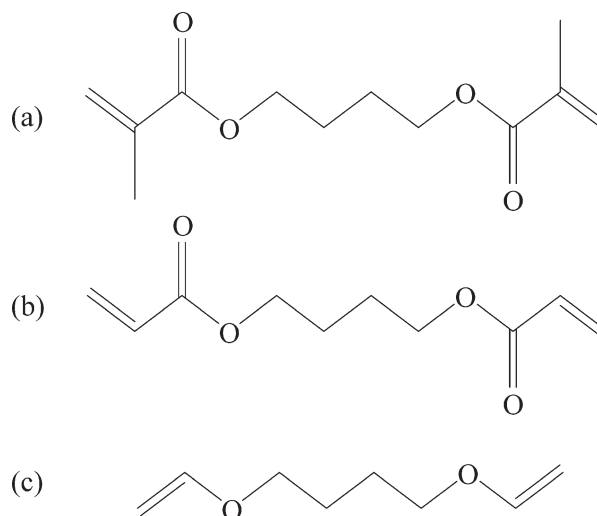
### Influence of the crosslinking on the expansion properties

Considering the nature of the thermally expandable microspheres, it is reasonable to believe that the viscoelastic behavior of the polymer shell is very important for the expansion properties of the microspheres.<sup>29</sup> One obvious method to alter the viscoelastic behavior, and thus the expansion properties of the microspheres, is the crosslinking density of the polymer shell.<sup>18</sup> Different concentrations and types of difunctional crosslinkers have therefore been studied in this particular system. Measuring the actual modulus in these samples would be very interesting for a deeper understanding of the expansion mechanisms. However, we have so far been unable to develop a method for measuring the modulus directly in the polymer shell. Instead, TMA and TGA have been used to study the effects on the expansion properties of the microspheres from variations in the crosslinking.

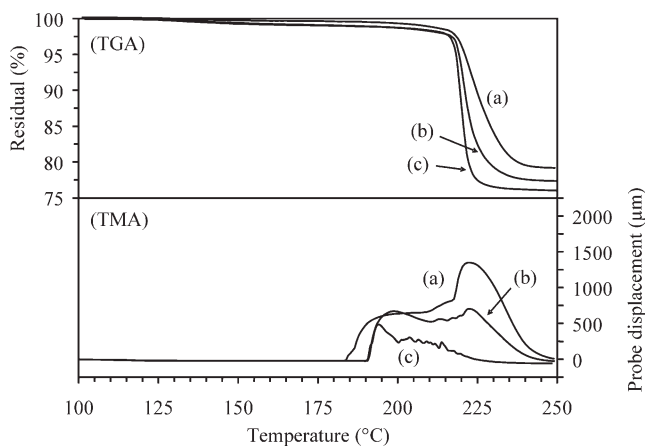


**Figure 8** TGA and TMA of microspheres containing various amounts of BDDMA as crosslinker (Entries 3, 14–16, Table I). The TGA thermogram for sample (c) is excluded from the figure as it is very similar to the thermograms of sample (b) and (d). (a) No crosslinker (b) 0.1 mol %, (c) 0.2 mol %, and (d) 0.3 mol %.

The expansion properties of a sample containing no crosslinker (Entry 14, Table I) are clearly inferior to samples (Entries 3, 15–16, Table I) containing BDDMA as a crosslinking agent (Fig. 8). The addition of 0.1 mol % BDDMA (based on the molar amount of monomers and crosslinker in the system) gives a tremendous improvement in the expansion,  $T_{\text{start}}$  is raised  $20^\circ\text{C}$  whereas  $T_{\text{max}}$  is raised as much as  $45^\circ\text{C}$ . Increasing the amount of BDDMA to 0.2 mol % reduces the expansion, not only does the maximum expansion decrease, the temperature range for good expansion shrinks. A small decrease in  $T_{\text{start}}$  can be observed as well. The maximum expansion is highly limited with an even further increase of the amount of BDDMA to 0.3 mol %. The expansion rapidly reaches a plateau that is held to



**Figure 9** Structure of crosslinkers used in this study: (a) BDDMA, (b) BDDA, and (c) BDDVE.



**Figure 10** TGA and TMA of microspheres containing 0.2 mol % of different crosslinkers based on 1,4-butanediol (Entries 13, 17, 18, Table I): (a) BDDMA, (b) BDDVE, and (c) BDDA.

approximately 225°C when the microspheres collapse, similar to the samples containing less BDDMA. The general trends of these TMA results are similar to those found by Kawaguchi and Oishi,<sup>18</sup> although they have used a different crosslinker (dipentaerythritol hexaacrylate) and a combination of blowing agents (*n*-pentane/*n*-hexane (70/30 wt/wt)). The effects of introducing crosslinks in the polymer shell are further shown by TGA (Fig. 8). A tremendous increase in the onset temperature for IO loss is seen when a crosslinker is used when compared with the sample where no crosslinker is used. When comparing the samples with different amounts of crosslinker, only minor differences in the IO loss rate can be observed.

We have found that not only is the amount of crosslinker crucial, but also the nature of the crosslinker seems to be important for the microsphere properties. This is illustrated by the addition of crosslinkers having different reactive groups although being structurally very similar as they are all based on 1,4-butanediol (Fig. 9). The maximum expansion of a microsphere sample containing 0.2 mol % BDDMA (Entry 13, Table I) is clearly superior to microspheres containing equivalent amounts of BDDVE or BDDA (Entries 17 and 18, Table I, Fig. 10). The expansion of the sample containing BDDA is actually as poor as when no crosslinker is added [Fig. 10(c) vs. Fig. 8(a)]. However, the large difference in  $T_{\text{start}}$  and the different appearance of the TGA thermogram for the sample without crosslinker indicates that BDDA (and BDDVE) have been incorporated in the polymer shell. From TGA, it can be seen that the rate of IO loss differs significantly for the different crosslinkers. It is very rapid for microspheres containing BDDA when compared with microspheres containing BDDMA, although the onset temperature is almost identical. Further stud-

ies are currently under way to find a plausible explanation for these differences in the expansion properties of microspheres containing different crosslinkers.

## CONCLUSIONS

This study demonstrates that the expansion properties of thermally expandable microspheres depend on several concurrent parameters. The expansion properties are strongly affected by the amount of crosslinker. We have also seen that the structure of the crosslinker may have a large impact on the expansion behavior. Another vital component for the expansion properties of microspheres is the blowing agent.  $T_{\text{start}}$ ,  $T_{\text{max}}$ , and the maximum expansion depend on the ability of the blowing agent to create sufficient internal pressure to expand the microspheres. The boiling point, the vapor pressure, and also the structure of the blowing agent have been found to be the important parameters affecting the expansion properties of the microspheres. Bulky blowing agents have a lower diffusion rate through the polymer shell, and thus, a higher maximum expansion can be reached. Furthermore, the expansion properties depend on the particle size of the microspheres. It is therefore important to have good control of the particle-size distribution to optimize the microsphere properties.

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