

Influence of Crosslinking on the Characteristics of Thermally Expandable Microspheres Expanding at High Temperature

Magnus Jonsson,^{1,2} Ove Nordin,² Anna Larsson Kron,² Eva Malmström¹

¹KTH Fibre and Polymer Technology, School of Chemical Science and Engineering, Royal Institute of Technology, TR 56-58, SE-100 44 Stockholm, Sweden

²Eka Chemicals AB, Box 13000, SE-850 13 Sundsvall, Sweden

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ABSTRACT: Free-radical suspension polymerization was used to synthesize thermally expandable microspheres (TEMS); in this process, a poly(acrylonitrile-co-methacrylonitrile) shell encapsulated isooctane. Different amounts of dimethacrylate, diacrylate, or divinyl ether functional crosslinker were added to investigate the effects on the crosslinking density of the polymer and the expansion properties of the TEMS. The optimum amount of crosslinker was found to be approximately 0.05–0.1 mol %. However, a significantly better expansion could be obtained with 1,4-butanediol dimethacrylate as a crosslinker, compared to 1,4-butanediol divinyl ether or 1,4-

butanediol diacrylate. From monitoring the conversion of monofunctional analogues by gas chromatography, we suggest that the differences in expansion obtained with different crosslinkers, originated from the difference in the reactivity of the radicals in the system toward the vinyl functionalities of the crosslinkers. This regulated the incorporation of the crosslinker into the polymer and, thereby, the mechanical properties of the microsphere shell. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1219–1229, 2010

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INTRODUCTION

In the early 1970s, Dow Chemical Co.¹ developed *thermally expandable microspheres* (TEMS), which are polymeric core-shell particles with a typical diameter of 5–50 μm , in which a hydrocarbon is encapsulated by a thermoplastic polymer shell.^{2–5} A unique property of TEMS is the tremendous increase in volume that is obtained when they are heated. This results in a density reduction, from about 1100 kg/m^3 to approximately 30 kg/m^3 . The expansion is not reversible upon cooling because of the plastic deformation of the polymer shell. The polymer shell softens when the TEMS are heated above the glass-transition temperature (T_g) of the polymer shell, and when the vapor pressure of the encapsulated hydrocarbon exceeds the modulus of the polymer shell, vaporization of the hydrocarbon causes the TEMS to expand.⁶

TEMS are used in a vast number of industrial applications. For example, they are commonly used to achieve weight reduction, bulk increase, or tailored material properties, such as light-weight products with improved elasticity.^{7–10} The addition of TEMS to printing inks enables three-dimensional textures on wall papers and textiles and Braille-type printing. In the automotive industry, they are used in underbody coatings to provide both weight and noise reduction¹¹ and in adhesives used for windshields to enable easy dismantling.¹² Also, thermoplastic materials, such as poly(vinyl chloride) (PVC), thermoplastic elastomer (TPE), polyethylene (PE), polypropylene (PP), and thermoplastic polyurethane (TPU), can be foamed with TEMS with conventional polymer processing methods, such as extrusion or injection molding.⁸ Because the hydrocarbon is encapsulated within the polymer shell, homogeneous, closed-cell foams with excellent stability can be obtained without the need of any special equipment.

TEMS have been commercially available for nearly 30 years, and although many patents have been filed over the years, studies regarding their synthesis and properties are scarce in the literature.^{6,13–18} It is, therefore, interesting to further explore the properties of TEMS for which the thermal characteristics are especially important.

Additional Supporting Information may be found in the online version of this article.

Correspondence to: E. Malmström (mavem@kth.se).

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Studies regarding the influence of crosslinking and polymer composition on the thermal properties of microspheres were presented by Kawaguchi, Oishi, and coworkers.^{16,17} By determining the swelling ratio and gel fraction of a dipentaerythritol hexaacrylate crosslinked shell, they found that the expansion properties of the microspheres depended on the crosslinking density of the polymer.¹⁶ Recently, our research group investigated the properties of TEMS expanding at temperatures around 200°C.⁶ One interesting observation was that different types of difunctional crosslinkers could give surprisingly different expansion properties of the microspheres when 1,4-butanediol dimethacrylate (BDDMA), 1,4-butanediol diacrylate (BDDA), and 1,4-butanediol divinyl ether (BDDVE) were compared at a concentration of 0.2 mol % (on the basis of the monomer and crosslinker).

The objective of this study was, therefore, to further investigate the correlation between the crosslinking of the polymer shell and the expansion properties of TEMS. If the expansion properties only depend on the crosslinking density in the polymer shell, as indicated by Kawaguchi and Oishi,¹⁶ it is reasonable to believe that similar expansion properties can be obtained, regardless of the chemical structure of the crosslinker, merely by the optimization of the crosslinker content. However, if the expansion properties depend on the crosslinking on a molecular level, the structure and reactivity of the crosslinker will be important as well because this affects how the crosslinker is incorporated into the polymer shell. Thus, in this study, correlations among the crosslinker concentration, gel fraction, and expansion properties were examined with three different crosslinkers, BDDMA, BDDA, and BDDVE. The concentration was varied between 0 and 0.4 mol %, on the basis of the total amount of monomer and crosslinker. Furthermore, to gain a deeper understanding of the polymer shell formation, the conversion of monofunctional analogues (Fig. 1) was monitored during polymerization in an attempt to mimic the incorporation of the crosslinkers into the polymer shell.

EXPERIMENTAL

Materials

Acrylonitrile (AN; Aldrich, >99%), methacrylonitrile (MAN; Acros, 99%), BDDMA (Aldrich, 95%), BDDA (Alfa Aesar, >99%), BDDVE (Aldrich, 98%), isooctane (Alfa Aesar, 99%), methyl methacrylate (MMA; Aldrich, 99%), methyl acrylate (MA; Aldrich, 99%), ethyl vinyl ether (EVE; Fisher Scientific, 99%), dilauryl peroxide (AkzoNobel Polymer Chemicals, 99%), sodium hydroxide (Sharlau Chemie, >99%), magnesium chloride (Prelabo, 97%), and sodium 2-ethylhexyl sulfate (Fluka, ~50% in water) were used as received.

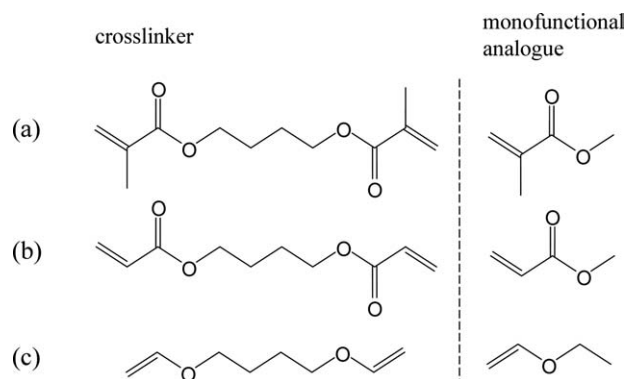


Figure 1 Crosslinkers (left) and their monofunctional analogues (right) used in this study: (a) BDDMA and MMA, (b) BDDA and MA, and (c) BDDVE and EVE.

Polymerizations

In a typical experiment, polymerization was performed according to a general procedure described elsewhere.² A magnesium hydroxide dispersion was prepared by the mixture of sodium hydroxide [0.55 g of NaOH (s)] with magnesium chloride [1.94 g of MgCl₂·6H₂O (s)] in deionized water (30.0 g), which was followed by vigorous stirring for 30 min. This dispersion, together with 0.10 g of sodium 2-ethylhexyl sulfate (1 wt %, aqueous) was mixed with an organic phase containing AN (5.26 g), MAN (2.83 g), isooctane (2.03 g), BDDMA (0.064 g), and dilauryl peroxide (0.16 g). The mixture was emulsified with a Silverson high-shear mixer (8000 rpm, 45 s). Polymerizations were performed in 50-mL glass reactors (Tynclave from Büchi) under gentle agitation at 62°C for 20 h.

The conversion experiments were conducted in a similar manner. However, a sufficient amount of emulsion for six simultaneous experiments was prepared in one batch and subsequently distributed to the individual reactors before polymerization. Polymerizations were conducted at 62°C for the desired time periods followed by quenching through cooling.

The final dispersions were passed through sieves (20 and 32 μm in pore size) to produce samples with similar average particle sizes to limit the influence of the particle size on the expansion properties.⁶ The fraction collected by the 20-μm sieve was used for further analysis after it was dried at 50°C over night.

Measurements

The expansion properties of the TEMS were determined by thermal mechanical analysis (TMA) with a Mettler Toledo TMA/SDTA 841^e. The samples (0.7 mg) were heated from 30 to 250°C at 20°C/min under a nitrogen atmosphere with a 0.06-N load

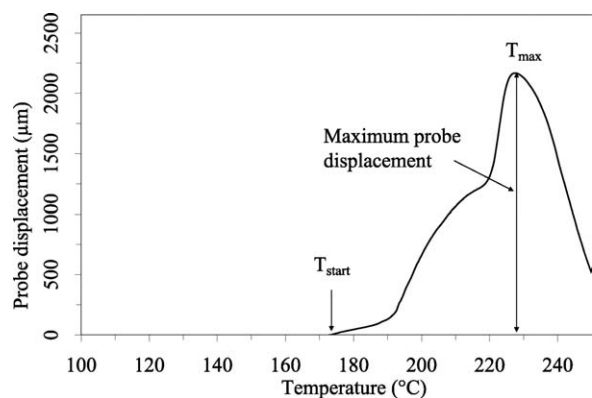


Figure 2 Representative thermogram from the analysis of TEMS by TMA demonstrating the expansion. The probe displacement was a measure of the expansion of the sample.

applied to a probe in contact with the sample within a confined chamber. The determined parameters were the onset temperature of expansion (T_{start}), the temperature at maximum expansion (T_{max}), and the maximum expansion presented as the maximum displacement of the probe (Fig. 2). All of the thermograms and values presented in this study were normalized with respect to the sample amount to enable comparison. T_{start} was defined as the lowest temperature at which the first derivative of the thermogram exceeded 3.

The particle sizes [presented as the volume mean diameter (0.5)] and particle size distributions were determined with a Malvern Mastersizer Hydro 2000 SM light-scattering apparatus.

The monomer conversions were determined by gas chromatography (GC) on an Agilent 6890 instrument equipped with a flame ionization detector (FID) and a CP-SIL 19CB (25 m \times 0.53 mm \times 2.0 μm) column from Varian. The dispersion (0.2 g) was withdrawn directly from the reactor and swollen in *N,N*-dimethyl acetamide (DMA; 10 mL) with 3-hexanone as an internal standard.

Isooctane contents were determined by GC-FID in a similar manner to the monomer conversions. However, a J&W Scientific HP-1 (60 m \times 0.32 mm \times 1.0 μm) column from Agilent Technologies was used, and dry microspheres (0.2 g) were swollen in DMA (10 mL) with cyclohexane as the internal standard.

Gel fractions were determined gravimetrically after repeated extractions with DMA. Microspheres (0.1 g, previously washed with dilute sulfuric acid to remove remaining suspension stabilizer on the microsphere surface¹³) were dispersed in DMA (10 mL) and stirred for 20 h at ambient temperature. The swollen mixture was centrifuged (5000 rpm, 15 min), and the upper solvent phase was removed. The remaining gel was washed three times by the following sequence: the addition of DMA, agitation

(2 h), centrifugation (5000 rpm for 15 min), and removal of the solvent phase. Finally, the gel fractions were determined gravimetrically after drying (ambient temperature overnight followed by 6 h at 135°C).

The polymer content in the samples was determined by thermogravimetric analysis with a Mettler Toledo TGA/SDTA 851^e. The samples were heated from 30 to 650°C at 20°C/min under a nitrogen atmosphere followed by isothermal analysis at 650°C for 15 min in an air atmosphere. The residual at 250°C was considered to represent the polymer content of the samples, whereas the volatile fraction escaping at temperatures up to 250°C mainly consisted of isooctane and minor amounts of residual monomers and moisture.

The particle morphologies were studied with a Philips SEM XL 20 scanning electron microscope. All samples were coated with a thin layer of gold before analysis with a BAL-TEC SCD 005 sputter coater (0.01–0.1 mbar, 230 s at \sim 35 mA). Particles were molded into an epoxy matrix cured at 40°C for 3 days to enable studies of the particle cross sections. These samples were prepared with a LKB ultramicrotome before sputter-coating.

The expansion behavior was studied by optical hot-stage microscopy at 100 \times magnification with a Zeiss optical microscope equipped with a hot-stage attachment from Leitz Wetzlar (Germany). Heating of the sample in the hot-stage equipment was controlled by manual regulation of the power supply at an overall average heating rate of approximately 10°C/min. The temperature was monitored by a thermometer attached to the hot-stage set up.

RESULTS AND DISCUSSION

Effect of the type and amount of crosslinker on the thermal properties

It has earlier been shown that, although the expansion properties of TEMS may be dramatically improved by the addition of a crosslinker, the expandabilities of TEMS with polymer shells crosslinked by 0.2 mol % BDDMA, BDDVE, and BDDA (Fig. 1) are vastly different.⁶ The TEMS containing BDDMA were found to expand well, whereas the ones containing BDDVE or BDDA displayed relatively poor expansion. Also, the expansion was improved by a reduction of the BDDMA concentration.

Because of the improved expansion shown for lower amounts of BDDMA,⁶ a comparison of the crosslinkers was performed with a crosslinker concentration of 0.075 mol %. Compared to the earlier results for 0.2 mol % crosslinker, the expansion was indeed improved for each crosslinker, although significant

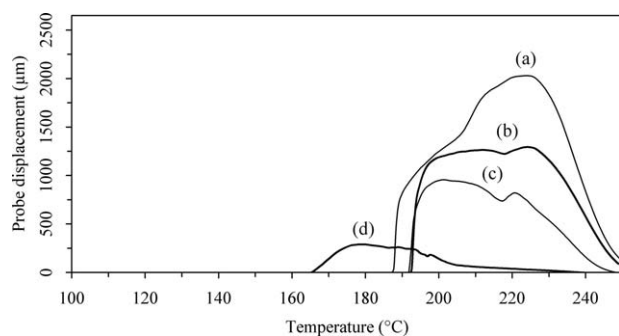


Figure 3 TMA thermograms showing the expansion characteristics of TEMS containing 0.075 mol % of BDDMA, BDDA, or BDDVE in comparison to a sample containing no crosslinker: (a) BDDMA, (b) BDDVE, (c) BDDA, and (d) without crosslinker.

differences in expansion still were observed when the different crosslinkers were compared (Fig. 3).

With these differences in expansion properties verified, a study over a wider range of concentrations (0–0.4 mol %) was conducted to investigate whether the expansion properties in general were better for TEMS containing BDDMA and, if so, to find a plausible explanation for these differences.

When comparing the maximum expansions of TEMS containing different amounts of either crosslinker (Fig. 4), we observed that the highest degree of expansion (i.e., the maximum volume increase of the sample) was reached when 0.05 mol % of crosslinker was used, regardless of the type of crosslinker. However, when comparing the effect of the different crosslinkers, we observed that a higher maximum expansion was obtained with BDDMA than with BDDVE or BDDA.

The optimum BDDMA concentration for maximum expansion seemed to be approximately 0.05–0.1 mol %. When comparing the effect of the different crosslinkers, we found that, when the concentration was 0.4 mol % or below 0.04 mol %, there were no apparent differences in the maximum expansion, regardless of whether BDDMA, BDDVE, or BDDA was used.

The general understanding of these different TMA data was improved by the monitoring of the expansion with an optical microscope coupled to a hot stage. Profound differences in the expansion behavior of particles in the investigated samples were found, although the particle size distribution was relatively narrow in the samples (Table SI in the Supporting Information). A striking feature was that, when the particles expanded, they popped just like popcorn and instantaneously reached maximum expansion. When the expanded particles shrank, they did it fast, regardless of composition. However, the resistance of the particles toward shrinkage varied significantly between samples. Although

all of the samples expanded over a similar temperature range; all of the samples consisted of two fractions of particles with different behaviors during the expansion. There was one fraction in which the particles shrank immediately after they reached their maximum expansion. In the other fraction, the resistance toward shrinkage of the particles was sufficient to retain the volume after expansion; for how long was dependent on the type and amount of crosslinker.

It was difficult to reveal whether the shrinkage of particles originated from a collapse of the polymer shell because it burst or from diffusion of the isooctane through the polymer shell, thus causing the pressure to drop. The observations were also tainted with uncertainties; temperature control as the temperature and heating were adjusted manually, and obviously, the observations were limited by the eye of the observer.

In the sample without crosslinker, the particles were found to expand just as well as those containing crosslinker. However, the expansion of these noncrosslinked particles was scattered over a wider range of temperatures, and although each particle expanded well, they all shrank immediately after they reached maximum expansion. This explained the poor expansion seen in the TMA thermogram [Fig. 3(d)], as there was only a limited number of expanded particles at any time [illustrated in Fig. 5(a)].

The superiority of TEMS containing BDDMA compared to the TEMS containing equal amounts of BDDVE or BDDA or no crosslinker was obvious in the optical hot-stage microscopy experiments as well. A characteristic property of BDDMA-crosslinked TEMS was the excellent resistance toward shrinkage for the vast majority of the expanded

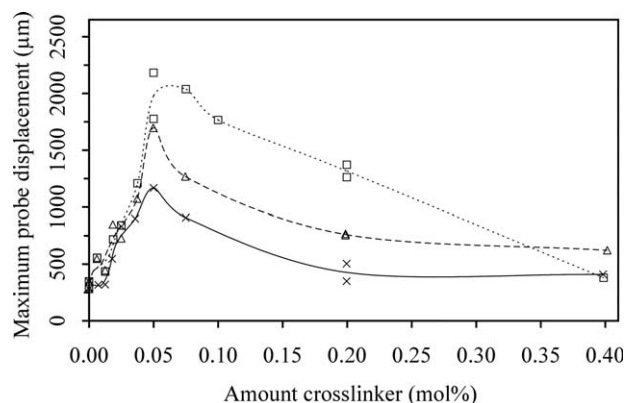


Figure 4 Maximum expansion of TEMS as a function of the crosslinker concentration. To increase the readability of the graph, lines have been inserted to guide the eye. Where there were multiple experiments, the lines pass through the average for each crosslinker at these positions: (···□···) BDDMA, (---△---) BDDVE, and (—×—) BDDA.

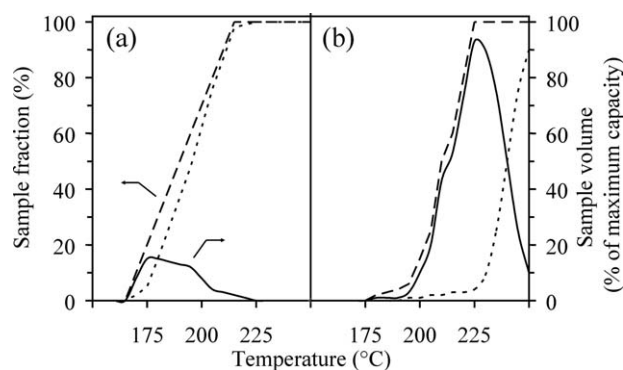


Figure 5 (a) Representation of a sample containing a large fraction of particles shrinking immediately after expansion. (b) Representation of a sample in which the majority of the expanded particles had excellent resistance toward shrinkage: (---) number of particles that expanded, (···) number of particles that collapsed, and (—) resulting total sample volume (100% corresponds to all particles being fully expanded at the same time).

particles. This allowed the overall volume of the sample containing 0.05 mol % BDDMA to increase tremendously because of the large number of simultaneously expanded particles [Fig. 5(b)]. However, as shown in Figure 4, there was a difference in maximum expansion for the duplicate samples containing 0.05 mol % BDDMA. When comparing these samples in the optical hot-stage microscope, we observed that there was a difference in the amount of particles having excellent resistance toward shrinkage, and thus, the corresponding total sample volume detected by the TMA was different.

In the samples containing either 0.2 or 0.4 mol % BDDMA, the large majority of the expanded particles had excellent resistance toward shrinkage. Still, these samples differed in maximum expansion when compared to TEMS containing less BDDMA (Fig. 4). For these samples, we also observed that the total expansion of each particle seemed to be affected. In all of the examined samples containing no more than 0.075 mol % crosslinker, the particles expanded to more than 60 times their original volume as the diameter of the particles increased from approximately 30 to around 120 μm . However, during the expansion of TEMS containing 0.2 mol % crosslinker, the expanded particles were restricted to approximately 100 μm in diameter; this corresponded to approximately 40 times their original volume. The TEMS containing 0.4 mol % BDDMA were only able to expand to approximately 80 μm in diameter (20 \times volume increase). Presumably, the extensive crosslinking of the polymer shell in these particles limited plastic deformation during expansion. Increasing the crosslinking density of the polymer shell also had an apparent effect on the particle morphology (Fig. 6). The particles in the sample containing no crosslinker were nearly spherical with some minor dents; with

increasing crosslinker concentration, these dents increased in size and number, and the particles containing 0.2 mol % were best described to have a raisinlike morphology, whereas the particles containing 0.4 mol % showed no resemblance to a spherical shape. However, all particles became spherical when expanded, regardless of their initial shape.

When BDDVE was used as a crosslinker, the highest degree of expansion was obtained with a 0.05 mol % concentration, although the expansion was not as good as with BDDMA (Fig. 4). In the optical hot-stage microscopy, we observed that a slightly larger fraction of particles shrank immediately upon expansion as compared to when BDDMA was used, and the resistance toward shrinkage of the remaining expanded particles was not as good, although the particles expanded to a similar extent. Also, with BDDA, the highest degree of expansion was obtained with 0.05 mol %, but it was not nearly as good as with BDDMA or BDDVE. In the optical hot-stage microscopy, we observed that a large fraction of particles shrank immediately upon expansion, and the resistance toward shrinkage of the expanded particles was inferior compared to particles containing BDDMA or BDDVE.

T_{max} depends not only on the crosslinking but also on several other parameters, such as monomer composition of the polymer shell, particle size, and type, and amount of the blowing agent is just as important.^{6,16} In this particular system, there seemed to be an upper limit in T_{max} around 225°C, which was nearly 45°C higher than without crosslinker (Fig. 7). The highest T_{max} was reached with 0.05 mol % crosslinker, regardless of type. Interestingly, this was the same concentration that gave the best expansion (Fig. 4).

The resistance of the expanded particles toward shrinking was obviously important for T_{max} . For instance, the dramatic drop seen in T_{max} when the BDDA content was increased from 0.05 to 0.075 mol % (Fig. 8) originated from a large increase in the fraction of particles shrinking immediately upon expansion. T_{max} seemed to be less affected by increasing amounts of BDDMA and BDDVE, although too a high crosslinker content was detrimental for T_{max} . Also, T_{max} varied significantly between repeated analyses for some samples, especially for TEMS with a very flat TMA thermogram, as exemplified in Figure 3(b).

T_{start} was also affected by the crosslinking (Fig. 9). An increase of about 20°C was obtained by the addition of crosslinker compared to when no crosslinker was added. One interesting observation was that a higher T_{start} was obtained with BDDVE or BDDA as a crosslinker compared to BDDMA. This was especially apparent at crosslinker concentrations of 0.2 mol % and above, where T_{start} decreased for TEMS

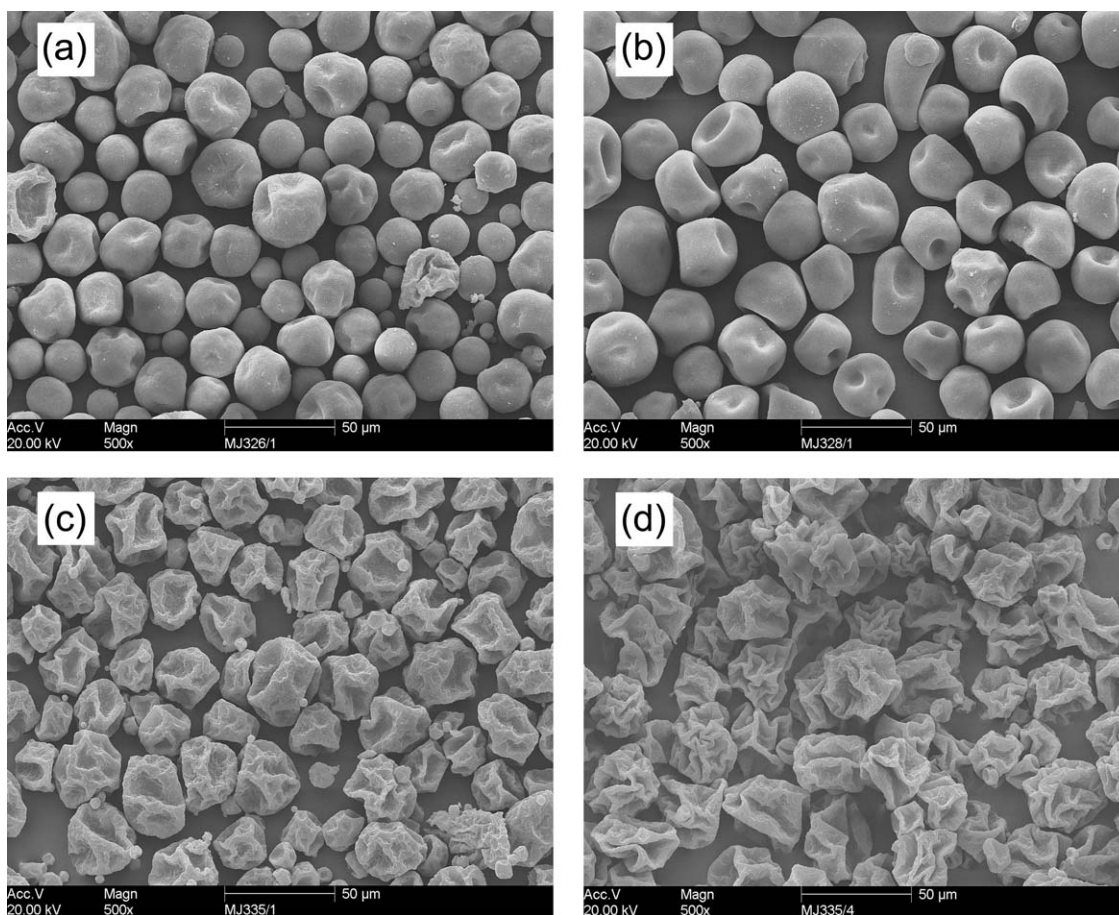


Figure 6 Scanning electron microscopy images showing the influence of the BDDMA concentration on the particle morphology: (a) no crosslinker and (b) 0.05, (c) 0.2, and (d) 0.4 mol %.

containing BDDMA, whereas it remained virtually unaffected for samples containing BDDVE or BDDA (Fig. 9).

In optical hot-stage microscopy, we observed that noncrosslinked particles expanded over a wide temperature range (nearly 50°C). The introduction of crosslinks in the polymer shell not only shifted this

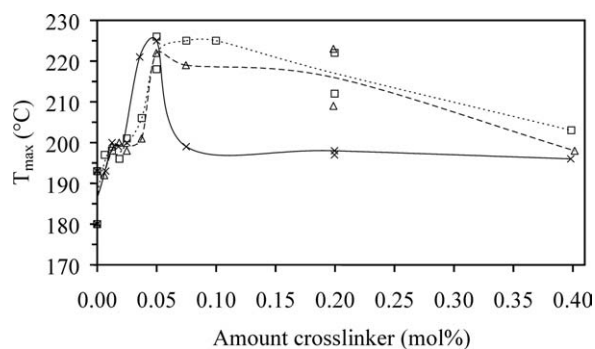


Figure 7 T_{\max} as a function of the crosslinker concentration. To increase the readability of the graph, lines have been inserted to guide the eye. Where there were multiple experiments, the lines pass through the average for each crosslinker at these positions: ($\cdots\Box\cdots$) BDDMA, ($- \triangle -$) BDDVE, and ($- \times -$) BDDA.

temperature range upward, but it also seemed to narrow the temperature span in which the particles began to expand.

The results show that crosslinking of the polymer shell had a profound impact on the expansion properties of TEMS. Therefore, the gel fraction in all samples was determined to gain a deeper understanding of the influence of the crosslinker type and concentration. This was conducted gravimetrically after the

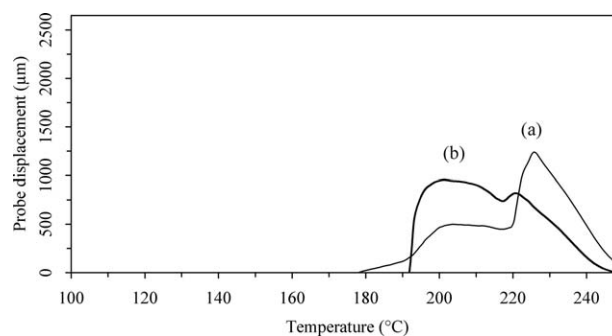


Figure 8 TMA thermograms of TEMS containing 0.05 and 0.075 mol % BDDA displaying the large differences in T_{\max} caused by variations in the collapsing mechanism of the particles: (a) 0.05 and (b) 0.075 mol %.

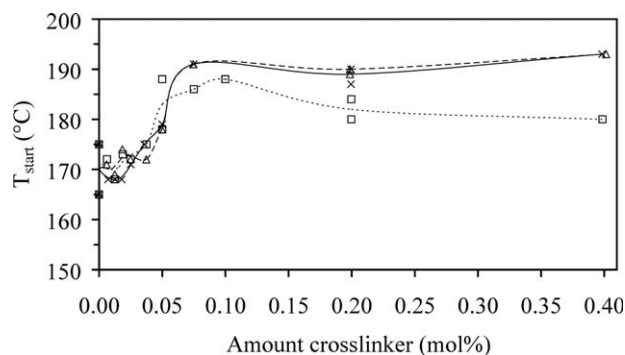


Figure 9 T_{start} as a function of the crosslinker concentration. To increase the readability of the graph, lines have been inserted to guide the eye. Where there were multiple experiments, the lines pass through the average for each crosslinker at these positions: ($\cdots\square\cdots$) BDDMA, ($- \Delta -$) BDDVE, and ($- \times -$) BDDA.

noncrosslinked free polymer was removed in the polymer shell by repeated extractions with DMA.

Below 0.05 mol %, there were significant differences in the gel fraction, where the lowest values were obtained with BDDMA, followed by BDDVE and BDDA in increasing order (Fig. 10). At the lowest concentrations investigated in this study, no gel fraction could be isolated for BDDMA or BDDVE, but around 0.01 mol %, a gel fraction could be detected with all crosslinkers, although it was about 30 wt % larger with BDDA than with BDDMA. This difference in gel fraction diminished as the crosslinker concentration increased, and when the crosslinker concentration reached 0.05 mol %, no significant differences in the gel fractions were observed for the different crosslinkers. Clearly, the gel fraction alone could not explain the differences in expansion obtained with the different crosslinkers.

One obvious reason behind the different gel fractions observed for the different crosslinkers could have been differences in the monomer conversion, which resulted in different yields of polymer. However, the monomer conversions in these experiments were similar and could, therefore, not explain the differences in gel fraction at low crosslinker concentrations. A plausible explanation may be presented on the basis of the following assumptions:

1. The reactivity of the vinyl groups in the crosslinkers was similar to the reactivity of the vinyl groups of monofunctional monomers, with structures resembling those of the crosslinkers (Fig. 1).
2. The reactivity of both vinyl groups in the crosslinkers was equal.

The reactivity of the AN and MAN radicals toward MMA was relatively high compared to EVE

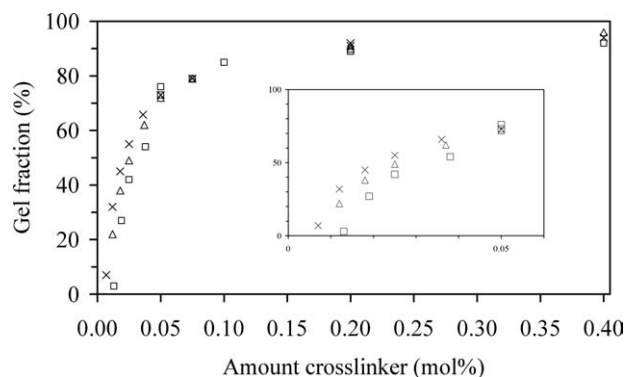


Figure 10 Gel fractions in the polymer shell of microspheres containing various amounts of BDDMA, BDDVE, or BDDA as the crosslinker. Inserted is an enlargement covering the region of 0–0.05 mol % crosslinker. (\square) BDDMA, (Δ) BDDVE, and (\times) BDDA.

and MA, according to the r_1 values or these monomer pairs (Table I). Consequently, we could assume that BDDMA was consumed early in the polymerization.¹⁹ This implicates that a small fraction of polymer had a relatively high amount of BDDMA incorporated, whereas the average chain length between the crosslinking points was relatively low. As a result, the gel fraction could be expected to be low at low BDDMA concentrations.

In contrast, the reactivities of the AN and MAN radicals toward MA were lower compared to the reactivity toward MMA (Table I), why it was reasonable to assume that the incorporation of BDDA was slower during the polymerization. This would result in a polymer having a higher molecular weight between the crosslinks, and thus, a larger weight fraction of the polymer was crosslinked at low BDDA concentrations. The reactivity of the AN radical toward BDDVE could be expected to be higher than toward BDDA but lower than toward BDDMA, whereas the MAN radical could be expected to have a low reactivity toward both BDDVE and BDDA (Table I). Therefore, a faster network formation might be expected with BDDVE than with BDDA but slower than with BDDMA.

TABLE I
Reactivity ratios (r_1 and r_2) for the Monomers Used in this Study as Calculated by the Patterns of the Reactivity Scheme²⁰

Monomer 1	Monomer 2	r_1	r_2
AN	MAN	0.42	1.67
AN	MMA	0.16	1.33
AN	MA	1.21	0.85
AN	EVE	0.67	0.06
MAN	MMA	0.63	0.85
MAN	MA	2.34	0.49
MAN	EVE	10.9	0.05

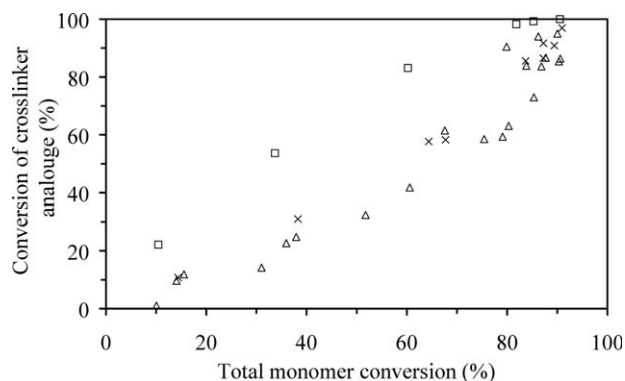


Figure 11 Conversion of the crosslinker analogues added to the system to study the incorporation into the polymer shell: (□) MMA, (△) EVE, and (×) MA.

Polymer shell formation during polymerization

To deepen the understanding of the polymer shell formation during polymerization, we mimicked the incorporation of the crosslinkers by monitoring the conversion of monofunctional monomers with structures resembling those of the crosslinkers (Fig. 1). Thus, 1 mol % of the crosslinker analogue (on the basis of the total amount of monomer and crosslinker) was added to a system containing 0.05 mol % crosslinker. MMA was added to the system containing BDDMA, EVE to the system containing BDDVE, and MA to a system containing BDDA. Polymer shell formation is an *in situ* process, for which even minor alterations in the system can affect the thermal properties and particle morphology.^{6,13} However, we assumed that the addition of 1 mol % of these monomers did not significantly affect the properties of the TEMS or the conversions of AN, MAN, and crosslinker during polymerization.

The conversion data determined by GC during polymerization showed that MMA was consumed at a much higher rate than EVE and MA (Fig. 11) and that after 12 h, 98% of the MMA was incorporated into the polymer. This was expected, on the basis of the previous discussion, that is, the high reactivity data of both AN and MAN radicals toward MMA (Table I). In the experiments involving EVE, we encountered unexpected problems with reproducibility, and it was, therefore, difficult to distinguish the differences in the conversion rate between EVE and MA. The monomer conversion varied significantly between repeated experiments, not only for EVE but also for AN and MAN. However, whereas the conversion of EVE varied throughout the study, the conversion of AN and MAN primarily varied in the samples collected after 9 h of polymerization. Although a thorough investigation was conducted to prevent the problems, we were not able to fully understand the origin of these variations.

The high reactivity of the radicals involved in the polymerization toward BDDMA compared to BDDVE or BDDA was corroborated by the gel fractions in samples collected at different conversions. As shown in Figure 12, the gel fraction was over 70% already after 3 h of polymerization with 0.05 mol % BDDMA as crosslinker, although the total monomer conversion was only around 10%. As the polymerization proceeded and the conversion increased, the gel fraction was fairly stable between 70 and 80 wt %. In our opinion, these data confirmed that BDDMA was incorporated early in the polymerization. However, because the effect on the gel fraction with increasing monomer conversion was minimal, there must have been unreacted pendant groups in the polymer available for crosslinking even at high conversions. If not, the gel fraction would have passed through a maximum as polymer formed beyond this point would have not been incorporated in the gel phase.

The gel fraction at low monomer conversion in systems containing 0.05 mol % crosslinker shows a different behavior with BDDVE and BDDA when compared to BDDMA (Fig. 12). It was apparent that the reactivity of these crosslinkers was lower and that the polymer was crosslinked later in the process. However, these differences in gel fraction diminished as the conversion increased, and no apparent differences in the gel fraction were detected as the conversion exceeded approximately 50% in the system containing BDDVE and nearly 70% in the system containing BDDA.

It was obvious that the timing of incorporation of crosslinking in the polymer shell was very important when we studied the evolution of the expansion properties during polymerization (Fig. 13). These properties differed significantly with the different crosslinkers, although the monomer conversions and

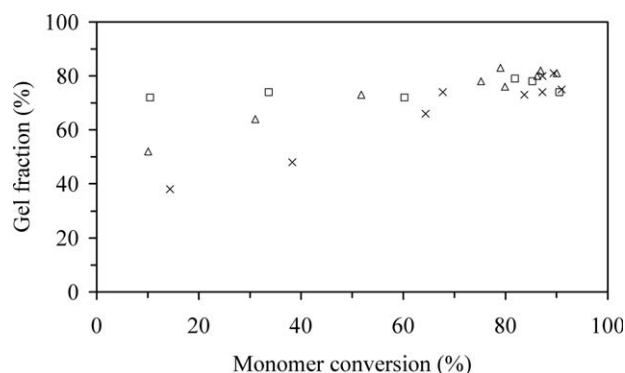


Figure 12 Gel fraction as a function of total monomer conversion during the polymerization for up to 20 h with 0.05 mol % BDDMA, BDDVE, or BDDA as the crosslinker. The crosslinker analogue (1 mol %) with a structure resembling that of the crosslinker were added in these experiments: (□) BDDMA, (△) BDDVE, and (×) BDDA.

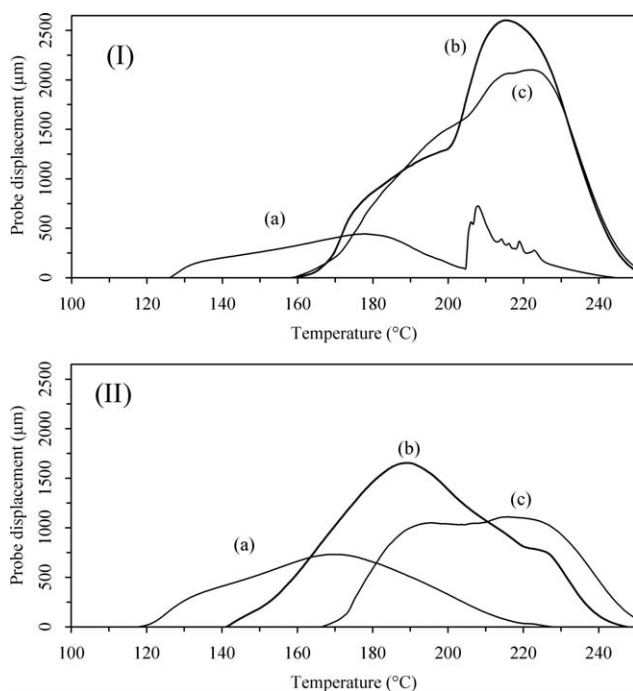


Figure 13 Evolution of the expansion properties with the polymerization time and conversion, as demonstrated by TMA for TEMS containing (I) 0.05 mol % BDDMA and (II) 0.05 mol % BDDVE. The monomer conversion and gel fraction were approximately the same in the corresponding samples: (a) 50–60% conversion after 9 h, (b) 80% conversion after 12 h, and (c) 90% conversion after 20 h.

gel fractions were approximately the same. The TEMS collected after 9 h of polymerization were beginning to expand, although the expansion was poor. T_{start} was very low at this stage and close to the T_g of the polymer forming the particle shell (T_g was approximately 105°C according to the Fox equation²¹). When the conversion reached 80% after 12 h, there was no doubt of the superiority of BDDMA. The expansion was by far the best with BDDMA, and T_{start} was increased by more than 20°C (Fig. 13).

We believe that this was due to a higher polymer strength²² in the shell being crosslinked with BDDMA at this stage of the polymerization. Furthermore, the ductility of the polymer shell containing BDDMA was better suited for good expansion. When the yield stress of the polymer shell was overcome by the internal pressure during heating, the shell was biaxially extended as the particle expanded. However, the stress endured by the polymer shell during expansion was not static because the large volume increase affected the internal pressure of the microspheres. The high expansion capability of TEMS with BDDMA as a crosslinker and the observation by optical hot-stage microscopy that the resistance toward shrinkage of these particles was good suggest that the expansion was not limited by a rupture of the polymer shell. The expansion of

these particles was more likely limited by either too low an internal pressure or the diffusion of the encapsulated isooctane through the thin shell of the expanded particle.

For the BDDVE sample, the polymer strength improved significantly when the polymerization time was extended from 12 to 20 h, as shown by the 20°C increase in T_{start} (Fig. 13). According to Figure 12, the gel fraction did not change significantly during this time period; this suggested that there were no big changes in the crosslinking density. However, the conversion of EVE (Fig. 11) increased rapidly during the late stages of polymerization; this suggested that the incorporation of BDDVE continued after 12 h of polymerization, which explained the observed increase in T_{start} . On the other hand, the expansion capability was negatively affected; this indicated that the polymer shell was not as ductile with BDDVE as with BDDMA.

It was not only the crosslinking of the polymer shell that varied during the polymerization. Previously, we showed that the isooctane droplet was encapsulated early during the polymerization process because the polymer rapidly precipitated from the monomer solution and arranged at the droplet interface.¹³ Subsequently, the polymer shell was built up from the outside in. Furthermore, there was a drift in the polymer composition as the polymerization proceeded because MAN was more reactive than AN (Table I) and was, therefore, consumed faster than AN (Fig. 14). We believe that this is another key factor for achieving excellent expansion properties in TEMS. When BDDMA was used as a crosslinker, the outer parts of the polymer shell consisted of mostly amorphous crosslinked MAN-rich copolymers. However, when most of the MAN was

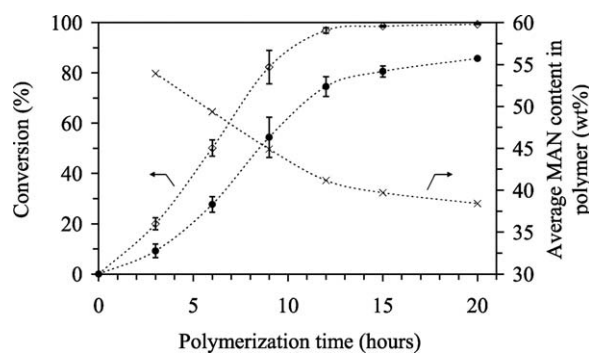


Figure 14 Average conversions of AN and MAN in experiments in which 1 mol % crosslinker analogue were added to the system before polymerization. Also presented in the figure is the drift in the polymer composition depending on the monomer conversion. To increase the readability of the graph, lines have been inserted to guide the eye: (•••••) AN, (•••◇•••) MAN, and (•••×•••) average MAN content (by weight) in the polymer shell.

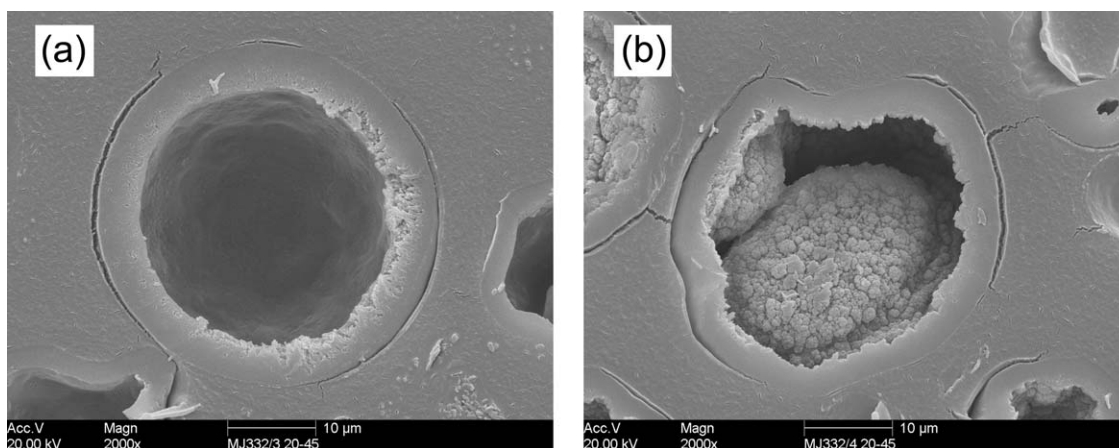


Figure 15 Scanning electron microscopy images of particle cross sections of TEMS containing 0.05 mol % BDDMA and 1 mol % MMA at different total monomer conversions: (a) 60% conversion after 9 h of polymerization and (b) 82% conversion after 12 h of polymerization.

consumed, the AN content in the polymer being formed gradually increased. When BDDVE or BDDA was used as a crosslinker instead of BDDMA, the initial MAN-rich copolymer was less crosslinked, and instead, more crosslinks were incorporated in the later stages of the polymer shell formation. Apparently, this was less effective when it came to improving the expansion properties.

In the final stage of the polymerization (>80% monomer conversion), noncrosslinked polyacrylonitrile were mainly formed. Because polyacrylonitrile is a semicrystalline polymer, we assumed that the crystalline domains were incorporated into the polymer shell; this, thereby, affected important parameters, such as the mechanical and barrier properties of the shell. The internal morphology of the particle shell was changing at this stage of the polymerization, altering from a smooth surface into a surface with pronounced topography (Fig. 15). Apparently, all of these different steps in the polymer shell formation affected the final properties of the TEMS. According to our findings, the reactivities of the AN and MAN radicals toward the three different crosslinkers were crucial for the polymer characteristics and, thus, the resulting expansion.

CONCLUSIONS

This study showed that more desirable expansion properties in TEMS were obtained when the polymer shell was crosslinked with 0.05–0.1 mol % (on the basis of the monomer and crosslinker) BDDMA compared to when no crosslinker or when BDDVE or BDDA was used.

All particles expanded to a similar extent when no or up to 0.2 mol % crosslinker was added, regardless

of type, and the behavior of the expanded particles differed, depending on the crosslinking of the polymer shell. Some particles shrank immediately upon expansion, whereas others were more resistant and remained expanded. With no crosslinker added, all particles shrank immediately upon expansion. With 0.05–0.1 mol % BDDMA, the particles exhibited excellent resistance toward shrinkage, and only a limited number of particles shrank immediately upon expansion. When BDDVE was used instead of BDDMA, the resistance toward shrinkage was not as good, and the fraction of particles shrinking immediately increased. With BDDA, this was even more pronounced.

The proposed reason for these observations was that the different reactivities of the radicals involved in the polymerization toward the crosslinkers affected the incorporation of the crosslinker in the polymer and, thus, the mechanical properties of the particle shells.

References

1. Morehouse, D. S. J.; Tetreault, R. J. U.S. Pat. 3,615,972 (1971).
2. Lundqvist, J. Eur. Pat. 0,486,080 B1 (1996).
3. Yokomizo, T.; Tanaka, K.; Niinuma, K. Jpn. Pat. 9,019,635 (1997).
4. Kron, A.; Sjögren, P.; Bjerke, O. International Patent application WO2001/083100A1 (2001).
5. Ejiri, T. Eur. Pat. 1,964,903 A1 (2008).
6. Jonsson, M.; Nordin, O.; Larsson Kron, A.; Malmström, E. *J Appl Polym Sci*, 2010, 117, 384.
7. Jönsson, L. Proceedings of Blowing Agents and Foaming Processes. Rapra Technology: Munich, Germany, May 2006.
8. Jönsson, L.; Rosskothén, K. R. *Kunststoffe* 2003, 93, 40.
9. Kron, A.; Jönsson, L.; Elfving, K.; Ahmad, M. Proceedings of High Performance Fillers; Rapra Technology: Cologne, Germany, 2005.
10. Ahmad, M. *J Vinyl Addit Technol* 2001, 7, 156.
11. Tomalino, M.; Bianchini, G. *Prog Org Coat* 1997, 32, 17.

12. Nishiyama, Y.; Uto, N.; Sato, C.; Sakurai, H. *Int J Adhes Adhes* 2003, 23, 377.
13. Jonsson, M.; Nordin, O.; Malmström, E.; Hammer, C. *Polymer* 2006, 47, 3315.
14. Jonsson, M.; Nyström, D.; Nordin, O.; Malmström, E. *Eur Polym J* 2009, 45, 2374.
15. Huang, Y. Ph.D. thesis; Lehigh University, 2004.
16. Kawaguchi, Y.; Oishi, T. *J Appl Polym Sci* 2004, 93, 505.
17. Kawaguchi, Y.; Itamura, Y.; Onimura, K.; Oishi, T. *J Appl Polym Sci* 2005, 96, 1306.
18. Hu, J.; Zheng, Z.; Wang, F.; Tu, W.; Lin, L. *Pigment Resin Technol* 2009, 38, 280.
19. Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2004; p 523.
20. Jenkins, A. D.; Jenkins, J. In *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999. p. II-321.
21. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
22. van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1997; p 413.