# Increased Onset Temperature of Expansion in Thermally Expandable Microspheres Through Combination of Crosslinking agents

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**ABSTRACT:** Free-radical suspension polymerization was used to synthesize thermally expandable microspheres (TEMS) in which a poly(acrylonitrile-co-methacrylonitrile) shell encapsulates isooctane. TEMS were prepared with 1,4-butanediol dimethacrylate (BDDMA), in combination with 1,4-butanediol divinyl ether (BDDVE), diallyl carbonate (DAC), or allyl methacrylate, as crosslinkers. It was found that a significant increase in the onset temperature of expansion ($T_{start}$) could be obtained when a combination of BDDMA and BDDVE or DAC was used, compared to when only BDDMA was used as crosslinker. The expansion capacity of the TEMS was excellent when BDDMA and DAC were combined. One benefit of the increased $T_{start}$ was demonstrated when poly(vinyl chloride)-plastisols containing TEMS could be cured at higher temperatures without premature expansion. The differences in expansion obtained with different combinations of crosslinkers originate from the difference in reactivity of the vinyl-functionalities of the crosslinkers, which regulate the incorporation of the crosslinker into the polymer and thereby, the mechanical properties of the microsphere shell. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 369–375, 2011

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

## INTRODUCTION

Thermally expandable microspheres (TEMS), which were developed in the early 1970s by Dow Chemical Co.,[1] are core/shell particles with a typical diameter of 5–50 μm, in which a thermoplastic polymer shell encapsulates a volatile hydrocarbon.[2–5] When heated above the glass transition temperature ($T_g$) of the polymer shell, the particles expand as the hydrocarbon vapor pressure overcomes the yield strength of the polymer shell.[6] Vaporization of the hydrocarbon generates a tremendous volume increase, which is retained upon cooling because of plastic deformation of the polymer shell. As a result, the density of the microspheres can be reduced from about 1100 kg m$^{-3}$ to ~ 30 kg m$^{-3}$.

TEMS are used by the industry for many different purposes, for example, weight reduction, material savings, or tailoring of product properties such as thermal-, sound-, and electrical insulation.[7] For instance, TEMS are used in printing inks to enable 3D textures on wall papers and to tailor surface properties such as matting or antislip. Material savings, improved corrosion resistance, and noise reduction are all benefits of using TEMS in under body coatings for cars.[8] Thermoplastic materials such as poly(vinyl chloride) (PVC), thermoplastic elastomer, polyethylene, polypropylene, and thermoplastic polyurethane can be foamed with TEMS in conventional polymer-processing methods, such as extrusion or injection molding.[9] Because the microspheres are available as dry powder or masterbatch, no special equipment is needed for the manufacturing of foamed products.[7]

In the scientific literature, there are only a few studies regarding the synthesis and properties of TEMS.[6,10–15] A PhD thesis by Huang[11] covers the synthesis of TEMS expanding at temperatures below and around 100°C, with an emphasis on particle formation and expansion properties. Kawaguchi and Oishi[15] investigated the influence of crosslinking of the polymer shell on the expansion properties and were able to correlate the expansion properties to the gel fraction and swelling ability of the polymer shell. Kawaguchi and Oishi with coworkers[13] have also been able to improve the thermal properties of

TEMS, by altering the monomer composition of the polymer shell. A paper from Kawaguchi in collaboration with Ohshima and coworkers[14] investigates the correlation between the viscoelastic properties of the polymer shell and the expansion properties of the TEMS. Recently, Hu et al.[10] published a paper on the synthesis of TEMS utilizing nitrogen from the decomposition of encapsulated *p*-toluenesulphonyl-hydrazide to expand the microspheres. Our research group has studied the polymer shell formation during polymerization with respect to monomer composition and polymerization temperature and were able to determine differences in the shell forming mechanism depending on the polymerization parameters.[12] Furthermore, our research group just recently investigated the properties of TEMS expanding at temperatures around 200°C with respect to the amount and structure of the encapsulated hydrocarbon as well as crosslinking of the polymer shell.[6,16] It was found that the expansion properties of the microspheres differ significantly depending on the crosslinker structure, when comparing 1,4-butanediol dimethacrylate (BDDMA), 1,4-butanediol divinyl ether (BDDVE), and 1,4-butanediol diacrylate (BDDA).[6,16] BDDMA, which is incorporated early during the polymerization, provides superior expansion properties compared to BDDVE or BDDA, which are incorporated later. Presumably, the difference in reactivity of the radicals in the system toward the different vinyl functionalities of BDDMA, BDDVE, and BDDA affects the crosslinker consumption and, thus, the incorporation into the polymer shell.[16]

Based on our previous findings, the objective of this study has been to elucidate whether the expansion properties can be manipulated by combining crosslinkers having different incorporation rates. Thus, in this study, TEMS have been synthesized with BDDMA as the primary crosslinker in combination with BDDVE, diallyl carbonate (DAC), or allyl methacrylate (AMA) (Fig. 1).

## EXPERIMENTAL

### Materials

Acrylonitrile (Aldrich, >99%), methacrylonitrile (Acros, 99%), BDDMA (Aldrich, 95%), BDDVE (Aldrich, 98%), DAC (Aldrich, 99%), AMA (Aldrich, 98%), isooctane (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), and PVC (PVC P682 from Hydro Polymers AB, Sweden). All chemicals were used as received.
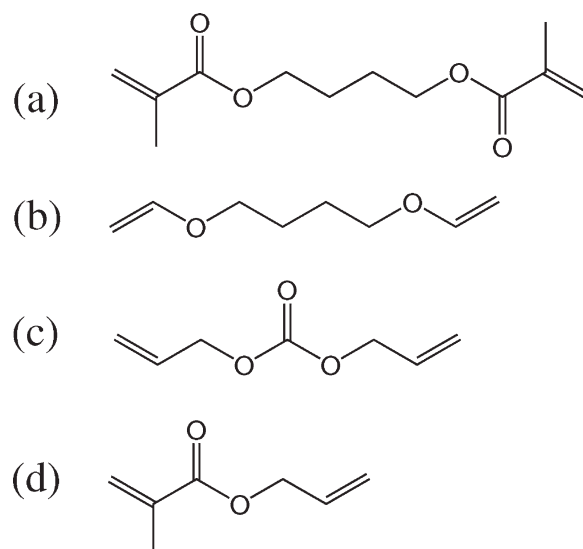
**Figure 1** Structure of crosslinkers used in this study. (a) 1,4-butanediol dimethacrylate (BDDMA), (b) 1,4-butanediol divinyl ether (BDDVE), (c) diallyl carbonate (DAC), and (d) allyl methacrylate (AMA).

## Polymerizations

In a typical experiment, polymerizations were performed according to the general procedure described in Ref. 2. A magnesium hydroxide dispersion was prepared by mixing sodium hydroxide [0.55 g NaOH (s)] with magnesium chloride [1.94 g MgCl$_2$ × 6 H$_2$O (s)] in deionized water (30.0 g) followed by vigorous stirring for 30 min. This dispersion, together with 0.1 g of sodium 2-ethylhexyl sulfate (1% by weight, aq), was mixed with an organic phase containing acrylonitrile (5.26 g), methacrylonitrile (2.83 g), isooctane (2.03 g), BDDMA (0.064 g), DAC (0.015 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 (Tinyclave from Büchi) under gentle agitation at 62°C for 20 h.

After cooling to ambient temperature, the dispersions were fractionized with regards to particle size using sieves (45 and 20 μm in pore size) to limit the influence of the particle size on the expansion properties. Finally, the fraction collected by the 20-μm sieve was dried at 50°C over night.

## Plastisol evaluations

The expansion properties of the microspheres were evaluated in a PVC-plastisol [main components; PVC (100 parts by weight), and diisononylphtalate (60 parts by weight)]. The microspheres (6.4 parts per weight) were gently mixed with the plastisol to minimize air bubbles in the mixture. Draw downs were prepared manually using a film applicator

**TABLE I**
**Amounts of Crosslinkers and Analytical Data for the TEMS Prepared in This Study**

| XL[a] 1 | Mol % | XL[a] 2 | Mol % | Particle size (μm) | PSD[b] | Gel fraction (%) | $T_{start}$ (°C) | $T_{max}$ (°C) | Probe displacement (μm) |
|---|---|---|---|---|---|---|---|---|---|
| – | | – | | 31.4 | 0.7 | 0 | 165 | 180 | 300 |
| BDDMA[c] | 0.075 | – | | 33.7 | 0.7 | 79 | 175 | 225 | 2500 |
| BDDMA | 0.15 | – | | 39.0 | 1.1 | 91 | 175 | 215 | 1500 |
| DAC | 0.075 | – | | 33.5 | 0.7 | 39 | 176 | 194 | 800 |
| DAC | 0.15 | – | | 32.9 | 0.7 | 58 | 188 | 202 | 900 |
| AMA | 0.075 | – | | 34.3 | 0.8 | 77 | 169 | 194 | 1200 |
| AMA | 0.15 | – | | 32.3 | 0.7 | 89 | 176 | 208 | 1000 |
| BDDMA | 0.075 | DAC | 0.075 | 33.5 | 0.7 | 85 | 180 | 225 | 2300 |
| BDDMA | 0.075 | DAC | 0.075 | 35.2 | 0.7 | 85 | 178 | 226 | 2200 |
| BDDMA | 0.075 | DAC | 0.15 | 34.1 | 0.7 | 86 | 189 | 223 | 1700 |
| BDDMA | 0.075 | BDDVE | 0.075 | 35.4 | 0.7 | 90 | 180 | 211 | 1400 |
| BDDMA | 0.075 | BDDVE | 0.15 | 35.2 | 0.7 | 88 | 186 | 211 | 800 |
| BDDMA | 0.075 | AMA | 0.075 | 35.7 | 0.7 | 90 | 174 | 225 | 1500 |
| BDDMA | 0.075 | AMA | 0.15 | 36.4 | 0.8 | 92 | 180 | 222 | 1000 |

[a] Crosslinker.
[b] Particle size distribution, $[D(0.9) - D(0.1)]/D(0.5)$.
[c] Average of five experiments; std. dev.: particle size 1.8 μm, PSD 0.01, gel fraction 0.5%, $T_{start}$ 7°C, $T_{max}$ 1°C, probe disp. 130 μm.

with a fixed gap (500 μm) and subsequently cured for 5 min at 150, 170, and 190°C. Cross sections of the cured films were investigated by scanning electron microscope (SEM) to get a qualitative measurement of any premature expansion of the microspheres. As microsphere bubbles are easily distinguished from artifacts such as air bubbles in the SEM images, the results are conclusive. SEM images with larger magnifications are available in the Supporting Information. The cured PVC/TEMS composites were later foamed by heating at 210°C for 1, 3, and 5 min. The foam densities were determined by Archimedes' principle.

## Measurements

Thermomechanical analysis (TMA) was conducted on a Mettler Toledo TMA/SDTA 841[e]. The samples were heated (30–250°C) at 20°C min^{-1} under nitrogen atmosphere with a 0.06 N load applied to the TMA probe. The determined expansion parameters include the onset temperature of expansion ($T_{start}$), the temperature of maximum expansion ($T_{max}$), and the maximum expansion (presented as the maximum TMA probe displacement). All values and thermograms presented are normalized with respect to sample weight to enable comparison.

Gel fractions were determined gravimetrically after repeated extractions with N,N-dimethyl acetamide (DMA). Dry microspheres (0.1 g, previously washed with dilute sulfuric acid to remove remaining suspension stabilizer) 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; addition of DMA, agitation (2 h), centrifuge (5000 rpm, 15 min), and removal of the solvent phase. Finally, the gel fractions were determined gravimetrically after drying at ambient temperature over night followed by 6 h at 135°C.

The polymer content in the samples was determined by thermogravimetric analysis (TGA), using a Mettler Toledo TGA/SDTA 851[e]. The samples (without suspension stabilizer) were heated (30–650°C) at 20°C min^{-1} under nitrogen atmosphere followed by isothermal analysis (650°C) for 15 min in an air atmosphere. The residual at 250°C was considered to represent the polymer content of the samples, while the volatile fraction escaping at temperatures up to 250°C mainly consists of isooctane but also minor amounts of residual monomers and moisture.

SEM imaging was performed using a Philips SEM XL 20. All samples were coated with a thin layer of gold prior to analysis using a BAL-TEC SCD 005 sputter-coater (0.01–0.1 mBar, 230 s at ∼ 35 mA).

Particle sizes were determined using a Malvern Mastersizer Hydro 2000 SM light scattering apparatus and are presented as the volume mean diameter $D(0.5)$.

## RESULTS AND DISCUSSION

It has been shown earlier that the incorporation rate of the crosslinker into the polymer shell significantly affects the properties of the microspheres.[16] BDDMA is incorporated early in the polymerization compared to, for example BDDVE, because of the high reactivity of BDDMA towards the AN- and MAN-radicals in the system. To the best of our knowledge, there are no studies reported regarding how a combination of two crosslinkers having different
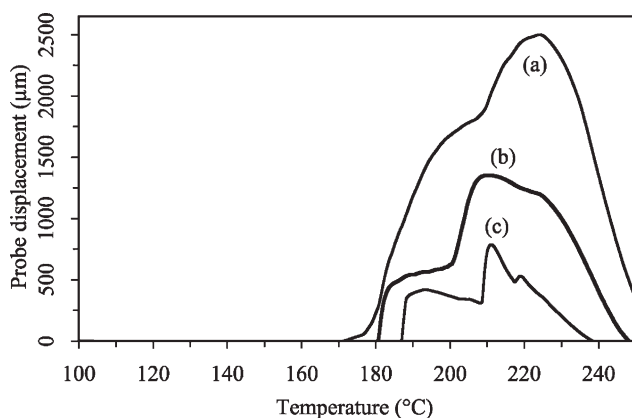
**Figure 2** TMA-thermograms showing the expansion properties of TEMS with different crosslinker combinations. (a) 0.075 mol % BDDMA, (b) 0.075 mol % BDDMA and 0.075 mol % BDDVE, and (c) 0.075 mol % BDDMA and 0.15 mol % BDDVE.

reactivity influences the expansion properties of microspheres. AN have a very low reactivity toward allyl functionalized monomers according to the reactivity data from copolymerization of AN with allyl acetate ($r_1 \sim 7$ and $r_2 \sim 0$).[17] DAC was therefore chosen as an example of a crosslinker, which can be expected to have even lower incorporation rate than BDDVE.

When combining 0.075 mol % BDDMA with 0.075 or 0.15 mol % BDDVE or DAC, $T_{start}$ increases significantly with increasing amount of BDDVE (Table I and Fig. 2) or DAC (Table I, Figs. 3 and 4). However, there are significant differences in expansion behavior between microspheres containing BDDVE or DAC. Although both crosslinkers increases $T_{start}$ to a similar extent, the maximum expansion is impaired with BDDVE, especially at 0.15 mol % (Fig. 2). However, with DAC, there is only a slight decrease in the maxi-
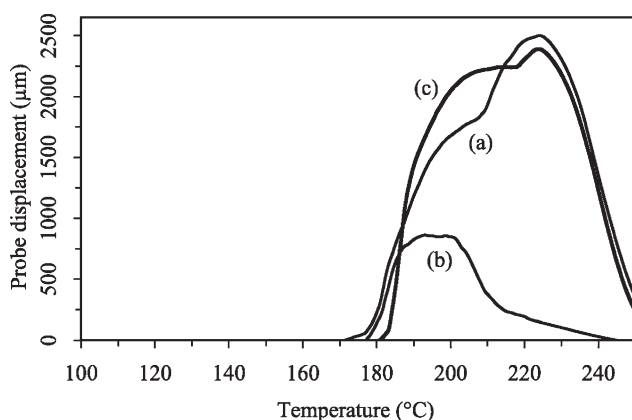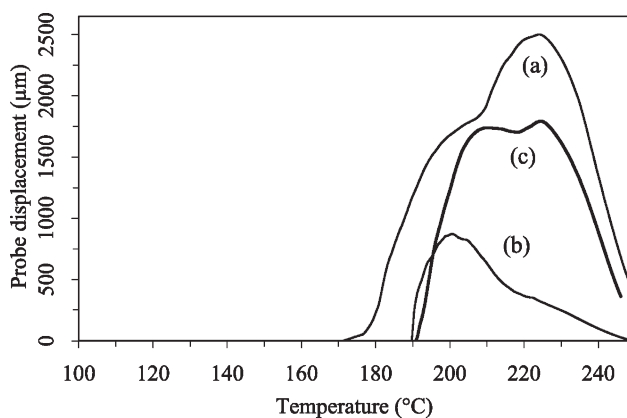


**Figure 4** TMA-thermograms showing the expansion properties of TEMS with different crosslinker combinations. (a) 0.075 mol % BDDMA, (b) 0.15 mol % DAC, and (c) 0.075 mol % BDDMA and 0.15 mol % DAC.

mum expansion compared to the sample containing only 0.075 mol % BDDMA (Figs. 3 and 4). Furthermore, it is obvious from Figure 5 that such expansion properties cannot be obtained simply by increasing the amount of BDDMA to 0.15 mol %.

Microspheres containing 0.075 or 0.15 mol % DAC as the only crosslinker were also prepared and analyzed by TMA. As can be seen from Figures 3 and 4, $T_{start}$ increases with increasing amount DAC, but the maximum expansion is quite poor compared to the corresponding samples containing the combination of DAC and BDDMA.

These results indicate that DAC and BDDMA are incorporated in separate parts of the polymer shell. Also, the ductility of the polymer fraction crosslinked with BDDMA is suggested to be relatively unaffected by the addition of 0.075 or 0.15 mol % DAC, as the expansion capability of these samples are quite good.
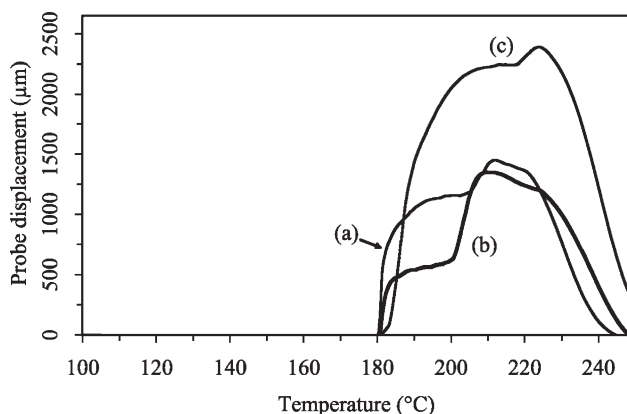


**Figure 3** TMA-thermograms showing the expansion properties of TEMS with different crosslinker combinations. (a) 0.075 mol % BDDMA, (b) 0.075 mol % DAC, and (c) 0.075 mol % BDDMA and 0.075 mol % DAC.



**Figure 5** TMA-thermograms showing the expansion properties of TEMS with different crosslinker combinations. (a) 0.15 mol % BDDMA, (b) 0.075 mol % BDDMA and 0.075 mol % BDDVE, and (c) 0.075 mol % BDDMA and 0.075 mol % DAC.
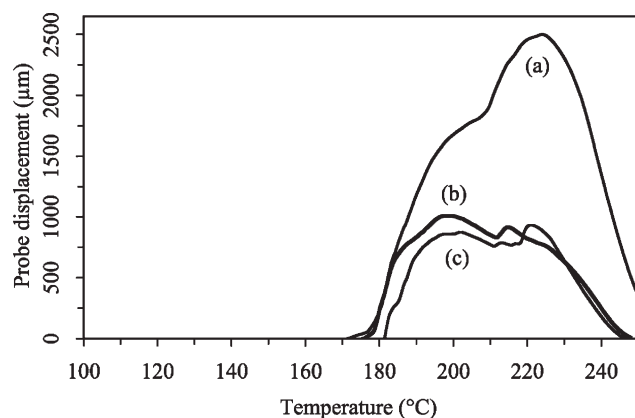
**Figure 6** TMA thermograms showing the expansion properties of TEMS with different crosslinker combinations. (a) 0.075 mol % BDDMA, (b) 0.15 mol % AMA, and (c) 0.075 mol % BDDMA and 0.15 mol % AMA.

When analyzing the effect of the crosslinking on the gel fraction in the polymer shell, it was found that the gel fraction increases nearly 10 wt % by the combination of BDDMA and BDDVE, when compared with TEMS containing 0.075 mol % BDDMA, to constitute around 90% of the polymer shell (Table I). When using DAC in combination with BDDMA, the gel fraction increases about 6 wt %, which indicates that DAC is not incorporated to the same extent as BDDVE or BDDMA. This is also supported by the low gel fractions obtained in the samples containing only DAC as crosslinker (Table I).

AMA was used as crosslinker to further elucidate the difference in incorporation between BDDMA and DAC. This crosslinker combines the functiona-
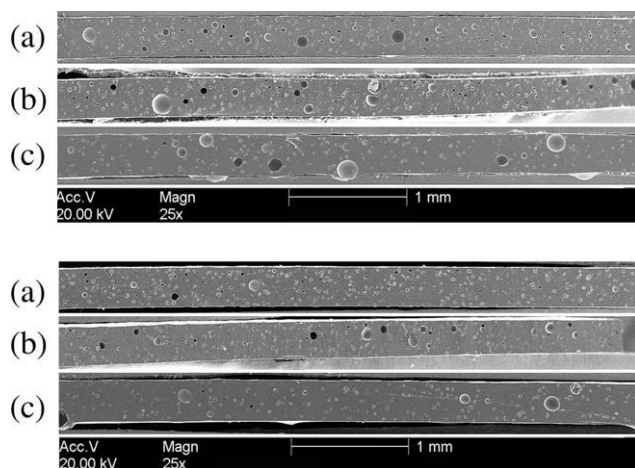


**Figure 7** SEM images showing the cross sections of PVC-plastisols containing TEMS (4 wt %) cured at different temperatures for 5 min. The upper series contain TEMS crosslinked with 0.075 mol % BDDMA and the lower series contain TEMS crosslinked with 0.075 mol % BDDMA and 0.15 mol % DAC. (a) Cured at 150°C, (b) cured at 170°C, and (c) cured at 190°C.
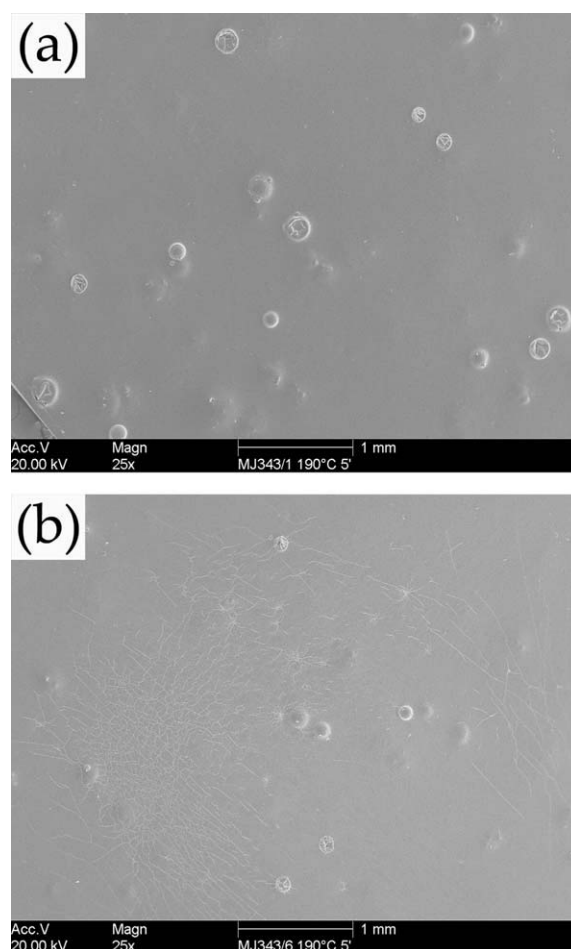


**Figure 8** SEM images revealing the surface roughness of PVC-plastisols caused by premature expansion of TEMS during curing at 190°C for 5 min. (a) TEMS crosslinked with 0.075 mol % BDDMA and (b) TEMS crosslinked with 0.075 mol % BDDMA and 0.15 mol % DAC.

lities of both BDDMA and DAC. It will probably be incorporated into the polymer simultaneously with BDDMA, while it might be expected not to contribute to the crosslinking until much later into the process, based on the assumption that the reactivities of the two different vinyl-functionalities in AMA are similar to the corresponding ones of

**TABLE II**
**Foam Densities of PVC-Plastisols Containing TEMS (4 wt %) After Heating at 210°C**

|  | Foam density (g mL$^{-1}$) | |
|---|---|---|
|  | BDDMA[a] | BDDMA + DAC[b] |
| After curing[c] | 1.15 | 1.15 |
| 1 min at 210°C | 0.50 | 0.49 |
| 3 min at 210°C | 0.37 | 0.42 |
| 5 min at 210°C | 0.37 | 0.43 |

[a] About 0.075 mol %.
[b] About 0.075 mol % BDDMA, 0.15 mol % DAC.
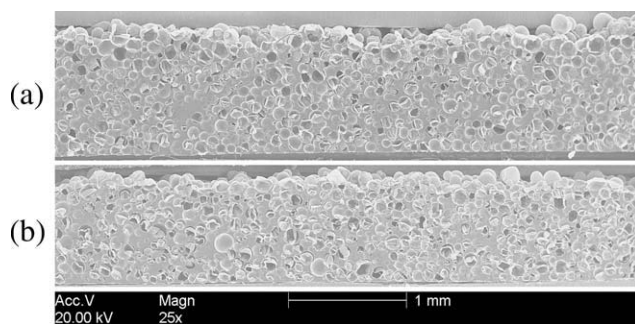[c] Cured at 170°C for 5 min.

**Figure 9** SEM images of the cross section of PVC-plastisols foamed by TEMS showing the closed cell structure. The plastisols have been cured for 5 min at 170°C after which the TEMS have been expanded by heating the plastisols for 3 min at 210°C. (a) TEMS crosslinked with 0.075 mol % BDDMA and (b) TEMS crosslinked with 0.075 mol % BDDMA and 0.15 mol % DAC.

BDDMA and DAC. Furthermore, it is unclear whether the incorporation of AMA into the polymer through the methacrylate moiety affects the reactivity of the allyl moiety. However, it is noticeable that the expansion properties of TEMS containing BDDMA and AMA show no resemblance to those containing BDDMA and DAC; instead the expansion is severely limited (Fig. 6). This further strengthens our belief that the improved expansion properties from the combination of BDDMA and DAC comes from the incorporation of these crosslinkers in separate parts of the polymer shell. BDDMA is mainly incorporated into the amorphous MAN-rich polymer fraction formed early in the polymerization, while DAC, which is incorporated much later, is incorporated into the AN-rich parts of the polymer shell.[16] The significant increase in $T_{start}$ indicates that this AN-rich polymer fraction is important for the yield strength of the polymer shell, while the ductility of the amorphous MAN-rich polymer fraction is crucial for the expansion of the TEMS. Thus, by the proper combination of different crosslinkers in the polymer shell, the properties of the TEMS may be altered.

The benefit of increasing $T_{start}$ is demonstrated when these TEMS are used as foaming agents in a PVC-plastisol. The plastisols can be cured at higher temperatures with low probability of premature expansion of microspheres when TEMS containing the combination of 0.075 mol % BDDMA and 0.15 mol % DAC are used, compared to TEMS containing only 0.075 mol % BDDMA. This is exemplified in Figure 7, in which it can be seen that there are only a few expanded particles in the plastisol containing TEMS (4 wt %) crosslinked with BDDMA and DAC, even after curing for 5 min at 190°C. In the plastisol-containing TEMS crosslinked with BDDMA, there are TEMS beginning to expand even when curing at 170°C for 5 min, and after curing at

190°C, there are numerous expanded TEMS in the plastisol. It is desirable to avoid such premature expansion, because it may cause problems with product quality as exemplified in Figure 8, in which premature expansion of TEMS has affected the surface finish of the plastisols during curing at 190°C. However, it is clearly seen that this is less of a problem in the plastisol containing TEMS crosslinked with BDDMA and DAC. After curing at 170°C for 5 min, the platisol samples were foamed at 210°C to yield fine closed cell structured foams (Table II and Fig. 9). In both samples, the density decreased from 1.15 g mL$^{-1}$ to about 0.4 g mL$^{-1}$. The microspheres containing only BDDMA gives slightly lower densities in the final foamed plastisol, which was expected considering that these microspheres had a higher maximum expansion in TMA.

## CONCLUSIONS

This study shows that the expansion properties of TEMS can be altered by combining crosslinkers having different reactivities toward the radicals in the system. It was found that both high $T_{start}$ and high expansion capacity could be achieved, when a combination of BDDMA and DAC was used as crosslinker.

Based on these results together with our earlier findings,[16] it is suggested that DAC is incorporated late during the polymerization and thereby mainly into the AN-rich parts of the polymer. This influences the yield strength of the polymer shell and increases $T_{start}$. BDDMA is incorporated earlier into the MAN-rich parts of the polymer shell, which influences the ductility of the polymer shell and thereby the expansion capacity of the TEMS.

It was also shown that the increased $T_{start}$ obtained with the combination of BDDMA and DAC is beneficial, because PVC-plastisols containing TEMS could be cured at higher temperatures without premature expansion.

## SUPPORTING INFORMATION

Supporting information containing analytical data associated with this article can be found, in the online version, at wileyonlinelibrary.com/journal/30035/home.

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