

1 **Silica-coated poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing organic**  
2 **phase change materials**

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16

17 **Abstract**

18 Macroporous sorbents differing in size were prepared by the 2,2'-azobis(isobutyronitrile)  
19 (AIBN)-initiated suspension radical polymerization of glycidyl methacrylate and ethylene  
20 dimethacrylate in the presence of an inert porogen. The microspheres were loaded with paraffin  
21 and cetyl alcohol phase change materials (PCMs) and coated with silica by sol-gel method using  
22 trimethoxy(methyl)silane hydrolysate. The energy storing capacity of the PCM-containing  
23 composite particles was monitored by differential scanning calorimetry. Accelerated thermal  
24 cycling tests were carried out to determine the thermal reliability of the microencapsulated  
25 PCMs. Paraffin and cetyl alcohol content in the microcapsules was 42.9 wt.% and 48.9 wt.%,  
26 respectively. The microcomposites with higher PCM content showed correspondingly higher  
27 latent heat storage capacity (melting and solidification enthalpies were 96.1 J/g and 94.5 J/g,  
28 respectively). However, there was low enthalpy change observed after 1000 thermal cycles of  
29 cetyl alcohol-containing capsules, which indicated that PCM leakage from the microspheres was  
30 minimal.

31 **Keywords:** porous poly(glycidyl methacrylate-ethylene dimethacrylate) beads, paraffin, cetyl  
32 alcohol, phase change material, silica shell.

33  
34 **Nomenclature**

35

36 AIBN	2,2'-Azobis(isobutyronitrile)
37 $D_v$	volume mean diameter
38 DSC	differential scanning calorimetry
39 EDMA	ethylene dimethacrylate
40 GMA	glycidyl methacrylate
41 $M_w$	molecular weight
42 PCM	phase change material
43 P(GMA-EDMA)	poly(glycidyl methacrylate-ethylene dimethacrylate) beads
44 P(GMA-EDMA)-CA-Me-SiO <sub>2</sub>	silica covered poly(glycidyl methacrylate-ethylene 45 dimethacrylate) beads containing cetyl alcohol

46	P(GMA-EDMA)-P-Me-SiO <sub>2</sub>	silica covered poly(glycidyl methacrylate-ethylene
47		dimethacrylate) beads containing paraffin
48	PVA	poly(vinyl alcohol)
49	PVP	poly( <i>N</i> -vinyl-2-pyrrolidone)
50	$S_{\text{BET}}$	specific surface area
51	TMMS	trimethoxy(methyl)silane
52	$V_p$	pore volume

53

## 54 **1. Introduction**

55

56 Thermal energy storage has received increasing attention during the past decades due to the  
57 importance of energy saving. Latent heat storage is one of the most efficient ways of thermal  
58 energy storing. The main benefits of latent heat storage compared with that of sensible heat are  
59 the much higher storage density accompanying with a smaller temperature difference between  
60 storing and releasing heat. Phase change materials (PCMs) are used for latent heat storage. Most  
61 promising applications of PCMs are waste heat recovery, solar heating, building energy  
62 conservation and air-conditioning systems. Most of the organic PCMs are non-corrosive and  
63 chemically inert (stable), recyclable and compatible with numerous building materials. They have  
64 desirable cohesion, a high latent heat per unit weight, low vapour pressure, no supercooling, and  
65 offer congruent melting and self-nucleation. They have disadvantages such as low thermal  
66 conductivities, flammability and high changes in volume during phase change. In order to  
67 overcome these problems, their microencapsulation can be an efficient tool. Microencapsulation  
68 is the entrapment of PCMs in natural or synthetic polymer capsules. The advantages of the  
69 microencapsulated PCMs are their protection against the environmental effects, the enhancement  
70 of specific heat-transfer area, and the elimination of the volume change of the PCM during phase  
71 change by providing void space [1].

72 Most frequently applied microencapsulation techniques of organic PCMs are simple  
73 coacervation, *in situ* polymerization of, e.g., methacrylates [1,2], other acrylic polymers [3] or  
74 melamine–formaldehyde [4]. Emulsion methods/phase separation [5,6] and interfacial  
75 coacervation and crosslinking [7] can be also efficient to prepare PCM-containing capsules of  
76 core-shell structure.

77 Organic/inorganic composite form-stable phase change materials combine the advantages of the  
78 inorganic and the organic components [8,9]. The inorganic supporting material provides  
79 structural strength and prevents the leakage of the organic PCM component. Several preparation  
80 methods of the organic/inorganic composite form-stable phase change materials were described.  
81 The most important ones are absorption [8,10], solution intercalation [11] and sol–gel method  
82 [12,13]. Among them, the main benefit of the sol–gel method is the simplicity and low cost.  
83 In the present work, the form-stabilization of PCM was achieved by imbedding cetyl alcohol or  
84 paraffin in porous poly(glycidyl methacrylate-ethylene dimethacrylate) P(GMA-EDMA) beads,  
85 and the leakage of PCM was prevented by a silica shell prepared by sol-gel method. The carrier  
86 beads synthesized from this copolymer by suspension radical polymerization have not been used  
87 as support for PCMs so far. However, Chen et al. [14] covalently bound poly(glycidyl  
88 methacrylate) (PGMA) to poly(ethylene glycol) PCM through the ring-opening crosslinking  
89 reaction of oxirane groups in PGMA and end-carboxyl groups of poly(ethylene glycol).  
90 The main benefits of our prepared form-stable composite is that the porous organic beads provide  
91 shape-stable environment for the PCMs, and due to the capillary forces they are able to keep the  
92 latent heat storing material even in the liquid phase, while the inorganic silica shell inhibits the  
93 leakage that would definitely occur during long term application.

94

## 95 **2. Experimental**

96

### 97 **2.1. Materials**

98 Glycidyl methacrylate (GMA; Aldrich; St. Louis, MO, USA) and ethylene dimethacrylate  
99 (EDMA; Ugilor S.A., France) were distilled before use under reduced pressure. 2,2'-  
100 Azobis(isobutyronitrile) (AIBN; recrystallized from ethanol), [(2-  
101 hydroxypropyl)methyl]cellulose (Methocel 90 HG), (2-hydroxyethyl)cellulose, poly(*N*-vinyl-2-  
102 pyrrolidone) K 90 (PVP;  $M_w = 360,00$ ) and cetyl alcohol (CA) were obtained from Fluka (Buchs,  
103 Switzerland), poly(vinyl alcohol) (PVA; Polyviol W 25/140;  $M_w = 80,000$ ) was from Wacker  
104 (Germany). Trimethoxy(methyl)silane (TMMS) and Tween 20 were from Sigma-Aldrich and  
105 paraffin (P), melting-solidification range 53-55 °C, from Paramo (Pardubice, Czech Republic).  
106 Other chemicals and solvents were purchased from Lachner (Neratovice, Czech Republic).

107

## 108 **2.2. Synthesis of macroporous beads**

109 Macroporous sorbents were prepared in a 10-l reactor equipped with anchor-type stirrer by the  
110 AIBN-initiated suspension radical polymerization of GMA and EDMA using an inert porogen  
111 [15]. Aqueous 0.2 wt.% PVP, 0.2 wt.% hydroxyethyl cellulose and 0.006 wt.% PVA solution (6  
112 l) formed the continuous phase, while the dispersed phase consisted of GMA (480 g), EDMA  
113 (320 g), AIBN (4 g) and porogen. The porogen was composed of the mixture of toluene (885 g)  
114 and 1,2-dichloroethane (315 g) or that of cyclohexanol (1180 g) and dodecan-1-ol (20 g). While  
115 the polymerization employing the first mixture was used for production of large beads (~ 700  
116  $\mu\text{m}$ ), the reaction using the second porogens yielded small beads (~ 150  $\mu\text{m}$ ) due to different  
117 stirring. The reaction mixture was stirred at 90 rpm (large beads) or 150 rpm (small beads) and  
118 heated to 75 °C for 6 h. The resulting beads were washed with water, toluene and methanol to  
119 remove porogens, unreacted compounds, and other soluble admixtures.

120

## 121 **2.3. Loading of phase change materials in the beads and formation of silica shell**

122 It is advantage that macroporous P(GMA-EDMA) beads are hydrophobic, which enables their  
123 wetting with PCM; as a result, the pores are well-filled with cetyl alcohol or paraffin avoiding  
124 thus need of vacuum degassing. Briefly, macroporous beads (2 g) were dispersed in molten cetyl  
125 alcohol (5 g) or paraffin (5 g) which were loaded at 65-100 °C. The PCM-loaded particles were  
126 separated by centrifugation using a stainless sieve to remove free cetyl alcohol or paraffin and  
127 again dispersed in aqueous 0.1 wt.% Methocel 90 HG solution (20 ml) at 70 °C in 50-ml reaction  
128 vessel under stirring with an anchor-type stirrer (500 rpm).

129 The silica shell was formed around the beads to keep PCM inside and to prevent particle  
130 aggregation at elevated temperatures. TMMS (1.36 g; 10 mmol) was thus hydrolyzed in 0.01 M  
131 HCl (0.54 g; 30 mmol) at room temperature to yield  $\text{SiMe(OR)}_3$  hydrolysate. The volume of the  
132 mixture was adjusted to 5 ml by adding distilled water. The TMMS hydrolysate (1 ml) was added  
133 to the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change beads (P(GMA-  
134 EDMA)-PCM), the suspension was stirred at 70 °C for 3.5 h and the product eight times washed  
135 in 0.01 wt.% Tween 20 (100 ml each). Finally, the poly(glycidyl methacrylate-ethylene  
136 dimethacrylate)-phase change material-methyl silica particles (P(GMA-EDMA)-PCM-Me-SiO<sub>2</sub>)  
137 were dried in air. The preparation of beads and the loading of PCMs as well as the formation of  
138 silica shell are drawn in Fig. 1.

139

## 140 **2.4. Characterization methods**

141 Carl Zeiss optical microscope (Germany) was used for the imaging of the particles. The size  
142 distribution of the beads was measured by Mastersizer 2000 (Malvern Instruments, Malvern, UK)  
143 applying laser diffraction method.

144 The specific surface area ( $S_{\text{BET}}$ ) of the microspheres was determined by nitrogen adsorption (77  
145 K) using a Gemini VII 2390 Analyzer (Micromeritics; Norcross, GA, USA). Pore volume was  
146 determined from cyclohexane or 1-chlorododecane regain using centrifugation method [16]. The  
147 PCM content of the beads was calculated after weighing 100 mg of the beads, and extracting the  
148 PCM 3 times from the microcapsules by each 5 ml n-hexane.

149 The thermal properties of the microcapsules compared to the neat PCMs were determined by a  
150 Setaram  $\mu$ DSC3evo differential scanning microcalorimeter. The samples (10.2 mg cetyl alcohol,  
151 12.8 mg paraffin, 17.6 mg of each of the microencapsulated PCM) were weighed into 100  $\mu$ l  
152 aluminium crucibles, and ethylene glycol as a heat transferring medium was added, which  
153 covered the microparticles, and then the system was closed by crimping a cap. The samples were  
154 cycled with a scanning rate of 0.6  $^{\circ}\text{C}/\text{min}$ . The results were processed by the thermoanalyzer's  
155 Calisto Processing (v1.38) software. The corresponding melting/freezing enthalpies and onset  
156 temperatures were determined by the baseline integration method (Tangential sigmoid baseline  
157 type).

158 The covered beads were tested via accelerated thermal cycling in order to study whether they are  
159 capable to retain the PCM after several phase transition. One thermal cycling test included  
160 heating till the complete melting and cooling till the complete freezing of the phase change  
161 materials in the capsules. The tests were performed consecutively up to 1000 thermal cycles by  
162 heating and cooling using a Peltier element. DSC analysis was repeated after the thermal cycling  
163 using Setaram  $\mu$ DSC3evo.

164

## 165 **3. Results and Discussion**

### 166 **3.1. Porosity, size and PCM content**

167 Macroporous sorbents were prepared by the AIBN-initiated suspension radical polymerization of  
168 GMA and EDMA. The mixture of toluene/1,2-dichloroethane and cyclohexanol/dodecan-1-ol  
169 was used as porogen. While the former materials were preferred for preparation of large particles,

170 the latter one was suitable for synthesis of small beads. Copolymerization of GMA (60 wt.%)  
171 with EDMA (40 wt.%) produced particles possessing reactive oxirane groups. Two types of  
172 beads were thus obtained: large P(GMA-EDMA)L and small P(GMA-EDMA)S microspheres.  
173 Both of these beads had moderate specific surface area and pore volume, and these properties did  
174 not show significant differences (Table 1).

175 The P(GMA-EDMA) beads were rather hydrophobic, i.e., compatible (well-wettable) with the  
176 PCMs, which facilitated their fast imbibition, filling of the pores and air displacement thanks to  
177 the low interfacial tension. The large and the small beads were filled with paraffin and cetyl  
178 alcohol PCMs, respectively. After PCM loading, the particles were dispersed in the [(2-  
179 hydroxypropyl)methyl]cellulose solution and via hydrolysis and condensation of silane, a shell of  
180 silica was formed in sol-gel process using TMMS hydrolysate. Both large and small  
181 microcapsules had regular spherical shape (Fig. 2).

182 The large particles loaded with paraffin PCM and covered by silica were 300-1400  $\mu\text{m}$  in size  
183 (average size: 643  $\mu\text{m}$ ), while the small beads with cetyl alcohol and silica shell ranged between  
184 70 and 200  $\mu\text{m}$  (average size: 111  $\mu\text{m}$ ) (Fig. 3, Table 2).

185 Although the specific surface area and the pore volume of large and small beads were very  
186 similar (Table 1), the PCM content of the small beads was substantially higher than that of the  
187 large beads (Table 2). The reason for this finding must be that the cetyl alcohol-copolymer  
188 interaction is more favourable than the adsorption of paraffin to the carrier of the same  
189 composition.

190

### 191 **3.2. DSC analysis**

192

193 Thermal properties of the PCM-containing composites were studied by DSC measurements. The  
194 thermal energy storage capacities of pure paraffin and P(GMA-EDMA)-P-Me-SiO<sub>2</sub> are compared  
195 in Fig. 4a. The melting and crystallizing enthalpies of the P(GMA-EDMA)-P-Me-SiO<sub>2</sub> composite  
196 were found to be 78.0 J/g and 78.8 J/g, respectively, which was slightly lower than the calculated  
197 values according to paraffin content (42.9 wt.%). This difference might be explained by the  
198 thermal isolating effect of the silica shell. The melting and solidifying latent heats of P(GMA-  
199 EDMA)-CA-Me-SiO<sub>2</sub> microcapsules were 96.1 J/g and 94.5 J/g (Fig. 4b), respectively. These  
200 values were a bit lower again related to the ones which can be determined from their PCM

201 content (48.9 wt.%). The latent heat storage capacity of our developed composites is higher than  
202 the form-stabilized PCMs that were prepared from similar types of carriers or with similar  
203 procedures. E.g., the thermal energy storage capacity of poly(ethylene glycol) PCM crosslinked  
204 with PGMA was around 70 J/g [14]. Microencapsulated palmitic acid with titanium dioxide shell  
205 as shape-stabilized thermal energy storage material was formed through a sol-gel process. The  
206 microcapsules melted and solidified with latent heat of 63.3 J/g and 47.1 J/g, respectively [17].

207

### 208 **3.3. Thermal reliability**

209

210 If one would like to use PCM-containing microcapsules for latent heat storage, leakage must be  
211 avoided during the phase change. To analyze the potential leakage, the capsules were 1000 times  
212 heated and subsequently cooled. The heat storage capacity of the PCM-containing capsules was  
213 investigated by DSC before and after the thermal cycles. It was assumed that if the heat capacity  
214 of microcapsules did not change after the thermal cycling test, the PCM did not leak from the  
215 composites. In case of leakage significant decrease of heat capacity could be observed. In  
216 contrast, the melting and crystallizing enthalpies of cetyl alcohol (Fig. 5b) containing composites  
217 decreased only slightly after 1000 heating-cooling cycles, although the heat storage capacity  
218 reduction of silica-covered paraffin-containing beads was not negligible (Fig. 5a). This result  
219 verifies that the cetyl alcohol adsorption is stronger to the copolymer than that of the paraffin, and  
220 the leakage of latter PCM may be higher than acceptable for real use.

221

### 222 **4. Conclusions**

223 Large and small macroporous poly(glycidyl methacrylate-ethylene dimethacrylate) beads were  
224 synthesized by the suspension polymerization technique and imbibed with high amounts of  
225 paraffin and cetyl alcohol phase change materials. The PCM-loaded beads were coated with a  
226 protective shell of silica via sol-gel synthesis using trimethoxy(methyl)silane hydrolysate.  
227 According to the results obtained by differential scanning calorimetry, both composites showed  
228 high latent heat storage capacity. Due to the higher cetyl alcohol content, which was the result of  
229 its higher affinity to the carrier copolymer, larger melting and solidifying enthalpies were  
230 measured in cetyl alcohol containing beads coated by silica compared to those values found for  
231 similar composites but with paraffin phase change material. The beneficial latent heat storage

232 capability of the former beads could be preserved more effectively after the thermal cycling tests.  
233 Nevertheless, it should be emphasized that the used quick thermal cycling test is not appropriate  
234 to model the reliability of the microspheres in long-term (during years) application. In order to  
235 study long-term performance, investigations under longer stress would be useful, which can be  
236 suitable to simulate the real use.

237

## 238 **References**

239

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284

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289

290 Figure captions:

291

292 Fig. 1 Preparation process of the beads

293 Fig. 2 Optical micrographs of P(GMA-EDMA) beads containing paraffin (A) and cetyl alcohol  
294 (B) covered by silica. Squares indicate size of 0.5 mm x 0.5 mm.

295 Fig. 3 Size distribution of cetyl alcohol- (P(GMA-EDMA)-CA) and paraffin loaded (P(GMA-  
296 EDMA)-P) microspheres. Squares indicate size of 0.5x0.5 mm.

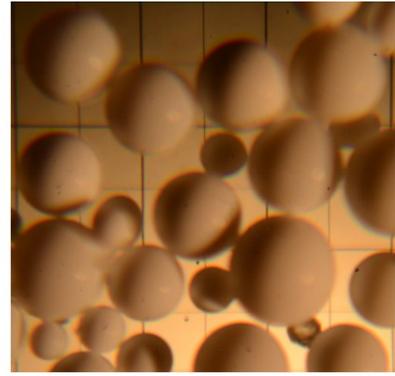
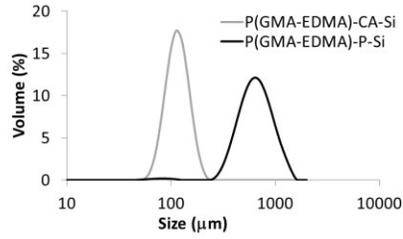
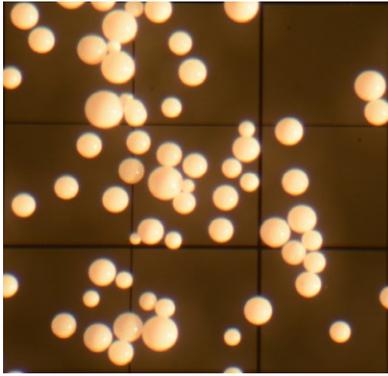
297 Fig. 4 DSC of paraffin and P(GMA-EDMA)-P-Me-SiO<sub>2</sub> (A), as well as cetyl alcohol and  
298 P(GMA-EDMA)-CA-Me-SiO<sub>2</sub> beads (B).

299 Fig. 5 DSC of beads containing paraffin (marked with P) (A) or cetyl alcohol (marked with CA)  
300 before (P(GMA-EDMA)-P/CA-Me-SiO<sub>2</sub>) and after (P(GMA-EDMA)-P/CA-Me-SiO<sub>2</sub>-1000c)  
301 1000 heating-cooling cycles.

302

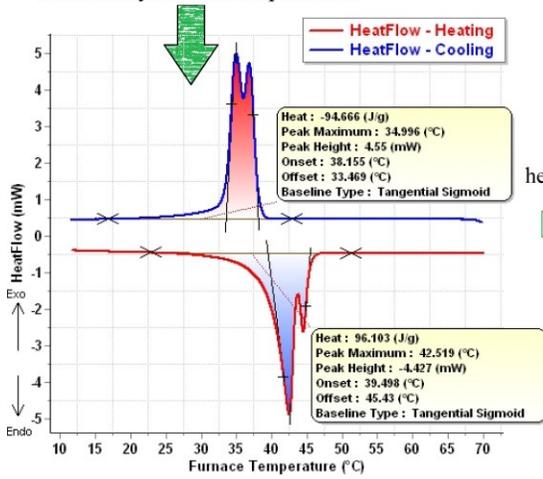
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304 Graphical abstract

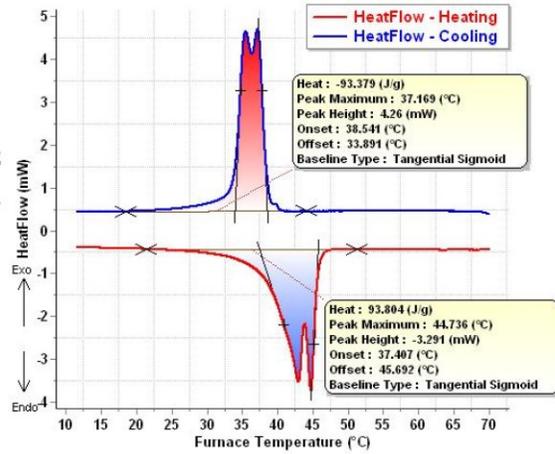


Small beads filled with cetyl alcohol covered by silica nanoparticles

Large beads filled with paraffin covered by silica nanoparticles



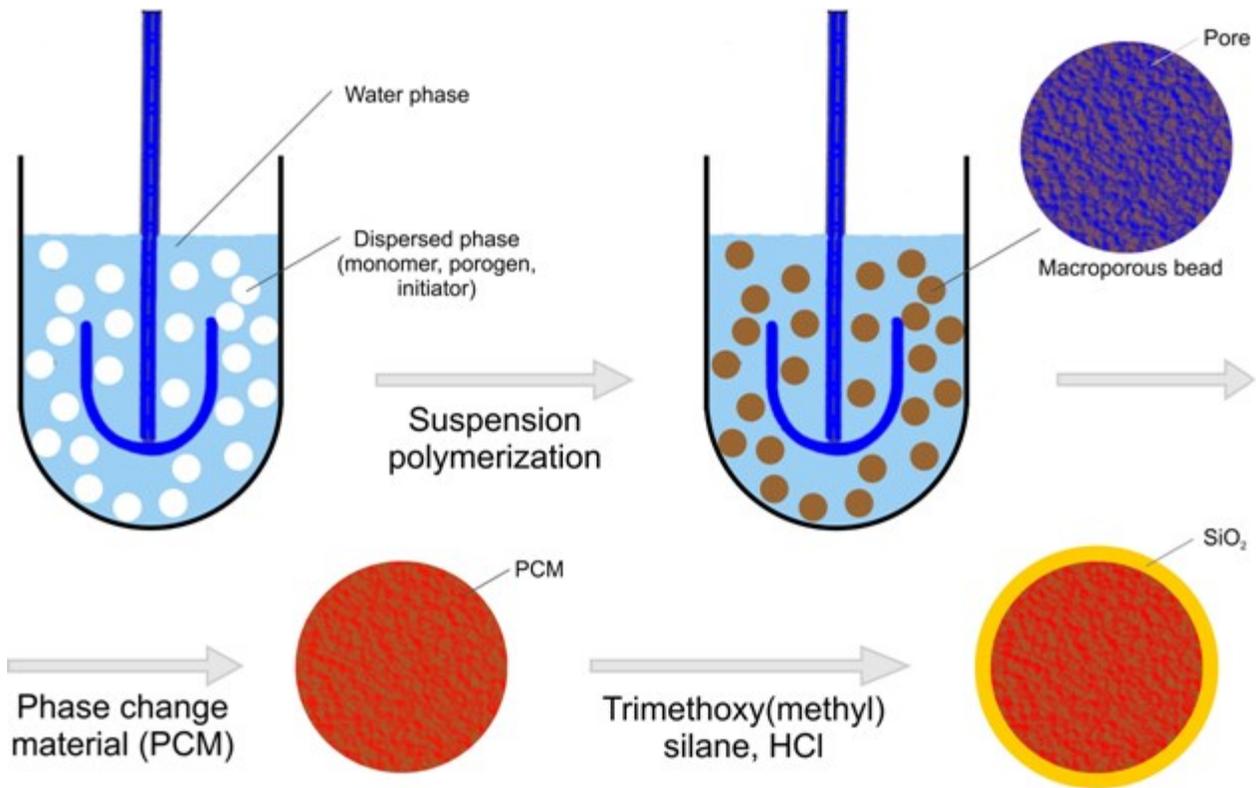
After 1000 heating-cooling



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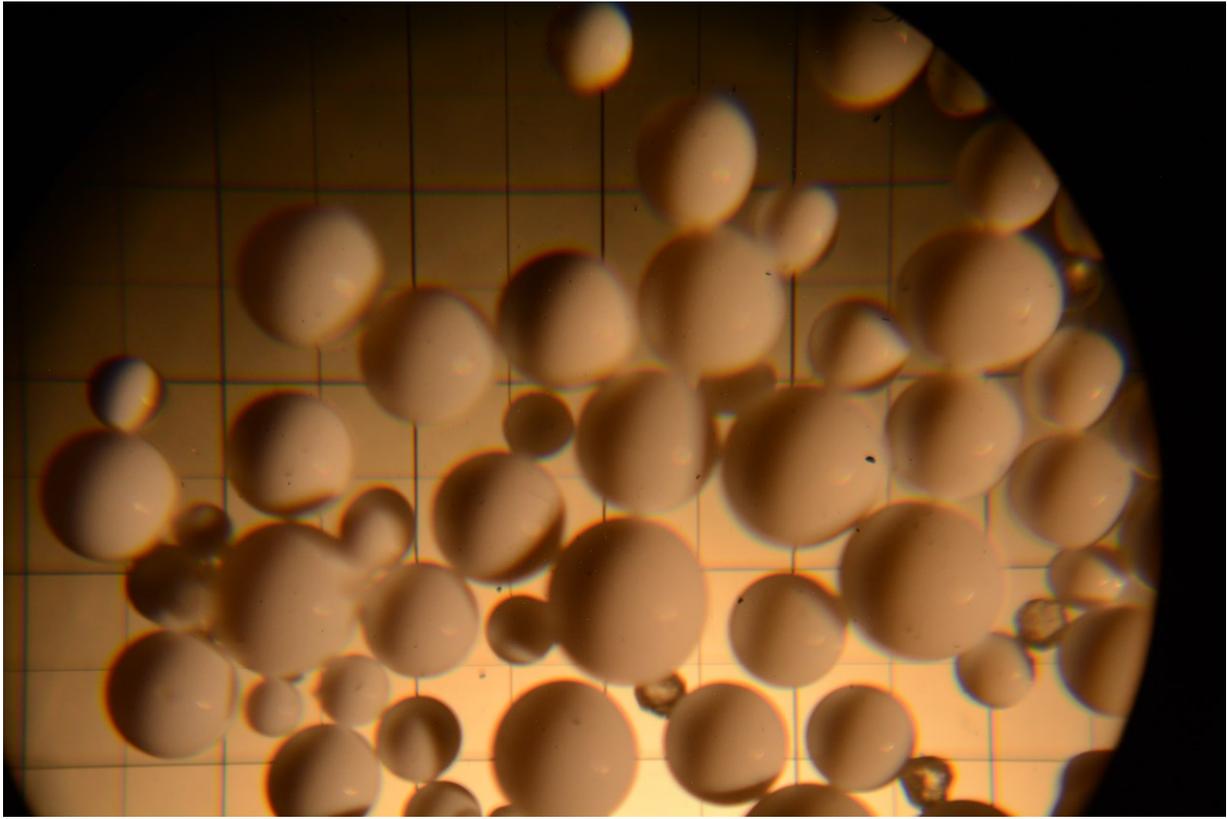
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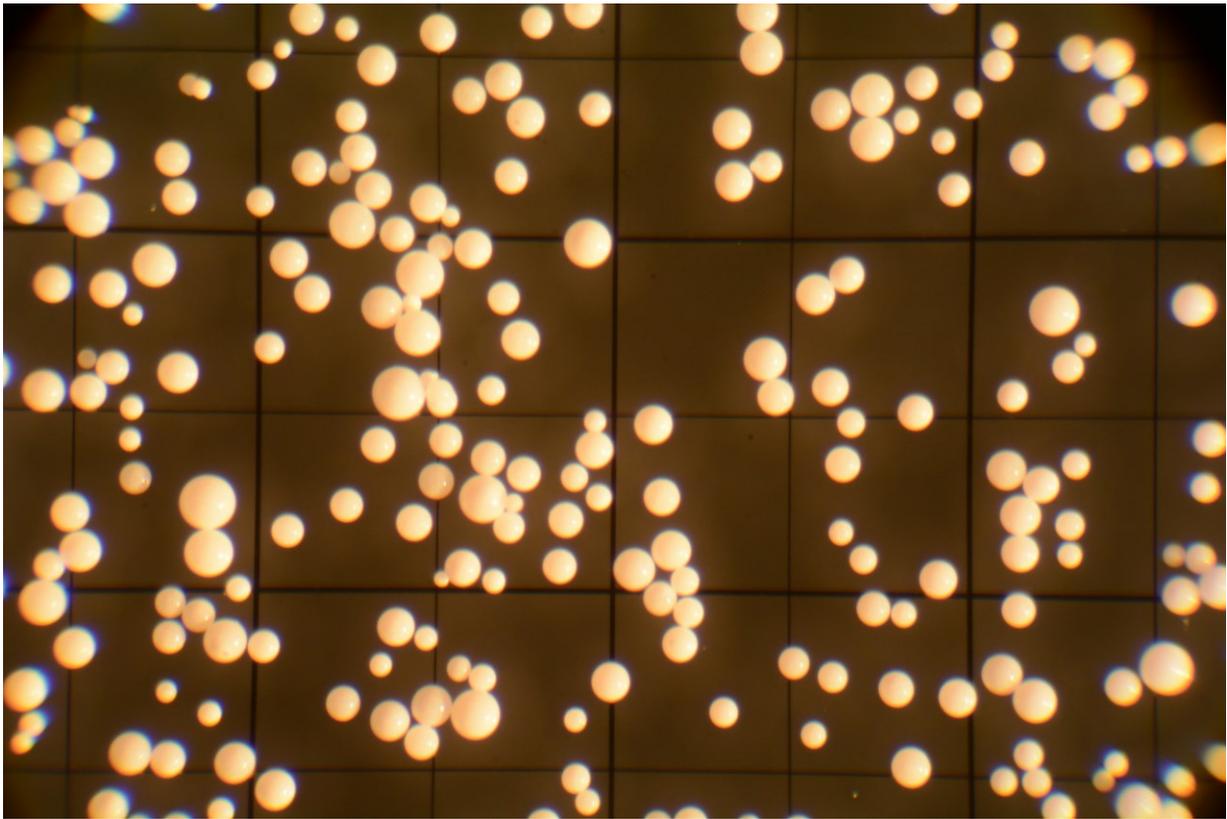
311 Fig2a



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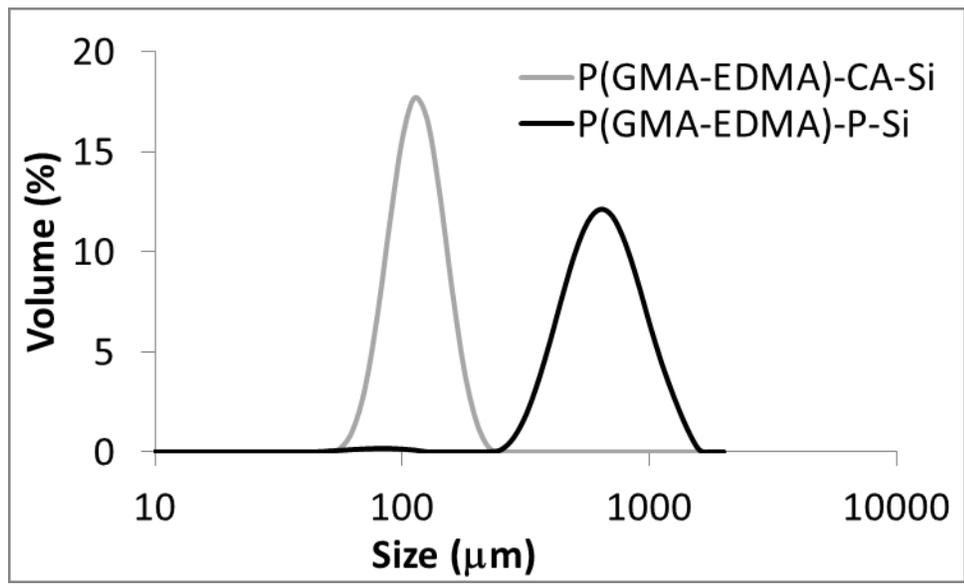
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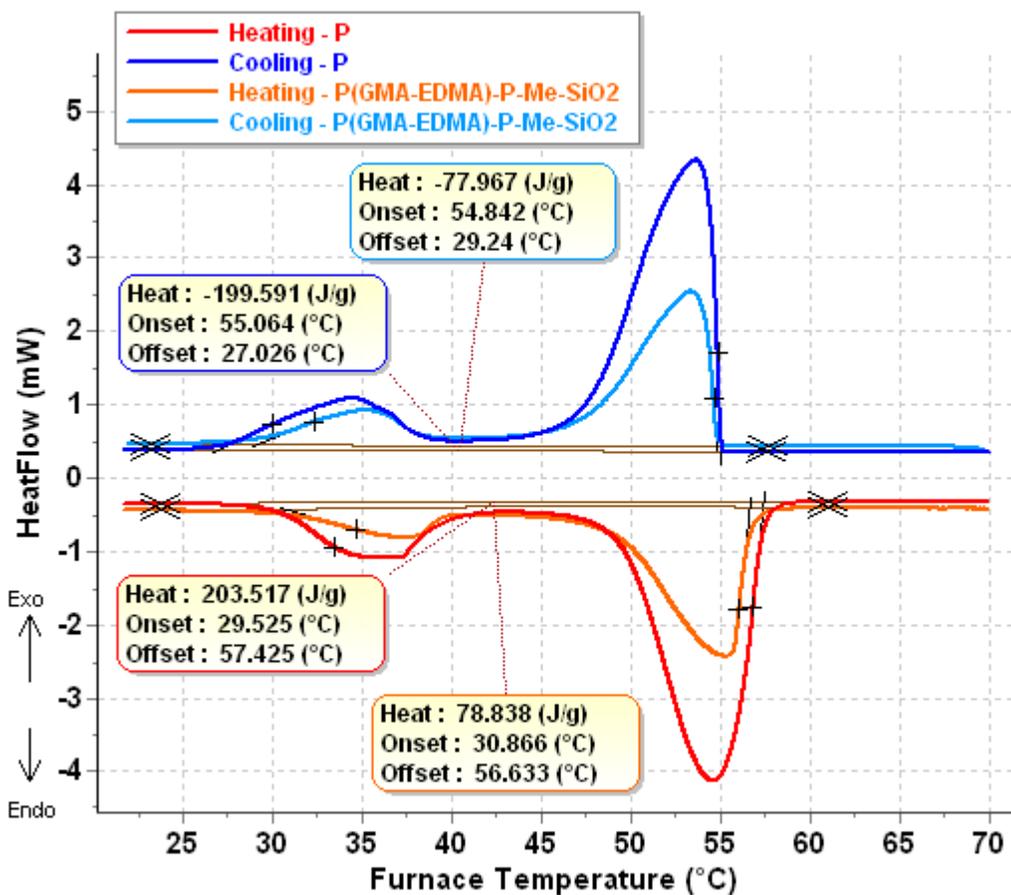
317 Fig3



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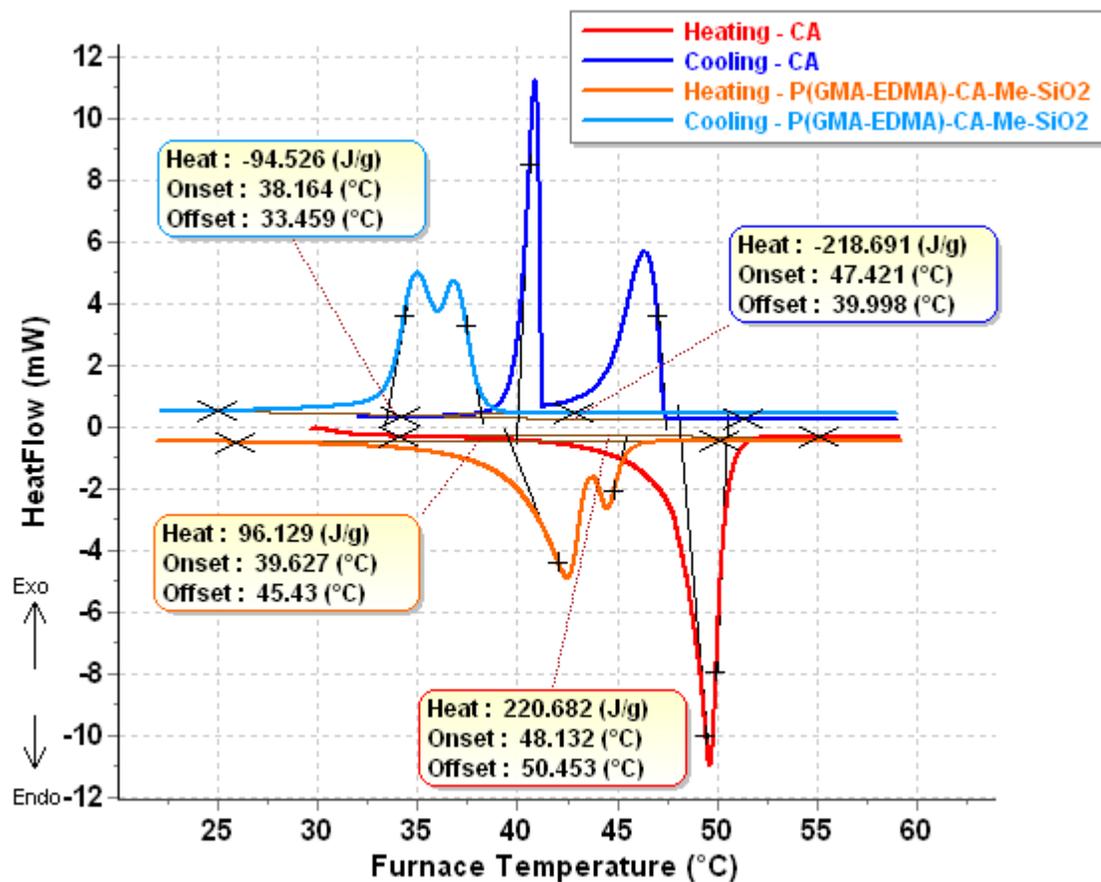
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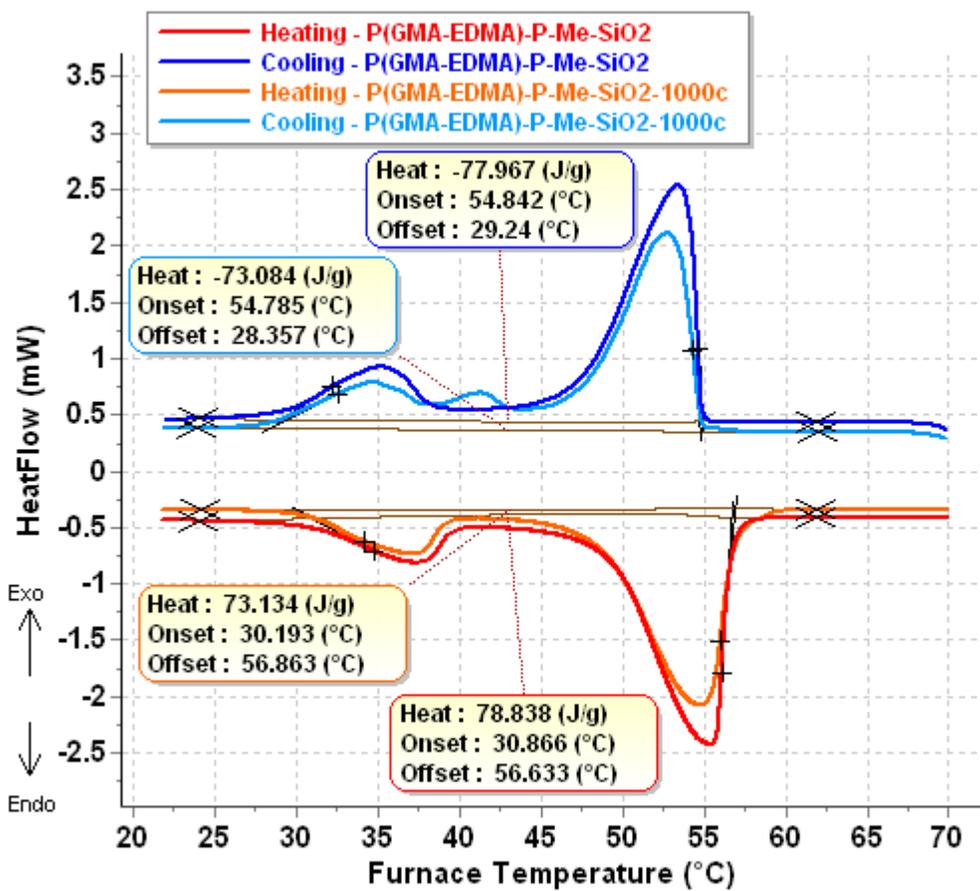
323 Fig4b



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326 Fig5a



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