1   **Silica-coated poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing organic**

2   **phase change materials**

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Abstract

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

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

Nomenclature

AIBN	2,2′-Azobis(isobutyronitrile)
D_v	volume mean diameter
DSC	differential scanning calorimetry
EDMA	ethylene dimethacrylate
GMA	glycidyl methacrylate
M_w	molecular weight
PCM	phase change material
P(GMA-EDMA)	poly(glycidyl methacrylate-ethylene dimethacrylate) beads
P(GMA-EDMA)-CA-Me-SiO$_2$	silica covered poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing cetyl alcohol

46	P(GMA-EDMA)-P-Me-SiO$_2$	silica covered poly(glycidyl methacrylate-ethylene
47		dimethacrylate) beads containing paraffin
48	PVA	poly(vinyl alcohol)
49	PVP	poly(*N*-vinyl-2-pyrrolidone)
50	S_{BET}	specific surface area
51	TMMS	trimethoxy(methyl)silane
52	V_p	pore volume

1. Introduction

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

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

2.2. Synthesis of macroporous beads

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

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

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

The silica shell was formed around the beads to keep PCM inside and to prevent particle aggregation at elevated temperatures. TMMS (1.36 g; 10 mmol) was thus hydrolyzed in 0.01 M HCl (0.54 g; 30 mmol) at room temperature to yield $SiMe(OR)_3$ hydrolysate. The volume of the mixture was adjusted to 5 ml by adding distilled water. The TMMS hydrolysate (1 ml) was added to the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change beads (P(GMA-EDMA)-PCM), the suspension was stirred at 70 °C for 3.5 h and the product eight times washed in 0.01 wt.% Tween 20 (100 ml each). Finally, the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change material-methyl silica particles (P(GMA-EDMA)-PCM-Me-SiO$_2$) were dried in air. The preparation of beads and the loading of PCMs as well as the formation of silica shell are drawn in Fig. 1.

139

2.4. Characterization methods

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

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

The thermal properties of the microcapsules compared to the neat PCMs were determined by a Setaram μDSC3evo differential scanning microcalorimeter. The samples (10.2 mg cetyl alcohol, 12.8 mg paraffin, 17.6 mg of each of the microencapsulated PCM) were weighed into 100 μl aluminium crucibles, and ethylene glycol as a heat transferring medium was added, which covered the microparticles, and then the system was closed by crimping a cap. The samples were cycled with a scanning rate of 0.6 °C/min. The results were processed by the thermoanalyzer's Calisto Processing (v1.38) software. The corresponding melting/freezing enthalpies and onset temperatures were determined by the baseline integration method (Tangential sigmoid baseline type).

The covered beads were tested via accelerated thermal cycling in order to study whether they are capable to retain the PCM after several phase transition. One thermal cycling test included heating till the complete melting and cooling till the complete freezing of the phase change materials in the capsules. The tests were performed consecutively up to 1000 thermal cycles by heating and cooling using a Peltier element. DSC analysis was repeated after the thermal cycling using Setaram μDSC3evo.

164

3. Results and Discussion

3.1. Porosity, size and PCM content

Macroporous sorbents were prepared by the AIBN-initiated suspension radical polymerization of GMA and EDMA. The mixture of toluene/1,2-dichloroethane and cyclohexanol/dodecan-1-ol 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 μm in size

183   (average size: 643 μm), while the small beads with cetyl alcohol and silica shell ranged between

184   70 and 200 μm (average size: 111 μm) (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$_2$ are compared

195   in Fig. 4a. The melting and crystallizing enthalpies of the P(GMA-EDMA)-P-Me-SiO$_2$ 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$_2$ 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 glycaol) 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

3.3. Thermal reliability

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.

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

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

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282   acid with TiO_2 shell as shape-stabilized thermal energy storage materials. Sol Energy
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284

285 **Acknowledgement**

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-SiO2 (A), as well as cetyl alcohol and

298   P(GMA-EDMA)-CA-Me-SiO2 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-SiO2) and after (P(GMA-EDMA)-P/CA-Me-SiO2-1000c)
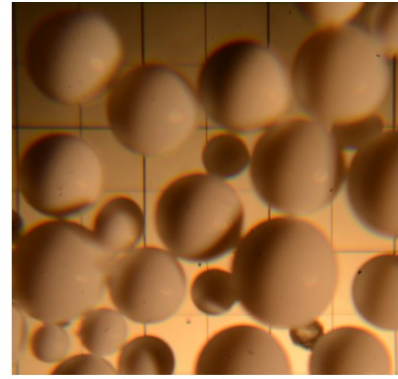
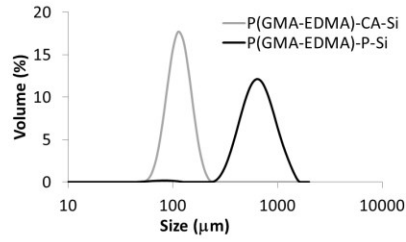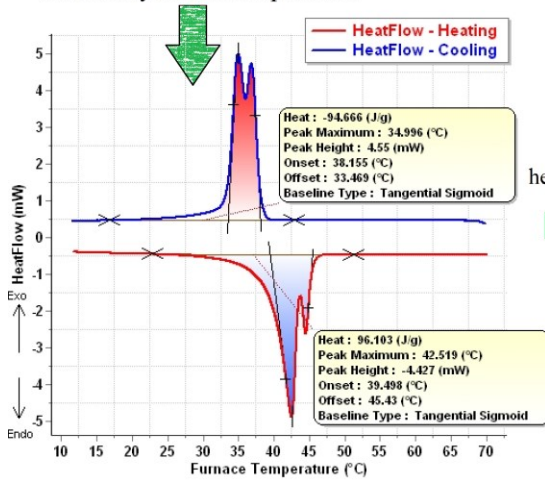301   1000 heating-cooling cycles.

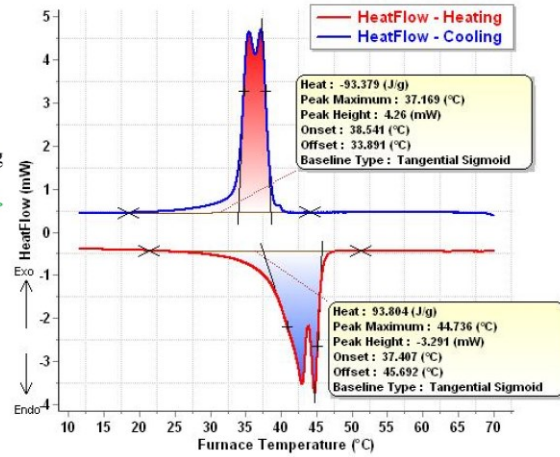302

303

304   Graphical abstract

Small beads filled with cetyl alcohol
covered by silica nanoparticles

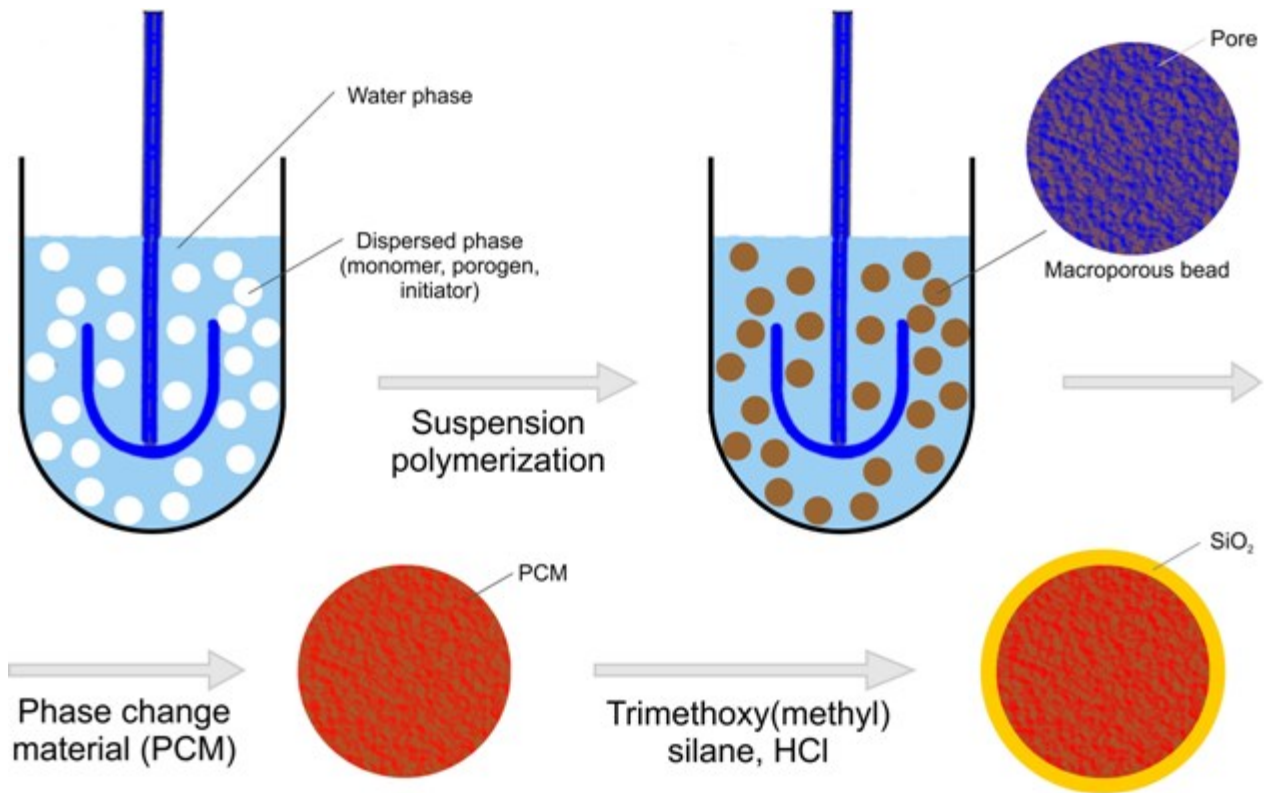Large beads filled with paraffin
covered by silica nanoparticles

After 1000
heating-cooling

305

306

307

308   Fig 1

Water phase

Dispersed phase
(monomer, porogen,
initiator)

Suspension
polymerization

Pore

Macroporous bead

Phase change
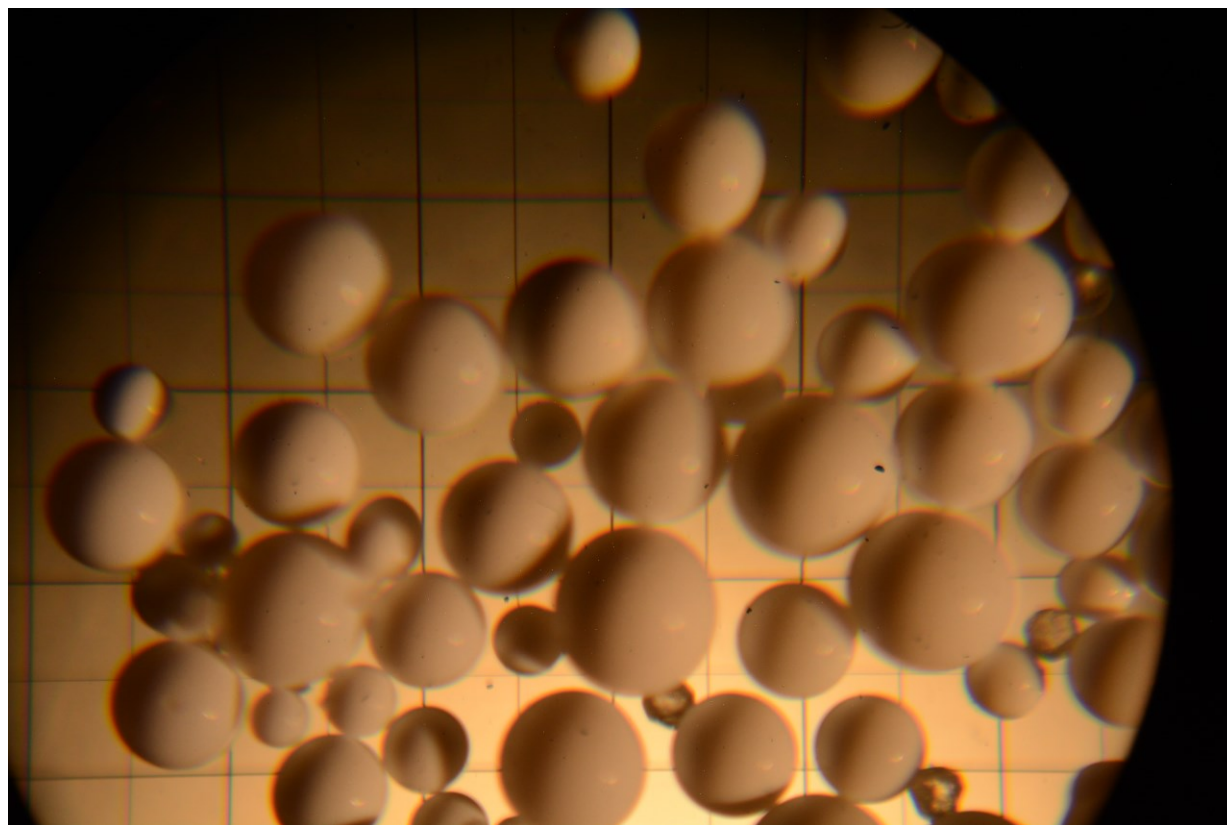material (PCM)

PCM
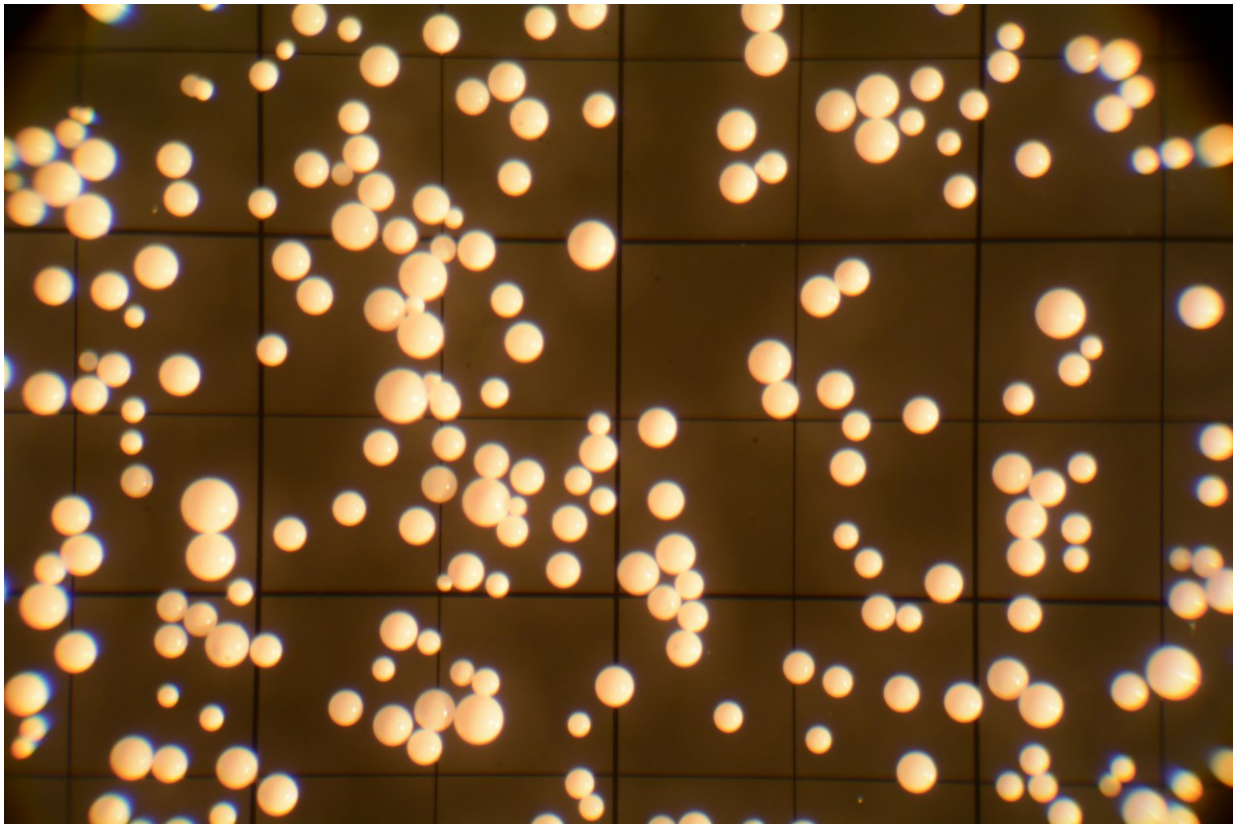
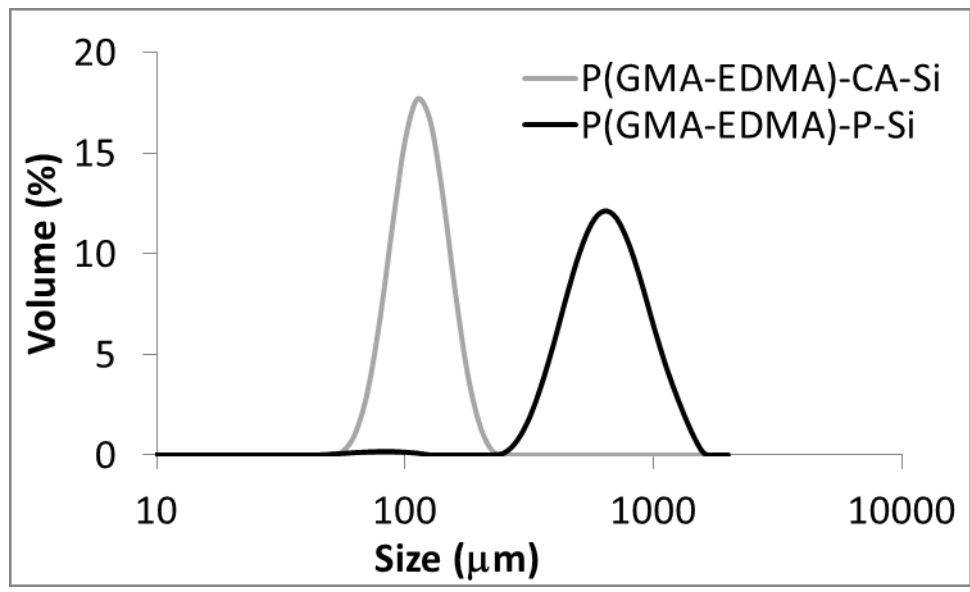Trimethoxy(methyl)
silane, HCl

SiO$_2$

309

310

311   Fig2a

312

313

314   Fig2b

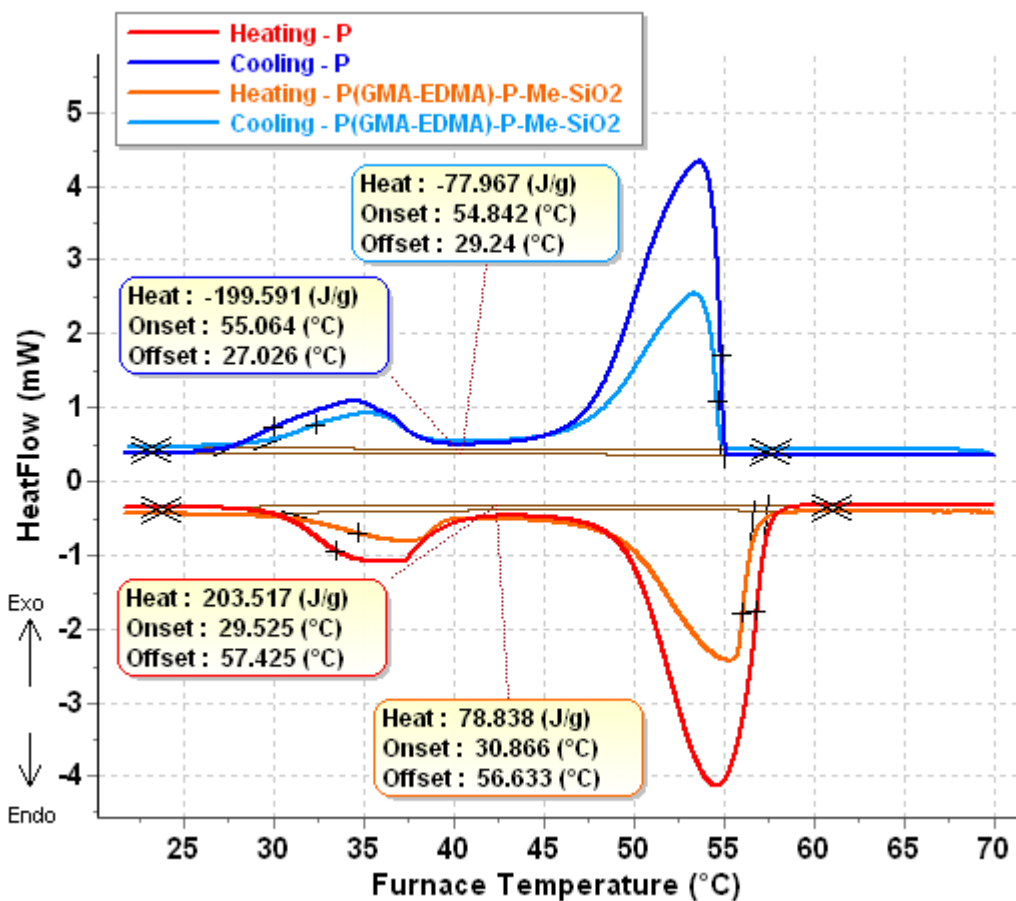315

316

317   Fig3

318

319

320   Fig4a

Heat : -77.967 (J/g)
Onset : 54.842 (°C)
Offset : 29.24 (°C)

Heat : -199.591 (J/g)
Onset : 55.064 (°C)
Offset : 27.026 (°C)

Heat : 203.517 (J/g)
Onset : 29.525 (°C)
Offset : 57.425 (°C)

Heat : 78.838 (J/g)
Onset : 30.866 (°C)
Offset : 56.633 (°C)

321

322

323   Fig4b

Legend:
- Heating - CA
- Cooling - CA
- Heating - P(GMA-EDMA)-CA-Me-SiO2
- Cooling - P(GMA-EDMA)-CA-Me-SiO2

Heat : -94.526 (J/g)
Onset : 38.164 (°C)
Offset : 33.459 (°C)

Heat : -218.691 (J/g)
Onset : 47.421 (°C)
Offset : 39.998 (°C)

Heat : 96.129 (J/g)
Onset : 39.627 (°C)
Offset : 45.43 (°C)

Heat : 220.682 (J/g)
Onset : 48.132 (°C)
Offset : 50.453 (°C)

Y-axis: HeatFlow (mW)
X-axis: Furnace Temperature (°C)
Exo ↑   Endo ↓

324

325

18

326   Fig5a

327

328

329   Fig5b

Heating - P(GMA-EDMA)-CA-Me-SiO2
Cooling - P(GMA-EDMA)-CA-Me-SiO2
Heating - P(GMA-EDMA)-CA-Me-SiO2-1000c
Cooling - P(GMA-EDMA)-CA-Me-SiO2-1000c

Heat : -93.346 (J/g)
Onset : 38.55 (°C)
Offset : 33.881 (°C)

Heat : -94.526 (J/g)
Onset : 38.164 (°C)
Offset : 33.459 (°C)

Heat : 93.817 (J/g)
Onset : 37.407 (°C)
Offset : 45.692 (°C)

Heat : 96.129 (J/g)
Onset : 39.627 (°C)
Offset : 45.43 (°C)

330