Recent advances in materials aspects of phase change materials in thermal energy storage

Charalampos Elias, Vassilis Stathopoulos

Laboratory of Chemistry and Materials Technology, School of Technological Applications, Technological Educational Institute of Sterea Ellada, 34400 Psachna campus, Evia, Greece

CYPRUS, Coral bay, 16-19.10.2018
• Merging of TEI of Chalkida (est 1983) & TEI of Lamia (est 1994) June 5th, 2013

- Karpenisi: 12,000m²/ 3,900m²
- Thiva: 800m²/ 770m²
- Amfissa: 12,000m²/ 3,500m²
- Lamia: 91,000m²/ 14,000m²
- Chalkida: 207,000m²/ 25,500m²

Laboratory of Chemistry and Materials Technology, School of Technological Applications, Technological Educational Institute of Sterea Ellada, Greece

RCUK Centre for Sustainable Energy Use in Food Chains
Energy - highlights

Sufficient and secure energy is the main enabler for welfare and economic development of a society. As energy-related activities have significant environmental impacts, it is indispensable to provide an energy system which covers the needs of the economies and preserves the environment.

“World Energy Resources 2016”
Energy highlights

Population without access to electricity (in millions)


Access to electricity will improve all over the world. Sub-Saharan Africa will struggle having the least.
Energy facts n figures

global energy needs rise more slowly but will be still +30% till 2040

carbon will still be intensively used in the future despite the small decrease in world production

Electricity sector is still mainly fossil fuel depended. Contributing high in global GHG emissions -- approx. 25%

Industry is consuming about 28% of energy demand and is responsible for 21% of GHG emissions

As 34% of energy demand is consumed in buildings and urbanization still increasing in most areas of the world
Trilemma in Energy

Development of green energy technologies and industrial waste heat recovery are becoming more and more important to face the problems of energy demand and environmental pollution.

“Since the Paris Agreement last year on action to fight climate change, virtually every country in the world is now conscious of the need to meet the challenge of the Energy Trilemma: providing households with supplies of energy that are accessible, reliable and affordable, and delivering energy to businesses at competitive prices, while at the same time ensuring that we generate and use energy in a way that protects the environment”

Sir Philip Lowe, Executive Chair, Energy Trilemma, World Energy Council
Energy – E storage

Sector of rapid change, driven by batteries reduced costs and increased industry requirement to manage system volatility.

Global installed storage capacity was 146 GW (including pumped hydroelectric storage) (2015)

Bottom-up projections suggest a global storage market of 1.4 GW/y by 2020 (excluding pumped hydro storage).

The storage of energy in suitable and clean forms, which can conventionally be converted into the required form, is today a challenge to the technologists.

✔ thermal energy storage
Thermal Energy Storage

- Excess thermal energy stored and be used hours, days, or months later,
- Individual process, building, multiuser-building, district, town, or region. Balancing of energy demand between daytime and nighttime,
- Storing summer heat for winter heating, or winter cold for summer air conditioning (Seasonal thermal energy storage).

Storage media: water or ice-slush tanks, masses of native earth or bedrock accessed with heat exchangers eutectic solutions and phase-change materials PCMs
Phase Change Materials & Thermal Energy Storage

SCOPUS hits on “TES” AND “PCMs”
Thermal Energy Storage

• **Sensible thermal (heat) storage (SHS)** - increase or decrease of temperature of a storage medium, such as water, oil, or ceramic materials.
  – Dependent on the specific heat capacity of the material. Linear relationship with temperature. Commercialized (industrial applications, residential water heaters or hot water storage on district-heating networks). Drawback of sensible thermal storage is low energy density and loss of thermal energy at any temperature.

• **Latent thermal (heat) storage (LHS)** involves heat transfer due to a phase transformation taking place in a suitable material (PCMs) in a specific and rather narrow temperature window e.g. molten salt, paraffin, or water/ice.
  – The temperature for heat capturing or release can be tailored by the material selection. (energy stored - chemical bonds rearranging) High energy storage density, More efficient than SHS.

• **Thermochemical storage (TCS)**: reversible chemical reaction involved.
  – The highest energy density of all TES approaches. Stability issues. Not constant efficiency / degradation over time. Lacks in depth understanding.

Buffering role / regulating thermic loads
Emerging sector and a growing market
A phase change material (PCM) is a substance with a high heat of fusion which, melting and solidifying at a certain temperature, is capable of storing and releasing large amounts of energy.

PCMs are a group of materials which exchange amount of thermal energy as latent heat within a narrow temperature range involving a phase transformation (S-L, S-S) [S-G or L–G limited].

Outside this temperature window PCMs may exchange typical sensible heat.
Phase Change Materials

Nano  Micro  Macro

Shape Stabilization
Encapsulation

PCMs

Solid - Solid
Solid - Liquid
Solid - Gas
Liquid - Gas

Phase Transition

Chemical Nature

Organic
Inorganic
Eutectics

Temperature

Low  Medium Low  Medium  High

-20 °C  +5 °C  +40 °C  +80 °C  +200 °C

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RCUK Centre for Sustainable Energy Use in Food Chains
## Main properties of groups of PCMs

<table>
<thead>
<tr>
<th>Material type</th>
<th>Type of transition</th>
<th>Phase change temp range (°C)</th>
<th>Latent heat (J/cc)</th>
<th>Density (g/cc)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic compounds</td>
<td>Solid-liquid (wet)</td>
<td>-12 to +187</td>
<td>125-400</td>
<td>0.75-1.54</td>
<td>Paraffins, fatty acids, alcohols, sugars, etc</td>
</tr>
<tr>
<td>Inorganic: salt hydrates</td>
<td>Solid-liquid (wet)</td>
<td>20-140</td>
<td>270-650</td>
<td>1.5-2.2</td>
<td>$\text{CaCl}_2\cdot 6\text{H}_2\text{O}$, $\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ etc</td>
</tr>
<tr>
<td>Inorganic salt</td>
<td>Solid-liquid (wet)</td>
<td>&lt; 150</td>
<td>200-500</td>
<td>1.7-2.5</td>
<td>$\text{LiNO}_3$, $\text{NaNO}_3$, $\text{MgCl}_2$, $\text{K}_2\text{CO}_3$</td>
</tr>
<tr>
<td>Inorganic salt solutions</td>
<td>Solid-liquid (wet)</td>
<td>&lt; 0</td>
<td>130-330</td>
<td>Around 1</td>
<td>$\text{KCl}$ 19.5% + $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Solid-solid organic compounds</td>
<td>Solid-solid (dry)</td>
<td>21-100</td>
<td>140-200</td>
<td>1.1</td>
<td>TCC</td>
</tr>
<tr>
<td>Metal eutectics</td>
<td>Solid-liquid (wet)</td>
<td>30-125</td>
<td>200-800</td>
<td>6-10</td>
<td>Eutectcs of $\text{Bi-Pb-Cd-Sn-In}$</td>
</tr>
<tr>
<td>Micro-encap. PCM</td>
<td>Solid-liquid (dry)</td>
<td>6-101</td>
<td>95-186</td>
<td>0.9-1.1</td>
<td>Micro encap. paraffin, fatty acid</td>
</tr>
</tbody>
</table>

Kumar et al DOI: 10.14429/dsj.61.363
Phase Change Materials –

- Phase transition temperature in the desired operating range
- High latent heat of phase transition per unit volume
- High specific heat to contribute in sensible thermal storage
- High thermal conductivity of both phases
- Limited volume change on phase change
- Low vapour pressure at the operating temperatures
- Favourable phase equilibrium
- High nucleation rate
- Adequate rate of crystallization
- Chemical stability
- Fully reversible freeze/melt cycle
- Compatibility with the construction materials
- Non corrosive to the construction materials
- Non-toxic, non-flammable and non-explosive for safety
- Readily available in large quantities and at low cost
Phase Change Materials

Shape stabilization & Encapsulation → properties enhancement

Mikrotek lab inc.

Nano Micro Macro
Common macro-encapsulation forms used in building envelopes

(i) PCM panel  (ii) PCM panel  (iii) PCM panel  (iv) PCM panel

(v) PCM panel  (vi) PCM brick  (vii) PCM brick  (viii) PCM slab

(ix) PCM slab  (x) PCM slat  (xi) PCM blade  (xii) PCM pouch

(xiii) PCM pouch  (xiv) PCM sphere  (xv) PCM sphere  (xvi) PCM tube

Table 3
Common PCM and shell materials for macro-encapsulation used in building envelopes.

<table>
<thead>
<tr>
<th>PCM</th>
<th>Melting point (°C)</th>
<th>Heat of fusion (kJ kg⁻¹)</th>
<th>Specific heat capacity (kJ kg⁻¹ K)</th>
<th>Density (kg m⁻³)</th>
<th>Thermal conductivity (W m⁻¹ K⁻¹)</th>
<th>Market pricea ($ kg⁻¹)</th>
<th>Shell material</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT 28 HC</td>
<td>27–29</td>
<td>245</td>
<td>1.65</td>
<td>880</td>
<td>0.24</td>
<td>2.21</td>
<td>Aluminum</td>
<td>[57,60,61]</td>
</tr>
<tr>
<td>RT 35</td>
<td>28–35</td>
<td>135</td>
<td>2.00</td>
<td>880</td>
<td>0.20</td>
<td>2.71</td>
<td>Aluminum</td>
<td>[62]</td>
</tr>
<tr>
<td>RT 42</td>
<td>38–43</td>
<td>174</td>
<td>2.00</td>
<td>880</td>
<td>0.20</td>
<td>2.71</td>
<td>Stainless steel</td>
<td>[51]</td>
</tr>
<tr>
<td>RT 18</td>
<td>18</td>
<td>134</td>
<td>2.00</td>
<td>756</td>
<td>0.20</td>
<td>2.71</td>
<td>Steel</td>
<td>[63]</td>
</tr>
<tr>
<td>RT 27</td>
<td>28</td>
<td>179</td>
<td>1.80</td>
<td>870</td>
<td>0.20</td>
<td>2.71</td>
<td>CSM</td>
<td>[64]</td>
</tr>
<tr>
<td>C₁₃H₃₄</td>
<td>22</td>
<td>223.66</td>
<td></td>
<td></td>
<td></td>
<td>2.23</td>
<td>Copper</td>
<td>[65]</td>
</tr>
<tr>
<td>Capric acid (CA)</td>
<td>30.20</td>
<td>142.70</td>
<td></td>
<td></td>
<td></td>
<td>3.01</td>
<td>Aluminum</td>
<td>[58]</td>
</tr>
<tr>
<td>Fatty acids/glycerides</td>
<td>16.50–26.50</td>
<td>116.70</td>
<td></td>
<td>503.30</td>
<td>4.82</td>
<td>HDPE</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>PEG 600</td>
<td>21–25</td>
<td>148</td>
<td>2.49</td>
<td>1128</td>
<td>3.01</td>
<td>PVC</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Hydrated salt</td>
<td>31.40</td>
<td>149.90</td>
<td></td>
<td></td>
<td></td>
<td>Polymer</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>CaCl₂·6H₂O</td>
<td>26 ± 1</td>
<td>180</td>
<td>2.13</td>
<td>2130</td>
<td>0.98</td>
<td>PVC</td>
<td>[68]</td>
<td></td>
</tr>
<tr>
<td>SP25 (hydrate salt)</td>
<td>26</td>
<td>180</td>
<td>2.50</td>
<td>1380</td>
<td>0.60</td>
<td>CSM</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>TD-MA (tetradecanol and myristate)</td>
<td>29.51–31.83</td>
<td>183–186</td>
<td></td>
<td></td>
<td></td>
<td>PE-RT</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td>Capric acid and 1-Dodecanol (95 wt %-5 wt%)</td>
<td>26.50</td>
<td>126.90</td>
<td></td>
<td>754</td>
<td></td>
<td>Aluminum</td>
<td>[58]</td>
<td></td>
</tr>
<tr>
<td>CA-PA (85 wt%-15 wt%)</td>
<td>27.48</td>
<td>151.54</td>
<td></td>
<td></td>
<td></td>
<td>PE-RT</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td>CA-LA (65.12 wt %-34.88 wt%)</td>
<td>19.67</td>
<td>126.56</td>
<td></td>
<td>1033</td>
<td></td>
<td>Stainless steel</td>
<td>[71]</td>
<td></td>
</tr>
</tbody>
</table>

a The market price was searched at www.alibaba.com and was provided as reference.
## Manufacturers of MPCMs.

<table>
<thead>
<tr>
<th>Trademark name</th>
<th>PCM</th>
<th>Shell material</th>
<th>PSD</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cristopia</td>
<td>Eutectic salts</td>
<td>Polyolefin</td>
<td>77 mm</td>
<td>Industrial refrigeration, building, conditioning</td>
</tr>
<tr>
<td>ClimeSel/climator</td>
<td>Sodium acetate, sodium sulfate</td>
<td>–</td>
<td>–</td>
<td>Medicine transportation, clothing, air-conditioning, electronic cooling, fire protection</td>
</tr>
<tr>
<td>Rubitherm</td>
<td>Paraffin, salt hydrate in granulate, pow-</td>
<td>Plastic</td>
<td>–</td>
<td>Storage and transport food, medical equipments, storage materials for textile</td>
</tr>
<tr>
<td></td>
<td>der and compounds forms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latest™/TEAP Energy</td>
<td>Glauber's salt, soda ash, sodium acetate,</td>
<td>Polyethylene</td>
<td>25.4 mm</td>
<td>Hot pads and solar heating telecom enclosure, back-up air-conditioning, cold storage</td>
</tr>
<tr>
<td></td>
<td>and paraffin wax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCM Products Ltd.</td>
<td>Eutectics, salt hydrates, organic materi-</td>
<td>Rubber, HDPE plastic</td>
<td>40 mm</td>
<td>Space International space station, automotive passive cooling, solar heating and heat recovery</td>
</tr>
<tr>
<td></td>
<td>als, and high temperature salts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPCM Microtek Labor-</td>
<td>Paraffin</td>
<td>Polymer</td>
<td>17–20 μm</td>
<td>Active wear clothing, woven and non-woven textiles, building materials, packaging, and electronics</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micronal°/BASF°</td>
<td>Paraffin wax</td>
<td>Polymer</td>
<td>5 μm</td>
<td>Building conditioning, surface cooling</td>
</tr>
<tr>
<td>Aegis</td>
<td>Inorganic salts</td>
<td>High density polyethylene</td>
<td>75 mm</td>
<td>Cold storage, boilers, solar water heaters, transport of blood, frozen food, fruits and vegetables</td>
</tr>
</tbody>
</table>

Manufacturers and their specifications of encapsulation of PCMs with maximum operating temperature above 100 °C.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>PCM</th>
<th>Shell material</th>
<th>Container</th>
<th>Average container size</th>
<th>Applications</th>
<th>Operating temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEAP</td>
<td>Glauber’s salt, soda ash, sodium acetate and paraffin wax</td>
<td>Aluminum, steel and polyethylene</td>
<td>Bottles, balls</td>
<td>25.4 mm</td>
<td>Storage and transport of food, medical equipment, storage, materials for textile</td>
<td>25–100</td>
</tr>
<tr>
<td>Rubitherm GmbH</td>
<td>Paraffin, salt hydrate in granulate, powder and compound forms</td>
<td>Aluminum, plastic</td>
<td>Box, bag</td>
<td>N/A</td>
<td>Storage and transport of food, medical equipment, storage, materials for textile</td>
<td>30–100</td>
</tr>
<tr>
<td>PCM Products Ltd.</td>
<td>Eutectics, salt hydrates, organic materials, and high temperature salts</td>
<td>Rubber, HDPE plastic</td>
<td>Tube, ball, pouches, plate</td>
<td>40 mm</td>
<td>International space station, automotive passive cooling, solar heating and heat recovery</td>
<td>90–885</td>
</tr>
<tr>
<td>Microtek Lab. Inc.</td>
<td>Paraffin</td>
<td>Polymer</td>
<td>N/A</td>
<td>17–20 μm</td>
<td>Active wear clothing, woven and non-woven textiles, building materials, packaging, electronics</td>
<td>25–250</td>
</tr>
</tbody>
</table>

Note: N/A means it is not reported on the company’s website.
Nanoencapsulation
(capsules <1 μm)
PCMs in capsules of 1 mm in size would increase the surface area by 300 m²/m³ when compared with the bulk PCM.
Encapsulated PCMs

Encapsulation Methods
Chemical
Physico-chemical
Physico-mechanical

Shell
Organic (>50 polymers)
Inorganic (clay, SiO₂, Al₂O₃)

The morphology of the microcapsules in PCM (a-irregular shape, b- simple, c- multi-wall, d- multi-core and e- matrix particle)

Up to now, mainly organic PCM have been encapsulated, with a focus in paraffin and fatty acids

Nanoencapsulated

organic shells – very low thermal conductivity + low thermal conductivity of organic PCMs = very slow heat exchange, supercooling and overheating.

inorganic shells!

SiO₂ nanocapsules with octadecane and n-dodecanol core via a sol–gel process.

Capsule thermal conductivity: 0.621 W m⁻¹ K⁻¹ (0.151 W m⁻¹ K⁻¹ octadecane).
Silica shell of 1.296 W m⁻¹ K⁻¹, (polymers approx. 0.20 W m⁻¹ K⁻¹)

Polystyrene-silica/n-tetradecane Nanocapsules (150 nm, 83.38 J/g latent heat)
+ 1wt% SiO₂ to the capsule shell increased thermal conductivity +8.4%.

Nanoencapsulated

Synthesis controlled SiO$_2$ content and hydrolysis rate, affect the morphology of PCM-loaded nanocapsules - thin shelled.

Mesoporous capsules with confined n-octadecane: variable nucleation & shift of crystallizing points.

Nucleation controlled by structure

High thermal reliability - Stable @ 500 melting/solidifying cycles,

Tunable hydrophobicity of the organosilica shell material

Materials for PCM-TES

Metal storage tanks / containers
- Availability, price, manufacturability (carbon steel, Al and/or Cu alloys)
- Organic PCMs: not(?) aggressive to metal container
- Inorganic PCMs: aggressive to metal container
- No corrosion of stainless steel (cost!)

Polymer materials tanks / containers / capsules
- PP, PET, HDPE and LDPE
- PET and PP reported as better for the organic PCM tested while HDPE for the inorganic PCM tested
- failure of commercial HDPE spheres encapsulating organic PCM
- compatibility issues of organic PCMs in contact with HDPE and PP (degradation)
- mass variations & Deformations of polymers in contact with PCMs

References:
- Chalkia et al., RSC Adv., 8 (2018) 27438
Challenges for materials for PCM-TES

Polymer materials for shells in capsules

>50 types

- Forming thin films
- Cohesive with the core material
- Inert with the environment, tasteless, pliable
- Soluble in a liquid media
- Chemically compatible and non-reactive with the core material
- Strength, flexible, impermeable, optical properties and stability
- Non-hygroscopic, with medium/low viscosity, and low cost.

Natural & synthetic
Market HDPE spheres with PCM A58

Undesired results obtained in the water tank set-up → PCM leakage in water

Suggestion of 25 heating cooling cycles to reach a stable state of the HDPE spheres to prevent leakage OR a coating (not defined)
Influence of organic phase change materials on the physical and mechanical properties of HDPE and PP polymers

Vasiliki Chalkia, Nikolaos Tachos, Pavlos K. Pandis, Aris Giannakas, Maria K. Koukou, Michalis Gr. Vrachopoulos, Luis Coelho, Athanasios Ladavos and Vassilis N. Stathopoulos

Organic PCMs: PCM Products Ltd with market names A44, A46, A53, A58

melting points in the temperature range 44–58 °C

Contact @ 70°C with high density polyethylene (HDPE) and polypropylene (PP) and epoxy-based resin (Ampreg 21)
Fig. 1 Weight change over time for HDPE samples (a) in left, for PP samples (b) in right and for Ampreg 21 samples in both (a) and (b), in contact with PCMs.

Variation of percentage strength change of all tested HDPE (A) in top (a) and PP (B) samples in bottom (b) as a function of treatment time.
HDPE and PP are affected
- PCMs adsorbed in a different level and speed (A44)
- Time depended molecular interaction / distribution.
- Decreased and partly restored HDPE strength (D28)
- PP results are without a similar trend for all PCMs indicating the need for further investigation.
- epoxy-based resin (Ampreg 21) is stable

DSC results on heating and cooling cycles in 35–65 °C region on HDPE in contact with PCMs (left) and PP in contact with PCMs (right).
PCMs and PLA

3D printing (FFD) technology → towards the replacement of standard structural parts on various industrial processes

PLA: Poly lactic acid

PLA material
- State of the art for additive manufacturing
- NOT TESTED for use in PCM/TES
PLA in contact with PCM - Results

The use of PLA in contact with two organic PCMs (A44 & A58) for the first time

- 3D printed PLA structure is found stable and inert towards the organic PCMs
- 3D printed PLA improves its crystallinity over working time at 65°C
- PLA proved so far very promising for organic PCM encapsulation or latent heat storage tank structural material

- Insignificant mass uptake

structure on-demand encapsulation & tank design by PLA 3D printing additive manufacturing

DSC Experiments

Laboratory of Chemistry and Materials Technology, School of Technological Applications, Technological Educational Institute of Sterea Ellada, Greece

RCUK Centre for Sustainable Energy Use in Food Chains
Large number of papers are reaching publication dealing with various aspects of PCMs in thermal energy storage technologies.

Enhancement of PCMs properties and applicability by shape stabilization and encapsulation approaches

Cautious use in contact with polymers is recommended

Nanoencapsulation is a dynamic and maybe the most promising sector for the enhancement of PCMs properties - ?Cost?

Non fossil fuel derived organic, renewable, recyclable and safe PCMs

Environmental as well as health and safety aspects are becoming of paramount important and should be closely followed
Thank you for your attention

Vassilis Stathopoulos
Professor

vasta@teiste.gr
http://lcmt.teiste.gr

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