Applied Thermal Engineering 127 (2017) 1427–1441

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Review on solid-solid phase change materials for thermal energy storage: Molecular structure and thermal properties

Ali Fallahi [a,d], Gert Guldentops [a], Mingjiang Tao [a], Sergio Granados-Focil [b], Steven Van Dessel [c,*]

[a] Civil and Environmental Engineering Department, Worcester Polytechnic Institute, Worcester, MA, United States
[b] Department of Chemistry, Clark University, Worcester, MA, United States
[c] Architectural Engineering Program, Civil and Environmental Engineering Department, Worcester Polytechnic Institute, Worcester, MA, United States
[d] Department of Civil & Architectural Engineering, College of Engineering, Lawrence Technological University, Southfield, MI, United States

HIGHLIGHTS

- Comprehensive review of the 4 major types of solid-solid phase change materials.
- Review relationship between molecular structure and phase transition mechanisms.
- Review relationship between molecular structure and thermal properties.
- Discuss challenges and future opportunities of solid-solid phase change materials.

ARTICLE INFO

Article history:
Received 2 May 2017
Revised 15 August 2017
Accepted 25 August 2017
Available online 1 September 2017

Keywords:
Phase change materials
Thermal energy storage
Solid-solid PCM
Solid-state PCM

ABSTRACT

Solid-solid phase change materials (SS-PCMs) for thermal energy storage have received increasing interest because of their high energy-storage density and inherent advantages over solid-liquid counterparts (e.g., leakage free, no need for encapsulation, less phase segregation and smaller volume variation). Four main SS-PCMs for thermal energy storage are reviewed, with a focus on their thermal properties and the relationship between molecular structure, processes involved during phase transition, and thermal properties. This review aims to provide guidance for selecting appropriate SS-PCMs for various applications and tailoring the synthesis of SS-PCMs with desired thermal, physical and mechanical properties. Challenges and opportunities to use of SS-PCMs for thermal storage and other applications are also discussed.

Contents

* Corresponding author.

http://dx.doi.org/10.1016/j.applthermaleng.2017.08.161
1359-4311/

1. Introduction

Thermal Energy Storage (TES) has been a key technology in energy systems for conserving energy and increasing energy efficiency by addressing the discrepancy between energy supply and demand. TES involves storage of high- or low-temperature thermal energy in the form of sensible heat, latent heat, or through thermochemical reactions or processes. An overview of major strategies for thermal energy storage is shown in Fig. 1. Sensible heat storage is based on storing thermal energy by heating or cooling a liquid or solid medium (e.g. water, sand, molten salts, rocks), with water being the most widely used because of its relatively high heat capacity, low cost, and being benign [1]. Sensible heat storage systems are relatively inexpensive compared to other forms of TES and are applicable to domestic systems, district heating, and industrial needs. However, in general sensible heat storage requires large volumes because of its low energy density (i.e. three or five times lower than that of latent and thermochemical energy storage systems, respectively) [2]. Furthermore, sensible heat storage systems require proper design to discharge thermal energy at constant temperatures.

Phase Change Materials (PCMs) have been receiving considerable attention for various thermal energy storage applications. PCMs provide much higher thermal energy storage density than sensible thermal storage materials, thus they have been widely used in various fields such as solar energy utilization [3], waste heat recovery [4], building air conditioning [5], electric energy-storage [6], temperature-control of greenhouses [7–9], telecommunications and microprocessor equipment [10], kitchen utensils [11], insulating clothing and textiles for thermal comfort applications [12], biomedical and biological-carrying systems [13], and food transport and storage containers [14].

Latent heat storage is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid, liquid to gas, solid to gas, or solid to gas, and vice versa. The most commonly used latent heat storage systems undergo solid-liquid phase transitions due to large heat storage density and small volume change between phases. These types of materials are often classified as inorganics, organics, and eutectic phase change materials, which have been covered in a few review papers and thus are briefly discussed herein [4,10,14–17].

Solid-liquid phase change materials (SL-PCMs) change their internal molecular arrangement from an ordered crystalline structure to a disordered amorphous one when temperature exceeds a critical threshold (i.e., the phase transition temperature). An increase in vibrational energy breaks the supramolecular bonds between individual molecules, causing the crystalline arrangement to become a randomly oriented liquid state (Fig. 2). In reverse, when temperatures fall below the phase transition temperature, a nucleation process starts whereby molecules re-arrange into a crystalline lattice. The shape and number of crystals that form during crystallization depends on many factors, such as cooling-rate, type of molecules, and the presence of impurities that can serve as nucleating agents. These phase changes are accompanied by a volume change, with volume typically increasing when the material becomes liquid. Solid-liquid PCMs commonly used for thermal energy storage include organic PCMs (paraffins) and Inorganic PCMs (salt hydrates), or various mixtures thereof (eutectics). Various strategies are often used to enhance the performance of SL-PCMs for thermal storage applications by addressing their inherent drawbacks. For example, the phase transition temperature of paraffin can be tailored by changing the length of the carbohydrate chain; and various additives with high thermal conductivity (e.g., aluminum powder, graphite, metal foams) were used to enhance

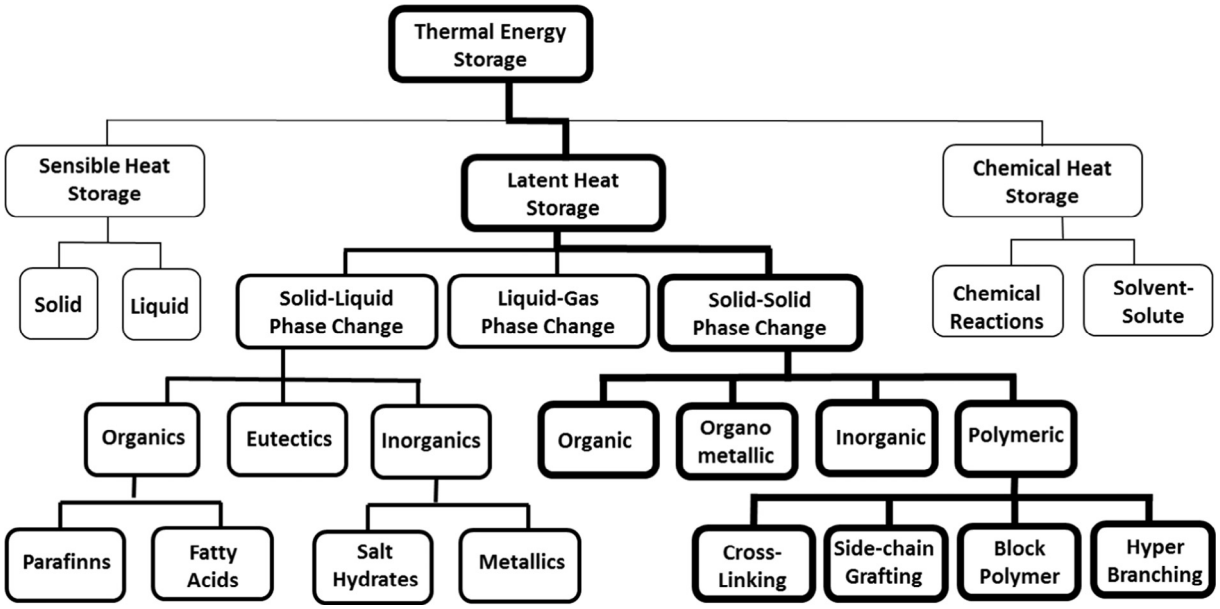

Fig. 1. Overview of thermal energy storage (TES) materials, solid-solid PCMs are highlighted in bold.

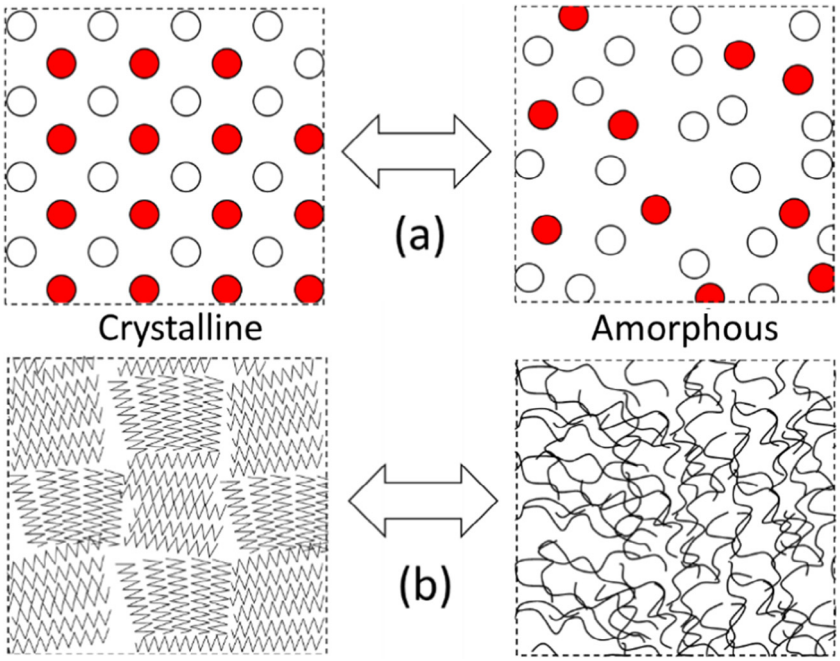

Fig. 2. Schematic representation of SL-PCM phase change processes for (a) salt-hydrate type system going from an ordered crystalline phase to a disordered non-crystalline phase, and (b) paraffin type system going from a lamellar crystal phase to a random disordered phase.

thermal response of SL-PCMs, many of which have low thermal conductivity that is the main barrier to many TES applications [18]. Some other practical challenges of using SL-PCMs include the need for containment or encapsulation when in liquid state to avoid leakage, the occurrence of phase segregation in mixed systems when going through multiple phase change cycles, material degradation, and hysteresis occurring between cooling and heating cycles.

Solid-solid phase change materials (SS-PCMs) absorb and release heat by reversible phase transitions between a (solid) crystalline or semi-crystalline phase, and another (solid) amorphous, semi-crystalline, or crystalline phase. Different from solid-liquid-PCMs, solid-solid-PCMs retain their bulk solid properties within certain temperature ranges and are therefore also referred to as "solid-state" PCMs [19]. The terminology of form-stable PCM (FS-PCM) or shape stabilized PCM typically refers to SL-PCMs embedded in an organic or inorganic matrix with higher melting temperature. The matrix in such FS-PCMs acts as a sponge for a SL-PCM, preventing it from flowing freely above its melting temperature [20]. Some authors also discuss SS-PCMs under the category of FS-PCMs in cases where the embedded PCM is a SS-PCM. Form-stable PCMs have been the subject of several review papers [18] and will not be covered in this review. This review focuses on the thermal properties of SS-PCMs that rely on solid state phase transitions. Since the fundamental phase transition mechanisms in SS-PCMs show similarities to those observed in SL-PCMs, the optimization strategies pursued in SL-PCMs are therefore also applicable to SS-PCMs.

SS-PCMs are of great practical interest for use in thermal energy storage applications as they avoid the leakage problems typically observed in SL-PCMs. This feature allows them to be blended with other materials without a need for encapsulation, for example for thermal energy storage in construction materials such as concrete or gypsum [21–24]. SS-PCMs typically also experience less phase-segregation and smaller volume change as their soft segments are immobilized [25,26]. This feature extends their durability by preventing degradation upon thermal cycling, which is important for applications that require long term performance (i.e. buildings).

SS-PCMs have received increasing attention for thermal energy storage in different fields because of the above advantages over SL-PCMs. Depending on chemistry and molecular structures, different types of SS-PCMs exhibit different phase transitions and can result in a wide range of enthalpy, transition temperature, and thermal conductivity values. While many review papers are available on solid-liquid PCMs, to the best of our knowledge, there are no reviews of solid-solid PCMs in the literature to date. This literature review summarizes the main SS-PCMs and is intended to provide timely guidance for selecting appropriate SS-PCMs for various applications and tailoring the synthesis of SS-PCMs with desired thermal properties. This review focuses on thermal properties of four major SS-PCMs and assesses the relationship between molecular structure, processes involved during phase transition, and thermal properties. This review is outlined as follows: The different approaches for obtaining SS-PCMs are reviewed in Section 2. The general trends in thermal properties of the different types of SS-PCMs are briefly discussed in Section 3. Thermal properties, including enthalpy, transition temperature, and thermal conductivity, and their dependence on molecular structure are reviewed and assessed in Section 4 for each of the different types of SS-PCMs. Efforts were made to identify quantitative or qualitative relationships between thermal, physical, and chemical properties of SS-PCMs. Challenges and barriers of more widespread use of SS-PCMs for thermal storage in various fields are discussed in Section 5.

2. Approaches for obtaining SS-PCMs

There are currently two main approaches taken to obtain SS-PCMs. In the first approach, the arrangement of relatively small molecules changes from one crystalline phase to another when absorbing or releasing heat [27]. These SS-PCMs materials are also referred to as "plastic crystal" solid-state PCMs, eluding to the solid state plastic deformation of their crystalline structures [28]. This approach includes the polyalcohol organic compounds (and mixtures thereof) that have tetrahedral coordination and whose phase transition, for example, involves a change from layered or

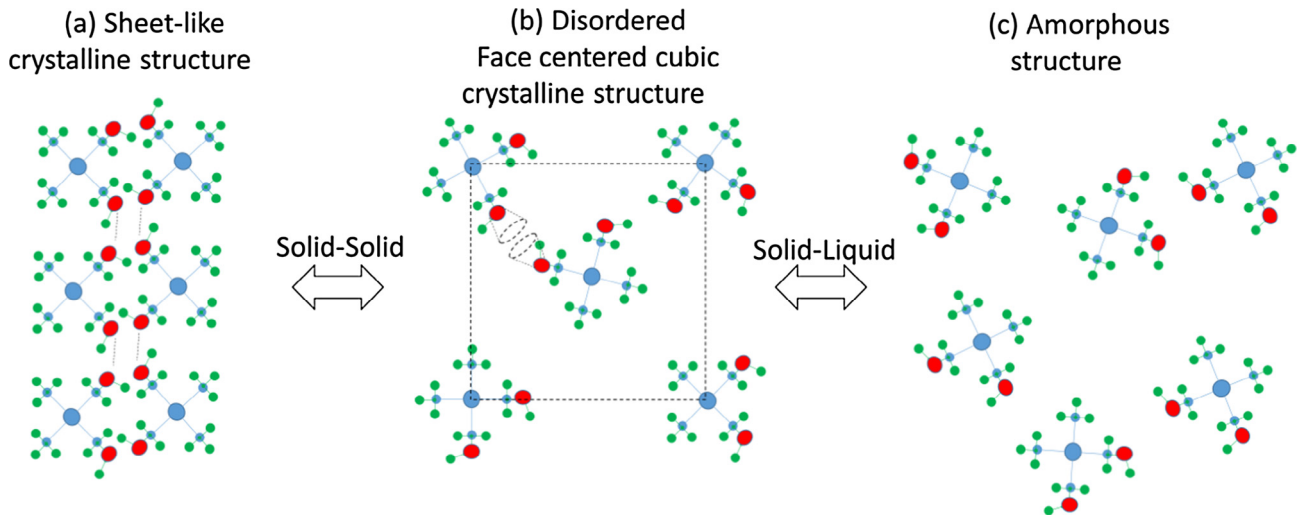

Fig. 3. Schematic representation of Polyalcohol type SS-PCMs with crystalline structure changing from (a) sheet like tetrahedral sheet configuration to (b) face centered cubic to (c) disordered amorphous structure (adopted from Ref. [27]).

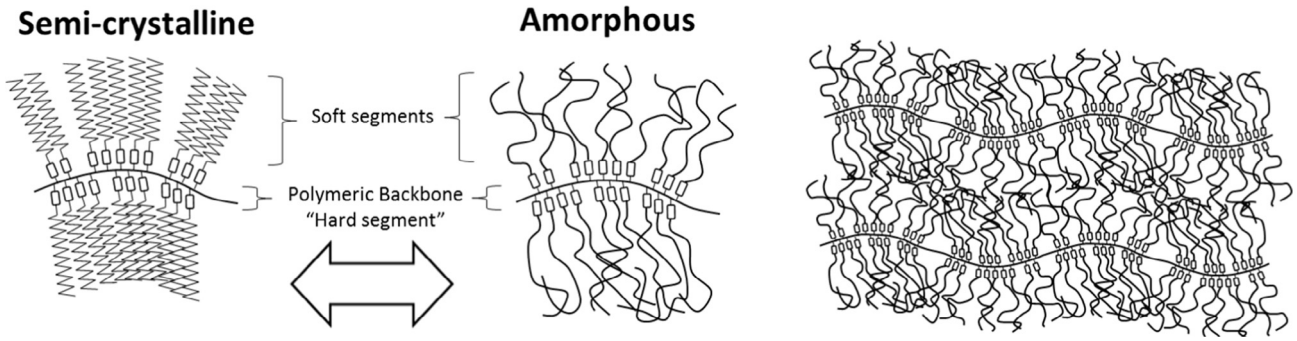

Fig. 4. Schematic representation of Polymeric Graft SS-PCMs and their phase transition.

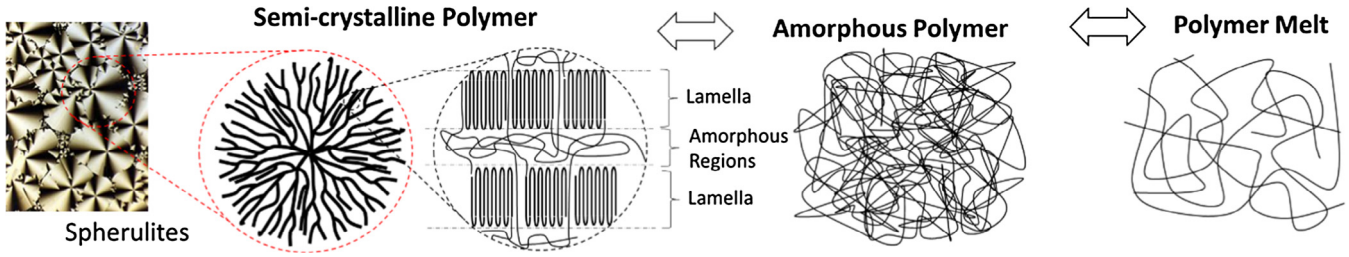

Fig. 5. Schematic representation of semi-crystalline SS-PCM.

chain-like internal tetrahedral arrangements at low temperature to a more disordered cubic crystalline arrangement at elevated temperatures [27–30]. When temperature continues to increase these systems eventually become liquid as all their supramolecular bonds break, see Fig. 3. The mechanisms underlying the phase transition of polyalcohol SS-PCMs resemble those of inorganic salt-hydrate SL-PCMs in that they entail a change in the crystalline arrangements of relatively small molecules. Solid-solid polyalcohol SS-PCMs differ however from SL-PCMs in their ability to undergo at least one crystalline-crystalline (solid-solid) phase change before becoming liquid. Different poly-alcohols can also be mixed, for example, to tune the phase transition temperature [31].

Another example of this approach includes the inorganic SS-PCMs that absorb and release thermal energy due to magnetically-induced transformations, crystalline phase transformations, or order–disorder transitions. For example, the phase change between ferrite and austenite of Fe encompasses a solid-solid phase change. Such transformations can also be tailored towards thermal energy storage applications, for example by developing Fe-Co binary systems [32]. More details about thermal properties of poly-alcohol and inorganic SS-PCMs are provided in Sections 4.2 and 4.4, respectively.

In the second approach, crystallizable moieties are incorporated through chemical bonding into a secondary structure that prevents them to flow freely when they are in their liquid non-crystalline state. Examples of this approach include polymeric SS-PCMs [33] and the perovskites [34]. In polymeric SS-PCMs, the phase change component is structurally incorporated into the macromolecular backbone via side-chain grafting [35–40], block-polymerization [41,63], hyper-branching [42], or crosslinking copolymerization

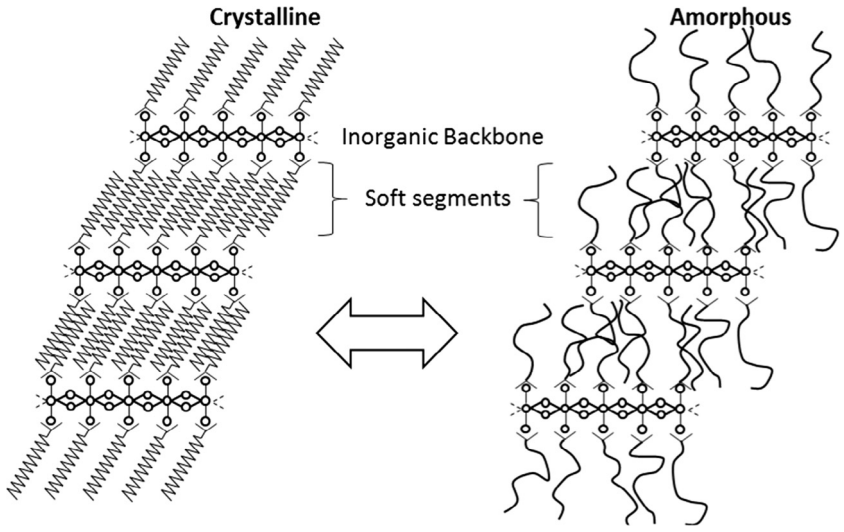

Fig. 6. Schematic representation of a Perovskite type SS-PCM (adopted from Ref. [59]).

with non-crystallizable motifs [20,36,43–48]. In one type of polymeric SS-PCMs, for example, linear chains, such as poly-(ethylene glycol) (PEG) or poly-(ethylene oxide) (PEO) serve as the "soft segment" and are grafted onto a polymeric backbone acting as the "hard segment" [49–53]. When the temperature reaches the melting point of the soft segment, the material absorbs heat through a latent heat mechanism while undergoing a first order phase transition. The mobility of these soft segments is restricted however as they remain attached to their polymeric backbone, which allows the system to remain solid overall. The transition temperature of these SS-PCMs can be tailored, for example, by adjusting the chain length of the soft segments or the rigidity of the polymeric backbone, see Fig. 4 [33].

Many linear polymers undergo reversible liquid-solid phase transitions upon cooling from their molten amorphous state. During the crystallization process, depending on the cooling rate, the flexible polymeric chains align into crystalline lamellar plates that nucleate into semi-crystalline spherulites (Fig. 5) [54]. Such an approach can also used to derive SS-PCMs whereby a "soft" polymer segment is connected by a "hard" polymer segment through block co-polymerization [41]. When the soft segments liquefy upon absorbing heat, they are kept together by the hard segments of the block co-polymer, thus preventing their free flow. Unless cross-linking is used, the hard segments eventually also melt when the temperature increases beyond the hard segment melting point. The ability to store and release heat as well as the phase change temperatures are controlled by changing the relative length and chemistry of the soft and hard segments. Many of the tools available from polymer synthesis, processing, and property optimization can also be leveraged towards the design and optimization of polymeric SS-PCMs, which has already resulted in different thermoplastic and cross-linked thermoset materials [46].

Another approach includes perovskites whereby inorganic 2D crystalline sheets serve as the scaffold onto which crystallizable soft segments are attached via non-covalent bonds [34,55–60]. When absorbing energy, the soft segments melt and store thermal energy, however their lateral movement is restricted due to attachment to the inorganic sheet-like scaffold. When cooling from their molten state the soft segments crystallize and release heat in a reversible process (Fig. 6). Thermal properties of polymeric SS-PCMs and those with perovskite structure are reviewed and discussed in more detail in Sections 4.1 and 4.3, respectively.

3. General trends in thermal properties for different SS-PCM types

The latent heat storage capacity of PCMs is ultimately linked to the packing density of molecules within the crystalline system, while the phase transition temperature is determined by the strength of the non-covalent bonding between molecules. Fig. 7 depicts the phase transition temperatures and enthalpies of the major types of SL-PCMs and SS-PCMs. As can be observed, SS-PCMs generally have lower phase transition enthalpies and/or undergo phase transitions at lower temperature when compared to SL-PCMs. The lower enthalpy trend can be explained by the mobility restrictions imposed within SS-PCMs, which hinders crystallization and therefore limits the packing efficiency. For example, paraffin based SL-PCMs have higher enthalpy and phase transition temperatures than polymeric SS-PCMs although both use similar soft segments that undergo phase transition are present in both PCMS. High packing density also affects the phase transition tem-

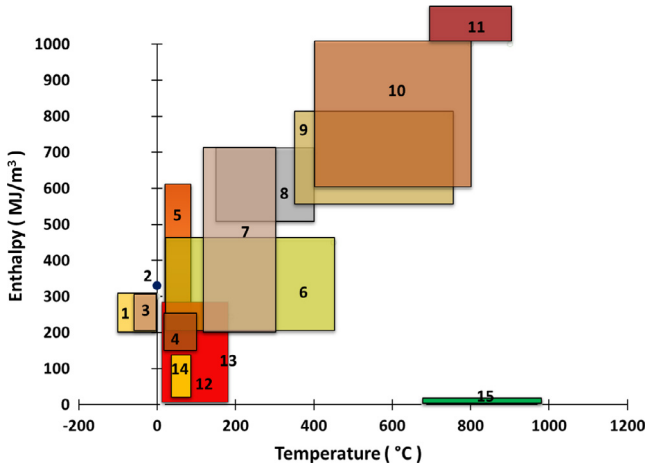

Fig. 7. Enthalpy and temperature ranges for SL-PCMs and SS-PCMs; L-PCMs: (1) Water-salt solutions; (2) Water; (3) Clathrates; (4) Paraffins; (5) Salt hydrates; (6) Sugar alcohols; (7) Nitrates; (8) Hydroxides; (9) Chlorides; (10) Carbonates; (11) Fluorides; (12) Polymeric; SS-PCMS: (12) Polymeric; (13) Organics (Polyols); (14) Organometallics; (15) Inorganics (Metallics).

perature as more molecules are in close proximity, their supramolecular bonding increases.

Differences in thermal properties also exist among the SS-PCMs. Fig. 8 depicts the enthalpy and temperature ranges for polymeric, organic, organometallic, and inorganic SS-PCMs. The phase transition temperature of organic SS-PCMs falls between 25 and 190 °C while their enthalpies range from 15 to 270 kJ/kg. This range is much wider than that observed in polymeric and organometallic SS-PCMs, which have phase transition temperatures between 15 and 65 °C and enthalpies between 10 and 205 kJ/kg. In the case of organic SS-PCMs, heat is stored and released when relatively small molecules undergo a crystalline to amorphous transition. Such small molecules can rearrange quickly to crystallize more efficiently and can adopt densely packed crystalline structures, which explains their higher enthalpies and phase transition temperatures. The crystalizing moieties in polymeric SS-PCMs on the other hand are much larger or exhibit restricted motion due to their attachment to a polymeric backbone, which limits their crystallization efficiency, slows the crystallization rate and makes the transition enthalpy more dependent on heating/cooling rate. The structure of organometallic SS-PCMs is very similar to some of the graft polymeric SS-PCMs, which explains the similarity in their thermal properties. Inorganic PCMs, on the other hand, operate at much higher phase transition temperatures indicating stronger interactions among their atoms. However, these materials have low enthalpies indicating that their different crystalline energy states are very close.

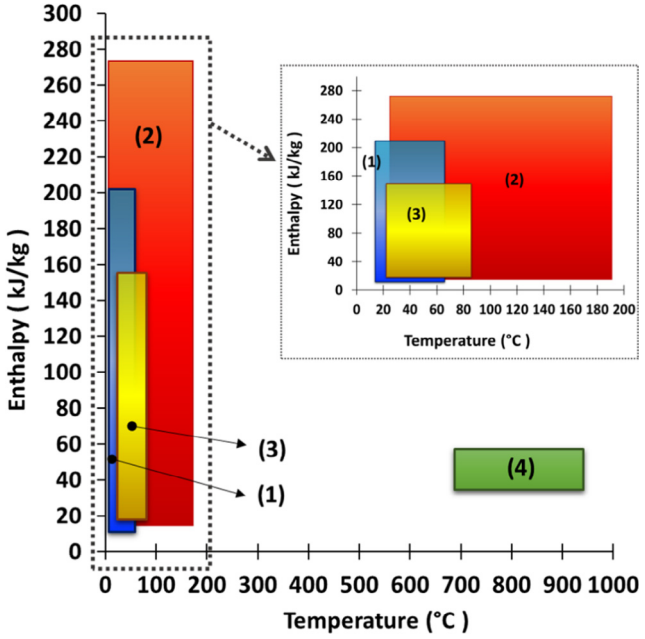

Fig. 8. Enthalpy and temperature ranges for SL-PCMs and SS-PCMs; (1) Polymeric, (2) Organic, (3) Organometallic, and (4) Inorganic SS-PCMs.

4. Thermal properties of different types of SS-PCMs

Tables 1–4 summarize thermal property information for approximately 66 different SS-PCM systems reported in the literature. The information is organized into four major SS-PCMs material types: polymeric, organic, organometallic, and inorganic SS-PCMs, based on the difference in their molecular structure. A discussion follows on the general trends observed for each material type, and the relationship between molecular structure, processes involved during phase transition, and thermal properties is assessed.

4.1. Polymeric SS-PCMs

As outlined in Section 1, attachment or incorporation of a phase changing motif into a polymeric structure will be accompanied by

Table 1
Thermal properties for Polymeric SS-PCMs.

PCM Type	Melting peak temperature [°C]	Melting enthalpy [J/g]	Crystallization peak temperature [°C]	Crystallization enthalpy [J/g]	Heating rate [°C/min]	Reference
Polymeric						
1. Grafted						
SAN-g-PA	29.2–37.5	11.6–23.7	31.3–41.5	11.7–24.4	10	[35]
SAN-g-Peg	30.0	66.8	49.0	68.2	10	[38]
PVA-g-C_{18}OH	55.1–56.5	41–65	45.3–49.4	40–63	10	[61]
polystyrene-g-PA	18.7–21.5	26.2–39.8	17.6–18.7	20–39.2	5	[37]
cellulose-g-PEG	42.8–60.1	77.6–203.2	25.1–40.6	44.7–203.2	10	[50]
Cellulose-g-E_2C_{16}	28.2–28.6	21–28	12.9–14.9	18–30	10	[52]
Poly(Styrene-co-Allyalcohol)-g-SA	27–29	34–74	25–30	28–71	1	[62]
Polystyrene-g-PEG_{6000}	44.9–58.0	111.5–179.5	34.4–38.5	99.4–143.6	5	[40]
2. Blocked						
PUPCM	65.28	138.7	38.58	126.2	10	[42]
3. Cross linked						
β-CD/MDI/PEG	57.6–60.2	92.3–115.2	43.5–47.8	90.3–11.6	2	[64]
Sorbitol/Dipentaerythritol/Inositol/PEG	36–59.9	91.0–107.5	44.0–45.8	86.1–102.9	2	[65]
PEG/MDI/PE	36	–	68	153	10	[43]
Melamine/Formaldehyde/Polyethyl Eneglycols (MFPEG)	49.1–57.7	91.1–109.4	28.3–36.9	85.3–103.9	10	[36]
PEG/MDI/PVA	61.1	72.8	34	–	10	[20]
4. Others						
PEO-CEL (Physical Blending)	62.5–63.4	40.6–134.7	32.5–39.5	40.2–127.3	10	[49]
PEO-CMC (Physical Blending)	58.4–62.5	52.8–140.2	35.3–41.3	5.2–138	10	[49]
MGPM	55.3	108.5	18.3	81.6	10	[66]
poly(polyethylene glycol methyl ether methacrylates) (BULCK POLYMERIZATION)	35.8–44.7	99.7–132.5	1.4–14.4	94.5–118.6	5	[67]
PD/Phenyl Ethylene (END GROUPS MODIFICATION)	53.2–57.7	47.2–108.5	1.5–18.3	33.9–81.6	10	[68]

Table 2
Thermal properties for organic SS-PCMs.

PCM Type	Melting peak temperature [°C]	Melting enthalpy [J/g]	Crystallization peak temperature [°C]	Crystallization enthalpy [J/g]	Heating rate [°C/min]	Reference
Organic (polyalcohol)						
PE-TAM						
PEAK 1	54–158	61.8–213.1	127.3–188.8	121.7–209.8	5	[69]
PEAK 2	184.6	14.2	188.6	14.3	5	
AMPD/TAM						[69]
PEAK 1	114.7–122.6	5.1–181.5	19.3–187.1	20–203.8	5	
PEAK 2	–	–	79.5	71.4	5	
NPG/TAM/PE						[69]
PEAK 1	25.8	21.0	166.9	29.7	5	
PEAK 2	121.1	121.5	175	24.3	5	
NPG/TAM/PE/AMPD						[69]
PEAK 1	34.7	62.6	117.1	44.8	5	
PEAK 2	171.6	14.1	169.6	17.4	5	
PEAK 3	178.1	13.1	–	–	5	
NPG/PE[1]						[72]
PEAK 1	32.0–37.4	18.8–68.2	25.9–31.3	18.8–51.7	5	
PEAK 2	160.3–169.8	83.0–147.7	169.5–172.3	81.4–125.3	5	
NPG/TAM						[72]
PEAK 1	35.6–38.6	27.1–143.3	22.1–30.0	33.0–150.1	5	
PE/PG						[73]
PEAK 1	82–187	139.0–270.3	–	–	–	
PG/NPG						[73]
PEAK 1	24–89	66.2–139.0	–	–	–	
PE/NPG						[73]
PEAK 1	39–187.0	49.9–270.3	–	–	–	
PE						[74]
PEAK 1	185.4	339.5	–	–	–	
NPG						[74]
PEAK 1	42.4	119.1	–	–	–	
TAM						[74]
PEAK 1	132.4	295.6	–	–	–	
NPG/PE						[74]
PEAK 1	32.0–37.4	18.8–68.2	–	–	–	
PEAK 2	160.3–169.8	18.8–26.2	–	–	–	
NPG/TAM						[74]
PEAK 1	35.6–38.6	27.1–143.3	–	–	–	
PEG						[51]
PEAK 1	60.4	148.1	47.6	139.3	–	
MDI						[51]
PEAK 1	56.7	108.7	46.1	106.7	–	
PEG/MDI						[51]
PEAK 1	60–61.4	120.5–131.9	45.5–46.3	116.3–121.4	–	

[1] DSC heating rate: 5 C/min & cooling rate: 18 C/min (below 30 C), 0.5 C/min (below 20 C), and 0.2 C/min (below 10 C).

Table 3
Properties of Organometallic SS-PCMs reported in the literature.

PCM formula	T_t (°C)	H_t (J/g)[a]	r_s (kg/m^3)	Reference
$C_{10}Mn$	32.8	70.34	–	[26]
$C_{10}Cu$	33.8–36.9	62.57	–	[26]
$C_{12}Cu$	52.5–63.8	70.15, 147.13[b]	1111	[26,77]
$C_{12}Mn$	54.1–56.4	80.8	–	[26]
$C_{12}Co$	60.7–88.0	92.89	–	[26]
$C_{14}Cu$	69.2–79.5	163.99	1186	[76]
$C_{15}Cu$	72.3–87.8	126.42	1245	[76]
$C_{16}Cu$	72.8–96.0	79.76	–	[26]
$C_{16}Mn$	73.1–91.0	104.48	–	[26]
$C_{10}Co$	77.7–82	74.28	–	[26,78]
$C_{10}Zn$	80.1–162.8	100.92	–	[26]
$C_{12}Zn$	88.2–156.0	120.23	–	[26]
$C_{16}Co$	93.4–164.1	153.79	–	[26,78]
$C_{16}Zn$	99.1–160.5	137.52	–	[26]

[a] Temperature range represents minimum and maximum temperatures over multiple solid transitions. Ht is the total enthalpy for all the transitions.
[b] Multiple enthalpy values represent discrepancy in reported heat release data between sources.

Table 4
Thermal properties for Inorganic SS-PCMs.

PCM Type	Melting peak temperature [°C]	Melting enthalpy [J/g]	Crystallization peak temperature [°C]	Crystallization enthalpy [J/g]	Heating rate [°C/min]	Reference
Inorganic						
FE-15CO	935	49	925	52	10	[32]
FE-20CO	950	49	942	50	10	[32]
FE-30CO	977	51	965	54	10	[32]
FE-40CO	988	53	979	57	10	[32]
FE-10CO-5CR	844	56	803	57	10	[32]
FE-7SI	683	34	685	32	10	[32]
FE-10AL	680	34	682	32	10	[32]

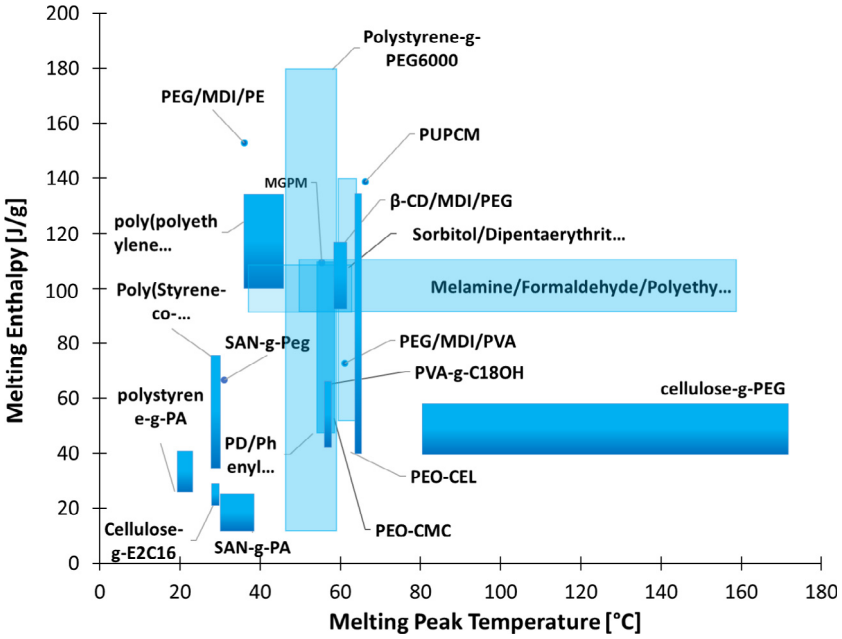

Fig. 9. Melting Enthalpy and melting temperature ranges for polymeric SS-PCMs.

a decrease in the observed latent heat. This reduction on the energy absorbed during the phase transition is due to several factors: (a) dilution of the phase changing moieties within a thermally inert polymeric matrix, (b) mobility or packing restrictions of the crystallizing groups due to attachment, (c) strong interaction of the phase changing moieties with the polymer backbone. The magnitude of the decrease in the observed latent heats depends on the choice of polymer backbone and phase changing motifs, see Fig. 9 and Table 1. As can be seen from the data in Table 1, covalent attachment of a phase changing group to a polymer chain broadens the temperature range where these transitions occur and widens the latent heats measured for these processes. The increase in the range of observable temperatures and latent heats for the polymeric SS-PCMs, compared to organic SS-PCMs is attributed to the decrease in rate of crystallization that results from the attachment of the crystallizing motifs to a high molecular, highly entangled, polymer backbone. Once the phase-changing moieties are covalently linked to the polymeric chains, the molecular motions required for efficient phase transition become slower and may not occur completely within the timescales associated with the DSC experiments. Furthermore, a fraction of the crystallizing motifs can become kinetically trapped in a conformation unfavorable for the phase transition, thus reducing the observed latent heats. Covalent attachment of the phase-changing moieties to polymeric backbones may increase the energy barriers that must be overcome to achieve the phase transition, resulting in higher transition temperatures than those for the same crystallizing motifs prior to their covalent inclusion within a polymeric material. Fig. 8 depicts the melting enthalpy and melting temperature ranges for polymeric SS-PCMs.

In an effort to understand the effect of macromolecular architecture on the heat storage capacity of the polymeric SS-PCMs, data were examined from several systems where the phase-changing moieties were incorporated into the polymers as either main chain cross-linkers, side-chain grafts or blend components. The observed latent heats increased as the mass fraction of the phase changing motif increased, while the specific connectivity to the polymer backbone (i.e. side-chain grafting, main chain cross-linking or physical blending) did not have a systematic effect on the resulting differences. See table 1. The effect of the specific chemical composition of both the polymer backbone and the active motifs were examined by comparing the observed latent heats, normalized to account for differences in mass fraction of the phase changing moieties, as a function of a normalized temperature scale (T_m observed/T_m pure phase changing motif). See Fig. 10.

Fig. 10 illustrates the data in terms of normalized enthalpy of melting as a function of normalized transition temperature. In that scale, values closer to 1 (on both normalized axis) indicate that the phase changing motifs undergo the thermally-induced transition as efficiently as they would if they were not attached or mixed with a thermally inert polymeric structure. Deviations below 1 in the normalized enthalpy scale indicate that only a fraction of the

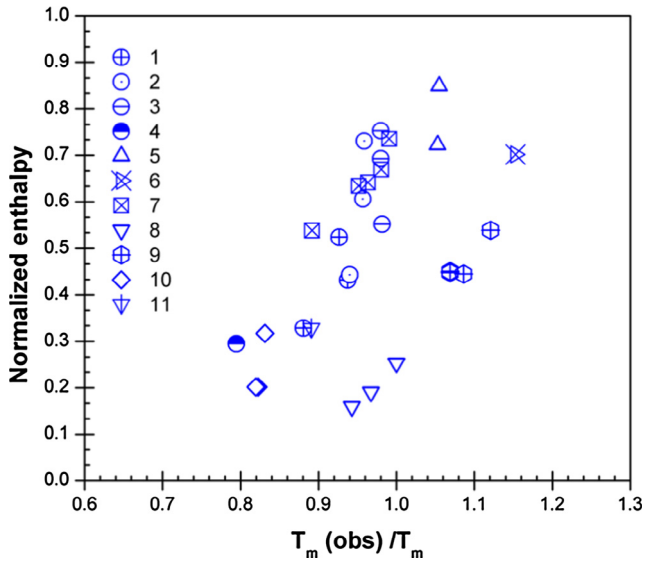

Fig. 10. Comparison of polymeric SS-PCMs using normalized enthalpy and temperature scales. Different symbols correspond to different materials. (1) PEG-grafted cellulose with PEG M.W. = 1 kg/mol [50], (2) PEG-grafted cellulose with PEG M.W. = 2 kg/mol [50], (3) PEG-grafted cellulose with PEG M.W. = 5 kg/mol [50], (4) Cellulose/PEG blend with PEG M.W. = 4 kg/mol [51], (5) Polyethylene glycol polymethylmethacrylate [67], (6) Crosslinked polyurethane with polyethylene and polyethylene glycol soft segments [44], (7) Crosslinked melamine-formaldehyde copolymer with PEG soft segments [36], (8) Poly(vinyl alcohol)-g-octadecanol copolymers [60], (9) Crosslinked polyurethane with β-cyclodextrin as hard segments and PEG as soft segments [64]. (10) Hexadecane-oxy-diethyleneglycol-grafted cellulose [52], (11) Poly(styrene-g-acrylonitrile)-g-polyethylene glycol copolymers [38].

available phase-changing moieties undergo the phase transition. Deviations below 1 in the normalized temperature scale indicate that the resulting crystalline phases exhibited weaker intermolecular interactions compared to the pure phase-changing component. In a few cases, deviations above 1 in the normalized temperature scale were also observed, these are attributed to slower phase transition kinetics in the SS-PCM compared to the pure phase-changing motifs. Longer melting or crystallization times result in an increase in the observed on-set temperature for these phase transitions.

Data from Fig. 10 also indicates that the use of ethylene oxide-based phase changing motifs produces SS-PCMs exhibiting higher latent heats of transition than the use of fully aliphatic crystallizing groups. A number of different backbones have been explored, with cellulose, polyacrylate, polyvinyl alcohol and polyurethane as the most common choices as polymeric matrices. The best heat storage efficiencies were observed in structures where the phase changing motif was grafted to a polyacrylate or a cellulose polymeric backbone. Different architectures where the polyethylene glycol phase changing motif was used as a "soft block" polyurethanes or as a cross-linked for a melamine formaldehyde resin showed similar heat storage efficiencies.

One key feature of these materials that is not captured in Fig. 10 is the absolute observed value for the heat absorbed during the melting transition. Ultimately this is the parameter that will determine whether a specific material is suitable as a SS-PCM for a target application. The absolute ΔH values are summarized in table 1. In the majority of the examples where the phase changing motif was covalently attached to the polymer backbone, part of the losses in heat storage efficiency (10–30%) were caused by the changes in the chemical structure that were required to produce the chemical linkage between the polymer backbone and the crystallizing motifs. Additional losses in efficiency ranging from 10% to 80% were measured after incorporation of the phase changing moieties into the polymer backbone. In general the best results were obtained when the linker between the crystallizing motif and the polymer backbone is flexible and no longer than 8 atoms. Use of aromatic linkers resulted in higher losses of heat storage efficiency, as did the use of hydrogen-bonding groups or strong dipoles. When using a polymeric phase changing motif, there is a compromise between accessing the highest heat of melting possible, while keeping the melt viscosity within acceptable ranges to allow the phase transition to occur to the maximum extent possible upon cooling. Diminishing returns are obtained once the molecular weight of the phase changing motif increases past 2 kg/mol when used as a grafted side chain or 6 kg/mol when the crystallizing motif is used as a cross-linker.

From a materials design perspective, the use of polymeric structures as a form stabilizing matrix and as mechanical support is definitively attractive. However, the observed decreases in the resulting phase change latent heats, compared to those for the unthetered phase-changing moiety suggest that direct covalent attachment of the phase changing motif to the polymeric backbone may not be the best course or action. Covalent bonding of the groups undergoing the phase transition to a polymeric backbone restricts their conformational freedom and negatively affects the ability of these groups to efficiently undergo the molecular rearrangements required for efficient phase transitions. Better results have been observed when blending a polymeric matrix with a phase changing organic molecule, though consistent characterization of the potential de-mixing of the polymer and the phase changing compound upon cycling was not always available [18]. Nonetheless the blending approach remains promising if the mixtures can be stabilized via a systematic tuning of the polymer-small molecule supramolecular interactions.

4.2. Organic SS-PCMs

Organic molecules capable of reorganizing their supramolecular interactions, typically hydrogen bonds, as a function of temperature, can potentially undergo highly endothermic solid-solid phase transitions. These highly symmetric and bulky alcohols, such as pentaerythritol (PE), neopentylglycol (NPG), trimethylol propane (TMP), and pentaglycerine (PG) have been reviewed extensively and we refer you to those works for specific details, see Fig. 11 and Table 2 [17,30,69].

The pure compounds exhibit relatively high latent heats for their solid-solid phase transitions (above 100 J/g), at temperatures ranging from 40 °C to 190 °C. The transition temperatures can be tuned by producing eutectic mixtures of two of these compounds, in general lowering both the transition temperature and the phase-change latent heats. Fig. 12 illustrates the data in terms of normalized enthalpy of melting as a function of normalized transition temperature. In that scale, values closer to 1 (on both normalized axis) indicate that the phase changing motifs undergo the thermally-induced transition as efficiently as they would if they were not mixed with a second compound to form a eutectic. Deviations below 1 in the enthalpy scale indicate that the phase transition occurred incompletely, while deviations below 1 in the temperature scale indicate that the resulting crystalline phases exhibited weaker intermolecular interactions compared to the pure phase-changing component. Attempts to improve the latent heat of these materials by adding inorganic salts, such as magnesium chloride or sodium sulfate have also been reported. The addition of these salts can in some cases increase the latent heat but results in a solid-liquid transition instead of a solid-solid transition [70]. An interesting alternative is the use of symmetric dialkylammonium salts with both organic and inorganic counterions, see Fig. 13. These compounds exhibit solid-solid phase change latent

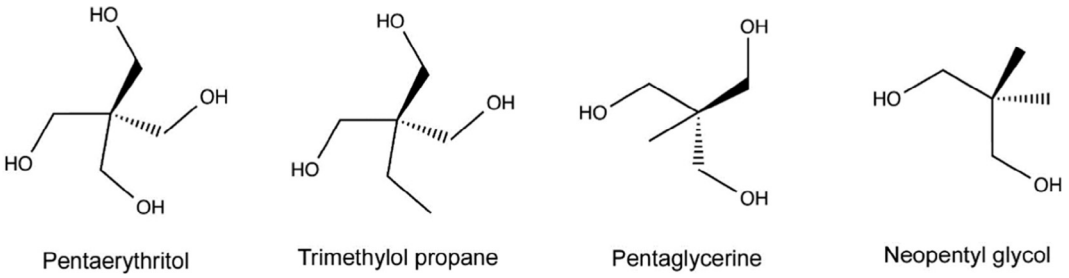

Fig. 11. Polyols SS-PCMs.

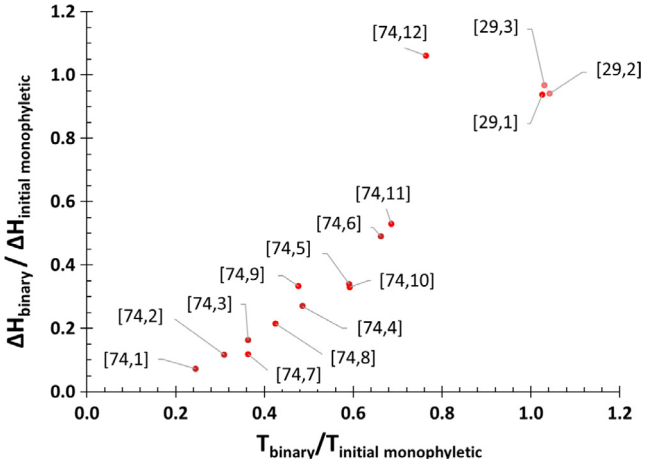

Fig. 12. Organic SS-PCMs using normalized enthalpy and temperature scales (Note: The first number in the brackets is the reference number and the second is the variation of the PCM in the formula or % weight of components).

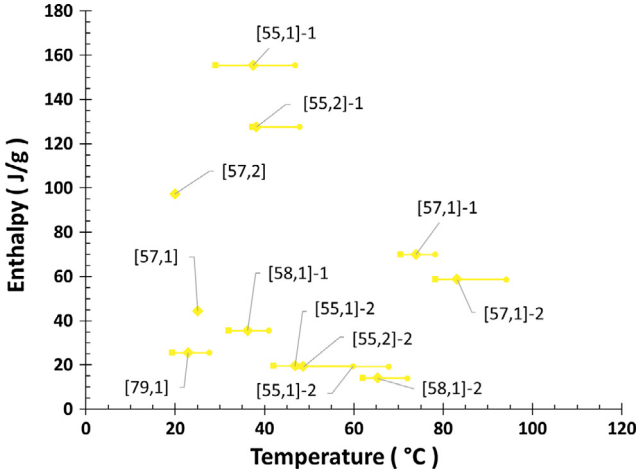

Fig. 14. Summary of enthalpy vs. transition temperature of organometallic SS-PCMs (Perovskites) reported in the literature (Note: The first number in the brackets is the reference number and the second is the variation of the PCM in the formula or % weight of components. The number behind the bracket is the melting peak number).

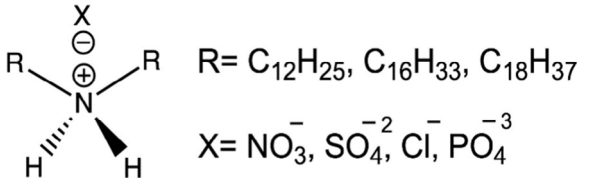

Fig. 13. Organic dialkylammonium-based SS-PCMs.

heats ranging from 102 J/g to 185 J/g, and transition temperatures ranging from 10 °C to 98 °C [71] .This behavior makes them particularly attractive for a wide range of heat storage applications, and warrants follow up work to characterize the long term stability and cyclability.

4.3. Organometallic SS-PCMs

Organometallic SS-PCM are a group of layer perovskite organometallics, which are composed of alternate inorganic and organic layers and have a sandwich-like crystalline structure. As illustrated in Fig. 6, the phase transition of organometallic SS-PCM only involves the alkyl chains (i.e., the organic region or soft segments) while the inorganic layers remain structurally unchanged since they are thermally inert [75]. When absorbing energy, the long alkyl chains melt and undergo a phase transition from an ordered formation, mainly in a planar zigzag arrangement (i.e., crystalline form), to disordered state (i.e., amorphous form). The hydrocarbon regions are in a liquid-like state at high temperature but their lateral movement is restricted by the attachment to the inorganic sheet-like scaffold, and thus the whole organometallic SS-PCMs remain in a solid form.

Organometallic SS-PCM can be described with a general chemical formula $(n\text{-}C_nH_{2n+1}NH_3)_2MX_4$, where M is a metal atom, X is a halogen, and n varies from 8 to 18.. The organic region consists of long paraffinic chains of n-alkylammonium groups, which are attached to the thin inorganic layer through ionic bonds (see Fig. 6). A series of organometallic SS-PCMs have been synthesized and characterized for X = Cl, shown in Table 3 [26,76,77], with their solid-solid transition temperature between 19.3 and 94.1 °C and enthalpy in the range of 62.6–153.8 J/g (see Fig. 14).

The thermal properties of binary mixtures of Co- and Zn-based organometallic SS-PCMs were also investigated. These binary mixtures exhibit behavior similar to the aforementioned polyalcohol blends, with the enthalpy between 74 and 115 J/g during solid-state transformations at temperatures between 70 and 105 °C for a C10–C16 blend [78]. Multiple, discrete solid–solid phase transitions were observed for many of the organometallic SS-PCMs over the ranges shown in Table 3, with the listed latent heat being the sum over those transitions.

The observed transition temperature and enthalpy change associated with the phase transition (latent heat) of organometallic SS-PCMs depend on the length of their alkyl chains, increasing with the number of carbon atoms in the chains, which also depends on the particular metal and halogen present in the inorganic region. Since the inorganic compounds do not undergo phase transition and remain thermally 'inert', they contribute only to the weight of organometallic SS-PCMs but not to their latent heat. Consequently, the enthalpies of the organometallic compounds per

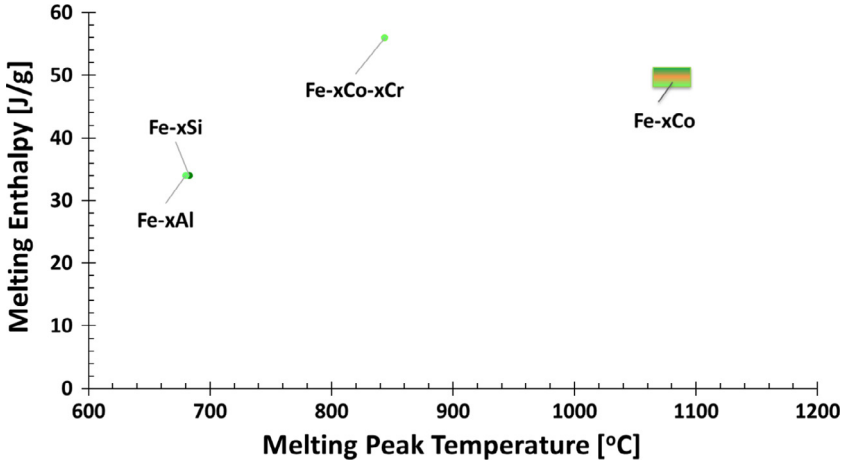

Fig. 15. Examples of melting enthalpy for several inorganic SS-PCMs.

unit mass are slightly lower than those for melting of the normal paraffin's. On the other hand, the thermal conductivity of organometallic SS-PCMs is higher than n-paraffin by an order of magnitude because of high thermal conductivity of the metals in the inorganic region, although no experimental results have been reported in the literature yet. However, the relatively high densities of organometallic SS-PCMs make them less suitable for weight sensitive applications.

Physical and chemical stability of organometallic SS-PCMs was also examined since they must be able to undergo many repetitive thermal cycles in practical thermal energy storage applications. Their solid-solid transition was found to be totally reversible after 1000 thermal cycles, with a volume change in the order of 5–10% during the transitions. These organometallic compounds are also chemically stable at moderately high temperatures and exhibit slow decomposition at temperatures above 500 K in presence of air.

4.4. Inorganic SS-PCMs

Inorganic SS-PCMs are able to store/release thermal energy in solid phase using one or combination of energy storage mechanisms including magnetic transformations, crystallographic structure transformations, order– disorder transformations, transformations between amorphous structure and crystal structure. In general, the amount of latent heat of inorganic SS-PCMs are smaller compared to other types of solid-solid PCMs reviewed in this paper.

Each single solid–solid transformation mechanisms exhibits a small amount of latent heat. Therefore, several solid–solid transformations should occur simultaneously to obtain large latent heats or heat storage/discharge at a specific temperature [32]. There are a limited number of materials able to undergo multiple and reversible solid–solid transformations at close temperatures. Transformations between amorphous structure and crystal structure are not reversible transformations as solid–solid transformations.

In the solid–solid transformations, crystallographic structure transformations and magnetic transformations have relatively large amount of latent heat. There are various metals showing crystallographic structure transformation; however, typical metals exhibiting magnetically-induced phase changes are limited to Fe, Co and Ni. The temperature of crystallographic structure transformation between ferrite and austenite of Fe and that of magnetic transformation of Fe are very close. These transformation temperatures can be controlled by the Co concentration in Fe–Co binary system [32]. Fig. 15 shows melting enthalpy of several inorganic SS-PCMs.

One of the applications of inorganic SS-PCMs is in industrial plants for heat recovery of the intermittently emitted high temperature waste heat. In this application, inorganic SS-PCMs utilizes one or two solid–solid transformations at high temperatures to store and later release of thermal energy in solid phase.

5. Challenges and opportunities

SS-PCMs are promising materials that have many useful attributes for heat storage applications, current literature reports have focused primarily on their basic thermal characterization. However, adoption of SS-PCMs in specific engineering applications requires more detailed characterization to fully understand their potential and limitations. Challenges and opportunities associated with the use of SS-PCMs for thermal energy storage and other applications are discussed in the following sections.

5.1. Thermal conductivity

Similar to their solid-liquid counterparts, SS-PCMs also exhibit relatively low thermal conductivity, especially the organic and polymeric types. Thermal conductivity of SS-PCMs plays an important role in thermal energy storage as it largely affects the charging and discharging rates. However, compared to other thermal properties (e.g., phase transition enthalpy, phase transition temperature, etc.), thermal conductivity of SS-PCMs has received much less attention. Whitman et al. [79] measured temperature-dependent thermal conductivity of Di-n-hexylammonium bromide ($(n\text{-}C_6H_{13})_2NH_2Br$) from −25 to 75 °C, which varied from 0.12 to 0.17 W/m/K and is discontinuous in the region of the phase transition temperature. Sari et al. [37] determined thermal conductivity of polystyrene-graft-palmitic acid (PA) copolymer SS-PCMs at room temperature based on the transient line heat source method.

Table 5
Summary of reported thermal conductivity of various SS-PCMs and SL-PCMs.

PCM types	K (W/m/K)	Reference No.
Polymeric SS-PCMs	0.10–0.20	[37,39,40]
Fatty acid SL-PCMs	0.15–0.17	[14]
Organic SL-PCMs	0.17–0.36	[14]
Organometallic SS-PCMs	~2	[18]
Inorganic SL-PCMs	0.32–5	[14]

Table 6
Summary of relative ratings of pros and cons for different types of SS-PCMs.

Property	Polymeric	Organic	Organometallic	Inorganic
Transition temp. (°C)	11–65	25–190	32–160	680–988
Enthalpy (J/g)	10–205	15–270	62–154	34–56
Thermal conductivity	+	+	+++	++++
Phase change kinetics	+	+	+++	+++
Phase separation	++++	++	+++	++++
Chemical & thermal stability	+++	+++	+++	++++
Volume change	++	++	++++	++++
Non-toxicity	+++	+	++++	++++
Fire resistance	+	+	++	++++
Ease of production	+++	+++	+	++++

+ Poor, ++ Fair, +++ Good, ++++ Excellent.

The measured thermal conductivities of the synthesized SS-PCMs depends on the mole percentage of PA, which are 0.13, 0.18, and 0.20 W/m/K for poly(S-PA-S) with 25%, 50%, and 75% PA, respectively. Sari et al. [39] and Sari et al. [40] reported thermal conductivity of polystyrene-graft-poly(ethylene glycol) and poly (styrene-co-allyalcohol)-graft-stearic acid SS-PCMs, ranging from 0.10 to 0.13 W/m/K and 0.12 to 0.15 W/m/K for polystyrene-graft-poly(ethylene glycol) and poly(styrene-co-allyalcohol)-graf t-stearic acid based SS-PCMs, respectively. In the case of these polymeric materials, their thermal conductivity also depended on the mass concentration of their respective soft segments (i.e., the side chains that undergo phase transition, *i.e.* polyethylene glycol and stearic acid, respectively). The polymeric SS-PCMs exhibited thermal conductivities comparable to their SL-PCM organic analogs, such as fatty acids, organic polyglycols and paraffins, but lower than those measured for the inorganic SL-PCMs, this was attributed to the similarities in molecular structure of the SS polymeric, and SL organic PCMs. Thermal conductivity of SS-PCMs reported in the literature is summarized in Table 5 which also includes typical thermal conductivity values for SL-PCMs commonly used for thermal energy storage [14]. The relative ratings of the thermal conductivity of the different SS-PCMs are presented in Table 6.

Enhancement of the thermal conductivity in SS-PCMs has been attempted using techniques like those used in SL-PCMs, such as the addition of thermal conductivity enhancing materials (e.g., carbon-based nano-materials, expanded graphite, copper, and other metal particles). Li et al. [50] added expanded graphite (EG) at different mass concentration in order to enhance thermal conductivity of cellulose graft poly(ethylene glycol) (cellulose-graft-PEG) copolymer SS-PCMs. The authors reported that thermal conductivity of the copolymer SS-PCMs increased linearly with the increase in the mass fraction of EG, ranging from 0.21 to 0.80 W/m/K at the EG mass fraction of 0–10%. However, they found that incorporation of EG at a higher mass fraction (~10 wt.%) reduced latent heat capacity significantly and recommended using EG at lower concentration for improving thermal conductivity without appreciable loss of latent heat capacity for cellulose-graft-PEG) copolymer SS-PCMs.

5.2. Phase change kinetics

In addition of their thermal conductivity, the charging/discharging rate of SS-PCMs also depends on the rate at which the heat-storing phase change occurs. Phase transition kinetics in SS-PCMs are influenced by the molecular weight, melt viscosity, and nature of the intermolecular interactions. Inorganic SS-PCMs exhibit the fastest phase-change rate due to the homogeneous nature of their molecular structure and the relatively low melt viscosity at the melting temperature. Organic SS-PCMs exhibit a broader range of phase-change rates with the polyols exhibiting the slowest transitions due to the presence of extended hydrogen-bonded supramolecular networks that interfere with the molecular rearrangements required for phase transition. Since the organometallic SS-PCMs contain paraffin-like phase changing motifs, their phase transition kinetics are similar to those observed for the paraffin-based SL-PCMs, thus exhibiting relatively fast phase change kinetics. The rate of phase transition for polymeric SS-PCMs depends on their molecular weight on the chemical nature of the phase-changing motifs. Increases in molecular weight typically lead to higher melt viscosities and slower phase change rates. A similar trend is observed when increasing the concentration of functional groups capable of generating strong supramolecular interactions, such as hydrogen bonds or ionic interactions. Slow phase transition kinetics can produce differences in the observed onset temperatures for melting and crystallization that increase as the heating or cooling rates increase. Super cooling of up to 40 °C has been reported for materials with slow phase-change kinetics, typically polymeric or organic SS-PCMs. A comparison of phase change rates is shown in Table 6.

5.3. Ease of production, cost and other factors

Wide-spread adoption of SS-PCMs will be linked to significant extent to their cost. Most of the organic and polymeric SS-PCMs have been synthesized from widely available, low-cost, starting materials that are commercially utilized for other applications, making a pathway to commercialization relatively straightforward. In contrast, the organometallic SS-PCMs required relatively more complex synthetic schemes and produce denser materials, thus increasing their cost per unit of mass. The inorganic SS-PCMs are derived from common metallic alloys and, when used within optimized, integrated processes can justify the additional production costs.

Many other factors affect the use of SS-PCMs in specific engineering applications. Some of the issues that may affect specific applications include phase separation, chemical and thermal stability, volume change, toxicity, and fire resistance. Current literature does not provide information on these factors. An initial assessment of the relative ratings for these factors is provided in Table 6.

5.4. Opportunities

Solid-solid PCMs can offer unique application opportunities that build upon their high latent heat storage capacity and the solid-solid nature of their phase transitions.

5.4.1. Structural-thermal functions

One of the arguments in favor of SS-PCMs is their ability to remain solid and prevent leakage. The term "solid" can be somewhat misleading, as most SS-PCMs become soft, wax-like, solids

with relatively low mechanical strength above their phase change temperatures. An evaluation of the mechanical properties of SS-PCMs as a function of temperature would be useful for engineering design purposes. Similar to the development of structural batteries [80], novel SS-PCMs can be envisioned that combine heat storage with useful mechanical properties. Several structural features must be balanced however to produce SS-PCMs with high latent heats and acceptable mechanical properties. For example, a higher degree of cross-linking can increase both the modulus and tensile strength in polymeric SS-PCMs, but may also reduce their chain mobility thus likely interfering with phase transitions and decreasing latent heat. A more thorough characterization of the effect of chemical structure on both thermal and mechanical properties would help with identifying general trends necessary for rational materials development. Current literature does not provide adequate information on mechanical properties and long-term shape stability at different temperatures, nor does it systematically report the glass transition temperature of SS-PCM polymeric compounds. Such information will be required to demonstrate, for example, that the glass transition temperature is sufficiently high for the expected application. As a general trend, addition of mechanically stabilizing materials (either via covalent modification or blending) to the phase changing motifs, decreases the resulting latent heat compared to the pure components. The majority of the literature reports have focused on minimizing the disruption to the crystalline structures resulting from the modifications required to convert a material undergoing solid-liquid transitions into one exhibiting a solid-solid phase change. A similar crystalline structure disrupting trend occurs when the organic PCMs are blended to increase their thermal conductivity, minimize hysteresis or fine tune the phase transition temperature. Even in the most promising cases, where the phase transition exhibits the latent heats comparable to solid-liquid systems, further characterization of the long-term stability of these compounds upon thermal cycling is still required.

5.4.2. Encapsulation and shape-stabilization

Encapsulation into plastics or absorption into porous materials are common approaches to prevent leakage of SL-PCMs [81]. These supporting materials, however, do not participate in the latent heat storage process and therefore lower the net heat storage capacity of such systems. Since SS-PCMs remain solid, they may also be used to encapsulate SL-PCM's, which would allow all constituents to contribute to the latent heat storage processes. Similarly, shape stabilized SL-PCMs using SS-PCM matrixes may also offer a viable path. Such approaches could offer cost benefits and higher heat storage capacity.

5.4.3. Smart and adaptive materials

Polymeric SS-PCMs show many similarities to various smart polymer systems, many of whom also employ phase transitions, for example to bring about changes in hydrophobicity or transparency. New multifunctional SS-PCMs can be developed that combine thermal energy storage with other useful functional attributes. Such integrated and multifunctional approaches can lead to the development of innovative adaptive materials that can self-regulate their heat storage and thermal transport properties in response to various external stimuli. Examples are abound in biological systems were optical, thermal, and structural functions render adaptive systems enabled by various phase transformations.

5.4.4. Thermo-chromic applications

Many SS-PCMs experience a change in transparency when undergoing phase transitions, such properties may be used to develop low-cost SS-PCM based thermo-chromic systems. A recent study investigated an adaptive passive solar building enclosure system using a thin layer of polymeric SS-PCM, which was used as a coating onto a highly reflective exterior façade material [82]. During winter, the SS-PCM is crystalline at low outdoor temperatures and remains opaque; thus absorbing solar radiation at the exterior surface (to reduce heating loads). During summer, the SS-PCM becomes amorphous and transparent at elevated outdoor temperatures, thus exposing the reflective layer, which reflects solar radiation (to reduce cooling loads). While many SL-PCMs also undergo transparency changes, their liquid state hinders such direct use in exposed surface applications. Additional studies are needed to assess the long-term shape stability and mechanical properties of such SS-PCM based exposed surface systems.

5.4.5. Radiation heat transfer

The ability to absorb heat using radiation heat-transfer can be used to circumvent the low thermal conductivity problems typically associated with PCM's. In such approach, as illustrated in the building envelope application described above, radiation penetrates the material at the surface and is turned into heat when it is gradually absorbed deeper into the material. The attenuation or absorbance of the SS_PCM, as well as its surface properties, will affect the rate and efficiency of such heat transfer processes. In some applications, low thermal conductivity may thus become beneficial as it allows the material to retain heat longer. New SS-PCMs systems may be developed with purposely-enhanced thermal resistance, for example by using blowing agents to produce cellular SS-PCM systems [82]. Such applications will require careful design and characterization of combined thermal and optical properties for SS-PCMs.

6. Conclusions

This paper reviews SS-PCMs for thermal energy storage applications, with a focus on thermal properties (i.e., enthalpy and phase transition temperature) of four types of SS-PCMs with different molecular structures reported in the literature. The processes underlying phase transition of these SS-PCMs were briefly explained. The relationship between molecular structures and thermal properties of these SS-PCMs was discussed and critically reviewed, which will provide guidance for synthesizing SS-PCMs with tailored thermal properties. Challenges to the practical implementation of SS-PCMs for thermal energy storage and heat management were also discussed. More effort is needed to characterize other thermophysical properties (e.g., thermal conductivity, mechanical strength, stiffness, etc.) of SS-PCMs in order to facilitate their engineering applications. SS-PCMs also offer unique opportunities to develop innovative materials that combine energy storage with other functional attributes.

Acknowledgements

Support from the National Science Foundation, award number CMMI-1662903 & 1662675, Directorate for Engineering, Division of Civil, Mechanical and Manufacturing Innovation (CMMI), Structural and Architectural Engineering and Materials program (SAEM), is much appreciated.

References

[1] N.R. Jankowski, F.P. McCluskey, A review of phase change materials for vehicle component thermal buffering, Appl. Energy 113 (2014) 1525–1561.
[2] EA-ETSAP, Thermal energy storage – technology brief.
[3] H. El-Dessouky, F. Al-Juwayhel, Effectiveness of a thermal energy storage system using phase-change materials, Energy Convers. Manage. 38 (6) (1997) 601–617.
[4] M.M. Farid et al., A review on phase change energy storage: materials and applications, Energy Convers. Manage. 45 (9–10) (2004) 1597–1615.

[5] H.G. Lorsch, K.W. Kauffman, J.C. Denton, Thermal energy storage for heating and air conditioning, future energy production system, Heat Mass Transf. Process. (1976) 69–85.

[6] R. Kandasamy, X.-Q. Wang, A.S. Mujumdar, Application of phase change materials in thermal management of electronics, Appl. Therm. Eng. 27 (17–18) (2007) 2822–2832.

[7] A. Bascetincelik, H.O. Paksoy, H.H. Ozturk, Y. Demirel, Seasonal latent heat storage system for greenhouse heating, in: Phase Change Materials and Chemical Reactions for Thermal Energy Storage First Workshop, Adana Turkey, 1998.

[8] H. Benli, A. Durmuş, Performance analysis of a latent heat storage system with phase change material for new designed solar collectors in greenhouse heating, Sol. Energy 83 (12) (2009) 2109–2119.

[9] M. Mazman et al., Heat transfer enhancement of fatty acids when used as PCMs in thermal energy storage, Int. J. Energy Res. 32 (2) (2008) 135–143.

[10] A. Sharma et al., Review on thermal energy storage with phase change materials and applications, Renew. Sustain. Energy Rev. 13 (2) (2009) 318–345.

[11] C. Alkan, A. Sarı, A. Biçer, Thermal energy storage by poly(styrene-co-p-stearoylstyrene) copolymers produced by the modification of polystyrene, J. Appl. Polym. Sci. 125 (5) (2012) 3447–3455.

[12] S. Mondal, Phase change materials for smart textiles – an overview, Appl. Therm. Eng. 28 (11–12) (2008) 1536–1550.

[13] P. Schossig et al., Micro-encapsulated phase-change materials integrated into construction materials, Sol. Energy Mater. Sol. Cells 89 (2+3) (2005) 297–306.

[14] B. Zalba et al., Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 (3) (2003) 251–283.

[15] D. Zhou, C.Y. Zhao, Y. Tian, Review on thermal energy storage with phase change materials (PCMs) in building applications, Appl. Energy 92 (2012) 593–605.

[16] G. Li et al., Review of cold storage materials for subzero applications, Energy 51 (2013) 1–17.

[17] M.M. Kenisarin, K.M. Kenisarina, Form-stable phase change materials for thermal energy storage, Renew. Sustain. Energy Rev. 16 (4) (2012) 1999–2040.

[18] V. Busico, et al. Solid-solid phase transitions for thermal energy storage. 1981. Nijhoff. "Thermal Storage of Solar Energy: Proceedings of an International TNO-Symposium Held in Amsterdam, The Netherlands, 5–6 November, 1980, p. 309-324

[19] J. Muntasell et al., Plastic crystals and their potential use in new technologies, J. Therm. Anal. 37 (10) (1991) 2395–2398.

[20] X.-M. Zhou, Preparation and characterization of PEG/MDI/PVA copolymer as solid-solid phase change heat storage material, J. Appl. Polym. Sci. 113 (3) (2009) 2041–2045.

[21] L.F. Cabeza et al., Advances in Thermal Energy Storage Systems: Methods and Applications, Woodhead Publishing, Cambridge, England, 2015.

[22] A.S. Fleischer, Springer Link, L.e.E. Springer, Thermal Energy Storage Using Phase Change Materials: Fundamentals and Applications, Springer International Publishing, Cham, 2015.

[23] H.C.L. Mehling, Heat and cold storage with PCM, Springer, Verlag, 2008.

[24] J. Kośny, PCM-enhanced building components: an application of phase change materials in building envelopes and internal structures, Engineering Materials and Processes, Springer, Cham, 2015.

[25] T. Bo et al., Thermodynamic investigation of a solid–solid phase change material: 2-Amino-2-methyl-1,3-propanediol by calorimetric methods, Energy Convers. Manage. 51 (10) (2010) 1905–1910.

[26] W. Li et al., Study of solid-solid phase change of (n-CnH2n+1NH3)2MCl4 for thermal energy storage, Thermochim. Acta 326 (1–2) (1999) 183–186.

[27] H. Singh et al., Continuous solid-state phase transitions in energy storage materials with orientational disorder – computational and experimental approach, Energy 91 (2015) 334–349.

[28] J. Timmermans, Plastic crystals: a historical review, J. Phys. Chem. Solids 18 (1) (1961) 1–8.

[29] W. Chen et al., Novel form stable phase change materials based on the composites of polyethylene glycol/polymeric solid-solid phase change material, Sol. Energy Mater. Sol. Cells 134 (2015) 80–88, http://dx.doi.org/10.1016/j.solmat.2014.11.039, ISSN 0927-0248.

[30] M. Barrio et al., Applicability for heat storage of binary systems of neopentylglycol, pentaglycerine and pentaerythritol: a comparative analysis, Sol. Energy Mater. 18 (1–2) (1988) 109–115.

[31] X. Wang et al., Heat storage performance of the binary systems neopentyl glycol/pentaerythritol and neopentyl glycol/tris(hydroxymethyl) aminomethane as solid-solid phase change materials, Energy Convers. Manage. 41 (2) (1999) 129–134.

[32] K. Nishioka et al., Development of Fe base phase change materials for high temperature using solid-solid transformation, ISIJ Int. 50 (9) (2010) 1240–1244.

[33] X. Du et al., Synthesis and thermal energy storage properties of a solid-solid phase change material with a novel comb-polyurethane block copolymer structure, RSC Adv 6 (48) (2016) 42643–42648.

[34] V. Busico et al., The layer Perovskites as thermal energy storage systems, Sol. Energy 24 (6) (1980) 575–579.

[35] S. Mu et al., A novel solid-solid phase change material based on poly(styrene-co-acrylonitrile) grafting with palmitic acid copolymers, J. Macromol. Sci., Part A 52 (8) (2015) 617.

[36] L. Yanshan et al., Preparation and characterization of melamine/formaldehyde/polyethylene glycol crosslinking copolymers as solid–solid phase change materials, Sol. Energy Mater. Sol. Cells 127 (2014) 92–97.

[37] A.A. Sarı, A. Biçer, A. Karaipekli, Synthesis and thermal energy storage characteristics of polystyrene-graft-palmitic acid copolymers as solid-solid phase change materials, Sol. Energy Mater. Sol. Cells 95 (2011) 3195–3201.

[38] S.-Y. Mu et al., Synthesis and thermal properties of poly(styrene-co-acrylonitrile)-graft-polyethylene glycol copolymers as novel solid-solid phase change materials for thermal energy storage, Chin. Chem. Lett. (2015).

[39] A. Sari, C. Alkan, O. Lafci, Synthesis and thermal properties of poly-graft-stearic acid copolymers as novel solid-solid PCMs for thermal energy storage, Sol. Energy 86 (9) (2012) 2282.

[40] A. Sarı, C. Alkan, A. Biçer, Synthesis and thermal properties of polystyrene-graft-PEG copolymers as new kinds of solid–solid phase change materials for thermal energy storage, Mater. Chem. Phys. 133 (1) (2012) 87–94.

[41] J.-C. Su, P.-S. Liu, A novel solid–solid phase change heat storage material with polyurethane block copolymer structure, Energy Convers. Manage. 47 (18) (2006) 3185–3191.

[42] Q. Cao, P. Liu, Hyperbranched polyurethane as novel solid–solid phase change material for thermal energy storage, Eur. Polym. J. 42 (11) (2006) 2931–2939.

[43] W.-D. Li, E.-Y. Ding, Preparation and characterization of cross-linking PEG/MDI/PE copolymer as solid-solid phase change heat storage material, Sol. Energy Mater. Sol. Cells 91 (9) (2007) 764–768.

[44] H.S. Zhang, Q. Wang, J. Guo, Y. Gong, Synthesis and characterization of polyethylene glycol acrylate crosslinking copolymer as solid–solid phase change materials, J. Appl. Polym. Sci. (2014).

[45] C. Chen et al., Synthesis of solid–solid phase change material for thermal energy storage by crosslinking of polyethylene glycol with poly(glycidyl methacrylate), Sol. Energy 85 (11) (2011) 2679–2685.

[46] X. Fu et al., Thermosetting solid–solid phase change materials composed of poly(ethylene glycol)-based two components: flexible application for thermal energy storage, Chem. Eng. J. 291 (2016) 138–148.

[47] X. Huang et al., Preparation and characterization of di-hexadecanol maleic/triallyl isocyanurate cross-linked copolymer as solid–solid phase change materials, J. Appl. Polym. Sci. 133 (40) (2016) n/a–n/a.

[48] X. Huang et al., Preparation and characterization of pentaerythritol/butane tetracarboxylic acid/polyethylene glycol crosslinking copolymers as solid-solid phase change materials, J. Macromol. Sci., Part A 53 (8) (2016) 500–506.

[49] K. Pielichowska, K. Pielichowski, Biodegradable PEO/cellulose-based solid-solid phase change materials, Polym. Adv. Technol. 22 (12) (2011) 1633–1641.

[50] Y. Li et al., Cellulose-based solid–solid phase change materials synthesized in ionic liquid, Sol. Energy Mater. Sol. Cells 93 (8) (2009) 1321–1328.

[51] W. Marta, W.T. M, Novel solid – solid phase change material based on polyethylene glycol and cellulose used for temperature stabilisation, in: MATEC Web of Conferences, vol. 18, 2014, p. 03009.

[52] N. Han et al., Synthesis and characterization of cellulose-g-polyoxyethylene (2) hexadecyl ether solid–solid phase change materials, Cellulose 23 (3) (2016) 1663–1674.

[53] S.B. Şentürk et al., Biodegradable PEG/cellulose, PEG/agarose and PEG/chitosan blends as shape stabilized phase change materials for latent heat energy storage, Carbohyd. Polym. 84 (1) (2011) 141–144.

[54] C.S. Brazel et al., Fundamental Principles of Polymeric Materials, third ed., Wiley, Hoboken, New Jersey, 2012.

[55] D.-F. Lu, Y.-Y. Di, J.-M. Dou, Crystal structures and solid–solid phase transitions on phase change materials (1−CnH2n+1NH3)2CuCl4(s) (n=10 and 11), Sol. Energy Mater. Sol. Cells 114 (2013) 1–8.

[56] D.F. Lu, Y.Y. Di, D.H. He, Crystal structures and thermodynamic properties of phase change materials, Renew. Energy 50 (2013) 498.

[57] W.-W. Zhong et al., Lattice potential energies and thermochemical properties of phase change materials (1-CnH2n+1NH3)2MnCl4(s) (n = 10 and 11), J. Chem. Thermodyn. 72 (2014) 100–107.

[58] D.F. Lu et al., Low-temperature heat capacities, and thermodynamic properties of solid–solid phase change material bis(1-octylammonium) tetrachlorocuprate, J. Therm. Anal. Calorim. 111 (1) (2013) 213–218.

[59] O.J. Almeida, B.G. Dixon, Lamellar metallo-alkylphosphonates as solid-state phase-change materials, Chem. Mater. 7 (11) (1995) 2039–2044.

[60] V. Salerno, A. Grieco, M. Vacatello, Ordered and disordered phases in mixed dodecylammonium and hexadecylammonium tetrachloromanganate(II), J. Phys. Chem. 80 (22) (1976) 2444–2448.

[61] H. Shi et al., Preparation and properties of poly(vinyl alcohol)-g-octadecanol copolymers based solid–solid phase change materials, Mater. Chem. Phys. 131 (1–2) (2011) 108–112.

[62] A. Sarı, C. Alkan, Ö. Lafçı, Synthesis and thermal properties of poly(styrene-co-ally alcohol)-graft-stearic acid copolymers as novel solid–solid PCMs for thermal energy storage, Sol. Energy 86 (9) (2012) 2282–2292.

[63] C. Alkan et al., Polyurethanes as solid–solid phase change materials for thermal energy storage, Sol. Energy 86 (6) (2012) 1761–1769.

[64] K. Peng et al., Preparation and properties of β-cyclodextrin/4,4′-diphenylmethane diisocyanate/polyethylene glycol (β-CD/MDI/PEG) crosslinking copolymers as polymeric solid–solid phase change materials, Sol. Energy Mater. Sol. Cells 145 (2016) 238–247.

[65] C. Chen et al., Synthesis and performances of novel solid–solid phase change materials with hexahydroxy compounds for thermal energy storage, Appl. Energy 152 (2015) 198–206.

[66] P. Xi, X.-H. Gu, B. Cheng, Studies on the synthesis, characterization and application of a novel copolymer macromonomer for polymeric solid-solid phase change materials, E-Polymers (2008).
[67] B. Tang, Z. Yang, S. Zhang, Poly(polyethylene glycol methyl ether methacrylate) as novel solid-solid phase change material for thermal energy storage, J. Appl. Polym. Sci. 125 (2) (2012) 1377–1381.
[68] P. Xi et al., Preparation and characterization of a novel polymeric based solid–solid phase change heat storage material, Energy Convers. Manage. 50 (6) (2009) 1522–1528.
[69] W. Gao et al., An experimental study on the heat storage performances of polyalcohols NPG, TAM, PE, and AMPD and their mixtures as solid-solid phase-change materials for solar energy applications, Int. J. Green Energy 4 (3) (2007) 301–311.
[70] C.H. Son, J.H. Morehouse, An experimental investigation of solid-state phase-change materials for solar thermal storage, J. Sol. Energy Eng. 113 (4) (1991) 244–249.
[71] S. Steinert et al., Thermal characteristics of solid–solid phase transitions in long-chain dialkyl ammonium salts, Thermochim. Acta 435 (1) (2005) 28–33.
[72] C. Wang et al., Heat storage performance of the binary systems neopentyl glycol/pentaerythritol and neopentyl glycol/trihydroxy methyl-aminomethane as solid–solid phase change materials, Energy Convers. Manage. 41 (2) (2000) 129–134.
[73] D.K. Benson et al., Materials Research for Passive Solar Systems: Solid-state Phase-change Materials, Solar Energy Research Institute, Prepared for the U.S. Department of Energy, 1985.
[74] X. Wang et al., Micromechanism of heat storage in a binary system of two kinds of polyalcohols as a solid–solid phase change material, Energy Convers. Manage. 41 (2) (2000) 135–144.
[75] H. Garg, S. Mullick, V.K. Bhargava, Solar Thermal Energy Storage, Springer Science & Business Media, 2012.
[76] D.-H. He et al., Crystal structures and thermochemistry on phase change materials (n-C n H 2n+ 1 NH 3) 2 CuCl 4 (s) (n= 14 and 15), Sol. Energy Mater. Sol. Cells 95 (10) (2011) 2897–2906.
[77] D.-H. He et al., Crystal structure, low-temperature heat capacities, and thermodynamic properties of bis (dodecylammonium) tetrachlorocuprate (C12H28N) 2CuCl4 (s), J. Chem. Eng. Data 55 (12) (2010) 5739–5744.
[78] D. Ruan et al., Phase diagrams of binary systems of alkylammonium tetrachlorometallates (II), J. Therm. Anal. Calorim. 45 (1–2) (1995) 235–242.
[79] C.A. Whitman, M.B. Johnson, M.A. White, Characterization of thermal performance of a solid–solid phase change material, di-n-hexylammonium bromide, for potential integration in building materials, Thermochimica Acta 531 (2012) 54–59.
[80] Filippo Dionisi, Ross Harnden, Dan Zenkert, A model to analyse deformations and stresses in structural batteries due to electrode expansions, Compos. Struct. 179 (1) (November 2017) 580–589, http://dx.doi.org/10.1016/j.compstruct.2017.07.029, ISSN 0263-8223.
[81] Alvaro de Gracia, Luisa F. Cabeza, Phase change materials and thermal energy storage for buildings, Energy Build. 103 (2015) 414–419, http://dx.doi.org/10.1016/j.enbuild.2015.06.007, ISSN 0378-7788.
[82] Gert Guldentops, Steven Van Dessel, Building envelope systems with transparent solid-solid phase changing material, towards resilient zero-energy buildings, in: Architectural Engineering Institute (AEI) Conference 2017, April 11–13, 2017, Oklahoma City, Oklahoma.