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Organic and Inorganic Phase Change Materials in Thermal Energy Storage: A Review on Materials Perspectives and Insights with a Case Study

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Abstract: Phase change materials (PCMs) are a significant class of contemporary materials that notably contribute to the effective use of solar energy and waste heat conversion and storage. PCMs are mainly utilized to collect thermal energy through phase transition of materials as latent heat. A high energy storage via latent heat capacity (*i.e.*, accumulation and release thermal energy) in a narrow temperature variation is more efficient than many commonly used heat storage method. Throughout the technical development of PCMs, a wide range of materials have been investigated, including organic and inorganic PCMs. Organic PCMs include paraffin, fatty acids, and polymeric, while inorganic PCMs comprised of salts, salt hydrates, and their mixtures. In this comprehensive review, all classes of PCMs are studied with an emphasis on their thermophysical properties, thermal stability, chemical stability, and methodologies for further development of these energy materials. Overall, this review article presents recommendations for mapping suitable PCMs for thermal storage applications. To conclude, inorganic salts and eutectic mixtures of salts such as chlorides were reviewed and considered most appropriate for thermal energy storage (TES) applications operating at high temperatures. Inorganic salts have attracted increasing amounts of scientific interest due to their promising contribution of economic value in the sustainable and renewable environment.

Keywords: Phase Change Materials; Thermal Energy Storage; Latent Heat; Encapsulation; Composites; Sustainable Materials

1. Introduction

The two foremost problems human beings face currently are the environment and energy. Energy demand is continuously increasing massively due to advancements in industries and the exponential increase in population over the next few decades. Fossil fuels are the main energy source, which has been used for a century now exhibit severe environmental impacts like greenhouse emissions. These concerns make us re-evaluate fossil fuels as a primary energy source. While considering these impacts, researchers have been motivated to work on alternative renewable energy technology to minimize climate change and attain sustainable development for our living environment. Solar, wind, and hydel are the three most widely used renewable energy sources. Among these sources, solar energy is good enough to fulfill the requirements of current energy consumption, while its intermittent nature is the most crucial factor, especially at night and during off-peak periods. To date, to discover novel efficient materials storing thermal energy for later use, plenty of research is in progress.

Thermal energy storage (TES) system stores heat energy to be consumed later depending upon several conditions such as location, temperature, power, etc. Mainly, three types of TES systems are used: sensible heat, latent heat, and thermochemical heat. Sensible heat storage materials store heat in their specific heat capacities without changing phase during the heat absorption process and the rise in temperature occurs. Materials that have the potential to be used as sensible heat TES systems are water, thermal oils, metals, melted salts, rocks, concrete blocks, etc. Sensible heat storage materials are mostly used in high-temperature applications due to their high enthalpy of fusion and thermal stability at high temperatures. Such types of materials are inexpensive except for thermal oils and metals. During the heat discharge process, the temperature stability of this type of material faces the main obstacle. Moreover, the heat capacity of these materials is smaller than that of latent heat storage materials, which leads to a smaller storage energy density [1-3]. The thermochemical heat type of thermal energy storage is the heat energy stored by reversible chemical reactions. If the chemical reaction is reversible, the solar heat can be retrieved and used to drive an endothermic reaction. The attractive features of a thermochemical system are high density of energy storage, infinitely extended storage times at temperatures close to atmospheric, and heat-pump functionality, which are some of its benefits. However, factors such as cyclic stability, high heat operational requirements, high expense, and toxic nature are some of the key limitations of thermochemical storage [4]. Another promising system to store heat energy is the latent heat TES system. Phase change materials (PCMs) are used in the latent heat storage system to store or release heat energy during phase transitions from solid to solid, solid to liquid, liquid to gas, or vice versa. Materials with a solid-solid state transition have less specific latent heat, however, they do not need encapsulation for leakage problems. Liquid-to-gas phase transitions possess the highest latent heat of fusion among all PCMs, however, huge volume expansion limits their use and has no use in general. If we compare PCMs with materials used in a sensible heat TES system, the specific heat of PCMs is 50-100 times greater than sensible heat storage materials. In light of these reasons, latent heat storage has attracted a lot of interest in energy storage applications [5, 6, 7]. The classification of latent heat storage materials is displayed in Figure 1.

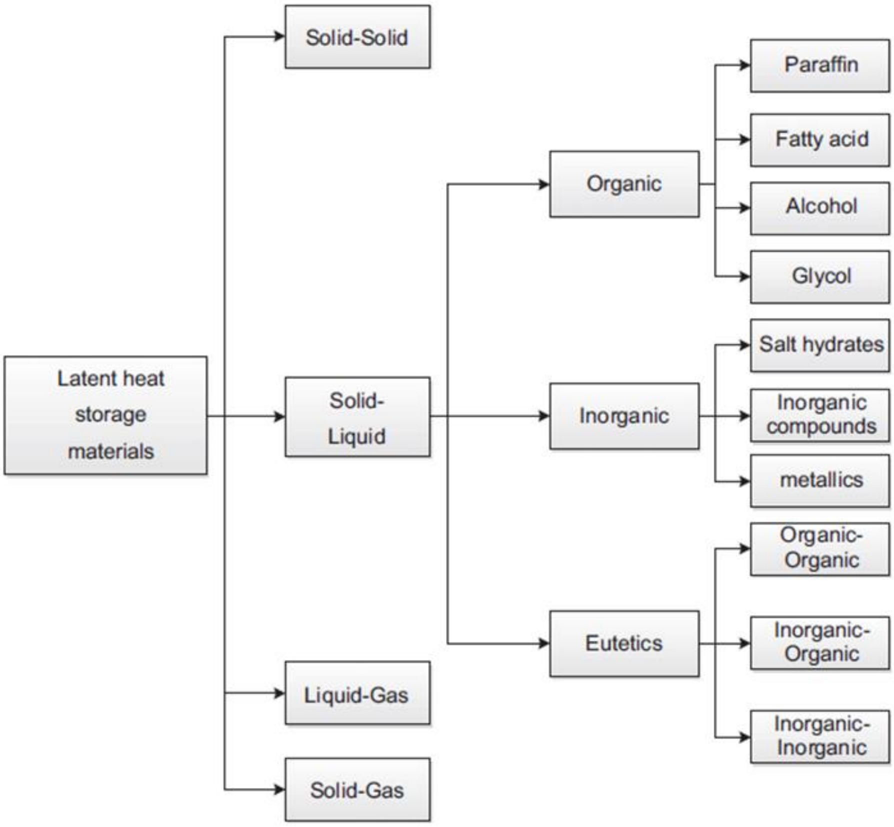

Figure 1. Classification of latent heat storage materials reproduced with permission from [7]; Elsevier.

Low and medium-temperature PCMs (with melting temperature < 200 ˚C) such as organics and salt hydrates of the inorganic class were the focus of research in the past. These PCMs are mostly used in building applications, personal cooling, electronics cooling, solar energy, and automotive applications. PCMs are commonly employed to mitigate and regulate thermal peak loads by releasing energy during cooler night hours and absorbing heat during warmer daytime hours. This is achieved through the processes of melting and solidification. When integrated into a building's envelope PCMs can enhance energy efficiency by effectively managing temperature fluctuations. Liu *et al.* [8] reported that PCMs be added to polyvinyl acetate wall tiles to increase the thermal efficiency of external walls. Their investigation showed that this novel technology might reduce peak heat flux by up to 80% and at least 70%. In another work reported by Chung *et al.* [9], establishes the efficiency of plates containing PCMs in temperature regulation. In the work on the thermal behavior of PCM-incorporated roofs, Reddy *et al.*, [10] found a decrease in heat gain of 25 – 36% compared to roofs without PCM layers. Zhou *et al.*, [11] tested the heat absorption/release capabilities and effects on interior heat gain of a microencapsulated PCM roof module enclosed in an aluminum honeycomb board. The integration of PCMs into Trombe walls offer several benefits, such as enhanced thermal efficiency and indoor comfort, optimized utilization of solar gain, improved storage of thermal mass, prevention of overheating problems, and increased energy conservation [12]. Subsequently, in several other studies, Leang *et al.*, [13], Liu *et al.*, [14], Tenpierik *et al.*, [15], Szyszka *et al.*, [16], and Lichołai *et al.*, [17] investigated the thermal performance of Trombe Wall incorporated with PCM to improve the overall performance. Building walls or roofs can support solar chimneys, which have open structures that circulate air through solar radiation. Traditional building materials for solar chimneys, like rock, brick, and concrete, require a sizable volume to provide adequate thermal storage. PCMs are used in solar chimneys to attain similar thermal storage benefits while using less material [18].

The cost-effectiveness of photovoltaic (PV) systems in producing power is the reason for their rapid global growth. PV systems are using PCMs to improve overall performance despite their competitive advantage. It is a well-known fact that when PV panels' temperature rises, so does their electrical efficiency. Therefore, to control the temperature increase brought on by incoming solar energy that cannot be converted into power, PCMs are used. This is the PV panel's thermal energy being absorbed by the PCM. Several researchers like Al-Waeli *et al.*, [19], Nada *et al.*, [20], Khanna *et al.*, [21], Soares *et al.*, [22], and Zhang *et al.*, [23] investigated PV systems with low and medium-temperature PCMs to improve their performance.

The solar collector is an established technology that is used all over the world. PCMs are integrated into the solar collector to improve thermal efficiency. This enhancement happens when some of the incoming solar radiation is absorbed by PCM using medium temperature, which stores thermal energy and lengthens the solar collector's operating life. Abuşka *et al.*, [24] established a solar air collector by integrating PCM with an aluminium honeycomb. According to their research, using a honeycomb core as a material to improve heat conductivity works very well in the discharge phase. Besides, several other works have also been carried out in the integration of PCMs in solar collectors such as Charvát *et al.*, [25], Palacio *et al.*, [26], Benkaddour *et al.*, [27], Aramesh *et al.*, [28], and Bejan *et al.* [29] emphasizing environmentally friendly solutions and their higher efficiency.

Recently, researchers have shown interest in developing high-temperature PCMs (with melting temperature > 200 ˚C) because they can store high-temperature heat, which lowers the total cost of thermal energy storage systems. Additionally, many concerns, including thermal stability, cycling stability, and corrosion problems with containing materials over an extended length of time, must be considered with high-temperature PCMs. During the selection of PCM for any TES system, some major requirements need to be considered, those are suitable thermophysical properties including melting temperature and heat of fusion, being thermally and chemically stable during many heating/cooling cycles, possessing higher thermal conductivity, and a lower cost [30, 31].

For high-temperature TES systems, metal alloys, and inorganic salts were employed as potential candidates due to their high thermal properties. Among them, metal alloys were rarely used in thermal storage applications due to their heavy weight, corrosion issues, and elevated cost [32]. Moreover, inorganic salts and eutectic mixtures of salts were investigated and considered as most appropriate for TES applications operating at high temperatures [31]. Inorganic salts like chlorides, carbonates, and sulfates have attracted increasing scientific interest due to their potential economic value. Although they are highly corrosive at high temperatures and have low thermal conductivity and thermal stability, these properties have made it challenging to utilize them in high-temperature applications. Classes of PCM with their melting temperature range and fusion enthalpy are displayed in Figure 2.

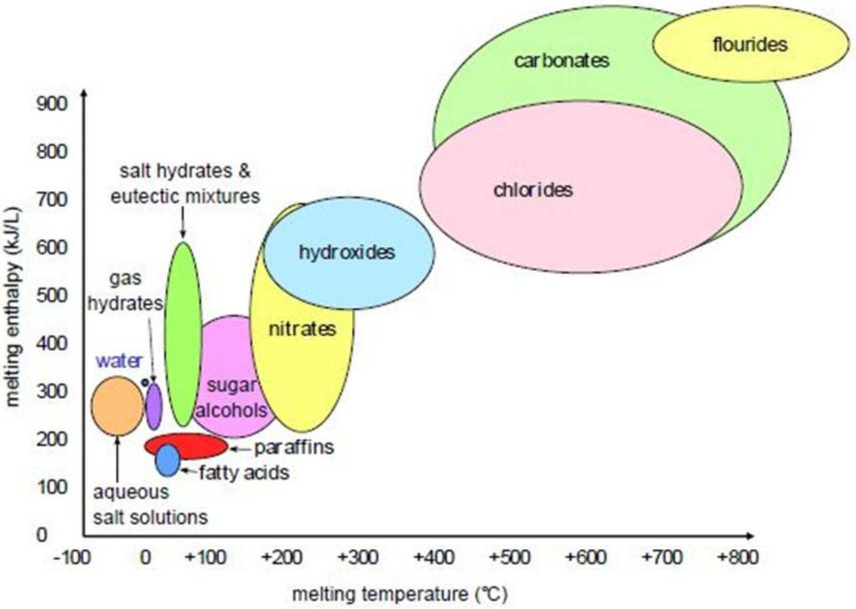

Figure 2. Classes of PCM with their melting temperature and heat of fusion range. Reproduced with permission from [33]; Elsevier.

One of the most important uses of solar energy is the generation of concentrated solar power (CSP), where high-temperature PCMs are used. In CSP plants, PCMs are frequently utilized for thermal energy storage. The PCM collects and stores extra heat during times of strong solar irradiation. When sunlight is scarce, this thermal energy can be released, enabling the continual production of power. PCMs can be added to CSP plant receiver systems to enhance heat storage and transfer. This aids in preserving constant temperatures and maximizing the heat transfer fluid's internal system efficiency. Previous works from Mahfuz *et al.*, [34], Zhao *et al.*, [35] Zhao *et al.*, [36] have mostly worked on developing CSP systems with high-temperature PCMs indicating their significance in the field.

In this review article, an in-depth analysis of both organic and inorganic PCMs along with their unique thermal properties have been synthesized. It provides a detailed summary of the various uses of PCMs in low-, medium-, and high-temperature applications while clarifying the unique requirements and benefits related to each temperature range. This review article also explores novel approaches to developing PCMs, such as composite forms and encapsulating strategies. With the comprehensive compilation of data on PCM thermal properties, application specifications, and fabrication techniques, this review provides useful details and an author viewpoint that advances our understanding of phase change materials in thermal energy storage systems.

The key features of the review on PCM materials are critically focused on organic and inorganic salts that were mapped based on their high thermal properties, low cost, and environmentally friendly. The most promising method that has been considered is the use of latent heat property to store energy, as internal energy of the materials, in molten salt PCM mixtures. The latent heat storage is considered to be an excellent choice for integrating with solar thermal energy applications. This literature review on PCMs may be less widespread on high-temperature salts for TES systems but focus on their thermal and chemical stability. Moreover, the thermal properties of single salts modified by making their mixtures are discussed in a case study. The role of binary salt mixtures, LiCl-LiOH and $CaCl_2$-LiCl, and the features of chloride salts are discussed.

Inorganic salts, such as nitrate, chloride, carbonate, and sulfate salts, exhibit attractive thermophysical properties such as an appropriate melting temperature and a promising fusion enthalpy. Moreover, these salts demonstrate superior energy density, and heat capacity and are thermally and chemically stable over an extended range of temperatures which makes them suitable candidates for TES applications. The chloride salts are potential candidates for thermal energy storage applications as these salts exhibit satisfactory thermophysical properties and lower cost. Salts such as LiCl, LiOH, and $CaCl_2$ are chosen in our case study and discussed. Single salts possess very good and reliable thermophysical properties, which in some cases do not lie within the general acceptable operational temperature of the TES system. However, by making eutectics/mixtures of high-temperature salts, the melting temperature is shown to be modified within the operating temperature of thermal storage applications. Several novel eutectic chloride salts, a type of TES material for high-temperature systems are reviewed here while addressing the key determining factors such as thermal properties and stability to verify its application in TES systems. The mixed salts have the merits of a low cost, easy fabrication, and wide temperature range compared with other molten salts; it has better stability and less degradation. To accelerate the commercialization of eutectic salts as PCMs, strategic approaches to improving the thermal properties and reducing the subcooling of eutectic salts, and selection of materials satisfying the properties such as suitable phase-transformation temperature, high latent heat of transition, and high thermal conductivity, are suggested in this review article.

2. Organic PCMs

Organic PCMs are composed of a wide range of materials, these include paraffin and non-paraffins (fatty acids, esters, alcohols, and glycols) as well as their eutectics. Apart from paraffin and non-paraffins, some other organic compounds possess the potential to be used as PCMs. These materials host a variety of properties that allow them to be used in latent heat storage applications. During several cycles, involving melting and freezing, these materials can melt congruently without phase separation. However, most notably, their best advantage is that they do not show much subcooling [1]. Many of these materials exhibit their phase transition temperature within the range of the human comfort zone, which makes them unique.

2.1. Paraffin

Paraffins are comprised of pure paraffins (alkanes) and technical-grade waxes. Paraffins are saturated hydrocarbons with the general formula C_nH_{2n+2}, where n indicates the number of carbon atoms. The melting point (mp) and enthalpy of fusion rely on chain length (the number of carbon atoms attached to the chain), with the temperature and enthalpy of the phase transition being higher if the chain is longer. Paraffins from pentadecane (15 C and 10 ˚C mp) to triacontane (30 C and 65 ˚C mp) are waxy solids and considered excellent candidates for TES applications. The most widely used paraffin for research work is n-octadecane with 18 C and 28 ˚C mp, which is a very comfortable temperature for humans. Thermophysical properties of pure paraffin are reviewed by Alva *et al*., [1], Pielichowska *et al*., [6], Sharma *et al*., [37], and a few are listed in Table 1. Blends of paraffin also show good performance in latent TES systems, as they melt at a single temperature. Mixtures of paraffin also show good performance in latent TES systems. Some of these mixtures and their thermo-physical properties are displayed in Table 2.

Table 1. Thermo-physical properties of pure paraffins.

Alkanes	C atoms	Melting Point (˚C)	Heat of Fusion (kJ/kg)
Pentadecane	**15**	10.0	206.0
Hexadecane	**16**	19.0	216.0-236.0
Heptadecane	**17**	22.50	164.0-214.0
Octadecane	**18**	28.40	200.0-244.0
Nonadecane	**19**	32.0	222.0
Eicosane	**20**	36.60	247.0
Heneicosane	**21**	40.20	213.0
Docosane	**22**	44.0	249.0
Trikosane	**23**	47.50	234.0
Tetracosane	**24**	50.60	255.0
Pentacosane	**25**	53.50	238.0
Hexacosane	**26**	56.30	256.0
Heptacosane	**27**	58.80	235.0
Oktacosane	**28**	41.20	254.0
Nonacosane	**29**	63.40	239.0
Triacontane	**30**	65.40	252.0

Table 2. Thermophysical properties of eutectic and non-eutectic mixture of n-alkanes.

Eutectics	Melting Point (˚C)	The heat of Fusion (kJ/kg)
Tetradecane-Hexadecane	1.70	156.20
Tetradecane-Geneicosane	4.50	200.20
Tetradecane-Docosane	1.50-5.60	234.30
Pentadecane-Octadecane	8.50-9.0	271.90
Octadecane-Heneicosane	25.80-26.01	173.92
Tetradecane-Octadecane	-4.0-2.0	227.50
Pentadecane-Heneicosane	6.20-7.20	128.24
Pentadecane-Docosane	7.60-8.90	214.82
Octadecane-Docosane	25.50-27.0	203.80

Pure paraffins are expensive as they require high refinement. As a substitute, inexpensive technical-grade paraffin, which comprises a blend of hydrocarbons obtained as a by-product of crude oil distillation, is used in TES systems. Commercially prepared paraffin waxes tested for 1000-2000 cycles present stable thermo-physical properties, with melting temperatures ranging from 5 ˚C to 100 ˚C and good thermal stability [1, 37]. Their thermo-physical properties and manufacturers, are listed in Table 3. Paraffins are non-toxic and ecologically harmless, and their heat storage capacities are high during phase changes over a narrow temperature range. Though they have some adverse properties, like being incompatible with plastic-containing materials, flammable, having low thermal conductivity, and experiencing high-volume expansion during phase transition, these materials are quite stable at temperatures under 500 ˚C. Additionally, they have an enormously low thermal conductivity (0.1 - 0.3 W/m.K) [3, 38].

Table 3. Thermophysical properties of technical grade paraffin manufactured by Rubitherm Gmb H.

Materials Rubitherm (RT) / Phase change Temp. (^{o}C)	Melting Point ˚C	Heat of Fusion kJ/kg
RT5	9.0	205.0
RT6	8.0	140.0
RT25	26.0	232.0
RT27	28.0	146.0
RT30	28.0	206.0
RT40	43.0	181.0
RT50	54.0	195.0
RT 60	58.0-60.0	214.0
RT65	64.0	207.0
RT80	79.0	209.0
RT90	90.0	197.0
RT100	99.0	137.0
RT110	112.0	213.0

Thermophysical properties of n-alkanes (C1 to C100) and technical-grade paraffin waxes have been previously investigated and characterized for use in low-temperature TES applications by Himran [39]. It is determined that n-alkanes have a wide range of enthalpy of fusion, phase transition temperature, density, and specific heat. This allows heat storage designers to choose normal alkanes for any specific low-temperature (24˚C – 50˚C) thermal energy storage application. Additionally, by inserting a metal matrix configuration, the thermal conductivity can be improved [40]. They also suggested a container that is fire barrier-rated would mitigate the issue of flammability. In another study, six paraffins, namely nonadecane, eicosane, docosane, and commercially prepared PW48, PW52, and PW58, were characterized by Kahwaji [38] for their thermo-physical properties. All six paraffins examined have demonstrated high latent enthalpies. For alkanes (nonadecane, eicosane, and docosane), the enthalpy of transition is greater than 200 kJ/kg, and for commercially prepared (PW48, PW52, and PW58), the latent heat ranges from 150-200 J/g. After long-term 3000 cycles involving melt/freeze, it is indicated that both the pure and commercial paraffin have good thermal stability, and no noticeable changes in thermo-physical properties were observed.

Encapsulation (micro, macro, and nano) and stabilization (making composites) are the most widely used techniques to increase thermal conductivity and avoid leakage of PCMs during melting. Moreover, additives, metal foams, fin configurations, and carbon materials are considered to improve the thermal conductivity of paraffin [41]. To improve thermal conductivity, paraffin waxes are impregnated into porous supporting materials such as graphite or silica. Many researchers have made composite materials of paraffin as PCMs and graphite as skeleton material to increase the thermal conductivity [42, 43]. A substantial amount of work has been carried out to encapsulate paraffin (pure, eutectics, or commercial grade) to enhance the properties required for latent heat TES applications, and a few are presented by Lu *et al.,* [44], Borreguero *et al.,* [45], and Sánchez *et al.,* [46].

2.2. Non-paraffins

Non-paraffin PCMs are primarily composed of fatty acids, esters, alcohols, and glycols. For the latent heat TES system, among the available materials, fatty acids are in primary use. They have some favorable properties, such as high enthalpy of fusion, no phase separation, and very low subcooling. However, these materials have low thermal conductivity and are flammable when exposed to high temperatures or oxidizing agents.

2.2.1. Fatty acids

This is the primary candidate for latent heat thermal energy storage applications. They have a carboxylic group (COOH) on the chain with the generic formula R-COOH, where R is the alkyl group. Natural oils are the main source of fatty acids, where it can be obtained. These materials, especially fatty acids with carbon atoms between 8 and 18, are used mostly in low-temperature applications because they have a suitable phase change temperature. Generally, fatty acids from 8 C atoms-8 (caprylic acid and melting temperature 16˚C) to 18 carbon (atoms-18) (stearic acid, melting temperature 70˚C) are mostly used in PCMs commercially. Their enthalpies of fusion range from 45 J/g to 210 J/g [1, 3, 6]. The list of some fatty acids with their thermophysical properties is shown in Table 4.

Table 4. List of some fatty acids with their thermal properties.

Materials	Melting Point (˚C)	Heat of Fusion (kJ/kg)
Caprylic acid CA (8 C atoms)	16.3	148
Caprylic acid CA (10 C atoms)	31.3-31-6	163
Lauric acid LA (12 C atoms)	41-44	183-212
Myristic acid MA (14 C atoms)	51.5-53.6	190-204.5
Palmitic acid PA (16 C atoms)	61-63	203.4-212
Stearic acid SA (18 C atoms)	70	222
Arachidic acid (20 C atoms)	74	227
Undecylenic acid (22 C atoms)	24.6	141

Fatty acids melt congruently and have good chemical and thermal stabilities. They are nontoxic. However, they possess some drawbacks, for instance, they are expensive, being 2 - 2.5 times more costly than commercially available paraffin waxes; they are corrosive; and they have an unpleasant odor. Moreover, some fatty acids have large volume expansion (greater than 10%) during phase change, which is not desirable [1, 6]. These materials tend to attain stability thermally after thousands of cycles of heating/cooling. The thermophysical properties of stearic acid (SA), lauric acid (LA), palmitic acid (PA), and capric acid (CA) are also assessed. These materials are considered satisfactory for space heating applications. The transition temperatures ranged from 30˚C to 65˚C and the enthalpy of fusion was 153 J/g to 182 J/g. Furthermore, their thermal stability was also examined with adequate results. Myristic acid's (MA) thermal stability is examined by Sarı *et al.,* [47], in which they concluded at a lower temperature, no notable change is observed in thermo-physical properties.

Fatty acids eutectic mixtures have also been widely investigated for their thermo-physical properties as potential PCMs for low and medium TES applications. A list of the thermophysical properties of possible eutectics is displayed in Table 5. Capric acid and stearic acid mixture were studied by Karaıpeklı *et al.,* [48]. It was reported that the mixture is thermally stable and has appropriate state transition properties for low-temperature building applications. Moreover, the eutectic of the fatty acids palmitic acid-stearic acid, myristic acid-palmitic acid, and Lauric acid-stearic acid is examined for thermal properties by Sarı *et al*., [49]. After 360 heating/cooling cycles, no variations in melting point or enthalpy of fusion are detected, and it is proposed as thermally stable which can be used for one year. Eutectics of lauric acid-palmitic acid, myristic acid-stearic acid, and lauric acid-myristic acid are also examined for thermal performance by Sarı *et al*., [50]. It is determined that the thermal stability of these materials is promising and that they can be used for an extended period of four years.

During the phase transition, solid-liquid materials can leak and interact with the external environment. Also, these have low thermal conductivity. To mitigate these issues, encapsulation and shape stabilization technology are the effective ways that should be considered.

Table 5. Thermophysical properties of eutectic mixtures of Fatty acids.

Material (wt.%)	Melting Point (˚C)	Heat of Fusion (J/g)
45%CA-55%LA	17–21	143
76.5%CA-23.5%PA	21.8	171.2
66%LA-34%MA	34.2	166.8
69%LA-31%PA	35.2	166.3
75.5%LA-24.5%LA	37	182.7
58%MA-42%PA	42.6	169.7
64%MA-36%SA	44.1	182.7
64.2%PA-35.8%SA	52.3	181.7
90%CA-10%LA	13.3	142.2
66.75%CA-33.25%LA	22.76	127.2
34%MA-66%CA	24	147.7
83%CA-17%SA	24.68	178.69
50%MA-50%SA	35.2-51.8	189.2
50%MA-50%PA	39.1-45.4	173.7

2.2.2. Esters

Fatty acid esters could also be used as PCMs in TES applications. R-COO-R' is the general formula for an ester, where R and R' stand for alkyl groups. They are formed through esterification, a catalytic reaction of alcohols and carboxylic acids [37]. These materials do not undergo phase separation, have little supercooling, and are chemically stable. Nevertheless, they have some undesirable properties, such as low storage density, and low thermal conductivity, and are expensive. Thermophysical properties of esters are collected from different literatures and listed in Table 6. The eutectics of esters can also be formed with negligible supercooling as the phase transition of esters occurs at a narrow range of temperatures. The thermal properties of methyl palmitate, methyl stearate, cetyl stearate, cetyl palmitate, and eutectics (methyl stearate-cetyl stearate, methyl stearate-cetyl palmitate, and methyl stearate-methyl palmitate) were examined by Nikolić *et al.*, [51] using DSC-TGA. These materials were tested in the 10˚C to 60˚C temperature range for 50 melting/freezing cycles, and another 50 cycles after 18 months. The results indicated no notable changes in their thermophysical properties. Esters of stearic acid were prepared and characterized for their thermophysical properties via DSC-TGA. The results showed that PCM was successfully synthesized without any remaining stearic acid. After performing 200 melting/freezing cycles, it was noted that there were no noticeable changes in its phase transition properties, under 100 cycles [52].

Table 6. Thermophysical properties of esters.

Materials	Melting point (˚C)	Heat of Fusion (kJ/kg)
Isopropyl palmitate	11.0	100.0
Butyl stearate	17.0-23.0	140.0-200.0
Isopropyl stearate	14.0	142.0
Methyl palmitate	27.0	163.20
Propyl palmitate	16.0-20.0	186.0-190.0
Allyl palmitate	23.0	173.0
Methyl stearate	39.0	160.70
Vinyl stearate	27.0	122.0

Fatty acid esters and eutectics of methyl palmitate and methyl stearate with different mass ratios are prepared and tested for their phase transition properties using DSC. Two endothermic peaks were detected (not shown in this review), one for melting and the other at 17.33 ˚C, for incongruent indicating that eutectics may have a residual component. Also, there are no changes in thermal properties after 360 thermal cycles [53]. Microencapsulation is also carried out for these materials to develop and limit their undesirable properties. A cross-linked shell microencapsulated phase change material using butyl stearate as the PCM and polyurethane as the shell material is synthesized using the interfacial polymerization process. In this process, pentaerythritol is added as a crosslinking agent. The results indicated that capsules have a spherical shape with surfaces that are observed as compact and smooth. These capsules also showed adequate thermal properties and stability [44].

2.2.3. Sugar alcohols

Among the organic phase transition materials, the highest enthalpy of fusion and phase transition temperature are recorded by the sugar alcohols which are mostly used for medium-temperature applications (90-200 ˚C). However, they have some undesirable properties like phase separation and subcooling, and due to this, they receive less attention [37]. On exposure of these materials to oxygen, they exhibit polymeric changes and oxidation [1]. Another important feature is that when they are used as conductive materials, they can undergo a degree of thermal shock [54]. The thermal properties of some sugar alcohols are listed in Table 7.

Table 7. Thermophysical properties of sugar alcohols.

Materials	Melting point (˚C)	Heat of fusion (J/g)
Xylitol	93.0	280.0
Erythritol	117.0	344.0
Mannitol	165.0	341.0
Sorbitol	97.0	110.0

Compared to the other materials within this family, xylitol, erythritol, and mannitol are promising materials, all of which possess high enthalpy of fusion. Adonitol, erythritol, xylitol, L-arabitol, and D-mannitol) and eutectics of sugar alcohols (L-arabitol-erythritol, erythritol-xylitol, and L-arabitol-xylitol) are examined by del Barrio *et al.*, [55]. Favorable phase transition properties were detected, such as melting temperature ranges between 77 ˚C and 168 ˚C, and enthalpy of fusion recorded between 226 and 341 J/g. Stable subcooling is determined for this material. Suitable thermal stability was achieved for erythritol, and D-mannitol was unstable during cycling. Thermal cycling tests for erythritol were performed, and the results indicated that the material could withstand up to 75 thermal cycles. The super-cooling of 15 ˚C was detected, and phase separation was also observed at a certain temperature in the liquid state [56]. Moreover, polymorphic transitions are an important characteristic that sugar alcohols exhibit, which can decrease the latent heat by discharging heat unpredictably during charging. Thermal cycling tests are performed for D-mannitol, myo-inositol, and galactitol. Between 50˚C and 260˚C, it was observed that some polymorphic changes appeared for myo-inositol; however, they almost vanished between 150˚C and 260˚C. Undesirable cycling stability is observed for galactitol, and its freezing temperature also dropped from 102˚C to 60˚C after cycling. D-mannitol, when reacted with atmospheric oxygen, exhibited a lower heat storage capacity and showed poor chemical stability [57].

Undesirable properties can be suppressed via shape stabilization or encapsulation. A composite of lauryl alcohol was prepared using kaolin as a skeleton material through a vacuum impregnation technique. The melting temperature of the prepared composite was measured at 19.1˚C, which is lower than that of pure lauryl acid (25˚C). The enthalpy of fusion of composite material was observed at 48.08 J/g, which is higher than the enthalpy of fusion of the pure lauryl acid. A cycling test is performed for one month and it is concluded that the transition temperature is reduced by 0.39˚C and the enthalpy of fusion is lowered by 0.7 J/g [58].

From the substantial amount of research conducted, sugar alcohols are seen as the most promising PCM. However, thermal endurance and super-cooling are two unresolved challenges that require further analysis to improve their utility in application.

2.2.4. Glycols

In this group of PCMs, polyethylene glycol (PEG) is the most widely used material commercially. PEG is a polymeric linear material with the generic formula $H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}H$. PEG exists with an extensive range of molecular masses like, PEG300 and PEG400, and can go up to PEG1000000. The numbers 300, 400, and 1000000 indicate the average molecular masses of PEG. The transition temperature and enthalpy increase as molecular mass increases. For instance, PEG400 has a 3.2˚C mp and an enthalpy of 91.4 J/g, PEG2000 has a 51 ˚C mp and exhibits a heat of fusion of 181.4 J/g, while PEG20000 has a 68.7˚C mp and an enthalpy of 187.8 J/g [1]. The degree of crystallinity is also influenced by molecular weight. The solubility of PEG in water is high as compared to other PCMs in this group, which makes PEG unique among other organic PCMs [37]. Some PEGs and their thermal properties are listed in Table 8. In one study, a wallboard filled with PEG600 was experimentally examined for thermal performance, and the results indicated that PEG filled in polycarbonate panels showed poor results for building applications. PEG600-filled polyvinyl chloride panels showed the best results and are considered promising for building applications. A Polyvinyl Chloride panel filled with PEG600 was tested for 400 melting/freezing cycles, and no change in thermal properties was observed [59].

Table 8. Thermophysical properties of Polyethylene glycols (PEG).

Materials	Melting Point (˚C)	The heat of Fusion (kJ/kg)
PEG400	4.20	117.60
PEG600	12.50	129.10
PEG1000	40.0	168.60
PEG3400	63.40	166.80
PEG10000	65.90	171.60
PEG20000	67.70	160.20
PEG35000	68.70	166.90
PEG100000	67.0	175.80
PEG1000000	70.0	174.0

PEG blends with other organic materials like fatty acids exhibit promising properties and have proven to be good PCMs for energy storage. A list of PEG blends with fatty acids is shown in Table 9. Mixtures of polyethers (polyethylene glycol, polypropylene oxide, and polytetrahydrofuran) with fatty acids (capric acid, myristic acid, palmitic acid, and stearic acid) were synthesized and characterized for their thermal properties. Their results on phase transition properties are disclosed as adequate performance. The melting temperature of these blends lies between 30˚C and 71˚C. The enthalpy of fusion ranges from 168 to 208 J/g, which are higher values to that of pure polyethers and fatty acids [60]. Supercooling is one of the most undesirable properties of PEG. Supercooling less than 10˚C is acceptable, however, PEG exhibits more than 10˚C supercooling temperature range. Most PEGs have the highest super-cooling degree among all organic PCMs. These materials have a huge difference between their melting and freezing points of 30˚C to 40˚C, which made them further less attractive

[37]. Aside from this, they also exhibit poor thermal conductivity. To enhance the poor thermal conductivity, researchers have developed inorganic PCMs, which will be discussed later in this review (section 3.2.2). A composite material composed of PEG (PCM) and SiO_2 supporting material is prepared and characterized using SEM, FTIR, and DSC. From the micrographs, SiO_2 is considered the best-supporting material due to its ability to prevent leakages of liquid PEG. However, the enthalpy of fusion of composites is notably lower, and their thermal conductivity is detected to be higher than that of pure PEG [61]. A list of polyethylene oxide (PEO) blends with fatty acids is shown in Table 9 [6].

Table 9. Thermophysical properties of Polyethylene oxide (PEO) blend with fatty acids.

Materials (wt%)	Melting Point (˚C)	Heat of Fusion (kJ/kg)
50%PEO3400-50%CA	32.20, 42.0	169.0
50%PEO3400-50%LA	47.10	188.0
50%PEO3400-50%MA	50.70, 54.90	207.0
50%PEO3400-50%PA	51.20, 58.00	209.0
50%PEO3400-50%SA	54.20, 60.30, 68.90	205.0
50%PEO10000-50%CA	33.30, 43.90	174.0
50%PEO10000-50%LA	46.40, 52.30	203.0
25%PEO10000-75%MA	57.10	190.0
25%PEO10000-75%PA	58.10, 63.30	206.0
50%PEO10000-50%PA	63.20	205.0
75%PEO10000-25%PA	61.60	192.0
25%PEO10000-75%SA	59.40, 72.20	252.0

2.3. Other Organic PCMs

Other PCMs that have the potential to be used in TES applications are listed in Table 10. In the literature, PCMs like halogen derivatives, sulfur compounds, amides, ketones, ethers, and oleochemical carbonates have been studied extensively. Thermo-physical properties of various organic PCMs including sodium acetate trihydrate, were studied by Kaizawa *et al.*, [62]. Thus, they possess promising properties and are considered good PCMs for energy storage applications. New oleochemical carbonate-based organic PCMs, investigated by Kenar *et al.* [63], indicated that these material have a sharp phase change and good thermal properties. Moreover, they are considered a valuable substitute for salt hydrates and paraffin waxes, which are currently the most widely used PCMs. Some of these materials, along with their thermophysical properties, are listed in Table 10.

Table 10. Thermophysical properties of other organic PCM.

Materials	Melting point (˚C)	Heat of fusion (J/g)
Acetamide	82.0	241.0
Decyl-carbonate	-2.20	144
Dodecyl-carbonate	19.30	200.0
Tetradecyl-carbonate	33.70	227.0
Hexadecyl-carbonate	44.90	219.0
Octadecyl-carbonate	51.60	223.0

The above-discussed PCMs in this section are the preferred TES materials due to their unique thermal and chemical properties with flexibility of temperature. However, their poor thermal conductivity and leakage limit their wide applications. To overcome these drawbacks of organic PCMs and to effectively integrate them into the building, shape-stabilized composite PCMs could be an option, or otherwise inorganic PCMs comprising salt hydrates, and eutectic mixture discussed in the next section are viable.

3. Inorganic PCMs

Inorganic PCMs mostly comprised of salt hydrates, salts, and their eutectics. Among the inorganic PCMs, salts, and their eutectics are mostly used in high-temperature TES applications. Salt hydrates are mostly used in TES applications operating at low temperatures as their melting range lies within the human comfort zone. Some other inorganic materials have the potential to be used as solid-solid phase transitions like metals, alloys, and some polymeric materials, however, these lie outside the scope of this project. These solid-solid PCMs have a higher melting temperature and higher thermal conductivity. Whereas, they are expensive, have low heat capacity per unit weight, and their large weight limits their applications.

3.1. Salt hydrates

Salt hydrates are the most commercially used PCM, especially for low-temperature applications. The generic formula for salt hydrate is “anhydrous salt $n.H_2O$”, where n is the number of water molecules. High enthalpy of fusion, small volume expansion, and high thermal conductivity are the most promising properties of salt hydrates. They show poor compatibility with plastic and are slightly toxic [1]. However, super-cooling and phase separation are the main issues associated with these PCMs [64]. The possible salt hydrates and eutectics with their thermal properties are listed in Tables 11 and 12.

The mechanism of melting of salt hydrates during heat storage is that heat is absorbed by salt hydrates, which causes them to either partially or completely dehydrate, as illustrated below of reactions Eq.1 and Eq.2.

Dehydration reaction:

$$\text{(Anhydrous salt)}\cdot(nH_2O) \longrightarrow \text{anhydrous salt} + nH_2O \quad \text{Eq.1}$$

Partial dehydration reaction:

$$\text{(Anhydrous salt)}\cdot(nH_2O) \longrightarrow \text{anhydrous salt}\cdot mH_2O + (n-m)H_2O \quad \text{Eq.2}$$

In the dehydration mechanism, if there is enough crystallization water to dissolve anhydrous salts completely then it is known as congruent melting. In partial dehydration, if there is not enough crystallization water available to dissolve anhydrous salts completely then it is known as incongruent melting. In partial dehydration, the remaining dissolved lower salt hydrates will remain in a solid phase. There must be congruent melting, as this necessitates the prevention of phase separation and sedimentation caused by the density difference between salt hydrates and water, which might make the system irreversible and cause the system to gradually lose latent heat with increasing cycles [6]. Calcium chloride hexahydrate ($CaCl_2.6H_2O$) has attracted much attention from researchers due to its low cost and promising thermal properties. Nevertheless, sub-cooling and its hygroscopic nature make this material limited for the long-term [65]. The phase transition properties of 18 salt hydrates were reviewed by Kenisarin *et al.,* [66], who found that these PCMs can add value to commercial heat storage applications due to their promising thermal properties. $CaCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ are widely studied due to their attractive transition properties.

Table 11. Thermophysical properties of Salt Hydrates.

Materials	Melting Point (˚C)	Heat of Fusion (kJ/kg)
$LiClO_3·3H_2O$	8.0	253.0
$K_2HPO_4·4H_2O$	18.50	231.0
$LiBO_2·8H_2O$	25.70	289.0
$LiNO_3·3H_2O$	30.0	250.0
$CaCl_2·6H_2O$	29.0	190.0
$LiNO_3·2H_2O$	30.0	296.0
$CaCl_2·12H_2O$	29.80	174.0
$Na_2SO_4·10H_2O$	32.0	254.0
$Na_2CO_3·10H_2O$	32.0	267.0
$Na_2HPO_4·12H_2O$	35.0	261.0
$KF·2H_2O$	42.0	266.0
$K_2HPO_4·7H_2O$	45.0	145.0
$MgCl_2·8H_2O$	42.0	133.0
$Na_2HPO_4·7H_2O$	48.0	170.0
$LiC_2H_3O_2·2H_2O$	58.0	300.0
$MgCl_2·4H_2O$	58.0	178.0
$LiCl·H_2O$	99.0	212.0
$MgCl_2·6H_2O$	117.0	167.0

For the desired melting temperature, binary inorganic eutectics can be made by mixing different salt hydrates for low-temperature TES applications. The typical salt hydrates are listed in Table 12. Non-eutectics salt hydrates experience incongruent melting, whereas eutectics salt hydrates melt incongruently, they do not segregate and also show less super-cooling [67]. Binary eutectics were prepared by adding $Na_2HPO_4·10H_2O$ to $Na_2SO_4·10H_2O$ and $Na_2CO_3·10H_2O$. It was determined that phase segregation of $Na_2SO_4·10H_2O$ and $Na_2CO_3·10H_2O$ was eliminated by adding $Na_2HPO_4·12H_2O$. The supercooling of eutectics was also reduced [68, 69] by effectively adding binary inorganic eutectics. The role of binary eutectics exhibited attracting thermal properties with enthalpy of fusion enhanced up to 140 kJ/kg and very small subcooling degree (less than 1°C after several cycles). On the other hand, adding nucleating agents also seems to be the most suitable way to limit the subcooling. The chosen nucleating agent must have close lattice parameters with the PCM. For example, in the case of $Na_2SO_4.10H_2O$, borax is the most appropriate nucleating agent, which can reduce the supercooling from 15˚C to 3˚C [70]. The supercooling degree of $C_2H_3NaO_2.3H_2O$ was reduced by fine graphite powder [71], borax [72], disodium phosphate dodecahydrate [73], and nano-silver particles [74]. Thus, graphite, silica, metal, and borax nanoparticles have been proven to be effective nucleating agents to reduce supercooling degrees.

The addition of thickeners is one of the most effective techniques to minimize phase separation. To attain an effective phase separation, in the past, researchers used cellulose [75, 76], polymers [77], PEG [78], and derivates of silicone [79] as thickeners. The novel binary eutectic of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was modified by adding a nucleating agent to limit supercooling. $SrCl_2 \cdot 6H_2O$ and $SrCO_3$ were observed to be suitable nucleating agents, while hydroxyethyl cellulose (HEC) was proved to be a good thickening agent to hinder the salt and avoid phase separation. Melting temperature and enthalpy of fusion of eutectic were measured at 21 ˚C and 102 J/g, respectively, and supercooling was decreased to 2˚C [80].

Table 12. Thermophysical properties of eutectics of salt hydrates.

Mixture (wt.%)	Melting Point (˚C)	Heat of Fusion (kJ/kg)
$45\%CaCl_2.6H_2O$-$55\%CaBr_2.6H_2O$	14.7.0	140.0
$66.6\%CaCl_2 \cdot 6H_20$-$33.3\%MgCl_2 \cdot 6H_2O$	25.0	127.0
$40\%CH_3COONa \cdot 3H_2O$-$60\%NH_2CONH_2$	30.0	200.50
$61.5\%Mg(NO_3)_2 \cdot 6H_20$-$38.5\%NH_4NO_3$	52.0	125.0
$53\%Mg(NO_3)_2 \cdot 6H_2O$-$47\%Al(NO_3)_2 \cdot 9H_2O$	61.0	148.0
$50\%CaCl_2$-$50\%MgCl_2 \cdot 6H_2O$	25.0	95.0
$58.7\%Mg(NO_3)_2 \cdot 6H_2O$-$41.3\%MgCl_2 \cdot 6H_2O$	59.0	132.0
$59\%Mg(NO_3)_2 \cdot 6H_2O$-$41\%MgBr_2 \cdot 6H_2O$	66.0	168.0

Additionally, encapsulation (macro and micro) and making composite material by impregnating PCM into porous material are attractive techniques to reduce phase separation and sub-cooling. This not only reduces the problems as stated above but also prevents leakage and improve thermal conductivity. Salt hydrates are highly polar and soluble in water, and the content of water can also be changed during melting/freezing. The latent heat of salt hydrates is dependent on these factors, due to which salt hydrates are difficult to encapsulate [81]. Liu *et al.* [82] prepared microcapsules of sodium phosphate dodecahydrate as PCM and silica as shell material. They used a combined interfacial polymerization and sol-gel process. The largest melting enthalpy of 177 kJ/kg was measured for microcapsules fabricated at a PCM-shell mass ratio of 4:1 and a thermal conductivity of 0.5004 W/m.K. According to TGA analysis, quick dehydration of salt hydrates was prevented by encapsulation, which showed good thermal stability after many thermal cycles. Salt hydrates should be impregnated into compatible porous materials to make them shape-stabilized. Expanded graphite, titanium dioxide, SiO_2, and diatomite proved to be promising porous materials for salt hydrates. Li *et al.* [83] prepared the nanocomposite of $CaCl_2.6H_2O$ and that composite with 1 wt.% supporting material had supercooling ranges of 0.3 to 1.1 ˚C. Also, the time of solidification decreased by 17.84%. A composite PCM was prepared by adsorbing liquid $CaCl_2.6H_2O$, into expanded graphite (EG). Alkylphenols polyoxyethylene-10 was added during preparation as an emulsifier to bind the PCM and salt hydrates. The thermal conductivity was also enhanced by 82% as compared to pure $CaCl_2.6H_2O$ [84].

3.2. Salts and salt eutectics

Among inorganic PCMs, salts possess a high melting point and high enthalpy. Therefore, these materials are considered most appropriate for high-temperature TES applications. Molten salts and their mixtures with low phase transition temperatures are generally used in sensible heat TES systems, which store thermal energy using sensible heat capacity in the liquid phase. Salts are selected by their melting temperature, which must be within the range of the TES operational temperature. Due to this, the volumetric thermal storage capability of energy storage systems can be greatly enhanced. For instance, if we choose $LiNO_3$ (melting temperature 250˚C) for TES operating between 300-500˚C then it only stores thermal energy using sensible heat and gives a volumetric storage capacity of 440 MJ/m^3. If we use KNO_3 (melting temperature 335˚C) for TES then it stores energy using sensible and latent heat and has a volumetric storage capacity of 935 MJ/m^3 [31, 85]. Table 13 lists the single salts that could be utilized as PCM in high-temperature applications.

Table 13. Thermophysical properties of high-temperature salts and hydroxide.

Materials	Melting Point (˚C)	Heat of Fusion (J/g)
$LiNO_3$	250.0	370.0
KNO_3	333.0	266.0
Na_2O_2	360.0	314.0
Na_2CO_3	854.0	276.0
LiOH	462.0	873.0
LiCl	610.0	441.0
LiH	688.0	2678.0
$MgCl_2$	714.0	454.0
Li_2CO_3	732.0	509.0
$CaCl_2$	772.0	253.0
NaCl	802.0	482.0
LiF	845.0	1044.0

Eutectics of salt is one of the most important PCMs that has received much attention from researchers recently. As the thermal properties of single salts are fixed, but to fulfill the requirements of the storage system, the thermo-physical properties of pure salts can be modified by eutectics. The phase temperature range is extended by eutectic mixtures. Some of the most important salt eutectics are listed in Table 14. It has been established via prior study and salt and salt eutectic selection for TES applications that salts and salt eutectics that melt at or above 250 ˚C are suitable for use in latent heat TES systems. The major drawbacks of salts are their low thermal conductivity and corrosiveness. Salts comprising fluoride, chloride, carbonate, nitrate, and hydroxide are proven as possible PCMs. Nitrate salts have a low melting temperature, and hydroxides melt between 250 ˚C and 600 ˚C, while fluoride, carbonate, and chloride salts melt above 600 ˚C. Lithium compounds were investigated by Milian *et al*. [86], and they found a large number of compounds with enthalpies above 200 kJ/kg, which raises the potential of lithium compounds as PCM. Lithium salts of chloride, hydroxide, and nitrate were proposed as the most attractive materials for latent heat storage systems. Nevertheless, additional examination of their thermal and cycling stability is necessary. Salts of fluoride and their mixtures were investigated for their thermo-physical properties, and it was concluded that these materials melted at temperatures above 700 ˚C and had a high heat of fusion, which made them suitable for applications operating at high temperatures. The thermal characteristics of salts and their eutectics were reviewed by Misra

[85], Kenisarin [31], Kenisarin *et al*. [87], Cárdenas *et al*. [88], Reed *et al*. [89], Mohamed *et al*. [90], Gomez *et al*. [91], and Gomez *et al*. [92]. 17 pure chloride salts and 33 possible binary chloride eutectic salts were investigated for their thermal properties and composition predictions through FactSage software. It was determined that all exhibited melting points greater than 400˚C were appropriate for high-temperature TES applications [93].

Table 14. Thermophysical properties of salt eutectics.

Materials (wt%)	Melting Point (˚C)	Heat of Fusion (J/g)
71%LiCl-29MgCl$_2$	571.0	418.0
72%LiCl-28NaCl	554.0	414.0
55%KF-45%KCl	605.0	407.0
73.6%LiF-26.4%LiCl	485.0	403.0
43.5%LiF-42.5%KF-10.7%NaF-2.8%KCl	445.0	688.0
48%NaCl-52MgCl$_2$	450.0	430.0
80%LiOH-20%LiF	427.0	1163.0
59%KF-29%LiF-23%NaF	463.0	590.0
67%KF-33%LiF	442.0	618.0
66.5%NaCl-33.5%NaF	675.0	572.0
67%LiF-33%MgF$_2$	746.0	947.0
68%NaF-32%CaF$_2$	810.0	600.0
75%NaF-25%MgF$_2$	832.0	627.0

Na_2CO_3-NaCl (59.45-40.55 wt.%) was characterized for their thermo-physical properties using DSC at a heating rate of 10˚C/min. Compositions and thermal properties were predicted by a phase diagram obtained from FactSage. The supercooling degree was determined by the difference between the melting point of 637 ˚C and the crystallization point of 626˚C. The enthalpies of fusion and solidification were measured at 283 J/g and 252 J/g, respectively. This difference between the enthalpy of fusion and solidification values might be from weight loss due to gas evolution. It was also tested in CO_2 and N_2 atmospheres and found that this eutectic can decompose in N_2 environment and be stable in a CO_2 environment. Thermal stability was tested at 50 to 100 thermal cycles, and it was concluded that Na_2CO_3-NaCl is thermally stable during 100 melting/freezing cycles with little deviation in phase transition properties [94]. A negligible deviation was determined for thermal properties (enthalpy of fusion and melting point) from the DSC curve of NaCl-$CaCl_2$-$MgCl_2$ after many thermal cycles. It was concluded that the material was not thermally stable under open air as $MgCl_2$ reacted with atmospheric moisture. A lid of alumina was used to cover the crucible, and less than 3% weight loss was determined below 700˚C [95]. Another salt mixture, KCl-NaCl-$CaCl_2$-$MgCl_2$, was characterized using DSC and TGA. One big endothermic peak was detected from the DSC curve illustrating the composition precision. From the DSC curve, the melting point (385 ˚C) and enthalpy of fusion were determined to be super high at 151.1 J/g, which agreed with the reported values. In thermal stability tests, this eutectic was recorded as unstable in a non-sealed environment, and only 1% of it was lost below 600 ˚C after 15 hours [96]. 53%$BaCl_2$-28%KCl-19%NaCl and 52.81%K_2CO_3-47.19%Na_2CO_3 are characterized to assess their thermal properties and stability. Melting temperature and enthalpy of fusion were slightly deviated from the reported values under melting/freezing cycles. Less than 1.2% weight loss was recorded when heating the salt mixtures to 750 ˚C, demonstrating excellent thermal stability [97]. Eutectic salt of 87% $LiNO_3$-13% NaCl was characterized by DSC and TGA for its thermophysical properties and cycling stability. In DSC experiments, 10 to 15mg of sample was heated and cooled between 50˚C and 250˚C at a heating/cooling rate of 10˚C/min and 15˚C/min. Promising results in terms of thermal properties were obtained at 10˚C/min. The material was tested for cycling stability by being heated 51 times between 50 and 250˚C at a rate of 10˚C/min. The melting point measurement showed deviations within ±0.4% and latent heat showed deviations within ±1.5%, which are acceptable to be used as PCM. Also, a weight loss of 0.26% was recorded for 50 cycles, excluding cycle 1. The thermal decomposition temperature was determined between 400˚C and 450˚C, as NaCl can bear high temperatures, but $LiNO_3$ decomposes at this temperature [98].

Lithium and sodium salts of the carbonate eutectic mixture (58%Na_2CO_3-42%Li_2CO_3) were characterized using DSC, TGA, and XRD. DSC-TGA. Tests were held from ambient temperatures up to 600 ˚C with a 10 ˚C/min heating/cooling rate in CO_2 and N_2 atmospheres. The heats of fusion and solidification were reported as 330.8±0.6 kJ/kg and 329.2±0.3 kJ/kg, respectively, which were quite similar. The measured temperature of melting was determined 498.3±0.1 ˚C higher than its solidification point by 14.4±0.2 ˚C. Subcooling degree was measured from these results. It also performed well in 500 thermal cycles and showed good thermal and chemical stability without any loss in weight in a CO_2 environment, and 0.8% weight loss was detected in an N_2 atmosphere. From XRD results, Na_2CO_3-Li_2CO_3 formed a uniform $LiNaCO_3$ phase after 100, 300, and 500 cycles. No chemical reaction between two salts is observed [99]. Four eutectics of carbonate salts (32%Li_2CO_3-35%K_2CO_3-33%Na_2CO_3, 28.5%Li_2CO_3-71.5%K_2CO_3, 35%Li_2CO_3-65%K_2CO_3, 22%Li_2CO_3-62%K_2CO_3-16%Na_2CO_3) and two eutectics of chloride salts (52%$MgCl_2$-48NaCl, 64%$MgCl_2$-36%KCl) were characterized for their thermal properties and thermal stability using DSC and TGA. Analysis was conducted in a nitrogen environment at a rate of 20 mL/min. It was difficult to get promising thermal properties for two chloride eutectics, as they strongly wet the graphite crucible. All carbonate salt eutectics showed promising results, while 28.5%Li_2CO_3-71.5%K_2CO_3 indicated a high degree of supercooling of over 10 ˚C, and phase separation was also observed. Due to the significant difference between the experimental and predicted values of the phase change properties, 22%Li_2CO_3-62%K_2CO_3-16%Na_2CO_3 was likely less desirable as PCM. For 52%$MgCl_2$-48%NaCl and 64%$MgCl_2$-36%KCl, the measured phase transition properties showed some differences from the reported values. Furthermore, after 40 cycles, almost all 64%$MgCl_2$-36%KCl were discovered to creep out, possibly due to the alumina crucible's high wettability [30].

Thus, lithium salts of chloride are considered the most promising among all inorganic salts and are potential candidates for TES applications. Not enough literature has been published on the fabrication and characterization of chloride, fluoride, and carbonate eutectic salts. A few researchers Wei *et al.* [100], Wang *et al.* [101], Li *et al.* [102], and Xu *et al.* [103] have focused on these salts, as well as eutectic salts.

3.2.1. Limitations of salts and eutectic salts as PCMs

3.2.1.1 Supercooling

The heat would be stored and released at the same temperature in ideal latent heat storage. Supercooling is the term used for the behavior that occurs in reality when a melted substance cools to crystallization temperature without solidifying until it is cooled below its freezing point. However, supercooling affects many salts, notably salt hydrates. The degree of supercooling might vary significantly depending on the salts used.

The inorganic salts' supercooling problem could significantly limit the salts' use as a heat storage medium in practical applications because it reduces the usefulness of PCM and, if sufficiently extreme, can impact heat recovery [104]. Salts of chloride and carbonate have less supercooling as compared to fluoride salts. One of the most serious concerns of salts as high-temperature PCM is the supercooling issue. All relevant strategies should be figured out for its mitigation. Subsequently, techniques for reducing supercooling have included the use of nucleating agents, contaminants, the cold finger method, encapsulation, and others [105, 106].

3.2.1.2 PCMs compatibility with containment materials

Another challenge for the efficient and reliable use of inorganic salts as PCM is their chemical endurance. During the phase transition process, the PCM should be stable and compatible with the confined materials without undergoing any chemical reactions. In the meantime, it shouldn't hinder heat transmission between the storage media and heat transport fluids [107]. To prevent storage material leakage and use for an extended period, the containment material should also be strong and thermally stable [108]. These qualities have been assessed using long-term corrosion tests. Although a little work has been undertaken, there is a severe delay in information regarding high-temperature salt storage for CSP plants, and most of the prior literature is from a long time ago [109, 110]. Six molten salts of chloride, fluoride, and nitrate with melting temperatures between 235˚C and 857˚C were tested for compatibility with four distinct types of steel. According to their findings, the containment materials were stable between 200˚C and 450˚C. NaCl, KF, and $MgCl_2$ showed good compatibility with steel and nickel alloys, resulting in negligible rates of corrosion at temperatures between 700˚C and 900˚C [111, 112]. To avoid these issues and make molten salts used in practical applications, techniques such as encapsulation and shape stabilization (composites) are used.

3.2.1.3 Thermal stability

The thermal energy storage system's service life is essential for practical implementation. Thermal storage materials are expected to exhibit stable qualities over many years of operation [6, 90]. One of the primary considerations limiting extensive use of latent heat storage at the moment is the ability of storage materials to go through a number of effective cycles of heating/cooling with no or slight variations in their thermal properties. There would be a reduction in fusion enthalpies and variations in transition temperatures under many heating/cooling cycles if the PCM decomposed in any way [113]. Therefore, materials must endure many heating/cooling cycles in addition to having thermally stable qualities at high temperatures. The literature has several works on material degradation behaviours and the thermal and cycling stability of the materials used for latent heat storage, despite the fact that relative experiments on high-temperature PCM are very rare.

3.2.1.4 Thermal conductivity

Other inorganic materials, like metals, have a very high thermal conductivity. Compared to that, salts and eutectics exhibit significantly low thermal conductivity, which is the main problem that needs to be addressed and solved. Phase change materials solidify during the discharging process, releasing energy that would otherwise be transmitted between the surface of the PCM and heat exchanger by a thick layer of solid [114]. As a result, the heat transfer coefficient of the solidified PCM is dominated by their thermal conductivity. However, most salts and eutectic salts have low thermal conductivity below 1 W/m.K, which causes inefficient heat transmission and lowers the pace of charging and discharging. Several appropriate thermal performance enhancement strategies have been researched to improve the PCM's thermal conductivity. In general, a few reviews summarise the desirable methods for thermal conductivity enhancement [114, 115].

3.2.2. Techniques to mitigate the issues with inorganic salts

3.2.2.1 Encapsulation

Like organic and inorganic salt hydrates, it is also necessary to encapsulate salts and salt eutectics to limit the problems mentioned above. Encapsulation can be nano, micro, or macro. A representation of core-shell encapsulation is shown in Figure 3.

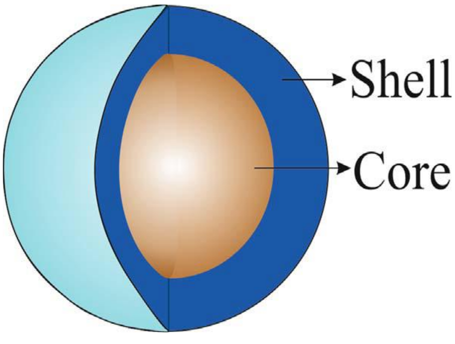

Figure 3. Demonstration of core-shell encapsulation. Reproduced with permission from [116]; Elsevier.

List of many encapsulation techniques follow: [117, 118].

Chemical techniques

- Dispersion polymerization
- In-situ polymerization
- Suspension polymerization
- Interfacial polymerization
- Emulsion polymerization

Physico-chemical techniques

- Sol-gel encapsulation
- Coacervation
- Supercritical CO_2 -assisted technique

Physico-mechanical technique

- Electrostatic encapsulation
- One-step technique
- Spray drying

Not all the above methods are favorable to encapsulating inorganic salts and their eutectics due to system stability and solubility issues. Chemical techniques that are viable for the encapsulation of salts and salt eutectics are emulsion, *in-situ* polymerization, interfacial polymerization, and electroplating. In physical techniques, only sol-gel is appropriate to encapsulate inorganic salts [119].

For core-shell encapsulation of PCM, compatibility between PCM and shell material should be required. In previous studies, researchers have proven specific shell materials that can be used for the encapsulation of inorganic salts [119]. Table 15 lists shell materials that are suitable for inorganic salts.

Table 15. Shell materials for encapsulation of inorganic salts.

Shell Materials	Advantages	Limitations
Inorganic shell materials		
SiO_2, TiO_2, $CaCO_3$, Sodium silicate, and Silica.	These materials have high mechanical strength, are less expensive, and are thermally stable at 1000 ˚C.	The only limitation is that they are porous, which can lead to leakage.
Polymer shell materials		
Melamine-formaldehyde (M-F), Vinyl trimethoxysilane VTMS, Urea-formaldehyde resin UFR, Butyl acrylate-divinylbenzene BA–DVB, Poly(methylmethacrylate-co-divinylbenzene) P(MMA-co-DVB), Butylmethacrylate-methylmethacrylate BMA–MMA copolymer, Poly(urethane–urea), styrene-methylmethacrylate St-MMA and Polystyrene.	They are less expensive and can be used in the temperature range of 300 ˚C-400 ˚C.	They have low thermal conductivity and are thermally unstable at high temperatures.
Metallic shells		
Chromium, Carbon or ruthenium Stainless steel or carbon steel.	The mechanical strength of these shells is high and thermally stable around 1000 ˚C.	They have a high potential for corrosion and are expensive.

Microcapsules of core $NaNO_3$ were prepared using a perhydropolysilazane (PHPS) shell by solvent extraction and ultrasonic dispersion processes. DSC tests resulted in onset melting temperature and heat fusion of microcapsules of 306.19±0.10˚C and 159.2±2.4 J/g, respectively, indicating little change in thermal properties. The thermal decomposition temperature of $NaNO_3$ in the microcapsule was improved by more than 36˚C, up to 648˚C [120]. Microencapsulation of KNO_3 [121] and eutectic 60%$NaNO_3$-40%KNO_3 [122] was performed using SiO_2 shell material by the sol-gel method. Microcapsules were successfully prepared and showed satisfactory results. Negligible changes in thermal properties were observed, and thermal conductivity was also enhanced.

3.2.2.2 PCM Composites

Incorporating PCM into the supporting materials, improved the thermal conductivity, and thermal stability. Additionally, some supporting elements can function structurally to minimize corrosion of the melted PCM with containment materials and avoid leaking of those materials during the phase change process. A typical demonstration of shape-stabilized PCM is shown in Figure 4.

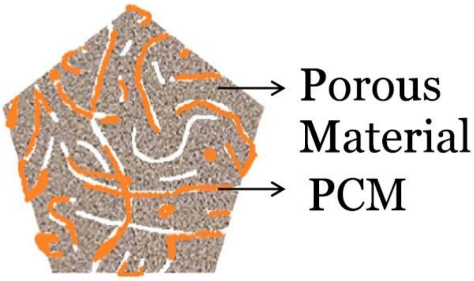

Figure 4. Demonstration of Shape Stabilized PCM. Reproduced with permission from [116]; Elsevier.

Moreover, six techniques are found to make shape-stabilized inorganic salts and eutectics: cold compression, vacuum impregnation, melt and cold infiltration, uniform mixing, and sol-gel [116]. Compatible supporting materials are required to make the composites of inorganic salts. Due to its high thermal conductivity and chemical compatibility, graphite is the most widely used skeleton material for shape-stabilized PCM. $LiNO_3$-KCl-$NaNO_3$ [123], KNO_3-$NaNO_3$ [124, 125], NaCl-$CaCl_2$ [126], and $LiNO_3$-KCl [127] were shape-stabilized using graphite as a skeleton material. All these pieces of literature reveal satisfactory results with enhancements in thermal conductivity many times greater than those of pure PCM. Appropriate supporting materials for inorganic salts are displayed in Table 16.

Table 16. Skeleton materials for inorganic salts and eutectics.

Skeleton materials	**Compatibility with salts**
Expanded Graphite (EG)	KNO_3–$NaNO_3$, $LiNO_3$, $Ca(NO_3)_2$-$NaNO_3$, NaCl–$CaCl_2$, NaCl–$CaCl_2$–$MgCl_2$ and $MgCl_2$–KCl. It is thermally stable with a maximum service temperature of up to 3000 ˚C.
Graphite Foam	$MgCl_2$ and $NaCl_2$
Expanded perlite (EP)	$NaNO_3$
Expanded vermiculite (EV)	$NaNO_3$, $LiNO_3$ and KNO_3
Diatomite	$NaNO_3$, KNO_3, $LiNO_3$, NaCl–KCl, and Na_2SO_4 with maximum service temperature of 1000 ˚C.
MgO	Li_2CO_3–Na_2CO_3, Na_2CO_3, and K_2CO_3–Na_2CO_3 with maximum stability temperature 1500 ˚C.
Al_2O_3	NaCl, Na_2SO_4–NaCl and Na_2SO_4. This skeleton material can endure a maximum temperature of 1400 ˚C.
SiC	KNO_3–$NaNO_3$ and Na_2SO_4 with high stability up to 1650 ˚C.
SiO_2	$NaNO_3$ and Na_2SO_4 with maximum service temperature 1500 ˚C.
$Ca(OH)_2$	$NaNO_3$ and stable up to 570.4 ˚C.

$MgCl_2$ was infiltrated in graphite foam using a pressure-assisted melt process. Two types of graphite, high density, and low density were used. $MgCl_2$ infiltered in high-density foam resulted in a higher thermal conductivity (200 times) than pure $MgCl_2$. Additionally, $MgCl_2$ with low-density foam exhibited 30 times higher thermal conductivity than pure $MgCl_2$. No change in melting temperature was observed [128]. Tetraethyl orthosilicate (TEOS) was used as a supporting material to make a composite of $LiNO_3$ and LiCl by the sol-gel method. Acceptable thermal properties were determined by characterization of the composite, which showed good thermal stability after 50 cycles [129].

In the next section (Section 4), chloride salts (an alternative to nitrate salts) are chosen as a case study, and the key features are discussed. The chloride salts demonstrate as promising candidates for TES applications. This is mainly due to their thermal stability and generally lower cost, and easy fabrication compared with nitrate counterparts. It has also been shown that the melting temperature of the chosen eutectic chloride salts is lower than that of the individual salts, indicating the merits of using the eutectic mixture. The initial screening of the binary eutectic systems of the pure salts was obtained through the FactSage software. This software has significantly assisted in elucidating the problem of TES materials election. The general categories based on simulated outcomes are chlorides of transition metals, alkali metals, rare metals, and earth metals. In the case study below, we focus on the salts of lithium, which is an abundant resource from Western Australian region, and to a certain extent of calcium. The potential downsides of their use in only high-temperature storage systems are discussed.

4. Insights from LiCl-based binary inorganic/eutectic salt mixtures for TES: A Case Studies

Case Study I

In one of our previous studies [130], we aimed to examine the thermal properties, stability, repeatability, chemical stability, morphology, elemental distribution, and composition of binary salts such as LiCl and LiOH. It is particularly noteworthy that the binary salt mixture comprising 32 mol% LiCl and 68 mol% LiOH exhibited a potential candidate for thermal energy storage application. The salts showed desirable thermophysical properties, including a melting temperature of 269˚C and a heat of fusion of 379 J/g. Moreover, the solidification temperature and heat of crystallization were found to be 265˚C and 375 J/g, respectively. These findings demonstrate the potential of these binary salts owing to their specific composition are suitable for thermal energy storage applications where these unique thermal properties are important. Thermal cycling experiments were conducted over 30 heating/cooling cycles to assess the repeatability of the binary salt mixture. Our results showed negligible deviations in the melting temperature and heat of fusion, indicating the consistent thermal behaviour of the material. This suggests that the binary salt mixture can maintain its thermophysical properties over repeated thermal cycles, which is crucial for energy storage applications involving thermal cycling. Furthermore, the thermal stability of the binary salt mixture was examined by monitoring weight loss during the heating/cooling cycles. It was observed that very little weight loss (<1.5%) occurred after cycles. This indicates that the binary salt mixture is thermally stable and undergoes minimal degradation or decomposition, making it a promising material for high-temperature applications. The decomposition behaviour of the binary salt mixture was investigated to determine its upper-temperature limit. It was found that the mixture remained stable up to 500˚C. Interestingly, a small peak corresponding to Li_2O was observed in the decomposed sample, resulting from the decomposition of LiOH at high temperatures. All these findings suggest that the binary salt mixture possesses good chemical stability, as only a minimal reaction leading to the formation of Li_2O occurred. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) analyses are employed to determine their surface morphology and elemental distribution. The analysis revealed a uniform morphology (Figure 5) with well-distributed elements in the salt mixtures before and after thermal cycling. No external impurities were detected, indicating the uniformity of the material. Both uncycled (see Figure 5a) and cycled samples (see Figure 5b) exhibited good morphological and chemical stability, with no observable impurities or structural degradation. Finally, X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical composition of the samples. The XPS results showed main peaks corresponding to the elements Li, Cl, and O, confirming the presence of LiCl and LiOH without any other impurities. The binding energies and the atomic percentages of each element in two samples (before and after thermal cycles) are listed in Table 17. The atomic percentage of O (1s) is higher in the as-prepared sample (53.34%) than in the cycled/decomposed sample (34.99%). This means that O1s in the form of LiOH, decomposed at higher temperatures and were later transformed into gas. A similar scenario is also observed for chlorine. This further confirmed the chemical stability of the prepared and decomposed samples, as no additional compounds or contaminants were detected. It is clear from the results that the binary salt is chemically stable up to 500 ˚C and is a potential candidate for thermal energy storage.

The comprehensive examination of binary salts LiCl and LiOH demonstrated their favourable thermal properties, thermal stability, chemical robustness, uniform morphology, and elemental distribution. These preliminary findings highlight the potential of LiCl and LiOH for a range of applications requiring reliable thermal behaviour and chemical stability.

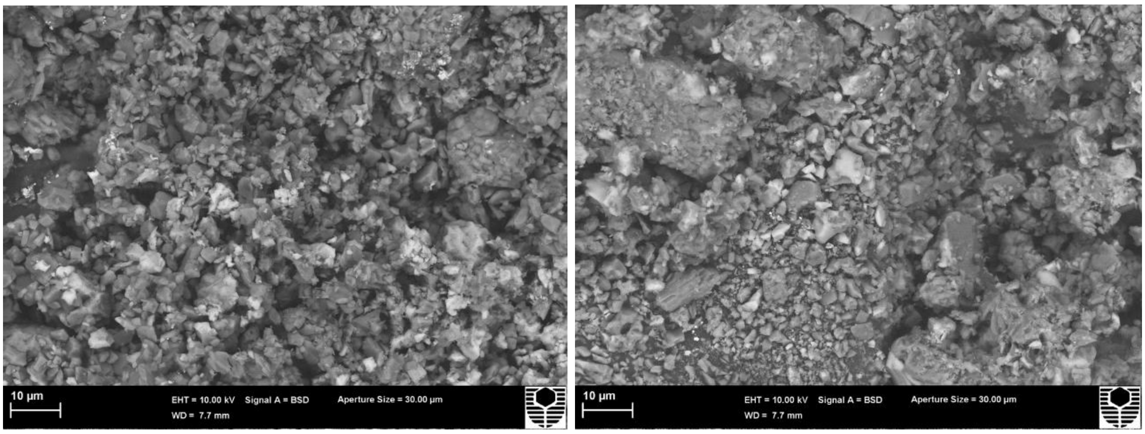

Figure 5. SEM of as prepared 32 mol% LiCl-68 mol% LiOH (a- left) before, and (b - right) after thermal cycles.

Table 17. Atomic percentages obtained by XPS of two samples (32 mol% LiCl-68 mol% LiOH with no cycle and decomposed at 700˚C).

Sample	Elements	Position eV	Atomic %
32 mol% LiCl-68 mol% LiOH (before cycles)	Li 1s	52	1.76
	Cl 2p	195	44.90
	O 1s	528	53.34
32 mol% LiCl-68 mol% LiOH (After cycling, decomposed at 700 °C)	Li 1s	53	2.08
	Cl 2p	196	62.93
	O 1s	528	34.99

Case Study II

In [131], thermophysical properties were evaluated for four different binary salt mixtures, and it was determined that the composition of 58 wt.% $CaCl_2$ and 42 wt.% LiCl exhibited satisfactory results. This composition demonstrated a melting temperature of 488˚C and a heat of fusion of 206.12 J/g. The solidification point and heat of crystallization were measured at 480 ˚C and 180 J/g, respectively. These findings highlight the potential of this specific composition for applications that require specific thermophysical properties. Thermal repeatability was assessed by subjecting the binary salt mixture to 30 heating/cooling cycles. Negligible deviations were observed in most parameters, except for the heat of fusion, which exhibited significant variations. This indicates poor thermal repeatability of the binary salt mixture, suggesting that the heat of fusion is more susceptible to fluctuations during thermal cycling. The thermal stability of the binary salt mixture was evaluated by monitoring weight loss during the 30 heating/cooling cycles. The results showed substantial weight loss, primarily attributed to the decomposition of LiCl. This indicates that the binary salt mixture is prone to decomposition and may not retain its stability under prolonged thermal cycling. Decomposition behavior was studied, and it was found that the binary salt mixture exhibited decomposition at 500˚C, which serves as the upper limit temperature. However, minor weight loss was still observed within the temperature range of 200 to 500˚C. The XRD patterns displayed additional peaks attributed to the decomposition of LiCl and $CaCl_2$, further confirming the chemical instability of the material. Morphological stability was examined through SEM/EDS analysis of both uncycled and decomposed samples of the binary salt mixture. The results shown in the SEM images (Figure 6) indicated good morphological stability for the samples before and after cycling with the elements were well distributed within the samples, suggesting uniformity and stability at the microscopic level. However, after a close examination of the image in Figure 6b, the particles are fused to that of the sample in Figure 6a.

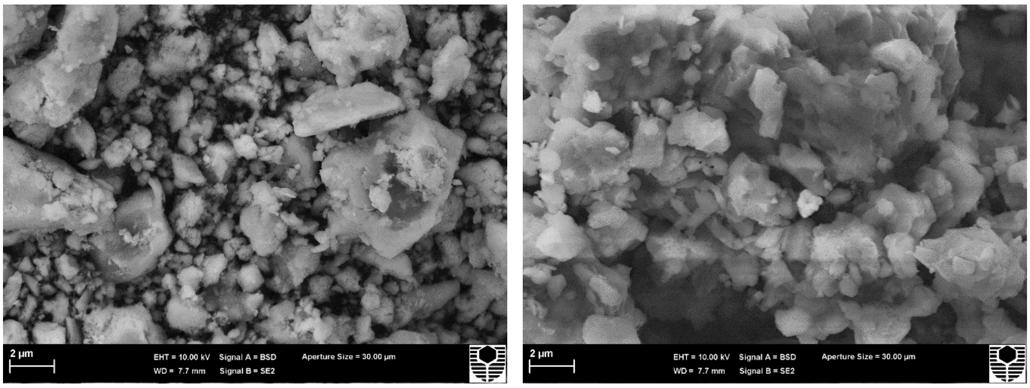

Figure 6. SEM of as prepared 58 mol% $CaCl_2$-42 mol% LiCl (a- left) before, and (b - right) after thermal cycles.

In summary, the characterization of the $CaCl_2$-LiCl binary salt mixture revealed satisfactory thermophysical properties for a specific composition and has advantages over nitrate salt counterparts. However, poor thermal repeatability, substantial weight loss during thermal cycling, decomposition at elevated temperatures, and chemical instability through contrast morphological images are a few limitations that we observed in the chloride inorganic salts. These findings shed light on the potential applications and limitations of the $CaCl_2$-LiCl binary salt mixture.

5. Conclusions

The organic class of phase change materials (PCMs) has a wide range of use in low and medium-temperature thermal storage applications due to their suitable melting temperature, high heat of fusion, high heat capacity, chemical stability, lack of corrosivity, and consistent melting and crystallization behaviour over many heating/cooling cycles. However, there are some demerits of organic PCMs such as decomposition at high temperature, poor thermal conductivity, and large volume expansion. These problems can be overcome by immersing the PCMs in porous materials or encapsulation.

Compared to the organic PCMs, the inorganic class of materials has a larger latent heat capacity and thermal conductivity. When referring to high-temperature thermal energy storage applications, inorganic PCMs play a significant role. However, limiting factors seen in inorganic PCMs such as low thermal conductivity, supercooling, corrosion, and phase segregation should be considered while selecting materials for thermal storage applications. Hence, further development is needed to cope with these drawbacks such as making composites, encapsulation, adding nucleating agents, and doping by higher thermal conductive particles. In the case study, the eutectic salts such as LiCl (32 mol%)-LiOH (68 mol%) and $CaCl_2$ (58 wt.%)-LiCl (42 wt.%) are found to be chemically stable and have the potential to be used as a PCM for thermal energy storage.

Overall, many efficient PCMs are available, and they have wide use in practical applications as a sustainable energy materials. However, there are some weaknesses due to lack of significant investigation efforts. Further research is needed to develop novel, less expensive, and more effective materials to provide better answers to technical issues including phase separation, supercooling, material compatibility, and thermal conductivity.

Conflicts of Interest

The authors declare no conflict of interest.

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