Journal of Advanced Research in Mechanical Engineering and Technology
Volume 7, Issue 3 - 2020, Pg. No. 1-8
Peer Reviewed Journal

Review Article

Opportunities in Latent Thermal Energy Storage by Phase Change Material for Lower Temperature Applications: A Review

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DOI: https://doi.org/10.24321/2454.8650.202003

I N F O

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How to cite this article:
Husainy ASN, Parishwad GV. Opportunities in Latent Thermal Energy Storage by Phase Change Material for Lower Temperature Applications: A Review. *J Adv Res Mech Engi Tech* 2020; 7(3): 1-8.

Date of Submission: 2020-06-11
Date of Acceptance: 2020-06-30

A B S T R A C T

Thermal energy storage through Phase Change Material has been used for wide applications in the field of air conditioning (cooling) and refrigeration, especially at the industrial scale for lower temperature applications like refrigeration and air conditioning, cold storage, cold chain, etc. Generally inorganic and eutectic type phase change materials are used because of long term temperature stability, good latent heat, chemical stability, etc. Latent energy storage technologies, which can improve the thermal inertia of the system, reduce indoor temperature fluctuations, improve thermal comfort, and are becoming an effective way to reduce reliance on traditional systems. In this review, paper attempts have been given to improve the refrigeration system performance by thermal storage with nanoparticles. The use of Phase Change Material may maintain the quality of food for a longer duration of time even though power outage exists. This review paper focuses on different phase change materials used for lower temperature applications. Compared with traditional materials, PCMs can store energy through the utilization of sensible latent heat. The PCMs selected for the system should possess a suitable melting point, high heat storage density, good thermal conductivity, small volume change; these materials mainly include paraffin waxes, fatty acids, salt hydrates, and eutectics, etc. The main objective of this review paper is to study different latent energy storage materials i.e. organic, inorganic, and eutectic phase change materials for lower temperature applications.

Keywords: Latent heat, PCM, Classification, Properties

Introduction

Thermal energy storage for lower temperature applications can be done by sensible, latent and thermochemical heat storage. Thermal energy storage by latent heat storage is a more superior method and it can be done by phase change materials. There are various phase change materials are available for lower temperature applications viz, organic, inorganic, and eutectic. Each phase change material is available in various temperature ranges for a particular application. Food and Agriculture Organization of the United Nations (FAO) displayed an estimate of around 795 million people were undernourished globally (FAO, 2015). According to (FAO, 2012) it is estimated that about 60% of more food production should increase to meet the demand of the rapidly increasing global population. Because one-third of overall food production is wasted globally.[1] As a result, overall food availability globally is lower than that of the demand. So either we have to produce extra added food to reach the demand otherwise we have to make sure about food security or cut the food losses/ waste. Thermal energy storage systems for both heat and cold are necessary for the good performance of many industrial processes.[2] High energy storage density and high power capacity for charging and discharging are desirable properties of any storage system. TES could be the most proper way and method to correct the gap between the demand and supply of energy and it has become a very attractive technology. Most of the PCM analyzed by the researchers and commercial companies with a melting temperature below 00C is eutectic water-salt solution, and above 0 0C is organic PCM. Eutectic salt solutions are good in terms of thermos physical properties, such as enthalpy of the phase change (since water is the main part) and they are cheap; however, due to the incorporation of the mixture with salts, they could be chemically unstable and may be corrosive. On the other hand, most organic PCM are non-corrosive and chemically stable, however, they have lower thermal conductivity, lower latent heat, larger volume change between the solid and liquid phase and they are relatively expensive. The use of PCM in many applications, and especially at low temperatures, requires the use of nucleation and thickening agents to decrease sub-cooling and phase segregation. Hence when a PCM is used in a new application, it is important to study its long term stability, phase segregation, corrosion, and sub-cooling effects. The enhancement of the heat transfer of many PCM has been thoroughly analyzed by the researchers and some of them showed a good performance, but specific to the case studied.[3]

Classification of Latent Thermal Energy Storage

Phase change heat storage materials; divided as organic and inorganic materials. Organic materials are further classified as paraffin and non-paraffins (fatty acids, eutectics, and mixtures) (Figure 1). Experiments (melting and freezing cycles) using these materials showed that they crystallize with little or no sub-cooling and are usually non-corrosive and very stable. Inorganic materials are further classified as compounds and eutectics. A eutectic material is a composition of two or more components, which melts and freezes congruently forming a mixture of the component crystals during crystallization. Eutectic nearly always melts and freezes without segregation, leaving little opportunity for the individual components to separate. The eutectic mixture melts almost at a constant temperature. Main inorganic materials are salts, salt hydrates, aqueous solutions, and water. The selection of a salt hydrate as a PCM can be eased by a good. The thermal conductivity of nanomaterials plays a vital role in enhancing the conductivity of PCMs. Nanoparticles were commonly used for incorporation in PCM which improves their thermos-physical properties like thermal conductivity, diffusivity, specific heat and latent heat capacity.

Organic PCM

A phase change material that has a carbon atom is known as organic PCM. It is classified into paraffin and non-paraffin. PCM materials with the general chemical formula CnH_{2n+2} are categorized under paraffin, where the heat of fusion and melting point increases with the increasing value of carbon atom number. Non-paraffin PCM is the compounds which contain functional groups such as alcohols, glycol, esters and fatty acids.

Inorganic PCM

Inorganic PCMs are materials that consist of salt hydrates, nitrates, and metallic. Inorganic PCM can also be used for higher temperatures up to 1500ºC. Inorganic PCMs are superior in terms of low cost, easy availability, sharp melting point, high thermal conductivity, the high heat of fusion, and lower volume change.

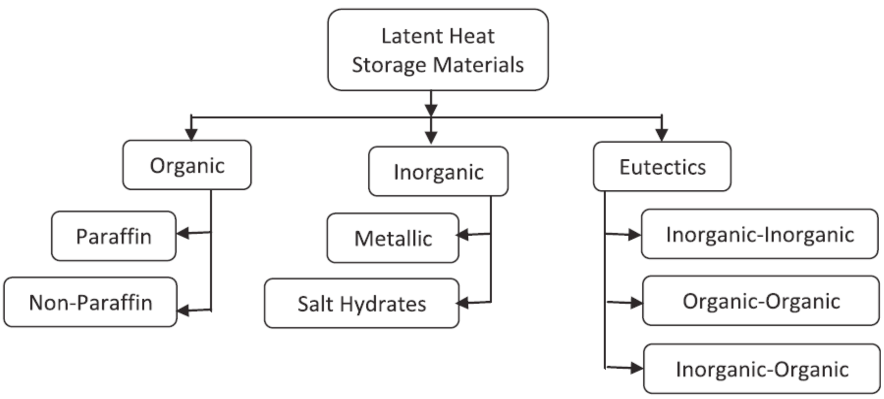

Figure 1.Classification of PCM for cold thermal energy storage[4]

ISSN: 2454-8650
DOI: https://doi.org/10.24321/2454.8650.202003

Table 1.Various organic PCM and its properties[4]

Materials	Melting point (°C)	Latent heat of fusion (KJ/Kg)	Density (kg/m³)
Formic acid	7.8	247	1226.7
Acetic acid	16.7	187	1050
Glycerin	17.9	198.7	1260
D-lattic acid	26	184	1249
Polyethylene glycol 600	20-25	146	1100
Cyanamide	44	209	1080
Methyl eicosanate	45	230	851
camphene	50	238	842
Chloroacetic acid	56	130	1580
Trimyristin	33-57	201-213	862
Bee wax	61.8	177	950
Bromcamphor	77	174	1449
Durene	79.3	156	838
Acetamide	81	241	1159
Succinic anhydride	119	204	1104
Benzoic acid	121.7	142.8	1266
Stibene	124	167	1164
Benzamide	127.2	169.4	1341
Alpha glucose	141	174	1544
Salicylic acid	159	199	1443
O-mannitol	166	294	1489
Hydroquinone	172.4	258	1358

Table 2.Various Inorganic PCM and its properties[4]

Materials	Melting point (°C)	Latent heat of fusion (KJ/Kg)	Density (kg/m³)
$NaNO_3$	306	182	2260
$RbNO_3$	312	31	3685
KNO_3	334	266	2109
KOH	380	149.7	2044
$CSNO_3$	409	71	2500
AgBr	432	48.8	110
$PbCl_2$	501	78.7	5600
$Ca(NO_3)_2$	560	145	2113
Licl	610	441	2070
$FeCl_2$	677	337.9	3160
$MgBr_2$	711	214	3720
Cal_2	783	142	3956
NaCl	802	482	2160
KF	858	468	2370
$BaCl_2$	961	76	3856

ISSN: 2454-8650
DOI: https://doi.org/10.24321/2454.8650.202003

$PbSO_4$	1000	133	6200
$MgSO_4$	1130	122	2660
MgF_2	1263	938	3150
BaF_2	1320	119	4890
CaF_2	1418	391	3180
$BaSO_4$	1512	188	4500
$SrSO_4$	1605	196	3960

Table 3.Various Eutectics PCM and its properties[4]

Material composition (wt %)	Melting point (°C)	Latent heat of fusion (KJ/Kg)	Density (kg/m³)
NaF-MgF_2 (75+25)	832	650	4660
NaF-MgF_2(67+33)	832	616	4650
LiF- MgF_2 (67+33)	746	947	-
NaF-CaF_2-MgF_2 (65+23+ 12)	745	574	-
LiF-NaF_2-MgF_2 (33.4+49.9 + 17.1)	650	860	1150
LiF-NaF_2-MgF_2 (46+44+10)	632	858	1200
Na_2Co_3-Li_2Co_3 (56+ 44)	496	368	2110
NaCl-$MgCl_2$ (50+50)	450	429	0960
$LiaCo_3$-K_2CO-Na_2CO_3 (31 +35+34)	397	275	2040
$MgCl_2$-NaCl-KCl (63 +22.3 + 14.7)	385	641	0950
NaCl- Na_2CO_3-NaOH (7.8 +64+ 85.5)	282	316	-
LiCl-LiOH (37+63)	282	485	1100
KCl-NaCl-$CaCl_2$ (5+29+66)	504	279	1000
KCl-$BaCl_2$-$CaCl_2$ (24 +47+29)	551	219	950

Eutectics PCM

Eutectic PCMs are a mixture of two or more compounds at a particular percentage of the composition. The compounds can be of any combination like organic-organic, inorganic–inorganic, and organic-inorganic. These types of PCMs melt and freeze congruently without any segregation. They freeze to an intimate mixture of crystals leaving less opportunity for the compounds to separate. Similarly during melting, different compound melts simultaneously which also gives less probability of compound separation.

The materials used in latent heat storage are known as phase change materials. There are some desirable thermo-physical, kinetic and chemical properties[5-6] for a material to be used as a PCM which are listed below:

- The melting temperature of the PCM should be in the range of operating temperature
- High Latent heat of fusion
- High thermal conductivity
- High density
- Low volume change during phase change
- Low degree of super cooling
- Less corrosive to the construction materials
- Low degradation
- Chemically stable
- Non-toxic and non-flammable
- Easily available
- Cost effective

What is Food Supply Chain (FSC), Food Loss, Food Waste?

Food supply change is the whole path line to bring the food commodities to the end consumer which includes all the necessary stages entitled, from basic production, post-harvesting handling and storage, processing, distribution, and at the end consumption. Food loss and food waste are decrements of food commodities in production, post-harvesting, processing from the food supply chain, and not exactly reaching the quantity of food material available to the consumer. Many efforts have been made to increase storage capacity while reducing storage volume for different materials. Using Phase Change Materials (PCM) as a latent heat Thermal Energy Storage (TES) system could be a new

ISSN: 2454-8650
DOI: https://doi.org/10.24321/2454.8650.202003

option for food storage purposes. Phase Change material is one of the most studied nowadays for the improvement of the storage ability of food storage. A Phase Change Material (PCM) is a latent heat thermal energy storage system which, melting and solidifying at a certain temperature. During the phase change time, the material is capable of storing and releasing large amounts of heat energy and that's why it is called a heat storage system (LHS). Water boils at a certain temperature and gets vaporized, the same like it freezes when the heat is absorbed/removed from it. Water is a type of PCM itself that can store the heat. Alike there are so many other materials which can store the heat. Quality of storing heat is nothing nut latent heat differs according to the material. Latent heat is the heat released or absorbed by a body or a thermodynamic system during a constant-temperature process.[7] Latent heat storage of PCMs has high energy density when compared to their sensible heat storage. The melting temperature of the PCMs and the latent heat storage are the important criteria when getting chosen for certain applications. Phase change material is not only selected based on higher latent heat storage but there are some of the essential properties which play a vital role. Such are desirable melting point; high thermal conductivity; stability in chemical proportionality; inflammable; non-toxic; lower cost and so on. Numerous sub-zero (Below Ice Freeze temperature) Phase Change materials are available which can be an employee as heat storage material in food refrigerator or freezer compartments. The use of two cycles which are high temperature and low-temperature refrigeration with accurate PCM selection is a better option than that of the conventional refrigeration cycle. The dual cycle works as the foodstuffs are being preserved using a high-temperature refrigeration cycle during on condition of the system and PCM will work as the low-temperature refrigeration cycle. As a result of this, the overall performance of the refrigeration system will increase up to 20–25% and also maintain the food quality for a long period by reducing compressor work as well. The incorporation of nanomaterials could increase the thermal conductivity of the PCMs with their high surface area to volume ratio. Various Oxides of Aluminum, copper, titanium, and the carbides, gold, silver, and so on are used as a nanoparticle in thermal applications.[8] Numerous sub-zero Phase Change materials are available which can be employed as heat storage material in food refrigerator or freezer compartments. As a result of this, the overall performance of the refrigeration system will increase up to 20–25% and also maintain the food quality for a long period by reducing compressor work as well.[9]

The use of PCM in different applications is presented, differentiating those that are already in the market from those that have been studied by researchers. PCM offers the possibility of thermal protection due to its high thermal inertia. This protection could be used against heat and cold, during transport or storage. The protection of solid food, cooked food, beverages, pharmaceutical products, blood derivatives, electronic circuits, and many others is possible. Some of the different applications for cold storage presented are the following ones:

- *Cooling*: Use of off-peak rates and reduction of installed power, ice bank.
- *Thermal protection of food*: Transport, hotel trades, ice-cream, etc.
- *Medical applications*: Transport of blood, operating tables, cold therapies.
- *Industrial cooling systems*: Re-gasification terminal.[10]

Literature Review

Md. Imran Hossen Khan and Hasan M.M. Afroz[11] used two different PCMs (Water and Eutectic solution of melting point 0 and -5OC) at different thermal loads. The experimental result shows that the Coefficient of Performance (COP) of the refrigeration cycle with PCM is considerably higher than that of PCM. Depending on thermal load and the types of PCM average compressor running time per cycle is reduced suggestively and it is found about 2-36% as compared to without PCM. Also, results show that with an increase in the quantity of PCM (0.003-0.00425 m8) COP increases by about 6%. In the situation of without PCM and with PCM the COP is higher at low thermal load while it decreases with the increase of thermal load.

Jenny Gustavsson Christel Cederberg Ulf Sonesson[12] the study suggests that roughly one-third of food produced for human consumption is lost or wasted globally, which amounts to about 1.3 billion tons per year. Food waste in industrialized countries can be reduced by raising awareness among food industries, retailers, and consumers. There is a need to find a good and beneficial use for safe food that is presently thrown away. The causes of food losses and waste in low-income countries are mainly connected to financial, managerial and technical limitations in harvesting techniques, storage and cooling facilities in difficult climatic conditions, infrastructure, packaging, and marketing systems.

Manas Puri[13] the main stages of the food value chain where increasing access to energy can play a dominant role in reducing food losses directly, by making food processing possible, as well as indirectly by acting as the main enabling factor affecting the rate at which cooling technologies are adopted. The cold chain is the key to tackling the loss of perishable produce. The primary challenge in developing a cold chain resides in the fact that in nearly all cases, cooling and refrigeration relies on access to a reliable and affordable source of either electricity or diesel fuel. The rural farmers to preserve and process food which consequently can have an immediate impact on food losses.

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K.Azzouz, D.Leducq, J.Guilpart, D.Gobin[14] in this paper, the case of a household refrigerator is simulated as an example. Compared to the classical vapor compression system, the new design shows a significant increase in the coefficient of performance, but also a limitation of the maximum refrigerating capacity transmitted to the refrigerated area. This model yields a 72% increase in the coefficient of performance and a 25% decrease in the global working time of the compressor.

C. Kaviarasu et al.[15] this review provides an outlook of various types of PCM, choices of nanomaterial for incorporation, and applications of nanomaterial incorporated PCMs. The most common types of PCM used are water, paraffin, hydrated salts, and bio-based PCM. Despite their high latent heat storage advantage, their low thermal property calls for the incorporation of nanomaterial. Nanomaterial with their high surface to volume ratio tunes the thermal properties of the base PCM. Nanomaterial used for incorporation in PCM includes Al, Cu, SiO2, TiO2, Carbon Nanotubes (CNT), Carbon Nanofibers (CNF), Al2O3, NaOH KOH, etc. In this review work thermophysical properties of PCM, Thermophysical properties of Nano-PCMs, Applications of Nano-PCMs are discussed.

Principi, et al.[16] in this paper, PCM is employed for transportation applications, where, a PCM layer was added to the external face of a refrigerator. Afterward, the experimental operation was aimed toward reducing the cooling energy needed to run a low efficiency-refrigerating unit. Results obtained by positioning a PCM air HX close to the evaporator highlighted a lower no. of compressors ON-OFF cycles. Specifically, within the first study, a PCM (35°C melting temperature) layer was added to the external side of an air HX wall to manage the cooling peak and reduce the daily energy rate. Outdoor experimental results showed that the added PCM layer helps to reduce (between 5.55% and 8.57%) and delay (between 4.30 h and 3.30 h) the peak load of incoming heat compared to the reference one. In the second study, the energy performance of a refrigerated chamber with an air heat exchanger containing PCM (50C melting temperature) was investigated. Test results showed that employing a PCM air HX addition, up to 16% of energy may be saved.

R. Liddiard, B. L. Gowreesunker, C. Spataru, J. Tomei and G. Huebner[17] the model described here provides an estimation of the amount of three foodstuffs that may be made unfit for human consumption, due to power supply interruptions. The present iteration of the model relies upon several assumptions that overcome some of the shortfalls in data accessibility. Principal among these shortfalls are the lack of good grid reliability data; information on patterns of food purchasing among consumers; data on how consumers store their food; seasonal availability and purchasing patterns; how consumers react to power interruptions; the effects of refrigerator types.

Pumin Hou, Jinfeng Mao, Fei Chen, Yong Li and Xian Dong[18] in this paper, a series of $Na_2SO_4.10H_2O$.KCl eutectic mixtures were prepared by adding different mass fractions of KCl (1 wt.%, 3 wt.%, 5 wt.%, or 7 wt.%) to $Na_2SO_4.10H_2O$. Polyacrylamide (PAM) was proposed as the thickener, Sodium Tetraborate Decahydrate (STD) was proposed as the nucleating agent, and Expanded Graphite (EG) was proposed as the high thermal conductivity medium for Na2SO4.10H2O–5 wt.% KCl eutectics. The results showed that in $Na_2SO_4.10H_2O$-5 wt.% KCl eutectics with 5 wt.% PAM and 5 wt.% STD, almost no phase separation occurred, and the degree of supercoiling was reduced to 0.4ºC. The thermal performance of $Na_2SO_4.10H_2O$.5 wt.% KCl Composite Phase Change Materials (CPCM) with varying contents of EG were explored. The results showed that EG could improve the thermal conductivity effectively and that the mass fraction of EG should be no more than 3%, otherwise the crystallization value and supercoiling would deteriorate. In this paper, a series of low-temperature eutectic CPCMs consisting of $Na_2SO_4.10H_2O$ and KCl was prepared. The $Na_2SO_4.10H_2O$–5 wt.% KCl eutectics were modified by adding PAM, STD, and EG. Then, the phase separation condition, cooling curve, DSC curve, and thermal conductivity of the $Na_2SO_4.10H_2O$ eutectic CPCMs were explored.

Randeep Singh, Sadegh Sadeghi and Bahman Shabani[19] in this paper, several techniques for enhancing the thermal conductivity of PCMs were experimentally studied. This included the addition of carbon powder and the introduction of aluminum and carbon fins to a PCM selected for this study. PEG-1000 PCM with a melting point of about 37ºC was used as a reasonable organic PCM for low-temperature thermal energy storage applications. Aluminum and carbon were used as heat transfer enhancers due to their low cost, light structure, and high thermal conductivity. In this study, 0.78–2.5% carbon powder was introduced to molten PCM containing PEG-1000, and the increment in the thermal conductivity was investigated. The effects of introducing aluminum and carbon fins on the thermal conductivity of the PCM were also investigated. For this purpose, aluminum heat sink with ~22.67% volume and ~41.5% weight of the total system and carbon heat sink with ~24.7% volume and ~34% weight of total (PCM + fin stack) assembly were used. The investigation will provide a twofold pathway, one to enhance the thermal conductivity of PCMs, and secondly 'relatively easy to set-up' methods to measure properties of pure and enhanced PCMs.

Conclusion

This review paper is focused on the available thermal energy storage technology with phase change materials for cold applications. Following conclusionare made from the above discussion:

- The use of phase change material helps to maintain a constant temperature for a longer duration of time even though power is cut off. Also, it prolonged the compressor ON-OFF time due to that electricity consumption reduces. Phase change materials are used as thermal storage in various applications like cold storage, transportation trucks, temporary storage unit, a pre-cooler, bulk cooler, deep freezer/chest freezer, chillers, domestic refrigerators, and commercial refrigerators, etc.
- From the above literature survey, it is understood that most of the above researchers choose eutectic type phase change material (Salt type) because it is easily available in a wide temperature range with lower prices. Also, latent heat of phase change material is good; however, due to the incorporation of the mixture of salts and water could be chemically unstable and may be corrosive.
- On the other hand, most organic PCM are non-corrosive and chemically stable, however, they have lower thermal conductivity, lower latent heat, larger volume change between solid and liquid phases. Hence, attention is given on limitations of organic and eutectic phase change materials by changing their combinations and by adding nanoparticles.
- The literature focuses on parameters like stability, phase change temperature, PCM thickness, cooling period, loading and unloading conditions, etc. Also, an attempt has been given on the long term stability of PCM and compressor ON-OFF time. Comparing the advantages and disadvantages of phase change material, Evaporator side PCM integration has some advantages which can cover the disadvantages of condenser side PCM and vice versa.
- Therefore, it seems that the simultaneous application of PCMs at condenser and evaporator could be more advantageous. The overall conclusion of the literature review is thermal energy storage is emerging technology for lower temperature applications and practice of this technology will improve cooling period for a longer duration of time, saves electric consumption, keep food quality good without spoilage, increasing in the Coefficient of Performance (COP), etc.
- The use of PCM for the transportation purpose of food supplies is also very helpful as it does not harm the food products in any manner. The hygiene of the food product is not hampered in any way.
- From all the studies it can be seen that the utilization of PCM for lower temperature applications has shown very successfully, promising results, and further it is also a very useful element for the refrigeration industry.
- Inorganic PCMs are more suitable for the low temperatures to high-temperature thermal energy storage but has got serious disadvantages of corrosion, incongruent melting, and super-cooling. Therefore organic PCM is mostly used for lower temperature applications.
- Eutectic salt solutions are great in terms of thermos physical properties, such as enthalpy of stage change and they are cheap; be that as it may due to the incorporation of the mixture with salts they can be chemically unsteady and may be corrosive.

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ISSN: 2454-8650
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