

A Systematic Review of Thermal Energy Storage and Phase Change Materials

Dinesh Kumar Saini* and Chandrashekara M

National Institute of Technology, Kurukshetra, Haryana, India

*Correspondence to:

Dinesh Kumar Saini
National Institute of Technology,
Kurukshetra, Haryana, India .
E-mail: dineshsaini1610@gmail.com

Received: November 24, 2022

Accepted: April 19, 2023

Published: April 20, 2023

Citation: Dinesh KS, Chandrashekara M. 2023. A Systematic Review of Thermal Energy Storage and Phase Change Materials. *NanoWorld J* 9(S1): S364-S368.

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Published by United Scientific Group

Abstract

An efficient solution to reach the demand for energy supply by implementing surplus solar energy, which is voluntarily available. An important class of modern materials, phase change materials (PCMs), is utilized to store available thermal energy from the sun. It can be stored in sensible and latent heat, considerably enhancing the effective use and conservation of waste heat, i.e., solar power. Utilizing thermal energy storage with PCMs has recently drawn much attention from the research community. Despite the storage method for sensible and latent heat that offers to store the higher energy density with a minimum temperature difference in its storage and release of heat. The paper integrates information on thermal energy storage needs and classifies some important PCMs with their types and properties. This article also includes a detailed description of organic PCMs like Paraffin and fatty acids, inorganic PCMs like salts and their salt hydrates and metallics, and eutectic PCMs. Also, discuss the PCM preparation techniques like macro and nanoencapsulation and composite PCMs (made using carbon filler and nanoparticles) to enhance the thermal conductivity of PCMs.

Keywords

Latent heat storage, Phase change materials, Sensible energy storage, Thermal energy storage

Introduction

The average worldwide temperature nonstop increases daily and reaches a worrying level, contributing to global warming and the greenhouse effect. This temperature increases due to the high dependence on producing energy from fossil fuels which are very harmful to the environment and human life. Steps need to be taken to control this increase in worldwide temperature immediately for a better sustainable environment on the earth [1]. An alternative (renewable) energy source is needed to balance the current energy production and demand and reduce emissions from burning fossil fuels. The most abundantly available energy on this planet, solar thermal energy, can be harnessed by direct and indirect renewable energy source methods [2]. The rate and timing of solar energy collection usually don't meet the load requirements of thermal applications because of solar radiation's intermittent, variable, and unpredictable nature. Hence, thermal energy storage (TES) systems are one of the best solutions to balance renewable energy production and consumption. The TES systems store the energy in the materials in various forms like sensible, latent, and thermochemical. Among these methods, Latent heat storage (LHS) system is the most popular and is known as Phase Change Materials (PCMs). The PCMs based on the Solid-Liquid transformation are used in various applications to store large amounts of energy [3]. The present review work focuses mainly on TES systems and Solid-Liquid PCMs.

Thermal Energy Storage

When the system receives the heat, TES systems store that heat as energy and release it as required. These systems can enhance the effective use of thermal energy obtained from the sun. We need TES to meet peak load demand, balance the adverse effects of changing electricity demand, ensure a consistent output from power plants, and supply energy at the thirst for intermittent generating technologies like wind and solar energy, where production varies with demand.

In the theoretical systems, three steps are required in the heat storage process, i.e., charging, storing, and discharging. Out of these three steps, one or more steps may occur concurrently in each storage cycle in the case of practical systems [4].

Thermal Energy Storage Methods and Materials

Figure 1 represents the classification of TES methods.

Sensible heat storage (SHS)

Sensible heat is the energy absorbed and released by a material due to increasing and decreasing temperature. The SHS system stores the energy in liquid or solid materials due to heating without changing its phase. The expression of the energy stored in SHS material is given as [5]:

$$E_s = \int_{T_i}^{T_f} mC_p dt = mC_p (T_f - T_i) \quad (1)$$

SHS systems are simpler in design than latent heat and thermochemical storage systems. For temperatures up to 100 °C, water is the best SHS liquid since it is cheap and has a high specific heat value. Water has three times more heat storage capacity than rock on a volume basis, which means rock requires three times more volume than water to accumulate an equal quantity of sensible heat. Molten salts, oils, and liquid metals are employed when the temperature exceeds 100 °C. The performance of SHS materials depends on two critical parameters: thermal capacity and diffusivity. Thermal capacity is the ability to store sensible heat, while thermal diffusivity is the rate of heat absorbing and releasing capacity of the material. These materials are inexpensive and chemically stable. Different materials have different working temperature ranges to hold the heat. The demerits of SHS Materials are the requirement of a large amount of volume and not working at an invariable temperature [6].

Latent heat storage (LHS)

LHS materials store latent heat from Solid-Liquid and Liquid-Gas transformation at a fixed temperature. The latent heat cannot be stored alone, as these materials had to undergo

an increase in temperature to reach the point of phase change temperature. The expression for stored energy at a range of temperature T_i to T_f is given by [5]:

$$E_s = \int_{T_i}^{T_f} mC_p dt = mC_p (T_f - T_i) \quad (2)$$

$$E = mC_{ps} (T_m - T_i) + mL + mC_{pl} (T_f - T_m) \quad (3)$$

Solid-Liquid transition LHS materials are used more effectively than other LHS and SHS materials due to charging and discharging at a fixed phase temperature and storing the high energy (energy density). The latent heat value of Solid-Liquid LHS materials is smaller than that of Liquid-Gas but used in many applications due to a slight change in volume of the order of 10% [7]. Some containers or encapsulations are required to avoid the leakage of liquid LHS materials. Encapsulation of storage material enhances cost and reduces the energy density of the storage system. Solid-Solid PCMs are used as an alternative that minimizes the encapsulation cost and the leakage problem. Hence, they are used for many TES applications with suitable melting temperatures and latent heat [8].

Thermochemical energy storage (TCES)

This method uses thermal energy to carry out the endothermic reaction where reactant A dissociates into B and C. This energy is recovered completely when the reverse (exothermic) reaction occurs. The reversible thermochemical equation is expressed as:



Where, A, B, and C are the reactants, and ΔH is the enthalpy of the reaction in kJ/mole [6].

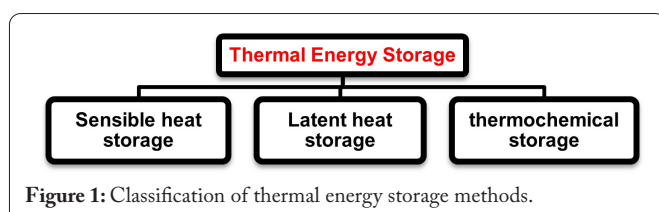
The advantage of this method is that it can be used for high storage energy density and indefinitely long storage duration near the surrounding temperature. This storage method offers an attractive choice for longer-term use and relatively low costs. This storage system is only suitable for medium or high-temperature applications [9].

Phase Change Materials

It can store tremendous energy during liquefaction (charging) and then release that energy during solidification (discharging) to provide useful heating and cooling within the specified temperature range. In 1983, Abhat et al. classified the materials used in the TES system [10]. PCMs have different properties and are used in various heating and cooling applications.

Desired properties of PCMs for selecting a PCM for a unique purpose are:

1. Thermal properties are high thermal conductivity, specific heat capacity, energy density and latent heat of fusion, good heat transfer, and melting temperature within the acceptable working temperature range.
2. Physical properties are high density, low vapor pressure, and a slight change in volume during phase transformation to minimize the storage container size and favorable phase equilibrium.



3. Chemical properties are high thermal cycling stability, toxic-free, non-inflammable, non-explosive, non-corrosive, no fire hazards and chemically steady to avoid chemical decomposition and oxidation degradation with the storage container material.

Along with these properties, PCMs should be commercially available at a reasonable cost, allow achievable improvement and not harm the environment. Along with the positive characteristics, the biggest challenge to using the PCM is having low thermal conductivity, which results in the slow storage and release of energy. Conversely, a different difficulty is that solid deposition reduces the heat transfer surface area [5, 11]. Researchers used experimental setups to evaluate the PCM characteristics during the melting and solidification processes by controlling the heat used for melting via a heating coil and thermostat. The heat transfer rate also increases by utilizing the fins inside the LHS unit [12]. Supercooling, which occurs when solidification begins in most PCMs at a temperature significantly below the melting point, results in a considerable loss in latent energy, which is unfavorable. The addition of suitable nucleating agents with a crystal structure and lattice properties similar to the PCM is the technique used to resolve the problem of supercooling. Materials supplied to the PCM as nucleating agents have similar crystal structures [13].

PCMs Classification

Figure 2 represents the classification of PCMs.

Organic PCMs

The PCMs which contain carbon atoms are known as organic PCMs. They are available in stable temperature ranges below 300 °C. Repeatedly melting (charging) and freezing (discharging) of Organic PCMs without phase separation results the latent heat degradation during fusion. PCMs have high fusion heat, low thermal conductivity and flash points, non-toxicity, non-corrosive, non-flammable and volatile at high temperatures. They are further categorized as Paraffin and non-Paraffin [10, 14, 15]. These PCMs have various advantages, but they also have certain drawbacks, such as lower thermal conductivity, which impacts the rate of melting and solidification, the problem of PCM leakage from containers, and the supercooling effect in thermal cycles. The flammability of organic PCM is also a significant problem. It can be minimized by including flame retardants in shape stabilized PCMs (ethylene propylene diene monomer, expanded graphite, silicon, and epoxy resin as a matrix in PCM), microencapsulated PCMs, and directly onto the PCM [16].

Paraffin

It consists of a long straight chain of hydrocarbons (primarily alkanes represented by C_nH_{2n+2}) with some small branching of methyl groups at the end of the chain. Alkanes comprise carbon atoms from 14 to 40 with melting points between 6 and 80, known as Paraffins. The melting point and latent heat also rise as the number of carbon atoms in the chain increase [10]. Due to essential properties like the availability of a wide temperature limit, high latent heat of fusion, minimal price, and no supercooling during freezing, Paraffins

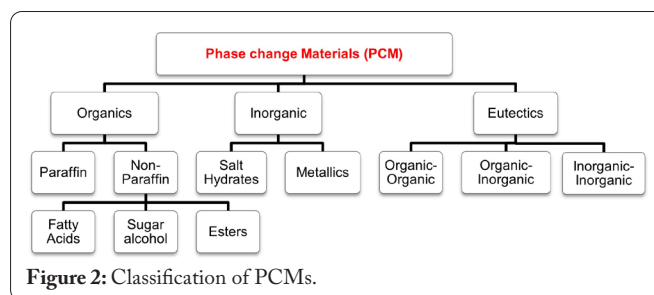


Figure 2: Classification of PCMs.

are used as a heat storage material in many applications [17]. Apart from these advantageous characteristics, Paraffin has very low thermal conductivity (0.2 W/mK), which confines its use in several solar applications.

Non-Paraffin

Abhat et al. [17] have done an extensive literature survey on non-Paraffin PCMs to shortlist the energy storage materials. They are classified as fatty acids, esters, glycols, and alcohols.

Fatty acids

These acids are essential organic PCMs represented by the general formula $CH_3(CH_2)_nCOOH$ and have high latent heat of fusion compared to Paraffin. These materials qualify as good PCMs for low-temperature TES applications due to their repeatedly melting and freezing behaviour and freezing without supercooling [17]. These materials are non-toxic, have high latent heat, and have a suitable temperature range. They are also chemically and thermally stable. Thousands of thermal cycles (charging and discharging) are performed on these materials without significant loss in their thermal characteristics [18, 19]. The major limitation of these materials is their cost (2 to 2.5 times more than Paraffin), low thermal conductivity, and mild corrosion. These materials are classified into six groups: caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid [10].

Sugar alcohols

Researchers have paid less focus to sugar alcohols, also called poly-alcohols, which are regarded as moderate temperature (90 - 200 °C) PCMs. Alcohols like xylitol, erythritol, and mannitol have a considerably larger latent heat value than other materials in this group. Over the past forty years, alcohol has been considered a suitable PCM for TES. Erythritol has a higher potential as a TES material among sugar alcohols. It has a 120 °C melting point and a 339.8 kJ/kg latent heat of fusion [20].

Esters

These are made from acids by substituting an alkyl (-O) group for one of the hydroxyls (-OH) groups. Over a limited temperature range, fatty acid esters exhibit the Solid-Liquid transition and can produce eutectics with little or no subcooling [21]. Large amounts of fatty acid esters are readily accessible on the market for use in polymers, cosmetics, and smart clothes [19].

Inorganic PCMs

This PCMs group includes salts, salt-hydrates, and metallics. Inorganic salt mainly considers salts and salt hydrates.

These salts are $A_xB_y \cdot n(H_2O)$, where n is the number of water molecules, and A_xB_y stands for chloride, oxide, nitrite, sulphite, acetate, phosphate, or metal carbonate [22]. These materials have high specific heat, latent heat, thermal conductivity, thermal stability, precise melting point, low vapor pressure, and viscosity. They work well in TES applications involving moderate and high temperatures [23, 24]. They have several drawbacks, such as corrosiveness, supercooling, significant volume changes during phase transitions, and phase segregation as an outcome of inadequate nucleating capacity and inconsistent melting [25].

Salt hydrates

Anhydrous salt and crystal water are the two components that make up inorganic hydrated salts, whether they be single or eutectic. After the raw salts are purified, the necessary anhydrous salts can be produced. In the Solid-Liquid transition phase, hydrated salts lose some or all of their water molecules and dissolve while adsorbing latent heat (LH) energy. This LH has recovered again when a reversal transition takes place. The most desirable features of salt hydrate include high latent heat per unit volume, moderate thermal conductivity (almost twice that of Paraffin), and little volume changes during melting. They are hardly toxic, plastic-compatible, and not highly corrosive. Many salt hydrates are suitably affordable for TES applications [7]. Some essential salt hydrates are $Na_2SO_4 \cdot 10H_2O$, $CaCl_2 \cdot 6H_2O$, Na_3PO_4 , and $MgCl_2 \cdot 6H_2O$.

Metallics

These PCMs are used in various applications due to higher volumetric heat of fusion than salt hydrates and organic materials, long-term stability, low specific heat, comparatively low vapor pressure, and minor change in volume during melting and freezing. The primary benefit of metallic PCMs is their high thermal conductivity, which may greatly simplify the design of thermal storage and eliminate the requirement for methods to improve heat transfer. Increased weight and cost are the primary disadvantages of these PCMs [26].

Eutectics

It is a mixture of two or more materials in suitable proportions. It can consist of organic-organic, organic-inorganic, and inorganic-inorganic materials. Each material melts and freezes concurrently during crystallization to produce a mixture. Since eutectic materials freeze into a near-crystal mixture, there is rarely a chance for the constituents to segregate during melting and freezing. Both components simultaneously liquefy when heated, making separation improbable. High latent heat capacity, thermal conductivity, non-flammability, and commercial availability are the benefits of these PCMs. A detailed description of different PCM types with their thermophysical properties is given below in table 1 [7, 15].

PCMs Preparation Techniques

Microencapsulation and nanoencapsulation of PCMs

PCMs can be shielded from outside influences and made into more useful TES materials using micro and nano-encapsulation techniques. During PCM meltdown, stabilizing the liquid phase to prevent leakage and migration is the most

Table 1: Thermophysical characteristics of a few significant PCMs.

Phase Change Material	Material type	Melting temperature (°C)	Latent heat of fusion (kJ/kg)
Caprylic acid	Organic	16.4	149
Capric acid	Organic	36.1	152
Lauric acid	Organic	49.1	178
Pentadecanoic acid	Organic	52.5	178
Myristic acid	Organic	58	199
Paraffin wax	Paraffin wax	64.2	173.6
Palmitic acid	Organic	55	163
Stearic acid	Organic	69.2	199
$Na_2SO_4 \cdot 10H_2O$	Salt hydrate	32.4	241
$CaCl_2 \cdot 6H_2O$	Salt hydrate	42	162
$MgCl_2 \cdot 6H_2O$	Salt hydrate	117	167

significant challenge in PCM applications. To solve this issue, PCM can be encapsulated in a polymeric shell of micron or nano-sized particles to create micro or nano-encapsulated PCM. The primary goals of PCM micro or nanoencapsulation are to increase thermal characteristics by expanding the heat transfer surface, minimize reactivity, and simplify and secure PCM handling. Many researchers explained the encapsulation of PCMs both experimentally and numerically [27-30].

Composite PCMs

Lower thermal conductivity and high potential of leakage problems in liquid form during phase transition are the downsides of the PCMs, which limit their practical use. These problems can be solved by using composite PCMs. Composite PCMs are formed by mixing carbon materials such as carbon nanotubes, carbon fibers, graphene, expanded graphite, and other porous carbons in ordinary PCMs. Dispersion of metallic nanoparticles such as copper sulfide (CuS), ferric oxide (Fe_2O_3), copper oxide (CuO), aluminium oxide (Al_2O_3), and titanium dioxide (TiO_2) by weight percentage in the ordinary PCM is the other way to enhance thermal conductivity. Nanoparticles are used in PCMs as the matrix and a heat conduction booster. Compared to pure Paraffin wax, the results demonstrate that the composite PCMs with 1.2 wt% CuO raise the thermal conductivity by 24.9% at 25 °C and 20.6% at 70 °C [30]. The mass percentage of Expanded Graphite (EG) improves the thermal conductivity of composite PCM. Pure Paraffin has a thermal conductivity of 0.355 W/mK, whereas Paraffin/EG80 (5 wt%) has a value of 1.492 W/mK [31]. Hence, TES capacity of the PCMs is increased by using micro and nanoparticles encapsulation and composite PCMs (adding metallic nanoparticles and carbon materials).

Conclusion

The current review article describes the principle of TES, PCMs, and their properties. Sensible heat, latent heat, and thermochemical energy storage are methods of TES. Solid-Liquid PCMs such as organic (Paraffin and fatty acids) and inorganic (salt hydrates and metallics) are primarily used as TES. Phase separation and supercooling problems with salt hydrates reduce the heat of fusion across consecutive cycles. In contrast, organic PCMs are flammable and have a low heat

of fusion. Low thermal conductivity is the main drawback of PCMs, which is enhanced by using metallic fins, dispersion of metallic nanoparticles by weight percentage in the basic PCM, micro and nanoencapsulation, and composition mixture of two or more PCMs.

Acknowledgments

The author wishes to express gratitude for the insightful conversations and suggestions received from the experts while writing this paper.

Conflict of Interest

None.

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