INNOVATIVE MECHANICAL ENGINEERING **ISSN 2812-9229 (Online)**
University of Niš, Faculty of Mechanical Engineering
VOL. 1, NO 2, 2022, PP. 116-129

Original scientific paper *

POTENTIALS OF CLAY AS A PHASE CHANGE MATERIAL

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Abstract. *Clay has a porous structure, a large specific surface and the ability to adsorb well. Clay and its composites are mechanically and thermally stable. Due to their robust mechanical properties and high chemical and thermal stability, they are compatible with various processes such as mixing, extrusion, molding, etc. Phase change materials interact with clay through hydrogen bonding surface tension and van der Waals forces. Clay is an integral part of building materials, which allows easy installation of PCM/clay composites. PCM/clay composites are prepared by vacuum impregnation, melt intercalation, melt adsorption and their combination. Properties that characterize PCM/clay composites are phase change temperature, heat of fusion and freezing, cooling temperature, thermal reliability and stability, and thermal conductivity. An important property of PCM/clay composites is the PCM loading efficiency, which represents the mass fraction of PCM in the composite container, as well as the crystallinity of the encapsulated PCMs, which affects the latent storage and heat release efficiency.*

Key words: *Thermal energy storage, Phase change material, Clay, Clay minerals*

1. INTRODUCTION

Natural clays are abundant throughout the world, formed as a result of the gradual chemical weathering of rocks on the earth's surface. They are a natural mixture of clay minerals and some other materials. Clay minerals represent hydrating silicates containing aluminum, potassium and other cations, and they give clay characteristic properties that depend on the quality of clay and its industrial use. Clay also contains traces of quartz, zircon, and granite, and is very stable in the moist oxidizing environment on the earth's surface [1]. When the term clay is used, it refers to a natural material composed primarily of fine-grained minerals, which is plastic at the appropriate water content and will harden when dried or baked.

*Received: November 25, 2022 / Accepted November 28, 2022.

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Clay minerals belong to the group of phyllosilicates, very small in size (several micrometers), whose formation occurs below the surface (alternates, soils, sediments) or underground (diagenesis, hydrothermal changes). They show a great diversity of composition due to the wide range of composition of solid solutions and their ability to form polyphase crystals [2]. Like any mineral species, phyllosilicates are characterized by a "unicellular" structure, which is a single layer structure. The layers are organized into larger groups: tetrahedral and octahedral "sheets". The leaf framework forms cation-anion bonds. Three types of coordination determine the elementary polyhedron that make up the different sheets of the crystal structure: 4-fold coordination (SiO_4^{-4} or $Al_2O_5^{-4}$ tetrahedron), 6-fold coordination (octahedron with centers Al^{3+}, Fe^{3+}, Fe^{2+} or Mg^{2+} cations for the most part - peaks formed by O_2^- or OH^- anions), 12-fold coordination (a dodecahedron whose center is occupied by a cation with a wide diameter: K^+, Na^+, Ca^{2+}, and the peaks are formed by O_2^- anions from two opposite tetrahedral sheets). The bonds of the silicate crystal framework are typically between ionic and covalent. Therefore, each bond is polar and characterized by electrical arrangement [3,4]. The crystal structure of all phyllosilicates consists of two types of layers: 1:1 layer in which one tetrahedral sheet is attached to one octahedral sheet, or 2:1 layer in which one octahedral sheet is inserted between two tetrahedral sheets. Layer structures depend on the hexagonal symmetry of tetrahedral and octagonal sheets that are connected to each other.

The term "clay mineral" refers to phyllosilicate minerals and to minerals that give plasticity to clay and harden when dried or fired. Like all minerals, clay is a natural substance. Synthetic materials having similar properties or any component of amorphous clay, even if it imparts plasticity or hardens after drying and firing, cannot qualify as a clay mineral. The currently known clay minerals belong to the phyllosilicate subclass of the silicate class. The basic structural unit of all silicate minerals is the SiO_4^{-4} tetrahedron in which each Si^{+4} is surrounded by four O^{-2} ions. Each SiO_4^{-4} tetrahedron has an unbalanced negative charge, which is neutralized by bonding to a cation (Mg^{+2}, Fe^{+2}, Al^{+3}, etc.) and/or by bonding two or more tetrahedrons. The silicate class is divided into subclasses based on the bonding and internal arrangement of the SiO_4^{-4} tetrahedron. In the non-isosilicate subclass, each SiO_4^{-4} tetrahedron is isolated.

In sorosilicates, two tetrahedrons are connected: cyclosilicates 3, 4 or 6 tetrahedrons are connected by a ring, while inosilicates are connected in a chain formation. In phyllosilicates, many tetrahedrons are connected to form a two-dimensional sheet. In tectosilicates, many tetrahedrons are linked into a three-dimensional framework. In phyllosiliphyllosilicate minerals, each SiO_4^{-4} tetrahedron is connected to three neighboring tetrahedrons to form a tetrahedral sheet. Each tetrahedron in that sheet thus shares three (out of four) apical oxygens and has the basic formula $Si_2O_5^{-2}$. The phyllosilicate subclass is divided into certain groups, such as mica, chlorite, talc, serpentine, kaolinite, smectite, etc. Clay minerals are not limited, by definition, to phyllosilicates.

2. PCM AS ENERGY STORAGE

Based on the law of conservation of energy, it is known that energy can neither be created nor destroyed but can be transformed from one form to another. It states that the total amount of energy in the system remains constant. Energy storage systems are based on this principle. Thermal energy storage (TES) is a concept that has been used for centuries and is one of the most important components of energy storage systems, Fig. 1.

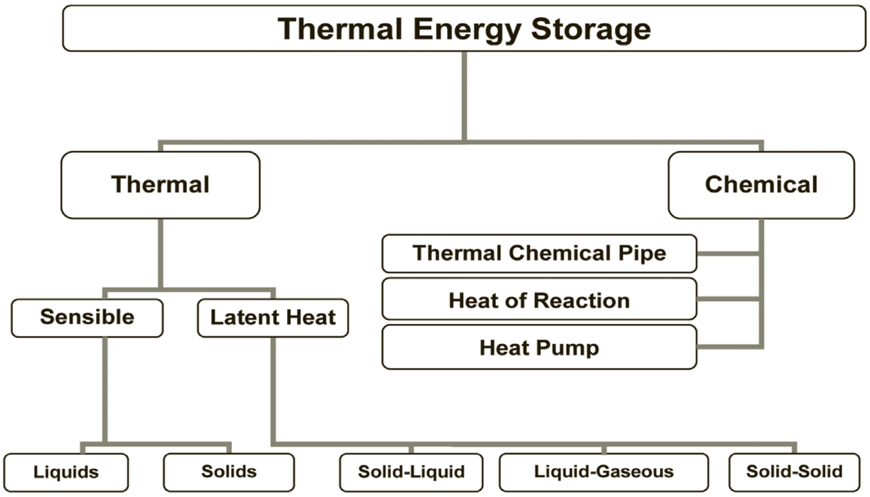


Fig. 1 Different types of thermal energy storage.

TES enables the temporary storage of thermal energy at high or low temperatures, allowing one to meet the energy needs and benefits for bridging the current lack of energy at any time, and therefore plays an important role in energy conservation [5,6].

With TES, energy can be stored in the system. At the highest demand, by releasing the stored energy from the system, it is delivered to the desired place. Continuous energy consumption shows dire effects on centralized energy distribution and grid instability under changing load conditions due to increased demand. These problems can be overcome by developing technologies related to energy storage. The overall energy storage capacity and operational performance of the energy storage system can be improved by integration with renewable energy sources [7, 8]. However, there are some limitations here when activating a storage system configured with renewable energy sources compared to conventional energy sources. Energy storage technologies can be a viable option for current as well as future energy needs as they concern both energy security and climate change. To bridge the gap between energy supply and energy demand, energy storage has gained much importance recently [9, 10].

The importance of TES is reflected in meeting short-term variable energy requirements, reducing the need for energy generators that consume primary energy sources, redistributing energy consumption, using energy produced from renewable energy sources, ensuring energy security and reducing the impact on the environment and improving the operational performance of energy systems. The main use of TES is energy saving [11-14]. Storage systems are active or passive [15]. An active storage system features forced convective heat transfer to the storage material, which circulates through a heat exchanger. Active storage systems can be direct, where the heat transfer fluid serves as the storage medium, or indirect, where a secondary medium is used for heat storage. Passive storage systems are generally dual storage systems, where the heat transfer fluid passes through the storage only to fill and drain the material.

Thermal energy storage in the form of sensible and latent heat has become an important aspect of energy management with an emphasis on the efficient use and conservation of waste heat and solar energy in industry and buildings. The use of phase change material (PCM) in a latent heat storage system is an efficient way to store thermal energy and has the advantages of high energy storage density and the isothermal nature of the storage process. TES can store energy with PCM in the form of sensible heat, latent heat and thermochemistry or their combination. In TES systems, energy is stored to be used later, implementing the whole process through three steps: charging, storage and discharge. Energy can be charged, stored and discharged daily, weekly, annually or in seasonal or rapid batch process cycles. High temperature storage is usually associated with solar energy or high temperature heating, and cold storage with air conditioning, refrigeration or cryogenic processes. In low-temperature heat storage, thermal energy can be stored and released using materials whose operating temperature is comparable to the temperature of the cooling/heating space. A medium temperature heat storage system uses materials whose operating temperature is generally higher than human comfort temperature. High temperature heat storage systems use molten salts to store and release thermal energy at very high operating temperatures (>300°C). Among the energy storage methods, TES is considered an advanced method of energy technology and is of great importance in a wide range of energy applications [16, 17].

The choice of a TES system mainly depends on the temperature level. Many research and development activities in energy are related to energy efficiency and energy saving. High energy density in the storage material (storage capacity), good heat transfer between the heat transfer fluid and the storage material, mechanical and chemical stability of the storage material, compatibility between the storage material and the container, complete reversibility of the cycle, all play a big role in the design of the TES system. The most important design criteria are the operation strategy, maximum required load, nominal temperature and enthalpy drop, as well as integration into the entire application system. The advantages provided by the application of energy storage are economy, energy efficiency, reduction of environmental pollution and CO_2 emissions. In construction, energy storage is most often used in seasonal solar thermal systems, district heating and passive cooling systems. In the industrial sector, these are the cases of combined heat and power (CHP, also called cogeneration), industry (heating and cooling systems), power plants and transport, and concentrated solar power (CSP). To determine the potential of TES, parameters related to energy and CO_2 emissions are needed. Within the energy field, two quantities show the potential to be determined: the reduction of heat load and the saving of heat/electricity. Heat load reduction refers to the reduction in capacity compared to that which would be consumed under the same operating conditions without the use of any type of energy storage. Energy conservation simply refers to heat or cold that is stored and can be reused.

2.1 Sensible heat storage

Sensible heat storage systems (SHS) typically use rock or water as the storage medium and are available for short-term and long-term storage. Thermal energy is stored by raising the temperature of a solid or liquid substance. The amount of stored heat is a function of the specific heat of the medium, the change in temperature and the stored mass of the medium:

$$Q = \int_{T_i}^{T_f} mC_p dT = mC_{ap}\left(T_f - T_i\right) \tag{1}$$

Q - amount of stored heat (J)
T_i - initial temperature (°C)
T_f - final temperature (°C)
m - mass of heat medium (kg)
C_p - specific heat (J/kg K)
C_ap - average specific heat between T_i and T_f (J/kg K)

Storage materials absorb heat by conventional heat transfer mechanisms by radiation, convection, and conduction. The SHS system utilizes the heat capacity and temperature change of the material during the energy charging and discharging process. Water is the best SHS fluid because it is cheap, readily available, and has a high specific heat. The amount of stored heat depends on the specific heat of the medium, the temperature change and the amount of storage material [18]. In addition to water, the storage material can be air, soil, rocks, bricks, concrete, etc. Each material has its advantages and disadvantages, and each material is selected according to its heat capacity and the availability of storage space. Properties that are important when choosing suitable materials are density, specific heat, thermal conductivity and diffusivity, vapor pressure, compatibility with container materials and chemical stability. Sensible heat can be stored in solid or liquid form (gaseous media are also used, such as air storage systems, but are much bulkier). Modern materials that are widely studied today to reduce energy consumption in buildings are concrete with phase change materials, as well as the use of solid particles for storage in concentrating solar power plants (CSP plants) [28,29].

2.2 Latent heat storage

Latent heat storage is the most efficient method of storing thermal energy. Latent heat storage (LHS) systems, which store energy in PCM (eg. salt hydrates and organic substances), are used for short-term storage. Latent heat TES is interesting because of its high energy storage density and constant temperature heat storage characteristics corresponding to the phase transition temperature of a PCM [6]. The amount of latent heat for storage of a phase change material system is given by the formula:

$$Q = \int_{T_i}^{T_\mathrm{M}} mC_p dT + ma_m \Delta H_m + \int_{T_\mathrm{M}}^{T_f} mC_p dT \tag{2}$$

where a_m - melting fraction and ΔH_m - heat of fusion per unit mass (J/kg).

Heat is stored when the material changes phase. Phase change in latent heat storage can be in the form of solid-solid, solid-liquid, solid-gas, liquid-gas and vice versa. In solid-solid transitions, heat is stored as the material moves from one crystal to another. Such transitions generally have low latent heat and small volume changes compared to the solid-liquid transition [19]. After melting, heat is transferred to the material, storing large amounts of heat at a constant temperature, to be released when the material solidifies.

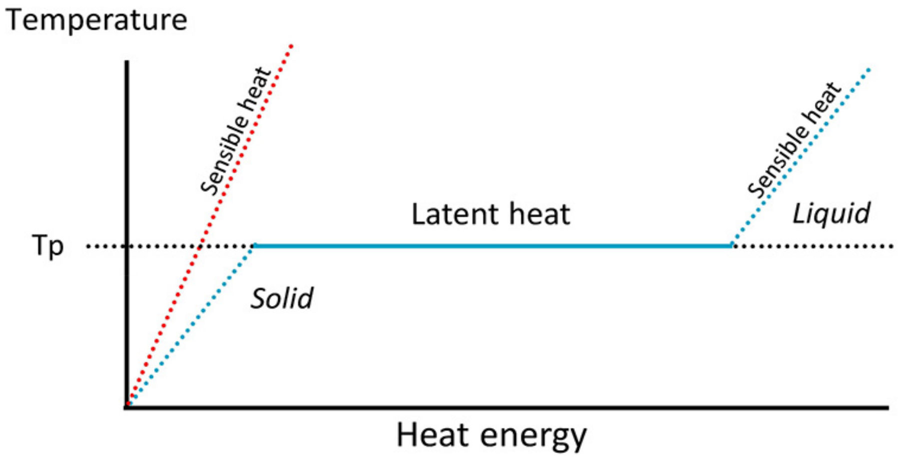


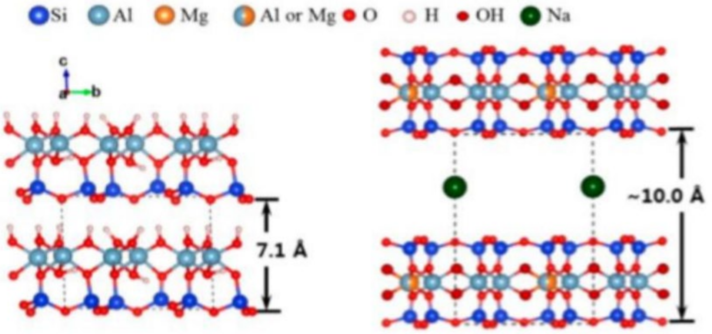
Fig. 2 Phase change of a material

The most well-known and used PCM is water, which has been used since early times as ice for storage in refrigerators. Many materials have been studied as PCMs, but only a few have been commercialized [11,14, 20, 21], mainly due to problems such as phase separation, undercooling, corrosion, long-term stability, low thermal conductivity, etc. PCMs are selected based on appropriate melting latent heat and temperature, availability and cost, required storage period, economic viability, operating conditions. Solid-gas and liquid-gas changes have high latent heat of phase transition, but their large volume changes at the phase transition are associated with problems [16]. A solid-liquid change produces relatively less latent heat than a liquid-gas change. However, these changes involve only a small change (10% or less) in volume. Solid-liquid changes have proven to be economically interesting for use in TES systems. PCMs cannot be used as a heat transfer medium. An additional heat transfer medium must be used to transfer energy from the source to the PCM and from the PCM to the load. The medium used must be specially selected, due to the low thermal diffusivity of PCM in general.

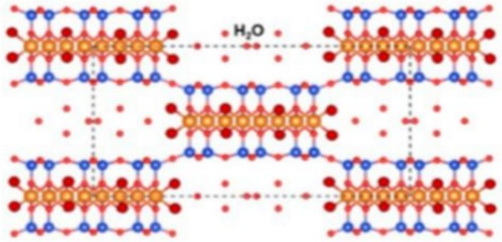
3. CLAY AS HEAT STORAGE

For heat storage, sensitive heat storage such as water or stones is most often used, due to its simplicity. This type of storage has disadvantages such as low energy density and insulation requirements. Stored energy can be lost in a short period of time due to the large temperature difference between the environment and the system. An efficient way to solve this problem is to store thermal energy in the form of chemical potential. This refers to a reversible chemical reaction, adsorption and a direct hydration process. PCMs, which are generally combined with other materials, are suitable for this purpose. Clay is a good base for this purpose. Clays are chemically inert, resistant to decay and available in large quantities. Due to these properties, clays can be used as key materials in the field of energy and environment, such as absorbents and energy storage and conversion systems. The storage principle is based on the possibility of working in a reversible hydration-dehydration mode.

Clay-based materials have good potential to become a kind of energy storage and conversion materials after optimizing the electrochemical properties. The activation of clay with alkalis enables the homogenization of materials capable of combining with PCM, whether organic or inorganic in nature. The main goal in the composite production process is to achieve stable thermal cycles without losing the average mass. By combining the mass ratio of the gel with hydrated clay salts and paraffin wax, composites are obtained that can have a higher capacity of thermal energy storage and the desired degree of cooling or heat recovery.



(a) Kaolinite (b) Montmorillonite



(c) Sepiolite

Fig. 3 Crystal structure of (a) kaolinite, (b) montmorillonite, and (c) sepiolite, where the dashed lines represent the unit cell.

Montmorillonite (MMT) clay is a member of the smectite group, a 2:1 clay, has two tetrahedral sheets of silica, with a negative layer charge, electrically balanced by exchangeable cations located between its silicate layers, between which is an octahedral sheet of alumina. The particles are in the form of a plate with an average diameter of about 1 mm and a thickness of 0.96 nm. Montmorillonite is a subclass of smectite, a 2:1 phyllosilicate mineral characterized by more than 50% octahedral charge; its cation exchange capacity is due to the isomorphic substitution of Mg for Al in the central plane of aluminum. By replacing a lower valence cation, it leaves nearby oxygen atoms with a net negative charge that can attract cations. The individual crystals of montmorillonite clay are not tightly bound together so that water can enter and cause the clay to swell. With variable water content montmorillonite increases significantly in volume when absorbing water. As it can absorb large amounts of water, it is suitable for energy storage.

MMT has a good ability to be encapsulated with organic PCM, while encapsulation with inorganic PCM does not show satisfactory properties. Thus, by adding organic RT20, a composite was obtained that has a phase change temperature of 23°C and a latent phase transition heat of about 80 J/g while showing good stability. This composite, when installed in plasterboard, shows a reduction in the fluctuation of the internal temperature in the room and the maintenance of a constant value. MMT composites are good in preparation with the addition of a surfactant-mediated n-hexadecane organic PCM insert [22]. The addition of surfactants to the composite shows an improvement in the thermal capacity and thermal conductivity of the composite. Also, composites can be obtained by adding lauric acid by melting and stearic acid by vacuum impregnation [23,24]. Both composites increase the heat storage efficiency and stability during the cycle, and the composites prepared by melt impregnation show better thermal reliability.

With the development of technology, more sophisticated models of composite-microcapsules have been created. Core/shell microcapsules are obtained by adding MMT to stearic acid emulsions [25]. This form of composite has a higher latent heat storage capacity about twice that of the composite, due to the higher content of stearic acid and the crystallization of stearic acid. In this way, good thermal reliability is achieved even after numerous cycles.

Only by assembling stearic acid latex particles and MMT nanosheets of different shell thicknesses, core/shell particles are obtained. The nanolayers are prepared by exfoliation, and the stearic acid particles are stabilized with sodium dodecyl sulfate. The thinner the shell of the particle, the higher the filling efficiency and LHS capacity with the best thermal conductivity of the shell and the whole composite particle. This composite has good shape stability and thermal reliability. By preparing the 3D structure of MMT nanoplates and stearic acid with the help of vacuum impregnation, the filling efficiency increases greatly, improving thermal conductivity and thermal reliability [26].

Table 1. Summary of the thermal properties of some PCM/ Montmorillonite composites

	PCM		PCM/ Montmorillonite Composite	
PCM	LHS, J/g	T_m/T_s, °C	LHS, J/g	T_m/T_s, °C
Lauric Acid	161.56	43/44	35.2	40.7
Paraffin	128.5	41/44	112.21	41.6
Stearic Acid	212.8	64.5	118.6	63.2
N-Dodecane	243	28	199.7	
RT20	136.3	23.24	79.25	23

Using the two-step intercalation method, other types of PCM/MMT composites are prepared. In the first phase, ion exchange of MMT intercalation with n-octadecyl amine salts is performed, and in the second phase, hydrophobic adsorption of n-dodecane is performed. This way, paraffin adsorption is controlled by changing the amount of salt to modify the MMT, as well as the thermal properties of obtained composites. A paraffin-bound hyperbranched polyester composite was generated to obtain an inorganically modified MMT with HCl that creates a gel-like structure that can be filled with paraffin [27, 28].

Sepiolite belongs to the phyllosilicate group; it is a bifoliate 2:1 clay mineral with a fibrous structure. Sepiolite is composed of alternating bands and tunnels. Tunnels containing water and other small molecules give sepiolite specific physicochemical properties such as high porosity and surface area, strong adsorption capacity and rheological properties [29, 30]. Treatment with inorganic acids modifies the properties of sepiolite, removes impurities and improves the pore structure, in order to prepare composites with organic or inorganic PCM. After treatment, the miscibility with PCM increases as well as the heat storage capacity by 50% compared to the untreated sepiolite. Ultrasonic treatment reduces the thermal properties of sepiolite due to its tubular structure, while microwave treatment allows obtaining composites with higher thermal conductivity [31].

Table 2. Summary of the thermal properties of some PCM/ sepiolite composites

PCM			PCM/ sepiolite Composite	
PCM	LHS, J/g	T_m/T_s, °C	LHS, J/g	T_m/T_s, °C
Lauric Acid	225.4	43.2/41.1	125.2	42.5/41.3°
Stearic Acid	206.1	70.8/69.1	118.7	68.0/60.1
Capric /Stearic Acid (83/17 wt%) Eutectic	184.43	24.47/23.12	76.16	22.86/24.51
$CaCl_2\cdot 6H_2O$	61	52	87.9	

Diatomite is a silicon mineral that, in addition to silicon dioxide, contains certain amounts of bound water (about 3-8%), aluminum and other minor ingredients. Diatomite has low mass, high specific surface area and porosity, excellent absorption capacity and good thermal and chemical stability at elevated temperatures. Due to many hydroxyl and hydrogen bonds on the surface, diatomite has good adsorption capabilities [32, 33]. These properties allow it to be used as a PCM additive at low temperatures. To be used as a PCM, diatomite is treated with calcium to remove organic impurities and improve the structures [34]. PCM/diatomite composites were made by adding organic PCMs such as PEG, fatty acid esters, and paraffin to diatomite particles by vacuum impregnation or adsorption. Organic PCM/diatomite composites exhibit good thermal and chemical reliability and shape stability, good LHS capacity and melting temperatures [34-36].

The inside of the tube can be filled with different substances, so it can be successfully combined with wax, stearic acid, capric acid, paraffin and polymers [37-39]. However, it needs to be processed before adding a PCM to the halloysite structure. It is prepared by mixing PCM and HNT in an ethanol solution. The optimal ratio of organic PCM to HNT that prevents leakage of PCM in the molten state is 60/40 % by weight.

The capacity of the LHS is directly related to the additional amount of PCM. For example, graphite can be added to modify the thermal properties of the composite by increasing the thermal conductivity, latent heat storage rate, and heat release rate. By adding paraffin wax in combination with graphite, a composite is obtained that has perfect shape stability even when heated at a temperature 30°C above the melting temperature of pure wax. The simultaneous addition of HNT and graphite leads to a significant increase in the thermal conductivity of the composite [40]. Changing the wettability of HNTs from hydrophilic to hydrophobic by treatment with polydimethylsiloxane (PDMS) improves the affinity of HNTs for organic PCMs such as paraffin wax and n-carboxylic acids [41]. Hydrophobization of HNT leads to higher addition of organic PCM. Composites prepared with HNTs treated with polydimethylsiloxane PDMS show higher LHS capacity compared to composites prepared with untreated HNTs. PEG/HNT composites with at least 30 wt% HNT significantly improve shape stability and thermal conductivity compared to PEG. In contrast, LHS capacity and melting point decrease along with the addition of the PEG fraction. By treating the inner surface of the HNT with selective acid etching, the alumina is partially dissolved and the specific surface area and pore volume are improved, while the outer surface of the silica remains intact [42]. The LHS capacity and melting point decrease along with the addition of the PEG fraction.

In order to increase thermal conductivity, carbon nanostructures or noble metal particles can be added. The preparation of Pickering emulsion of paraffin stabilized HNT with dopamine and Ag nanoparticles for light-thermal conversion of sunlight and thermal energy storage makes the composite have two-phase transition temperatures associated with solid-solid and solid-liquid phase changes of the encapsulated paraffin. The LHS capacity indicates that the encapsulation efficiency of paraffin is good, and the thermal conductivity of the composite is higher than that of pure paraffin due to the introduction of Ag nanoparticles [43].

Adding a small amount of encapsulated PCM has a positive effect on thermal capacity and conductivity, as well as mechanical properties. Adding a eutectic mixture of stearic and palmitic acid with diatomite as an additive to asphalt leads to a decrease in the temperature of the upper and lower surfaces [44]. More recently, high density polyethylene (HDPE) and wood fiber (HF) have been used as secondary encapsulated matrices to prevent paraffin leakage [45]. The LHS capacity of the new composites is adjusted by the paraffin/diatomite ratio and the proportion of composite particles in the polyethylene/wood fiber matrix. It has been proposed to coat diatomite particles filled with $CaCl_2 \cdot 6H_2O$ with paraffin [46] to decrease the melting enthalpy for $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$/diatomite, and 10 $CaCl_2 \cdot 6H_2O$/diatomite/paraffin composite while the melting temperature increases slightly. The thermal stability of $CaCl_2 \cdot 6H_2O$/diatomite composite is much better than pure salt hydrate, and the stability of $CaCl_2 \cdot 6H_2O$/diatomite/paraffin composite is further increased.

Sepiolite shows a good basis for the preparation of hydrated salt/diatomite composites with reduced cooling and increased thermal conductivity [47]. The cooling of salt hydrates is reduced after filling with diatomite particles. In turn, thermal conductivity increases compared to pure salt hydrates by adding graphite to the composition. Composites prepared by direct impregnation of pentadecane show the highest LHS capacity and thermal conductivity without cooling. Diatomite microwave treatment has a positive effect on pentadecane adsorption by increasing the LHS capacity. Composites prepared after microwave treatment with diatomaceous earth also show higher thermal conductivity [48]. Microwave and acid treatment resulted in an increase in the carrying capacity of diatomaceous earth compared to the untreated one. The modification of the surface and pore structure leads to better crystallinity of the filled lauric acid-stearic acid eutectic mixture. These factors lead to an increase in the LHS capacity of composites obtained from pretreated diatomite.

Table 3. Summary of the thermal properties of some PCM/ diatomite composites

PCM			PCM/diatomite Composite	
PCM	LHS, J/g	T_m/T_s, °C	LHS, J/g	T_m/T_s, °C
Dodecanol	170	22	75.8	23.3/21.2°
NaCl:KCl (1:1.02) Eutectic	259.6	665	179.3	661
Stearic Acid/Palmitic Acid Eutectic	196.9	54.33	106.7	52.93
Methyl Stearate	217.7	36.8/32.	111.8	36.5/33.1
Pentadecane	174.2	31.9/15.4	53.7	11.9/5.7

Halloysite (HNT) nano-clay is a natural and environmentally friendly material widely distributed. Halloysite is a natural tubular micro-container with a unique surface chemistry that enables selective modification of the lumen and outer surface. Halloysite is a 1:1 2-sheet clay mineral of the kaolin group, with a larger amount of water in the interlayer space. The small distance between alumina, silica and hydrated water leads to the twisting of the layers in multi-layered tubular structures [50-52], which distinguishes halloysite from other clay minerals [53].

Table 4. Summary of the thermal properties of some PCM/ halloysite composites

PCM			PCM/halloysite Composite	
PCM	LHS, J/g	Tm/Ts, °C	LHS, J/g	Tm/Ts, °C
Paraffin Wax	106.7	54.7	44.7	52.3
Myristic Acid	172.4	54.1	72.1	48.1
Palmitic Acid	187.3	62.4	58.4	46.2
Stearic Acid	166	55.2	70.3	52.7
PEG 1000	162.6	38.4/24.2	71.3	33.6/25.7
$Na_2HPO_4\cdot 12H_2O$/ $Na_2SO_4\cdot 10H_2O$ (1:1) Eutectic	211	38.5	142	35.8

4. CONCLUSION

Phase change materials are suitable for thermal energy storage, but they cannot be used in their pure form and must be modified to remove their limitations and improve performance. Combining clay with PCMs is a good way to overcome these problems. Low price and abundant reserves are the most competitive advantages. Clay minerals have a porous structure and a large specific surface area, and after the modification process, the desired pore structures are obtained, while also maintaining high thermal stability, mechanical stability and fire resistance. Clay minerals are conventional components of various construction materials, so PCM/clay composites can be used as functional additives without significant changes in construction materials technology. To date, the formation of organic PCM/clay composites has been the most studied and developed because the range of phase transitions of organic PCMs is attractive for thermal management in civil buildings. The preparation of composite PCMs with reliable shape and thermal stability has been developed along with the successful development of composite PCMs in the construction industry. Although inorganic PCMs are considered less useful due to phase stability and cooling problems, and despite better thermal properties and lower cost, the creation of composite inorganic PCM/clay materials with eutectic and nucleating agents has been shown to prevent these problems. This is particularly important due to the wide use of inorganic PCMs, including thermal energy storage at high temperatures. Improving the thermal conductivity of an organic PCM/clay to increase the rate of heat accumulation and release is another important area of research. Although inorganic clay minerals have better thermal conductivity than organic materials, their mass fraction in composites is generally lower than that of organic PCMs. Composite PCM/clay materials have higher thermal conductivity than non-composite PCMs.

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