Phase Change Materials

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Contributor: Alejandro Manzano-Ramirez, José Luis Reyes Araiza

The energy sector is one of the fields of interest for different nations around the world. Due to the current fossil fuel crisis, the scientific community develops new energy-saving experiences to address this concern. Buildings are one of the elements of higher energy consumption, so the generation of knowledge and technological development may offer solutions to this energy demand, which are more than welcome. Phase change materials (PCMs) included in building elements such as wall panels, blocks, panels or coatings, for heating and cooling applications have been shown, when heating, to increase the heat storage capacity by absorbing heat as latent heat.

Keywords: phase change materials ; construction elements ; heat storage

1. General Classification of PCM Materials, Comments

Materials for phase change thermal energy storage must have a large latent heat and high thermal conductivity. They should have a melting temperature lying in the practical range of operation, melt congruently with minimum subcooling, be chemically stable, low in cost, non-toxic and non-corrosive. The PCMs are grouped into organic, inorganic and eutectic mixtures of compounds that can yield different phase change temperatures. This classification has emerged from studies carried out over 40 to 50 years and, in that period, other authors have shown the advantages and disadvantages of PCMs. Different experimental techniques have been reported and used to determine these materials' behavior in melting and solidification. Hence, according to the analyzed papers [1][2][3][4][5][6][7][8][9][10][11][12][13][14][15][16][17][18][19][20][21], it is concluded that no material has all the optimal characteristics required for a PCM and selecting a PCM for a given application requires careful consideration of the properties of various substances.

Differential scanning calorimetry methods (DSC) are widely used to determine the thermophysical properties (heat of fusion, specific heat and melting point) of PCMs and have served to classify them. However, it may be suggested that other methods [19][20][21][22][23][24][25][26][27][28][29][30][31][32][33], such as the T-history method and conventional calorimetry methods, have also been used. The analysis of these properties is carried out with thermograms, in which we can identify the values of the phase transition temperatures during melting and freezing. However, as tiny samples are used to determine these properties' values, they may vary with large samples.

1.1. Organic

Three sub-types can be highlighted within the organic phase change materials: paraffins, fatty acids and polyethylene glycol (PEG). In general, these compounds have good thermal properties and convenient chemical stability [34]. As a result, it is seen how much of the research is currently related to different kinds of paraffin' uses in construction elements for buildings because their chemical stability facilitates the synthesis of materials and products' manufacture.

1.2. Inorganic

Compared to organic PCMs, there are fewer inorganic compounds that can be used in the construction industry. The two most widely used types are hydrated salts and metallic salts, where hydrated salts have been the most studied in all fields of research related to PCM's [35].

1.3. Eutectics

Eutectic PCM is a mixture of two or more PCMs to achieve a desirable melting point. Eutectic nearly always melts and freezes without segregation because the components are selected to freeze and melt simultaneously. These PCMs acquired great importance due to various eutectic compounds with different properties that can benefit thermal energy storage systems. In general, from the literature [30][31][32][33][36], it is clear that non-organic PCMs have better thermal storage characteristics; however, they tend to be more expensive than paraffin.

Table 1 shows some of the chemical components used for construction materials. Although these properties are the main ones, it is convenient to consider other secondary properties, which can be very important depending on the application, geographical area and number of cycles. The thermal properties of PCM suitable for buildings is described by Khudhair, A. M. and M. M. Farid [1], Memon, S. A. [33] and Cui, Y., J. Xie, J. Liu and S. Pan [36]; meanwhile the advantages and drawbacks from various PCMs are indicated in Khudhair, A. M. and M. M. Farid [1], A. Felix Regin et al. [37], Baetens, R., B. P. Jelle and A. Gustavsen [31] and Cui, Y., J. Xie, J. Liu and S. Pan [36].

Table 1. Characteristics of macro-encapsulated PCMs for buildings.

1. Melting temperature	Liquid–solid phase transition temperature close to the required operating temperature range
2. Phase change enthalpy	A high value improves the energy storage density in the system; value close to 200 kJ/kg
3. Specific heat capacity	In general, it should be more than 2.5 kJ/kg °K
4. Thermal Conductivity	High thermal conductivity will improve thermal charge and discharge speed; value greater than 0.6 W/m °C
5. Thermal Cycles	This must be able to experience over 5000 thermal cycles of charge and discharge
6. Over-cooling	This should not undergo over-cooling, because the PCM will not completely solidify below freezing. This could reduce heat removal during freezing
7. Change in Volume	This should experience minimal change in volume during phase change, a large change will increase the size of the container
8. Congruent fusion	Must be completely melted and frozen to ensure homogeneity in the solid and liquid phase. If this is not congruent, it will generate segregation due to the difference in densities
9. Vapor Pressure	You must have a low vapor pressure in the operating temperature range to avoid containment problems
10. Non-corrosive	It must not be corrosive or toxic to the environment
11. Economical and Availability	Must be available on a large scale and at an economical price
12. Non-flammable	Must not be flammable to avoid any fire hazard.

2. Encapsulation Processes for PCMs

A successful PCM thermal storage system should have a suitable container for the PCM (encapsulation of PCMs) and a heat exchange surface for transferring heat from the heat source to PCM and from PCM to the heat sink. It is necessary for proper operation that the encapsulation has strength, flexibility, corrosion resistance, thermal stability, structural stability and easy handling. Bulk storage in a tank (tank heat exchangers with more extensive heat transfer), macro-encapsulation and microencapsulation are the types of confinements most analyzed for PCMs.

2.1. Macro-Encapsulation

The most common type of PCM containment is macro-encapsulation, in which a significant quantity of PCM is encapsulated in a discrete unit (encapsulation in containers usually larger than 1 cm in diameter). The shape of the encapsulating shell can be any form (tubes, cylinders, pouches and cubes). The most cost-effective containers are plastic bottles (high density and low-density polyethylene bottles and polypropylene bottles), tin-plated metal cans and mild steel cans. The mass of PCM per unit may range from a few grams to a kilogram. The analysis of the revised papers [31][32][33][36][38][39][40][41][42][43][44][45] shows how macro-encapsulated PCM can be easily prepared in any shape and size to suit different applications. Unlike micro-encapsulation, where various methods and techniques are used to encapsulate the PCM, the PCM's macro-encapsulation does not require any pre-defined process.

By careful selection of the capsule geometry and the capsule material, the macro-encapsulation can be used for a wide variety of energy storage needs and can be to get incorporated easily into the building envelope of any shape, size and dimension. However, the compatibility of the shell material with building material and PCM is the area that still needs investigation for further improvement [31][32][33][36][38][39][40][41][42][43][44][45]. The advantage of the macro-encapsulation is its applicability to both liquid and air as heat transfer fluids and easier to ship and handle. In general, macro-capsules are incorporated on exterior walls and precast slabs since buildings' facades are in direct contact with weather conditions as well as to expose to solar radiation. Its operation depends on several factors:

- the location of the macro-capsule (the internal or external surface or within the construction element);
- the local weather conditions of the region (ambient temperature, solar radiation);
- the geometric characteristics of the construction part (concrete wall, partition masonry);
- the conductive characteristics of heat through the building material and the type of PCM.

Some reputable macro-encapsulated PCM manufacturers have been prepared and marketed as various forms of microencapsulates, such as Microtek Laboratories [46], Rubitherm technologies [47], Pure temp LLC [48], Shanghai Tempered Entropy New Energy Co. [49], MikroCaps [50], Winco technologies [51] and Teappcm [52], which individually market the following products: polymers, aluminum panels, polymer bags, pouches, aluminum tube, plastic blocks, breather membrane, stainless steel balls and HDPE (High Density Polyethylene) panels. Manufacturers of products ready for building applications are shown in Baetens, R., B. P. Jelle and A. Gustavsen [31], Kalnaes, S. E. and B. P. Jelle [53] and Vicente, R. and T. Silva [54], while the characteristics of macro-encapsulated PCMs for buildings are summarized in Table 1.

2.2. Microencapsulation

Microencapsulation refers to techniques in which small PCM particles or droplets (spherical or rod-shaped) are contained within a sealed, continuous shell (thin and high molecular weight polymeric film or inorganic film). This technique is an excellent solution to prevent leakage of the melted PCM in latent heat thermal energy storage systems, reduce PCM reactivity with the outside environment. The critical analysis of the literature [53][54][55] shows how micro-encapsulation improves heat transfer to the surrounding through its large surface to volume ratio and improves cycling stability since phase separation is restricted to microscopic distances; however, the cost of the microencapsulation system is high compared to other thermal storage methods. The coated particles can then be incorporated in a powder form or dispersed into a carrier fluid in any matrix compatible with the encapsulating film. It follows that the film must be compatible with both the PCM and the matrix [53][54][55].

The possible morphologies (shapes) of microcapsules can be diverse (irregular shape, spherical, tubular, multi-wall, multi-core and matrix particle) and depending on the arrangement of the core material and the deposition process of the shell. There can be four types of distribution: mononuclear (core/shell), polynuclear (many cores coated with a continuous shell material), matrix encapsulation (the core material is distributed homogeneously) and multi-film (a continuous core coated with multilayer continuous shell material) [56][57][58].

Organic PCM core has a suitable melting point near the thermal comfort range of humans around 20 °C and has several advantages over other types of PCM materials. Organic PCM includes different classes like paraffin (n-alkane), fatty acids, alcohols, esters and polyethylene glycol (PEG). Paraffin class materials of organic PCM are the most popular choice as core materials. On the other hand, polyethylene glycol (PEG) is difficult to encapsulate. Similarly, inorganic salts are also rarely encapsulated due to their solubility in water.

Shell materials form the capsules that contain the PCM and can be made from an organic or inorganic material or hybrid shell materials made of organic-inorganic combination. The majority of the shells are organic and prepared through chemical methods like polymerization. A shell material should not undergo a chemical reaction with the PCM core and should possess good chemical and thermal stability. Its surface morphology must be smooth hand it should have minimum porosity and prevent any leakage of PCM at temperatures above the melting point of PCM. The shell provides mechanical strength (so that thicker layers show a much better mechanical behavior) and also shape stability, and it is desirable to have shell material with high thermal conductivity.

Concerning the encapsulation process, from the literature, it may be pointed out that there are three different methodologies to microencapsulated PCM, and the most appropriate technique depends on the physical and chemical properties of the materials to be used [59][57][60][61][62]:

- (a) physical methods: pan coating, air-suspension coating, centrifugal extrusion, vibrational nozzle, spray drying and solvent evaporation;
- (b) physic-chemical methods: Ionic gelation, coacervation, sol-gel;
- (c) chemical methods: interfacial polymerization, suspension polymerization, emulsion polymerization.

Research reports [34] mention that the mean diameter, the thickness of the shell and the mass percentage of PCM compared to the total mass of the capsule is related to the quality of the microencapsulation process PCMs. This methodology for PCM still needs to be improved because the microcapsules can break when colliding with other microcapsules when used in active systems. Elsewhere, integrated carbon additives in building materials made of composite materials with PCM microcapsules have reported improvements in efficiency and the heat transfer rate [63][64]. In summary, in the literature revised so far, we can observe that many researchers have studied microencapsulation, but the literature is scattered [64][65].

With micro-encapsulated phase change materials products for buildings, two companies (BASF and Microteklab) have designed micro-capsules for home and office applications; furthermore, Rubitherm GmbH (Germany), Cristopia (France), TEAPEnergy (Australia), PCMProducts (UK), Climator (Sweden) and Mitsubishi Chemical (Japan) already offer commercial PCMs.

One of the objectives of using PCMs in mortars and concretes, regardless of the method of incorporation, is to improve their sustainability and durability [65][66][67][68]. Wei et al. [69] evaluated Portland cement-based mortars' durability with micro-capsules manufactured by Microteklab and Micronal-BASF. Their results showed a reduction of approximately 25% in the phase change enthalpy. Such a decrease was not ascribed to the microcapsules' mechanical affectation during the mixing process, but the chemical reactions with the sulfate ions. Moreover, this study shows how the chemical reaction between PCM and ions does not affect the durability of the mortar.

3. PCM with Lightweight Aggregate

Another interesting method is observed in the literature available so far for including PCMs in the building materials is incorporating PCM with lightweight aggregate (PCM-LWA). PCM can be added to concrete by shape-stabilized PCMs, direct incorporation and immersion and encapsulation. This PCM compound's manufacturing technique introduces the PCM into the lightweight aggregate (pumice, perlite, expanded shale/clay, expanded slate, expanded perlite, expanded vermiculite.). This technique is comparable to the shape stabilizing method, with some notable distinctions. In this case, the support material is the lightweight aggregate; in contrast, the shape-stabilized PCMs are used powder materials (fine aggregates), such as graphite powder or silica fume [70][71][72][73][74][75].

Vacuum impregnation and direct impregnation are the methods used to obtain PCM-LWA composite. In vacuum impregnation, a pump is used to remove the air from the pore of LWA, enabling better absorption capacity of aggregates. Memon et al. [71] reported that the absorption capacity of LWA using vacuum impregnation was 74%, in contrast with 18% using direct immersion. However, analyzing this process seems complicated and time-consuming; this technique is generally considered impractical [76].

There are some essential factors to obtain this PCM-LWA and for it to be considered as a constituent in mixing proportions for mortars or concretes, such as the type of lightweight aggregate and its absorption capacity (porosity, pore size, aggregate size and surface area, temperature and viscosity of liquid PCM), the method to impregnate, the materials for coating and support, as well as characterization and performance testing.

Numerous researchers [70][71][77][78][79][80][72][74][76][81][82][83][84][85][86][87][88][89] have proposed several porous aggregates as PCM hosts, distinct impregnation processes and various coating and support materials. It was observed that porosity is not the only measurable parameter for the PCM absorption capacity of LWAs. In addition, the pore and aggregate size can affect this property. Nonetheless, Aguayo et al. [76] took the surface adsorption of small particles into account and suggested removing particles finer than 150 mm from LWAs to prevent surface adsorption of PCMs in place of its absorption into the LWAs pores. Moreover, researchers have proposed adding supporting materials and other coatings (cement paste, silicone coating, bituminous emulsion, epoxy resin, graphite powder, silica fume) to moderate leakage molten PCM and make thermal and mechanical properties of the PCM better. In mixture proportioning with Portland cement, the gradual scape of PCM from pores of LWAs can make a difference to cement hydration reactions and consequently affect the compressive strength of concrete [70][71][77][78][79][80][72][74][76][81][82][83][84][85][86][87][88][89].

Regarding the covering placed on the PCM-impregnated porous material particles, it has been found that a low thermal conductivity of this can induce a short performance of the latent heat of the phase change within the encapsulation. Therefore, two study approaches emerge to take advantage of the thermal storage capacity: (a) determine the optimal thickness and area with which the aggregate should be covered, both to reduce damage in the mixing process and improve thermal transfer; (b) use smaller particles on the cover. Calvet et al. [90] and Wang et al. [91] observed a reduction in loading and unloading thermal energy time without affecting the capacity to store energy when graphite was incorporated in the PCM. However, these results are not wholly replicable for mortar mixtures with particles of 5 to 10 mm in diameter.

Other works such as that of Dumas et al. [92], Joulin et al. [93] and Sierra [94] report studies on the thermodynamic and thermal transfer processes of materials with PCMs. Likewise, research such as that of Haurie et al. [95][96] reports the flammability disadvantage of paraffin-based PCMs used in mortars and concretes under fire, despite their thermal advantages over hydrated salt-based PCMs. The work of Sierra [94] shows a differential calorimetry analysis of an organic PCM composed of butyl stearate and soy wax, which was vacuum impregnated in crushed pumice particles. In addition, graphite powder was added to promote thermal conductivity. The work's main objective was to evaluate the effect of thermal conductivity and latent heat stored in samples with different percentages of graphite powder when they are subjected to 100 work cycles with temperature variations using Peltier cells. The analysis showed that organic PCM-LWA stores heat energy.

Several investigations [70][71][77][72][74][76][81][82][83][84][85][86][87][97][98][99][100] have already carried out microstructural analysis (SEM, DSC, TGA and FTIR) of PCM-LWA and analysis of the thermo-mechanical properties (thermal performance, thermal conductivity, compressive strength, shrinkage strain and effects of freezing and thawing cycles) of concretes and mortars incorporating PCM. No matter the method of mixing PCMs in concrete, most of the research argues that it lowers resistance to compression. Elsewhere [101][102][103][104][105][106][107], it has been reported that when the encapsulation techniques for plain concrete are compared with others, the reduction in compressive strength of concrete incorporating microcapsule may be ascribed to two factors: the significant disparity between the intrinsic strength of the microcapsules and the concrete constituents and damage of microcapsules during mixing resulting in leakage of PCM. Due to these reasons, macro-encapsulation with a strong shell is preferred.

As a result, it may be inferred that more research is needed to obtain a structural PCM-LWA concrete with useful mechanical, thermal and heat storage properties, along with an understanding of their effects on the thermal and mechanical behavior of PCM-LWA with different coatings and supporting materials.

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