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Potential Applications of Phase-change Materials (PCM) in Building Energy Efficiency

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Abstract: *Phase-change material with high thermal capacity savings density is of great importance in building energy conservation, waste heat recovery, peak load shifting and other fields. We aim to guide the researchers of these problems and provide an underlying basis for the development of this new energy-saving material. We extensively reviewed the development history, classification, research methods and existing problems of the phase change materials system and discussed some potential research topics for the future. This study can promote the related research of the Phase-change materials.*

Keywords: Energy storage, Phase-change material, Building energy conservation, costs of average thermal energy storage

1. INTRODUCTION

At present, building energy consumption has been recognized as one of China's 'three big energy uses', along with industrial consumption and transportation consumption. Building energy consumption accounts for nearly 30% in total social energy consumption [1]. Along with the emergence of tall buildings and the improvement of people's living comfort requirements, the building energy consumption increases rapidly. Heating and air conditioning account for about 20% of the building energy consumption. It should be specially noted that winter heating in the north and summer air conditioning in south accounts for 50%-70% [2]. Therefore, storage and reuse of the building thermal energy is an effective way to improve the building energy efficiency.

In accordance with the storage mode, energy storage materials can be classified as sensible heat storage, chemical energy storage and latent heat energy storage [3]. The sensible heat storage method has advantages such as simple operation and low cost, but its heat storage density is small and it has significant temperature variation during the process of releasing the storage heat. Therefore, its application is very limited. Chemical energy storage, which stores reaction heat through the reversible reaction, has high heat storage density, but its technology is not yet sophisticated. Latent heat storage regulates the environment temperature through absorption or release of phase change heat when its materials status or internal particles change. Phase-change material (PCM) which not only has high energy storage density, is easily used, but can also keep approximate constant temperature in the process of changing phase. This can be used to control the temperature of the system. Latent heat energy storage is applied frequently in recent years, owing to its importance of energy storage.

The research of the PCM was initiated in a NASA's research project in the early 1980s, aiming to protect the astronauts and equipment from being destroyed by the rapid temperature changes in outer space. The United States energy storage allocations office drove this study in 1988 [4]. As building materials, the research of the PCM mainly experienced the following three stages: (1) the feasibility of phase-change material used as building materials; (2) the compatibility, stability and durability of the complex formed by mixing the PCM and traditional building materials; (3) the development of new types of PCM and type-setting material. As new materials, the phase change energy storage building materials are gradually being developed with its own complete system.

2. CLASSIFICATION AND PROPERTIES OF PCM

PCM can automatically absorb or release the latent heat to the environment through its change of phase or particle within certain limits of temperature, so as to regulate the environment temperature in the range that is comfortable for human beings. The detailed process of controlling temperature is as follows: When heated to melting temperature, the PCM will change phase from solid to liquid and store a large amount of latent heat. Conversely, in the cooling process of phase-change material, the phase will be

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changed from liquid to solid, resulting in sending the storing heat to the environment within a certain range. From the process, the storage or release energy becomes phase change latent heat. In the phase changing process, the temperature of the PCM is able to remain the same, which can produce a wide platform for the temperature.

There are many kinds of phase-change material with all types of forms, but only a few of them have commercial values. DOW Chemical Company in the United States tested nearly 2000 kinds of PCM and found only 1% of them have commercial value and are worth further study. Most of these PCMs are hydrate salt and organic phase change materials [5]. An appropriate PCM should have the following characteristics [6]: large phase change latent heat, favorable reversible phase change, small expansion and shrinkage, less over-cold or over-heat, appropriate phase-transition temperature, large thermal conductivity, high specific heat, non-toxic and non-corrosive, and low cost.

There are a lot of methods to classify the PCM. According to the nature of the material the PCM can be classified as inorganic phase change materials (alkaline metal, alkaline earth metal halide, nitrate/phosphate salts, etc.) and organic phase change materials (alkanes, fatty acids, alcohols, etc.). The thermal properties of the common organic and inorganic phase change material are shown in table 1.

According to the phase transition form, the PCM can be classified as solid-liquid phase change material, solid-solid phase change material, solid-air phase change, liquid-air phase change materials and shape stabilized phase change material. It should be pointed out that, although the solid-air phase change material and liquid-air phase change material have very large phase change latent heat, they are rarely used in practice because they can produce large amounts of gas and change their volume greatly in the phase change, which requires high expectations for the container and the using environment.

2.1. Solid - liquid PCM

The solid-liquid PCM absorb and release energy through phase changing between solid and liquid mutually, that is, the phase-change material absorbs heat and melts when the temperature is higher than its melting point, in the process of energy storage. Energy releases when the temperature is below the melting point.

The stearic acid, which is inexpensive, has the appropriate phase transition temperature, high phase change enthalpy, and good thermal stability. It is the perfect phase-change material. In the molten state, we replace the dimethyl sulphoxide, which is contained by alloysite-dimethyl sulfoxide, with the stearic acid (SA). The stearic acid will go into the halloysite. We can fabricate the SA-halloysite solid-liquid PCMs. Through this method, the solid-liquid PCMs have advantages such as: well thermal stability, compatibility, chemical stability.

2.1.1. Organic solid - liquid PCM

The organic solid - liquid PCM includes high aliphatic hydrocarbons, fatty acid, ester, salt compounds, alcohols and aromatic hydrocarbons. Organic solid - liquid phase-change materials have many advantages such as: good formation properties, little corrosion, no phase separation, no super-cooling in the phase change process, stable performance, etc. Disadvantages are also associated with this type of PCM such as: low thermal conductivity, low density, low energy storage density, high price, high volatilization, flammability and potential of oxidization. In order to overcome these drawbacks, researchers introduced the binary mix PCM or multi-component PCM with combinations of several kinds of organic matter. The organic PCM can also be combined with inorganic PCM so as to obtain the phase change material, which has a suitable phase change temperature and more suitable phase change heat for the application [7]. Generally, with the increase of carbon chains, the phase change temperature and phase change enthalpy of the corresponding homologous organic matter also increases, such that one can get energy storage material with a series of phase transition temperatures.

2.1.2. Inorganic solid-liquid PCM

The inorganic phase change materials mainly include: alkaline metal and alkaline earth metal halide, phosphate, nitrate, carbonate and acetate, etc. They have many advantages, such as: large phase change latent heat, wide phase transition temperature range (from a few degrees Celsius to hundreds of degrees Celsius), low cost, large thermal conductivity. The disadvantages include high precipitateness, poor durability, high corrosion to substrate.

2.1.3. High molecular polymer

The crystalline polymer is often being used as a solid-liquid phase polymer, such as high density polyethylene, polyethylene glycol, crystallization of polyvinyl chloride, etc. This kind of phase-change material can also be considered as organic. The high molecular compound of phase-change material is the mixture with a certain molecular weight distribution, and it also has a longer molecular chain, which leads to incomplete crystallization. Its phase change process has a melting temperature, rather than the low molecular weight substances, which has a melting peak.

2.2. Solid - solid PCM

Polyethylene glycol (PEG) is treated as the phase-change materi-

Table 1. The advantages and disadvantages of the thermal properties of the PCM

Material name	Type	Melting point (ºC)	Melting heat (J/g)	advantages	disadvantages
Heptadecane	Organic	27.5	224	No corrosion, high chemical and thermal stability, no sub-cooling degree	Low energy storage density, volatile, large volumetric change
n-octadecane	Organic	19	240		
hexadecanoic acid	Organic	62.9	54.3		
Paraffin C17	Organic	21.7	213		
$CaCl_26H_2O$	Inorganic	29	180	High energy storage density, good flame retardant, low price	sub-cooling degree, severe corrosion, phase separation, poor thermal stability
$Na_2SO_410H_2O$	Inorganic	32.4	250.8		

al; polyvinyl alcohol (PVC) is treated as the framework material. By using the chemical synthesis and blending method, the solid-solid PCMs can be created. The way that the chemical synthesis is used to fabricate the solid-solid PCMs are the graft copolymerization method and copolymerization method. The principle of fabrication of the solid-solid PCMs for the blending method is that fixing the solid-liquid PCMs into the carrier through physical means such as adsorption (molecular interaction or hydrogen bonding force) or enveloping (microcapsules or porous structure).

The absorption and release of heat for solid - solid phase change materials do not rely on the change of state during the phase change process but the change of the lattice. It can stay solid whether before or after the phase change, and does not reduce liquid or gas in the changing process. The advantages include non-toxic, non-corrosion, low under-cooling, and long life, which provides wide application prospects of the solid-solid PCM. Presently, the solid-solid phase change materials primarily include polyols, layered perovskite, crosslinked polymer resin, etc. Among those, polyols include pentaerythritol (PE); 2, 2-dimethylolbutyric alcohol (PG); neopentyl glycol (NPG); 2-nitrogen base 2-methyl-1, 3-propanediol; trimethylolethane, Tris (hydroxymethyl)-aminomethane, etc. The advantages of polyols include the low under-cooling, non-corrosion, high thermal efficiency, long life, etc. Therefore, it has great economic potential and development prospects.

On the basis of meeting the temperature requirements for storing heat, two or three kinds of polyols can be mixed with different proportions, and we can obtain the PCM that has a different phase transition temperature range. A serious drawback has to be considered, however: when the material is heated to the temperature above the solid-solid phase change temperature, the solid phase changes to plastic crystal, which has a high vapor pressure. As we know that the plastic crystal is easy to be sublimated, the phase change material must be kept in a sealed pressure vessel. This requirement mitigates the advantage of the solid - solid phase change materials [8].

2.3. The type-setting PCM

The type-setting PCMs consist of the phase-change material and support materials. When changing the phase, the type-setting PCMs can keep their type and their materials cannot be leaked. Using the micro-encapsulation technology, the solid-liquid PCMs, which have small size particles, can be fabricated easily. And by the type-setting technology, the solid-liquid PCMs, which have high mechanical strength, can be fabricated easily. Combining these two advantages, we treated the natural organic polymer sodium alginate, which can be biodegraded, and chitosan as the composite carrier material. We treated the inexpensive phase-change wax as the phase-change material. The alginate anion and divalent calcium ions can form the space network macromolecule. This macromolecule can fix the phase-change wax into the three dimensional grid. The alginate anion and chitosan ion have the opposite charge, so they can interact with each other, which can seal the space grid channel of the calcium alginate. The space grid structure sold-liquid PCMs, which has good sealing properties, can be fabricated.

Most of the solid-liquid phase change materials with good thermal performance have a potential problem in that liquid could leak after changing the phase. Many of the solid-liquid phase change materials are also corrosive, leading to indirect usage. The container of the materials brings problems such as the high cost, difficulty in operation etc. In order to solve these problems that are produced by the sole usage of solid-liquid PCM, a new material was developed, named “The type-setting PCM”, which can improve the application performance of the traditional solid-liquid PCM.

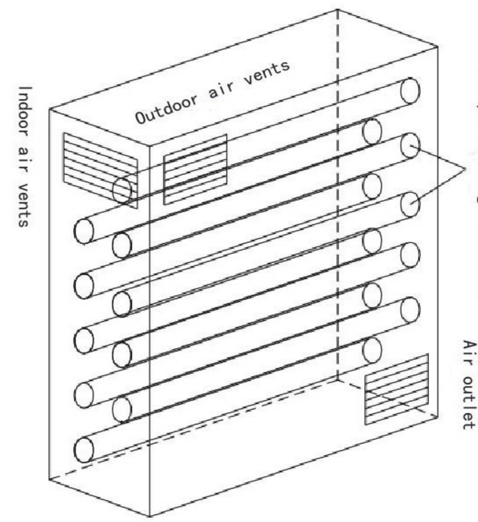

Figure 1. Schematic diagram of the phase change wallboard

The type-setting PCM consists of the phase change core material and base material, which is actually a kind of thermal functional composite material. The core materials can store and release heat in the phase change process. The base material can encapsulate the phase change materials, which can help to limit the flow of this PCM.

No container being required is one of the main advantages of the type-setting PCM. However, in this PCM, the working material is combined with the carrier substrate, which leads to the decreased regenerative capacity and reduced heat storage density. In long-term applications, the working material and the carrier substrate can be easily separated. The declination of mechanical properties of the carrier substrate can also cause the leakage of work material easily. In addition, the manufacturing costs of this kind of phase change material is high. Therefore, if the aforementioned bottleneck of manufacturing this PCM can be overcome, [9] a broad application future is possible.

3. APPLICATIONS OF PCM IN BUILDING MATERIALS

The research of the Phase change material (PCM) applications in building materials started from a NASA’s research project in the early 1980s. The United States energy storage allocations office further drove this study in 1988. The research on the phase change materials used in dealing with plasterboard, wallboard, and concrete building construction materials were developed in the 1990s [10]. In 1999, the PCMs were used in walls as well as light concrete precast slabs and floors, which maintain an appropriate indoor temperature. K.A.R. Ismail designed a kind of glass window

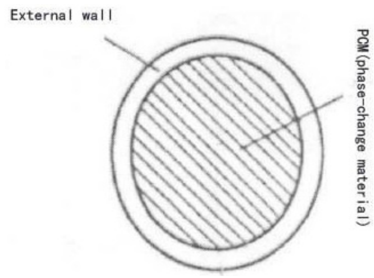

Figure 2. Structure of the microencapsulated PCM

which contained phase change materials in 2001 and proved the heating effect of the double glass windows filled with the PCM were better than the traditional window without PCM [11]. Currently, the methods of combining the PCM with the building material are as follows.

3.1. Sealing method of PCM

Feng et al. encapsulated the decanoic acid and lauric into the PE pipe at the mass ratio of 66:34 to produce the PCM wall, which can absorb outdoor cold air in the summer night [12]. It can be used to reduce indoor room temperature during the day. The experimental results show that the daily averaged temperature and fluctuations of the room with the PCM wall were significantly improved compared to that of the common room.

The microcapsule shaping phase change materials also belong to this kind of phase change material. With application of the microcapsule technology, a layer of the polymer film can be coated, leading to stable performance. Through this method, we can get a new type of composite phase change material with core-shell structures, as shown in Figure 2. The microcapsule technology solves the problem of the solid-liquid PCM changing its volume greatly when it changes phase. Furthermore, it protects the PCM from being in contact with the external environment directly, which can improve the efficiency of heat transfer. At the same time, the microcapsule technology can also greatly eliminate the phase separation and over-cooling phenomenon of the PCM, reducing the volatile toxicity of some PCMs, solving the compatibility with matrix materials, improving the durability of the material, and prolonging service life, etc. [13-14].

At present, due to relatively large capsule size, the microcapsule PCM have disadvantages such as: low thermal conductivity, abrasion and cracking, blocking pipe, unstable performance, etc.

In order to solve these problems, the capsule size needs to be further reduced. Therefore, ‘nano-capsules’, with particle size ranges between 1 to 1000 nano, were developed [15]. The nano-microcapsule PCM is the result of further development of the microcapsule PCM. It not only retains the microcapsule PCM’s technology advantage, but also overcomes the deficiency of the ordinary microcapsule PCM. The capsule size was reduced from the micron scale to Nano scale, leading to the increase of the ratio of the surface area to volume and improvement of the heat transfer rate PCM. All of them can further expand the applications of capsule type of PCM. At the same time, the damage caused by collisions between the particles can be greatly reduced, resulting in longer life spans [16-17].

3.2. Immersion method

The PCM can be penetrated into the building materials matrix through soaking, with the immersion method. It should be noted that this method is easily operated, and using this method can improve existing building materials. Zhang et al used a “two-step method” to prepare the concrete of the PCM. The procedure is to produce the PCM aggregate and then prepare the PCM concrete using the PCM aggregate. The experimental results show that using the “two-step” method can store enough liquid phase change materials in concrete. The storage function of the energy of the prepared PCM concrete is comparable to that using the commercial PCM.

3.3. Shaping and modification method

This method directly adds the modified PCM to the raw materials of building materials. For example, we can add semi-mobile silica powder to the PCM. The benefits of this method include simple structure, uniform nature and it is easy to be formed into many shapes and sizes for structural members so as to meet different needs. Feldman proved the rationality of this approach by using two contrasting methods. One of these methods is soaking ordinary plasterboard into the solution of the PCM, while the other is adding the PCM in the producing process. Feldman compared these two methods with a DSC analysis. The results proved that the inner and outer layers of the PCM made using the first method are not well distributed; the latter method provided well distributed layers and good heat accumulation effect. Currently, this method has attracted the interest of many researchers studying of PCM in building materials.

4. CONCLUSIONS

The phase-change materials have wide application prospects, but in practice, the utilization of PCMs also has many safety issues. The physical and chemical properties of the PCMs are unstable in the long term usage process: the solid-liquid PCMs can leak easily and are volatile, which can be corrosive to the accessories; many phase-change materials don’t have the appropriate phase transition temperature and phase change enthalpy. In order to solve the safety issues, we should study its packaging technology further. As well, the combining of the PCMs and base materials should be studied further.

At present, the applications of PCM in building energy conservation are still in the early stages. The composite building materials of the PCM are still have underlying durability and economic issues. Durability problems include: (1) the thermal physical properties of the PCM are weakened in the circulation process; (2) the low compatibility of phase-change material and the substrate material; (3) the corrosion effect of PCM on the substrate material. Moreover, the price of the PCM composite material is quite high which leads to high average thermal energy storage cost.

We suggest that future research should focus on the selection of the appropriate PCM according to the temperature of the different areas and studying the compatibility and the work stability between substrate material and PCM, aiming to the industrialization development of the PCM. The reasonable combination of the PCM and solar energy should be subjected to further investigation. This study provides a review and insights into the application of PCM in the future, as more attention is paid to improving building energy efficiency.

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