

Phase change materials and their use for energy accumulation

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Abstract. Problems with overheating and unstable temperature of industrial equipment are the reasons for generating significant costs that for companies. Solving the problems related to heat removal is a challenge in modern industry. Phase change materials are the solution to these challenges (PCM). These substances can accumulate and release large amounts of thermal energy during the phase change transition. The value of the phase transition enthalpy determines the energy storage capacity. The paper presents the results of phase transitions of selected materials. The measurements were carried out on a stand for testing phase change materials. The laboratory stand made it possible to determine the thermodynamic parameters of the phase transition. The substances analysed are kinds of paraffin of different chemical composition. Due to the diversity of substances, it is possible to analyse the influence of the chemical composition on possible uses in industrial applications for energy storage.

1 Introduction

Heat flow is a way of transferring energy to a thermodynamic system. The interaction between the system and the environment in the manner of heat flow causes a change in the internal energy of the system. The energetical effect on the way of heat transfer will continue until the systems are in a state of equilibrium, then the heat flow stops. Energy is stored as the system's internal energy level increases. However, the use of such accumulated energy is accompanied by a decrease in the internal energy level of the system. Storing and accumulating energy is usually difficult problem. A necessary condition for the correct and effective use of the heat emission is knowledge of the methods of energy accumulation.. The problem of heat storage is faced with phase-change materials (PCM). These substances (chemical compounds) are capable of absorbing, accumulating, and releasing energy.

2 Phase-change materials

Phase-change materials (PCM) are chemical compounds or groups of compounds capable of absorbing, accumulating, and giving back a large amount of energy in the range of 1st type phase transition temperatures. During the first type of phase transitions, discontinuities of the

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first derivatives of free specific enthalpy occur at the phase boundary, where the properties of the substance may change abruptly, e.g. specific volume.

The principle of operation of PCM is based on the absorption or release of excess heat from the environment during a phase transition. The process is repeatable but depends on the conditions in which the material is located. The most important parameter of PCM substance is the phase transition temperature. The material should be selected within the appropriate operating temperature range. This is an important parameter, because only the correct selection of substances guarantees effective heat accumulation.

Characteristics of phase transitions (Fig. 1) shows the material's ability to accumulate heat. Each PCM material has parameters such as specific heat or heat capacity, which determine the ability of PCM to store energy. The phase transition temperature range is also an important parameter during heat storage. During the phase transition, there is a change in internal energy. This means that energy in the form of heat flows between the system and the environment. The phase transition is usually connected with the visual effect. The substance can change its aggregate state, for example, become liquid or solid [1,2].

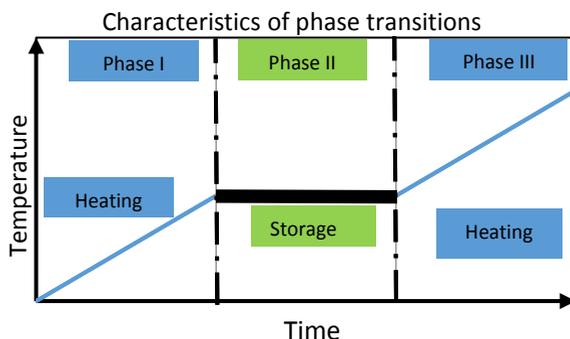


Fig. 1. Characteristics of phase transformation for the phase change materials

2.1 Classification of phase change materials

Phase change materials can be divided due to their chemical composition into: organic, inorganic, and eutectic.

Organic materials

Organic materials are stable in the melting cycles. The heat of phase change is about 200 to 250 kJ/kg. A common problem with organic PCM is the need for large temperature variations to achieve a phase change. Organic materials have low thermal conductivity but high volumetric expansion during the melting process. Examples of organic substances in PCM materials are: kinds of paraffin, esters, fatty acids and ionic liquids.

Inorganic materials

Inorganic PCM materials most often occur as hydrated salts, less frequently as metals. These types of PCM have a dense structure. Compared to organic materials, they are more efficient, but significantly more expensive. The disadvantage of inorganic materials is corrosiveness. There are also supercooling problems in inorganic PCMs. This means that they are not crystalline substances after a phase transition. An example of inorganic PCM materials are: hydrated salts.

Eutectic materials

Eutectic materials are created as mixtures of different substances. They have intermediate features. Most often they are made as mixture of substances:

- organic-organic;
- inorganic-inorganic;
- organic-inorganic.

2.2 Selection criteria PCMs

In order to obtain the correct properties of the phase change material for operation, the following parameters should be taken into account: thermodynamic characteristics, kinetic properties (conversion rate), chemical properties and economic profitability. When analysing thermodynamic properties, an important parameter is the melting point. This parameter must be within the appropriate temperature range and low vapor pressure at the phase transition temperature. This alleviates the problem of inhibition of the melting process.

Kinetic properties are important because they determine the rate of conversion. Knowing the kinetic parameters allows you to avoid inappropriate temperature increase and superconducting liquid phase.

Appropriate chemical properties should take into account the durability of the material in subsequent storage cycles. PCM should be resistant to multiple repeatability of phase changes. Despite many criteria, ease of access and economic considerations are very important. The cheaper the phase change material, the greater the probability of application [3].

2.3 Encapsulation of phase change materials

Most often, the "work of a material" in a phase change consists in cyclic transitions from solid to liquid, therefore encapsulation becomes natural. Phase change substances have different forms of "packing". You can distinguish capsules, larger packages or any other shaped structure. Most PCM substances do not contain water and can therefore be exposed to air. Water-based substances, i.e. various types of salt solutions, are encapsulated to prevent evaporation.

The first encapsulation structures were macrocapsules, which had large volumes, which proved to be a misconception since most PCMs have poor thermal conductivity. The materials tended to solidify at the edges, which prevented good heat transfer.

The smaller capsule dimensions are microcapsules, which proved to be the better solution compared to the larger macrocapsules as they did not show difficulties in clotting at the edges. Reducing the size of the capsules and developing the coating method made it possible to achieve a "suspend" effect in a given phase. Such systems are called "Phase Change Material Slurries (PCS)".

There is also a method of "molecular encapsulation", it is one of the technologies that allows the concentration of PCM in a polymer compound. The process of molecular encapsulation allows the material to be processed, e.g. drilling or cutting without leakage of the phase change material.

Encapsulation is a form of "packing" a phase change material that facilitates the application of phase change materials. Capsule materials are used in the construction and textile industries. The capsule consists of a core filled with PCM material and a shell of polymer material. An important feature of the capsule during its design is the planning of additional space taking into account changes in the volume of PCM during the phase transition.

The working cycle of a capsule with a phase change material (Fig. 2) is based on four stages: cooling, heating (charging), steady state (charging) and the heat release process. during

cooling, the PCM substance is solid and has a fixed temperature. As the temperature of the system increases, "charging" takes place, which is characterized by an increase in temperature inside the capsule and a change in the state of the PCM to liquid. The third stage is "state of charge". during this stage, the substance has a liquid state and a stable temperature. The last stage is the release of heat, during which the substance returns to a solid state as the temperature drops [4,5].

When designing warehouses related to PCM materials, an encapsulation solution is used. depending on the dimensions, you can create:

- nano-capsules with a size $<1 \mu\text{m}$
- micro-capsules with a size of $1 \mu\text{m} - 1000 \mu\text{m}$ (fig.2)
- macro-capsules with a size $> 1000 \mu\text{m}$.

The encapsulation of phase change materials depends on:

- phase transition temperature range
- maximum and minimum allowable temperature
- mass of the substance and thermal expansion during transformation
- cycle repeatability
- toxicity
- thermal conductivity
- ability to accumulate heat [6].

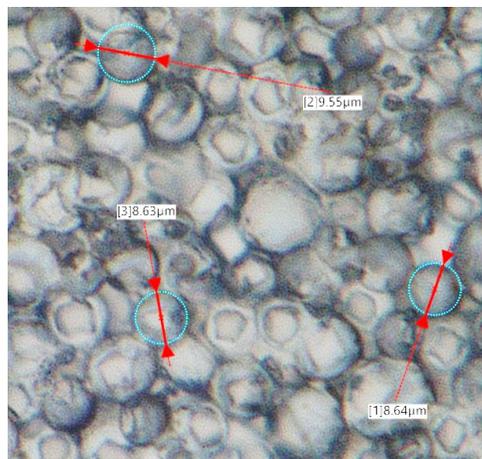


Fig. 2. Microscopic photo of capsules of the phase change material in dispersion

2.4 Application of phase change materials

Engine cooling systems

Research is being carried out on changing the cooling material in the cooling systems of automotive engines. Engine structures are built to withstand maximum thermal overloads. Currently, the design of cooling systems is too large under average driving conditions. This is due to the design of cooling systems for the most extreme situations that occur very rarely. The strategy developed by the scientists aims to reduce the cooling systems to about 35% of their original size, and the engine warm-up time to around 60%. The purpose of such a system is to increase economy in terms of fuel consumption. The advantage of such systems is weight reduction and shortening of the start-up time, while the temperature of the coolant is constant, thanks to which combustion is stable. [7]

Currently, there are cars with PCM applications on the market. An example of a brand that uses phase change materials is BMW. The manufacturer in the 5 series offers a hidden

thermal battery as an accessory. The principle of operation is simple. The phase change material is connected to the radiator and receives excess heat while the engine is running. The stored heat is available for the next "cold start" and improves the engine warm-up rate as higher temperature improves gas flow. An additional advantage of the heat storage is the use of heat for the interior of the car, which increases driving comfort. In order to extend the life of the battery, insulation is used, which allows you to maintain energy for up to two days at a temperature of up to -20°C . An additional solution is the use of PCM in vehicle exhaust systems.

This allows the catalysts to be kept at an appropriate temperature, which results in the reduction of hydrocarbon emissions during engine start-up [3, 8].

Electronics cooling systems

Electronic devices, such as telephones, tablets, computers have elements that get hot. The heat that is emitted from electronic devices is completely wasted and often has a negative impact on the durability of delicate components. Materials, PCM can be used in various ways, i.e. cooling, heating, stabilizing the system temperature [1].

The phase change material serves its purpose in systems that are exposed to short-term peak loads. The use of PCM allows for limiting the heating of components and reduces the occurrence of points of uncontrolled high temperature. It also allows you to limit the speed of running fans. PCMs also have disadvantages and difficulties in applying them. One of the disadvantages of the systems is the problem of design complexity and problems with the low thermal conductivity of PCM materials. Phase change materials are enriched with graphite or various types of metal filings in order to increase the ability to conduct heat. An additional disadvantage is the change in the volume of the system during the phase transition. Therefore, the use of this type of solutions requires appropriate design in order to minimize shortcomings and optimize project efficiency.

Other uses

There are also many other applications for phase change materials, e.g.:

- medical applications, i.e. the structure of operating tables, transport of blood and organs,
- life suits,
- textile industry - clothes intended for athletes
- thermal systems designed for spacecraft
- as a "warm" battery
- as a "cold" battery
- cooling, heating or temperature stabilization of building structures
- home "solar power plants"
- heat pump systems
- food cooling
- creating solar cookers.

3 Research on phase change materials

The structure of the test stand (fig.3) consists of three areas: the functional system, the regulating system and the software.

The assumption of the functional system is to obtain a heating and cooling chamber, thanks to which it is possible to create appropriate conditions for the phase transformation of the tested substance. The functional system includes: Peltier Moduls, fans, heat sinks, a PCM beaker and a housing. Peltier modules are semiconductor thermoelectric elements. On the outer sides, fire is composed of ceramic wafers, while the inner structure contains "n" and "p" type semiconductors. The effect of the current flowing through the structure is that one

side of the cell is heated while the opposite side is cooled. As a result, Peltier modules can be a heating or cooling heat source.



Fig. 3. Photo of a testing station for phase-change material

The research of phase change materials consisted registration of the phase change temperature, thanks to which parameters such as specific heat and heat of fusion can be determined. Samples of palm oil and paraffin were prepared. The material is placed in a glass beaker which is attached to the Peltier module with thermal paste. The task of the paste is to increase the heat flow from the heat source to the material placed in the beaker [13]. Temperature sensors record changes in temperature over time, so the phase change temperature can be determined. The device was used to determine the range of the transformation temperature. The melting point for paraffin is 49-50°C, respectively, while for palm oil it is 37°C.

Due to the knowledge of the tabular parameters and the substance tests performed, the specific heat and fusion heats (melting) values were determined. The obtained results were also compared with the theoretical coefficients (Fig. 4, Fig. 5). [9]

The algorithm for calculating the specific heat capacity

Determination of the heat necessary to heat the beaker

$$Q_Z = m_s \cdot c_s \cdot \Delta T \quad (1)$$

Calculation of the heat flux generated by the power supplies and the module:

$$\dot{Q}_{el} = U \cdot I + Q_{Peltier} \quad (2)$$

Calculation of the heating heat of the system:

$$Q_{el} = \dot{Q}_{el} \Delta t \quad (3)$$

Determination of the heat of the tested PCM material (heat balance):

$$Q_{el} = Q_{PCM} + Q_Z \quad (4)$$

$$Q_{PCM} = Q_{el} - Q_Z \quad (5)$$

Determination of the specific heat for the solid state of PCM material:

$$c_w = \frac{Q_{PCM}}{m \cdot \Delta T} \quad (6)$$

The algorithm for calculating the fusion heat capacity

Calculation of the heat flux generated by the power supplies and the module:

$$\dot{Q}_{el} = U \cdot I + Q_{Peltier} \quad (7)$$

Calculation of the heating heat of the system:

Determination of the heat of the tested PCM material (heat balance

$$Q_{el} = Q_{PCM} \quad (8)$$

Calculation of heat of transformation for PCM material:

$$Q_{fusion} = \frac{Q_{PCM}}{m} \quad (9)$$

The specific heat capacity and the fusion heat were determined on the basis of the research carried out for palm oil and paraffin. The experimental specific heat for palm oil is $2,00 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$ and is within the theoretical range. The obtained fusion heat is $117.28 \frac{\text{kJ}}{\text{kg}}$ and is slightly different from the theoretical values.

The same parameters were also determined for paraffin. The experimental specific heat is $2.87 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$ and exceeds the theoretical range. The obtained heat of transformation is $109.95 \frac{\text{kJ}}{\text{kg}}$ and is slightly different from the theoretical values. The obtained results (Table 1) prove the accumulating capacity of the tested substances. Mathematical determination of thermodynamic parameters can be used as an approximate determination of the properties of materials for heat accumulation [10].

Table 1. Comparison of theoretical values with those determined experimentally [10, 11, 12]

Substance	Parameters	Theoretical value	Determined value
Palm oil	Specific heat capacity	$1,8-2,4 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$	$2,00 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$
Palm oil	Heat of fusion	$130-210 \frac{\text{kJ}}{\text{kg}}$	$117,28 \frac{\text{kJ}}{\text{kg}}$
Paraffin	Specific heat capacity	$1,8-2,4 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$	$2,87 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$
Paraffin	Heat of fusion	$130-210 \frac{\text{kJ}}{\text{kg}}$	$109,95 \frac{\text{kJ}}{\text{kg}}$

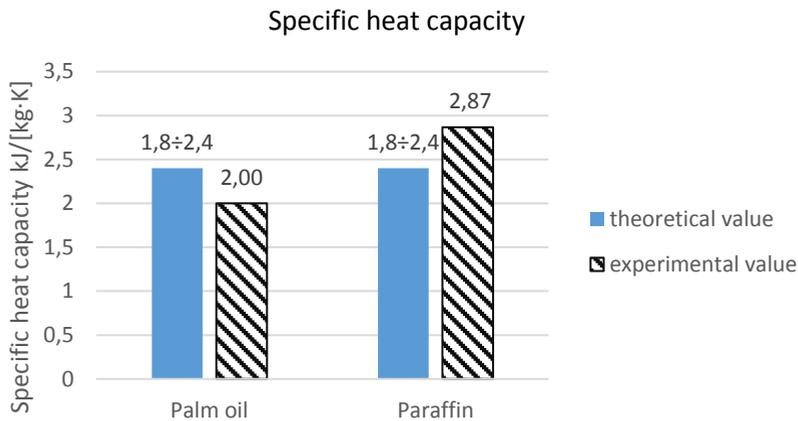


Fig. 4. Comparison of theoretical and experimental values of specific heat capacity

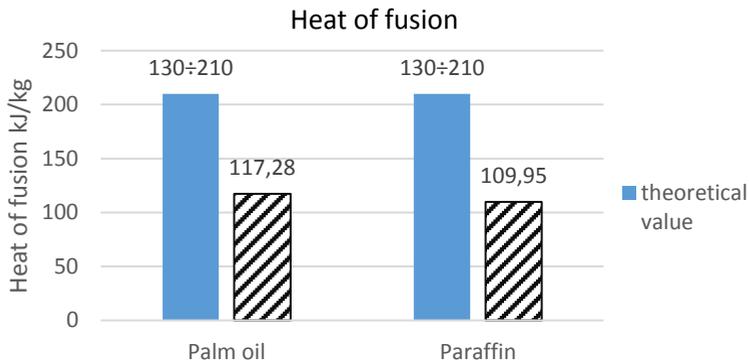


Fig. 5. Comparison of theoretical values with experimental heat of fusion [10]

4 Conclusions

The test results of selected substances are comparable to the theoretical values, which means that the system can be used as a tool for testing related to the determination of thermal parameters of PCM materials. There are thermal losses in the system, which is directly related to the stand structure. During the test, only Plexiglas insulation was used, because the observation of the tested PCM material facilitates the evaluation of the process. Thanks to the possibility of assessing the thermal parameters of phase change substances, it is possible to design an individual PCM application. An additional advantage of the tested substances is a slight change in the volume of the material during the transformation, which is an important performance parameter of the tested substances.

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