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CHARACTERIZATION OF SELECTED PHASE-CHANGE MATERIALS FOR A PROPOSED USE IN BUILDING APPLICATIONS

KARAKTERIZACIJA IZBRANIH MATERIALOV S FAZNO PREMENO ZA PREDLAGANO UPORABO V GRADBENIŠTVU

Milan Ostrý[1], Radek Přikryl[2], Pavel Charvát[3]

[1]Brno University of Technology, Faculty of Civil Engineering, Institute of Building Structures, Veveří 95, 602 00 Brno, Czech Republic
[2]Brno University of Technology, Faculty of Chemistry, Purkyňova 464/188, 612 00 Brno, Czech Republic
[3]Brno University of Technology, Faculty of Mechanical Engineering, Technická 2, 616 69 Brno, Czech Republic
ostry.m@fce.vutbr.cz

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The generally positive trend of ever-stricter requirements for the thermal insulation properties of building envelopes, leading to a significant reduction in the heat losses of modern buildings, has also brought about some negative aspects. Modern light-weight buildings with high-thermal-resistance envelopes are prone to overheating in the summer due to both solar and internal heat gains. This problem is often solved by installing mechanical cooling (air-conditioning) that leads to an increase in the energy consumption and, since electricity is mostly used to power the air-conditioning systems, the increase in the energy consumption for cooling can offset the heating-energy savings in terms of primary energy. A lot of attention has therefore been paid to the other means of temperature control in buildings, such as night-time ventilation and/or the building-integrated thermal storage. The phase-change materials that can store a rather large amount of heat in a narrow temperature interval around their melting point seem to be particularly suitable for this purpose. There are many ways of integrating PCMs into the building structures as well as the techniques that employ that extra thermal-storage capacity to provide thermal comfort for the occupants. This paper deals with the results of the laboratory testing of selected organic and inorganic phase-change materials for integration into building structures. Differential scanning calorimetry was used to obtain the melting ranges and enthalpies of fusion of the selected materials and thermogravimetry was used to explore the thermal stability (decomposition) of the materials at higher temperatures.

Keywords: thermal-energy storage (TES), heat-storage medium, phase-change materials (PCMs), organic materials, inorganic materials, sensible heat storage, latent-heat storage

Splošne pozitivne usmeritve v vedno ostrejše zahteve pri toplotni izolaciji poslopij vodijo k občutnemu zmanjšanju toplotnih izgub modernih zgradb in so prinesle tudi nekaj negativnih vidikov. Moderne, lahke zgradbe, z dobrim izolativnim ovojem so nagnjene k pregrevanju v poletju zaradi sončne in notranje toplote. Ta problem se pogosto rešuje s postavitvijo mehanskega ohlajevanja (air-conditioning), ki povzroči povečanje porabe energije, saj je elektrika najbolj pogosto uporabljena za pogon sistema ohlajanja, vendar pa se s stališča primarne energije povečuje poraba energije za ohlajanje, ki lahko celo preseže prihranke pri energiji za ogrevanje. Mnogo pozornosti je treba zato posvetiti drugim sredstvom za kontrolo temperature v zgradbah, kot so nočna ventilacija in/ali shranjevanje toplote integrirano v zgradbi. Materiali s fazno premeno lahko shranjujejo relativno velike količine toplote v temperaturnem intervalu okrog njihovega tališča in so zato videti posebno primerni za ta namen. Mnogo načinov je za vključitev PCM-materialov v strukturo zgradbe kot tudi tehnike, ki vključujejo shranjevanje ekstra toplotne kapacitete za zagotavljanje udobja stanovalcev. Članek obravnava rezultate laboratorijskih preizkusov izbranih organskih in anorganskih materialov s fazno premeno za njihovo vključitev v strukturo zgradbe. Diferenčna dinamična kalorimetrija je bila uporabljena za določanje področja taljenja in entalpije taljenja izbranih materialov, termogravimetrija pa za raziskovanje toplotne stabilnosti (dekompozicije) materialov pri povišanih temperaturah.

Ključne besede: shranjevanje toplotne energije (TES), sredstvo za shranjevanje toplote, materiali s fazno premeno (PCM), organski materiali, anorganski materiali, smiselno shranjevanje toplote, shranjevanje latentne toplote

1 INTRODUCTION

Thermal-energy storage systems have a wide variety of applications[1]. Heat (cold) can be stored by heating (cooling), melting (solidifying), vaporizing (liquefying) a medium or by reversible thermochemical reactions. Heat-storage media that undergo a phase change during the process of storage and release of energy are called phase-change materials (PCMs)[2]. The thermal-storage capacity of PCMs depends on the specific heat in each state and the latent heat of each phase transformation[3]. A large heat of fusion and the transition temperature in a required range are the two main characteristics determining the suitability of PCMs for a specific application. The determination of the selected properties of PCMs is the most important condition for a correct design of a new application of PCMs in buildings and for a prediction of the influence of the latent-heat storage on an indoor environment and energy savings. In practice there is a lack of reliable information about PCM properties and, therefore, only the results of validated laboratory experiments involving selected PCMs can help the investigators in designing and developing latent-heat storage systems. However, there are some limitations in the use of PCMs[4]:

- PCMs may interact with the building structure and change the properties of the building materials;

- there is a risk of a leakage of PCMs from the building structure;
- PCMs have a rather poor thermal conductivity in the solid state.

These problems are commonly solved with a proper PCM encapsulation.

Salt hydrates, paraffin waxes, fatty acids and eutectics of organic and non-organic compounds are the main categories of PCMs that have been considered for building use during the recent decades.

2 MATERIAL AND METHODS

Only the solid-liquid phase change of a material can be used when a material is integrated in a building structure. In some cases differential scanning calorimetry (DSC) is a standard method for a thermal analysis of PCMs. The most widely used scanning mode includes heating and cooling at a constant rate[5]. This dynamic method is used for the investigation of the melting and solidification enthalpies. **Figure 1** shows the solidification process of PCMs. The evolution of the released heat flux is the function of the external temperature T_{ext}, when this temperature is following a ramp[6]. The shape of the curve depends on the temperature rates. The latent heat of the phase change is calculated from the area under the curve and the external temperature rate that is constant in our case (e.g., 0.1 K min^{-1}, 1 K min^{-1}, 10 K min^{-1}):

$$l_f = \int_{t_1}^{t_2} Q(t)dt = \int_{T_e}^{T_0} Q(T_{ext}) \frac{\partial t}{\partial T_{ext}} = \frac{1}{v_{Text}} A_f \qquad (1)$$

where l_f is the latent heat of the phase transformation (J), Q is the heat flux (W), t is the time (s), T_o is the onset temperature (K), T_e is the end temperature (K), T_{ext} is the external temperature (K), v_{Text} is the external-temperature rate (K s^{-1}) and A_f is the area under the curve and the external-temperature rate (W K^{-1}).

There are inflections of the plotted curve on each side of the heat-flow peak temperature T_p. The onset temperature T_o and the end temperature T_e are the temperatures corresponding with the intersections between the tangents at the inflection points and the base line. The onset temperature and the peak temperature are often used for the characterization of PCMs.

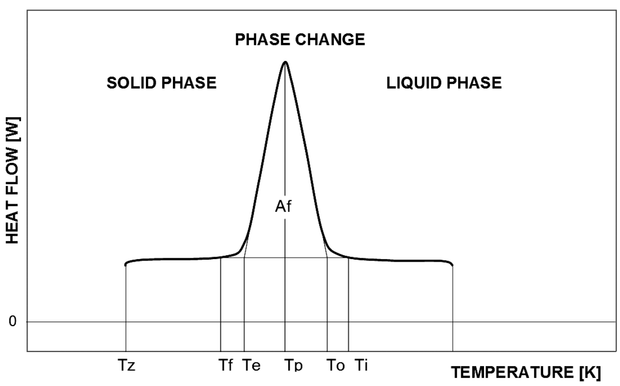

Figure 1: Characteristic temperatures for the solidification process
Slika 1: Značilne temperature pri procesu strjevanja

We have used selected non-commercial and commercial organic- and inorganic-based PCMs in our experiments. The list of selected PCMs is in **Table 1**. Perkin Elmer PYRIS1 DSC, equipped with a cooling device Perkin Elmer Intracooler 2P, was used for determining the thermal properties (the heat of fusion and the melting range). All DSC experiments were carried out at the temperature rate of 0.1 K min^{-1}.

A thermogravimetric apparatus (TGA) Q500 made by TA Instruments was used for the evaluation of the thermal stability of PCMs. The airflow rate was set to be 60 ml min^{-1} and the heating rate was 5 K min^{-1} from the room temperature to 600 °C. An open platinum pan was used as a sample holder. The weight of the samples was approximately 10 mg. The results of TGA determine the suitability of these materials in latent-heat-storage applications because the operating temperature must be below the thermal-decomposition temperatures of PCMs. The proposed operating-temperature range for building application was estimated to be between 18 °C and 30 °C.[7]

Table 1: PCMs tested in laboratory experiments
Tabela 1: PCM, preizkušeni v laboratorijskih preizkusih

Sample	Organic / inorganic	Source
$CaCl_2 \cdot 6H_2O$	inorganic	noncommercial
Parafol 16-97	organic	Sasol
Parafol 18-97	organic	Sasol
SP 22 A17	inorganic	Rubitherm
SP 25 A8	inorganic	Rubitherm
RT 21	organic	Rubitherm
RT 27	organic	Rubitherm
ThermusolHD26	inorganic	Salca

3 RESULTS AND DISCUSSION

Characteristics of all the samples were tested twice. The results in **Tables 2** and **3** represent the average values from both measurements. As already mentioned, all the experiments were carried out at the temperature rate of 0.1 K min^{-1}. Though the experiments carried out

Table 2: Peak temperatures of selected PCMs
Tabela 2: Vrhovi temperature izbranih PCM

Sample	Peak temperature in °C	
	Melting	Solidification
$CaCl_2 \cdot 6H_2O$	29.9	–
Parafol 16-97	18.8	16.1
Parafol 18-97	28.9	27.3
SP 22 A17	22.5	22.4
SP 25 A8	26.6	18.5
RT 21	22.8	22.6
RT 27	27.8	27.6
ThermusolHD26	27.0	21.5

at the temperature rate of 0.1 K min^{-1} take roughly 10 times more time than the experiments at the rate of 1 K min^{-1}, the slower rate was chosen because it is much closer to the real daily swing of indoor air temperature in summer in the rooms with natural ventilation without air-conditioning. PCM-based heat storage integrated in building structures is a way of controlling the indoor air temperature by storing and releasing the thermal energy from the solar radiation or internal heat gains.

Calcium chloride hexahydrate is a non-commercial salt-hydrate PCM. Parafol 16-97 is based on hexadecane, Parafol 18-97 is based on octadecane. Samples SP 22A17 and SP 25 A8 consist of a composition of salt hydrates and organic compounds. Samples RT 21 and RT 27 are based on n-paraffins and waxes. Thermusol HD26 represents a commercial group of salt-hydrate-based PCMs.

Table 3: Heat of fusion of tested PCMs
Tabela 3: Talilna toplota preizkušenih PCM

Sample	Heat of fusion in J g^{-1}	
	Melting	Solidification
$CaCl_2$–$6H_2O$	129.0	–
Parafol 16-97	223.6	–227.4
Parafol 18-97	221.3	–215.5
SP 22 A17	12.3	–11.9
SP 25 A8	71.4	–78.0
RT 21	116.7	–106.7
RT 27	139.7	–139.3
ThermusolHD26	132.4	–132.0

The possibility of a regeneration of PCMs (a rejection of stored heat) at night is very important for the building applications. The PCMs integrated with building structures absorb heat gains during the day and release the absorbed heat at night. If the heat absorbed during one day is not released at night the ability of PCMs to absorb heat the next day is reduced leading to a limited contribution to the room-temperature control. Two systems for the rejection of stored heat were studied at the Brno University of Technology in the past:

- a natural or mechanical ventilation of the indoor space;
- a circuit of cooled air or water integrated with the structure containing a PCM.

Only the PCMs with suitable melting- and solidification-temperature ranges can be used with each of the systems. As can be seen in **Table 2** calcium chloride hexahydrate is suitable only for the naturally ventilated spaces. The indoor temperature in the residential buildings and in the offices must be maintained between 20 °C and 26 °C. But a serious disadvantage of this material is its tendency to supercool during the solidification process. This kind of PCM cannot be used without a modification that reduces the supercooling effect. There are no results from the solidification process just because of the supercooling. On the other hand, Parafol 18-97, RT 27 and Thermusol HD26 could be used for the systems with ventilation of the interior. PCMs absorb cooling loads and release energy in the temperature range between 21 °C and 28 °C. This fact allows for cooling down the indoor environment only to 20 °C to reject the absorbed heat (the regeneration of PCMs). But these systems cannot commonly guarantee thermal comfort in the rooms during very hot summer days.

On the other hand, the temperature of cooled water or air in a separate circuit integrated with the building structures containing PCMs can be kept bellow 20 °C without a negative impact on the thermal comfort of the occupants. This fact allows for the use of the PCMs with a lower solidification range (e.g., SP 22A5 from the tested group).

As can be seen in **Figure 2** the samples of Parafol 16-97 and 18-97 have a very narrow range of melting and solidification temperatures, about 0.3 °C and 0.4 °C. This is an advantage for the short-term storage systems that represent building structures.

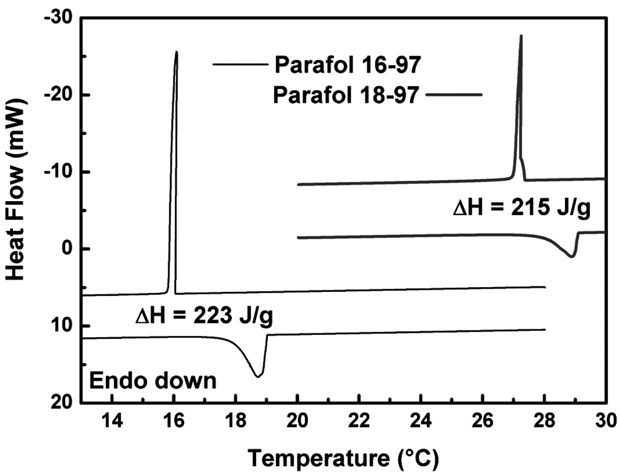

Figure 2: Results of DSC for Parafol 16-97 and Parafol 18-97
Slika 2: Rezultati DSC za Parafol 16-97 in Parafol 18-97

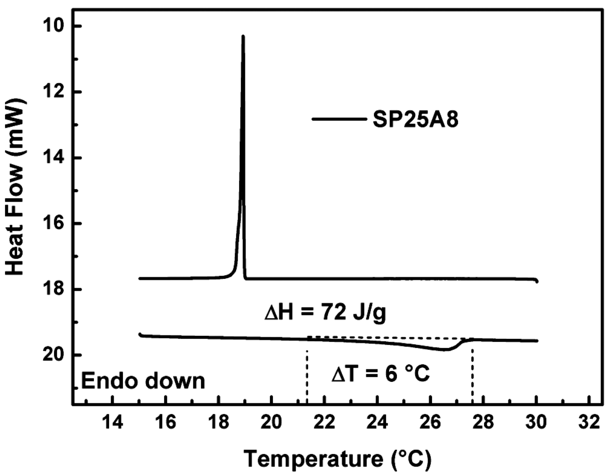

Figure 3: Results of DSC for SP 25A8
Slika 3: Rezultati DSC za SP 25A8

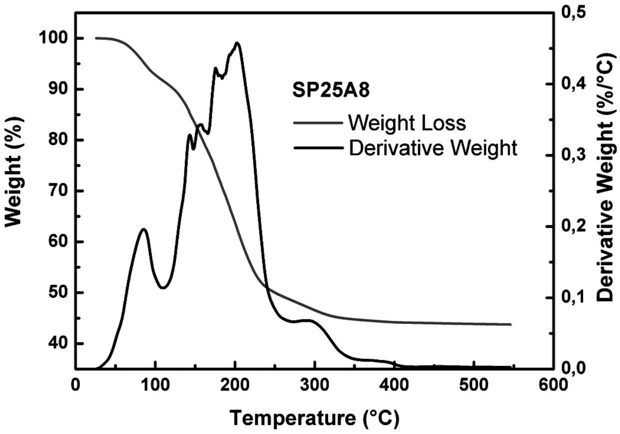

Figure 4: Example of results of a TGA analysis
Slika 4: Primer rezultatov TGA-analize

Compared to the paraffin-based PCMs, the PCMs that are a mixture of salt hydrates and organic compounds, tested in our experiment (**Figure 3**), have a wide range of melting temperatures and a rather narrow temperature range of solidification. This could be an advantage for the systems with a cooled-water loop, because the thermal energy can be slowly stored in a PCM during the day and quickly discharged at night by the cooled-water circuit.

All the materials tested in our experiments are suitable for building application from the point of view of thermal decomposition. The thermal decomposition of all the tested PCMs begins above the expected operation temperatures. The result for the sample composition of salt hydrates and organic compounds is shown in **Figure 4**.

The difficulties may occur with the use of salt-hydrate-based PCMs because of the changes in the water content. This effect was observed during the TGA at low temperatures. Therefore, salt-hydrate-based PCMs must be very tightly sealed in the containers.

4 CONCLUSION

A series of laboratory experiments was carried out to assess the suitability of the selected phase-change materials for the use in built environments. The purpose of a PCM-based building-integrated thermal storage is to contribute to the thermal stability or temperature control in buildings. All the tested materials were found suitable for this purpose from the point of view of thermal decomposition. That was due to rather low operating temperatures (mostly lower than 30 °C in buildings). All the tested materials exhibited the melting ranges that are suitable for building applications. However, the suitability of PCMs for integration with building structures from the point view of melting ranges and enthalpies of fusion depends, particularly, on the type of integrating and the type of rejecting stored heat.

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