Ceramics-Silikáty 60 (4), 291-298 (2016)
journal webpage: www.ceramics-silikaty.cz
doi: 10.13168/cs.2016.0044

PREPARATION OF PUZZOLANA ACTIVE TWO COMPONENT COMPOSITE FOR LATENT HEAT STORAGE

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Submitted May 16, 2016; accepted August 4, 2016

Keywords: Two component composite, Vacuum impregnation, Pozzolanic activity, Phase change material, Diatomite

Application of Phase Change Materials (PCMs) represents promising way for an increase of energy efficiency of industrial devices, reduction of energy demands for heating and cooling, waste heat recovery, solar energy storage and smart control of buildings interior climate. In this paper, the potential of diatomite as the bearer for the shape stable PCM was studied in order to develop material applicable in the mix composition of composite materials. Considering availability, endurance and compatibility of diatomite with the cement and lime based materials, preparation of diatomite/wax composite brings pozzolana active PCM with great promises at a reasonable cost. Prepared composite was analysed in detail using laser diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and differential scanning calorimetry. Also the pozzolanic activity was measured. The prepared two components composite exhibits high latent heat storage and particle size distribution compatible with cement and hydrated lime.

INTRODUCTION

Thermal energy storage (TES) can be considered as an effective tool for achieving an increase of building heat conservation [1]. One of the important advantages of the TES is overcome the mismatch between the supply and demand periods. Thermal energy storage system can be based on storage principles of the sensible heat (SHS), latent heat (LHS) and thermo-chemical reactions [2]. Sensible heat storage systems use materials of high specific heat capacity, good thermal conductivity and high density. On the other hand, LHS or free cooling are more efficient methods for storing the thermal energy which provide much higher storage density than SHS [3]. LHS is based on utilization of the released and absorbed heat energy during the materials phase change caused by the temperature fluctuation.

Phase Change Materials (PCMs) represent technology with the great potential for reduction of the energy consumption by utilization of the phase change processes [4]. PCMs can store thermal energy by the endothermic reaction of the material and on the other side release it, when ambient temperature drops under solidification temperature, by exothermic reaction. From the theoretical point of view, it is possible to exploit the thermal energy during solid-solid, solid-liquid, solid-gas, liquid-gas, and vice versa phase transition. Unfortunately, due to the further technical requirements on PCMs, application of solid-gas and liquid-gas transitions with high latent heat is not suitable due to the large volume changes which occur during phase transitions.

A large number of PCMs are known to melt with a high heat of fusion. Nevertheless, for their practical use as latent heat storage materials, these materials must exhibit certain desirable thermodynamic, kinetic and chemical properties as melting temperature in the desired operating temperature range, high latent heat of fusion per unit volume, small volume change on phase transition, congruent melting of the phase change material for a constant storage capacity of the material with each freezing/melting cycle, high nucleation rate to avoid super cooling, chemical stability, non-toxicity, no corrosiveness to the construction materials etc. [5]. For example leakage of PCM in its liquid phase into the material matrix represents serious problem for stability of material properties in time and reduces material durability and service life.

This problem was solved by commercial producers of PCM by encapsulation. Two main principles of encapsulation can be recognized, namely macroencapsulation and microencapsulation. The macroencapsulation containment method means inclusion of the PCM in plastic, metal or other material tubes, bags, pouches, spheres, panels etc. with volume from few cubic mililiters to several liters of encapsulated PCM [6]. On the other hand, micro encapsulation technique by polymer shell provides particle ranges from 1 μm to 1000 μm which allows simple incorporation into any matrix and sufficient heat transfer. Urea-formaldehyde resin, melamine-formaldehyde resin and polyurethane are the mostly used materials for microcapsules shell.

Several attempts aimed at the use of PCMs in concrete mix compositions were realised. Bentz and Turpin studied potential of PCMs in concrete technology and found promising results from the point of view of improvement of thermal energy storage [7]. Entrop et al. [8] reported on experimental research on the use of microencapsulated phase change materials in concrete floors to store solar energy for moderation indoor climate during evening and night. Performed experiments and modelling proved positive effect of PCM on thermal energy storage and consequent decrease in energy consumption.

Despite of the evident positive effect of microencapsulated PCMs on thermal energy storage of building components, their wider use is limited due to the inert polymer shell which decreases mechanical resistivity of cement based composites. A study published by Lucas et al. [9] discussed possibility of PCM incorporation into mortars. Authors found that microencapsulated PCM strongly influences macroporosity of mortars with increasing amount of incorporated PCM. Typically, higher amount PCM and thus increased porosity leads to the reduction of the mechanical parameters [10], [11]. In addition, polymer shell is also vulnerable during mixing because of collision and abrasion with other aggregates and fillers. These facts are limiting factors for addition of the adequate portion of PCM for the efficient thermal energy storage, higher influence on interior temperature fluctuation and delays of the temperature peaks. Finding the compromise between mechanical properties and energy efficiency reduces potential of PCMs for reduction of energy consumption for heating and cooling and thus environmental benefit of their use [12].

In order to avoid possible problems with inert polymer shell, development of shape stabilized phase change materials (SS-PCMs) was carried out [13]. Many researchers were attracted to application of inorganic materials as PCM bearer. Vacuum impregnation method [14] was used for preparation of shape stabilized PCM by incorporation paraffin into the porous materials as expanded graphite [15], glass powder [16], expanded perlite [17], vermiculite [18], clay minerals [19], cement [20] and diatomite [21]. Vacuum impregnation method enables the higher level of the bearer absorption against normal conditions [22].

Application of diatomite is extensively studied field having potential in several technical disciplines. Diatomite is a sedimentary siliceous rock formed by the fossilized skeletal remains of diatoms, unicellular aquatic plants. High porosity and resistivity of diatomite predestine its promising application in industry. It is commercially used e.g., as a filtration aid, mild abrasive, mechanical insecticide, absorbent for liquids, matting agent for coatings, reinforcing filler in plastics and rubber, porous support for chemical catalysts, thermal insulator etc. Additionally, diatomite is considered as a supplementary cementing material in cement blends. Here, the general term "the activity of additives" defines the chemical activity (usually pozzolanic activity) and microfiller effect [23]. The pozzolanic activity is the ability to react with portlandite ($Ca(OH)_2$) in the presence of an excess of water, which is expressed in the quantity of bound CaO mg per 1 g of additive [24], [25]. Moreover, the microfiller effect depends mainly on the shape and size of the particles, the particle size distribution, and specific surface area. These properties make diatomite applicable material for partial Portland cement substitution or additive in cement-based materials [26]. For example Ergun [27] measured improved mechanical properties of conventional concrete mixtures with partial cement replacement by diatomite using superplasticizing admixture. Moreover, possible use of diatomite for preparation of SS-PCM became recently an actual topic of material research. Jeong at al. [28] used for preparation of PCM on the diatomite base n-hexadecane, n-octadecane and paraffin. They obtained phase temperatures 23.7, 31.3 and 54.4°C respectively with corresponding phase change latent heat of 118.0, 112.9 and 59.7 $J \cdot g^{-1}$. Nevertheless, the pozzolanic activity of the developed PCM was not of the particular importance for material use.

In this paper, potential of diatomite as the PCM bearer for preparation of shape stable PCM composite applicable in composite mix design of building materials is studied. Considering availability, endurance and compatibility of diatomite with the cement and lime hydrate based materials, proposed solution on the basis of wax and diatomite represents promising way for an improvement of energy stability and efficiency of buildings at a reasonable cost of PCM composite.

EXPERIMENTAL

Materials and preparation of two component PCM composite

As bearing material for preparation of shape stabilized PCM was chosen filter diatomite produced by LB Minerals s.r.o. (Czech Republic). Chemical composition of diatomite used was determined by X-Ray Fluorescence (XRF). Chemical composition of diatomite was 82.9 wt. % of SiO_2, 13.2 wt. % of Al_2O_3, 1.5 wt. % of Fe_2O_3, 0.9 wt. % of K_2O, 0.6 wt. % of TiO_2, 0.3 wt. % of CaO and 0.2 wt. % of MgO. Other elements were present in concentrations below 0.1 wt. %. Phase composition of diatomite was accessed by X-Ray diffraction (XRD).

Diatomite contained 6 wt. % of quartz, 32.7 wt. % of kaolinite, 7.3 wt. % of muscovite. Remaining 53.9 wt. % was the amorphous phase. The measurement of chemical composition of the studied diatomite proved its high silica content as well as high amount of amorphous phase.

Palm wax was chosen as PCM due to its availability and high latent heat storage. The phase change temperature of palm wax is approx. 55.5°C during cooling and 57.3°C during heating. This data was given by wax producer Paramo a.s. (Czech Republic).

The diatomite/palm wax composite (DPWC) was prepared by a vacuum impregnation method. Mass proportion between diatomite and palm wax was selected as 0.9. Firstly, diatomite particles were placed into the oven and dried at 105°C for 48 hrs to remove moisture. 30 g of diatomite was placed in a filtering flask and evacuated. After this procedure, the liquid palm wax was injected to flask and PCM merged with diatomite. The valve was opened and air forced PCM to impregnate porous structure of diatomite. To obtain homogenous material of high specific surface, the developed powdered mixture was dried and milled after the impregnation. The whole procedure was performed two times. It means, the double impregnation was done.

Analytical methods

For experiments we used distilled water (16.8 MΩ), HCl (35 %, PENTA, Czech Republic, p.a.), NaOH (PENTA, Czech Republic, p.a.), EDTA (PENTA, Czech Republic, p.a.). Pressure air tank (99.9 %) was purchased from company SIAD (Czech Republic).

XRF analysis was done using X-Ray spectrometer ARL 9400 XP (Thermo) equipped with Rh lamp. It is fully automatic sequential XRF spectrometer for quali-tative and quantitative element analysis up to 83 elements of periodic table (B-C O-U) in the range from ppm to 100 %. The standardless analysis was performed using software UNIQUANT 5 integrated in Oxsas. Analysed sample was compressed to tablet with H_3BO_3. Tablets were 5 mm high and had diameter of 40 mm. They were filmed by polypropylene in thickness of 4 μm.

X-Ray diffractograms were measured with a diffractometer PANalytical X´PertPRO (PANalytical, Almelo) with Bragg-Brentano parafocusing geometry (CoK_a radiation source, voltage of 40 kV at 30 mA) and fast linear detector X´Celerator. Measured diffractograms were analysed by the computer code HighScore Plus 3.0.5 (PANalytical, Almelo). The amount of the particular crystalline phases was determined by the Rietveld analysis using the code DiffracPlus Topas 4.2. Here, models obtained from database ICSD, release 2012/1 (FIZ Karlsruhe, SRN) and American Mineralogist Crystal Structure Database were used. The amorphous fraction was found by the method of standard addition, with ZnO in an amount of 10 % of mass of the sample.

Particle size distribution was measured because of the evident effect of the fineness of pozolanic material on its pozzolanic activity and reactivity with cement hydrates. The measurement was done on a laser diffraction principle using the device Analysette 22 MicroTec plus (Fritsch). The measuring range is obtained with the utilization of two lasers with different wavelength. A green laser (wave length 521 nm) is used for the small particle range, whereas an IR-laser (wave length 940 nm) is utilized for the measurement of larger particles. The device is equipped with dispersive unit that enables measurement of dispersed particles in water and auto sampler for multiple measurements [29].-

As basic physical characteristics of diatomite and palm wax composite (DPWC), their matrix density, bulk density and specific surface were measured. The powder density was access on gravimetric principle from the measured sample mass and volume. The matrix density was measured by helium pycnometry, using a Pycnomatic ATC apparatus (Thermo Scientific). The specific surface was accessed using Blain apparatus according to the standard EN 196-6.

Morphology and rate of palm wax implementation into the diatomite porous structure was observed using Scanning Electron Microscopy (SEM). The analysis was done using microscope JSM 6510 LV (Jeol) with FEG electrons source with acceleration voltage 15 kV. To con-duct these measurements, the samples were placed on a carbon conductive tape.

Thermal properties were measured using Differential Scanning Calorimetry (DSC) with apparatus DSC 822e (Mettler Toledo) was applied. The following temperature regime was applied: 5 minutes of the isothermal regime (80°C); cooling of $5°C\cdot min^{-1}$ from the temperature 80°C to the temperature 0°C; 5 minutes of the isothermal regime (0°C); heating of $5°C\cdot min^{-1}$ from the temperature 0°C to the temperature 80°C; 5 minutes of isothermal regime (80°C). For the low temperature exposure of the studied samples, the cooling device FT 900 (Julabo) was used. The measurement was performed in a dynamic air atmosphere with flow rate 50 $ml\cdot min^{-1}$ [30].

Fourier Transform Infrared spectroscopy (FT-IR) was applied using FT-IR spectrometer Nicolet 6700 (Thermo Fischer Scientific) in ATR regime. The measuring device consists of He–Ne laser, high-intensity IR source EverGlo^{TM}, GE/KBr beam splitter, golden mirrors, pyroelectric detector HP DLaTGS and interchangeable sample compartment. This type of FT-IR spectrometer operates in spectral range from 7800 to 350 cm^{-1} with spectral resolution 0.4 cm^{-1}.

For the measurement of pozzolanic activity we chose Frattini test that is ranked between the direct methods of pozzolanic activity measurement applying standard methods of chemical analysis. This method is commonly used e.g., for the measurement of pozzolanic activity of crushed brick [31], metakaoline [32] and fly ash [33]. The Frattini test was done according to technical standard ČSN EN 196-5 – Methods of testing cement – Part 5: Pozzolanity test for pozzolanic cement. The test is based on a comparison of the amount of $Ca(OH)_2$ present in the liquid phase in contact with cement with the amount of $Ca(OH)_2$ that saturates the environment of equal alkalinity. The mass ratio of cement and DPWC (or diatomite) was 80/20. The tested mixture was mixed with 100 ml of boiled distilled water. Then, the sample was placed in a sealed plastic bottle and cured in thermostatic chamber at 40°C. After 8 days, samples were filtered with Buchner funnel. The filtrate was analysed to determine concentration of hydroxide ions with titration against HCl with bromophenol blue indicator. Finally, after pH adjustment to 12.5 using NaOH, the concentration of CaO was accessed by titration with EDTA solution using Murexide indicator [34]. For the examination of pozzolanic activity, the dependence of measured OH^- and Ca^{2+} (expressed as CaO) concentrations were graphed. The material is considered as pozzolana active when the graphed concentration point lies bellow the solubility isotherm of $Ca(OH)_2$.

RESULTS AND DISCUSSION

At first, particle size distribution of diatomite and diatomite/palm wax composite (DPWC) was measured (see Figure 1). It is apparent that the incorporation of palm wax into the diatomite particles affected the particle size distribution to a limited extent only. This gives evidence that no clumping or sticking of the particles took place within the vacuum impregnation process. The highest volume of the diatomite particles was identified at approx. 30 μm. The developed DPWC has the maximal volume of particles at 46 μm. The values of particle volume fractions 10, 50 and 90 % corresponding to the particle size distribution are presented in Table 1. From the qualitative point of view, the shape of particle size distribution curve of diatomite corresponded to the data accessed by Kuzielová et al. for Portland cement CEM I 42.5 [35]. In order to improve compatibility of DPWC with cement and increase its reactivity, the additionally milling to get the similar fineness has to be performed.

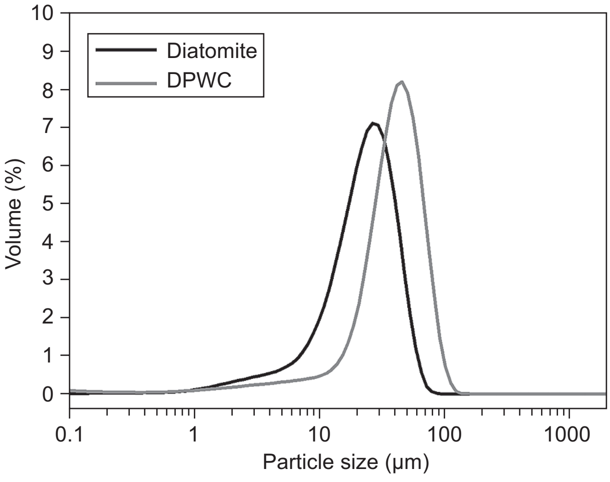


Figure 1. Particle size distribution of diatomite and DPWC.

Table 1. Particle size distribution – cumulative data.

Material	Size [μm] freq. d_{10}	Size [μm] freq. d_{50}	Size [μm] freq. d_{90}
Diatomite	7.7	23.0	46.2
DPWC	12.7	34.4	62.2

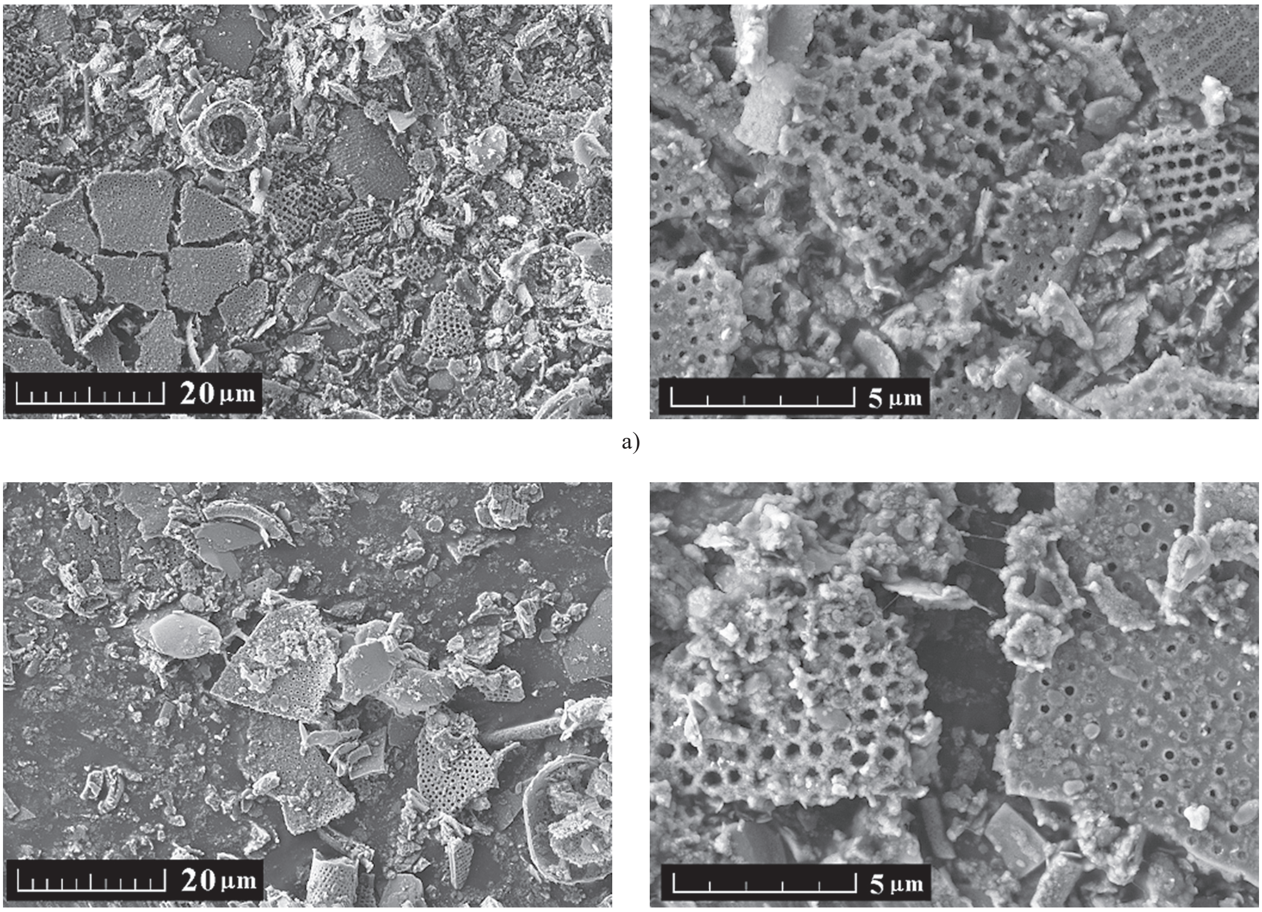
Basic physical characteristics of diatomite and DPWC are given in Table 2. The bulk density of DPWC is about 36 % higher compared to diatomite. This gives information on partial filling of pores of diatomite particles. On the hand, the matrix density of DPWC was lower than matrix density of pure diatomite powder. This is a result of a low density of palm wax that penetrated the open pores of diatomite. The specific surface values are for the both studied materials higher than those for ordinary Portland cements that are typically 300 - 350 $m^2·kg^{-1}$ for ordinary Portland cements and 400 - 450 $m^2·kg^{-1}$ for rapid-hardening cements [36]. The high specific surface obtained for the bot studied materials are in agreement with high porosity of diatomite. Since the palm wax partially filled the diatomite pores, the value of specific surface of the prepared composite was significantly lower compared to that of pure diatomite.

Table 2. Basic physical parameters.

Material	Bulk density [$kg·m^{-3}$]	Matrix density [$kg·m^{-3}$]	Specific surface [$m^2·kg^{-1}$]
Diatomite	307.5	2 416.4	1 632.1
DPWC	419.3	1 293.0	807.5

Anyhow, from the point of view of possible reactivity of the studied composite with cement and lime hydrates, its specific surface is quite sufficient.

Morphology of diatomite and DPWC is shown in Figure 2. It is evident that the structural changes in diatomite are almost imperceptible. Because of the high porosity of diatomite, one can observe partial filling of its pores by palm wax. Due to that the diatomite properties enabling its incorporation into the matrix of cement and hydrate lime-based composites were not significantly affected. Contrary to our results, Xu and Li [21] prepared PCM composite on the basis of diatomite and paraffin. They achieved material with fully encapsulated diatomite particles and high latent heat of phase change. Nevertheless, the high rate of impregnation of diatomite led to the significant decrease of mechanical



a)

b)

Figure 2. SEM micrographs of diatomite (a) and DPWC (b) at various magnifications.

parameters after incorporation of their PCM composite into the concrete. In our case, this negative effect of PCM incorporation into the composite matrix is eliminated.

The ability of diatomite to accommodate in its porous structure palm wax and to prevent its leakage during phase change was studied also by FT-IR spectroscopy. The results of FT-IR analysis are given in Figure 3. Spectral lines of diatomite and DPWC that underwent several phase changes correspond together in peaks at 3 694 and 3 618 cm^{-1} that characterize the inner layer stretching vibration of OH^{-}, in peak at 689 cm^{-1} of the deformation OH^{-} vibration and in peaks at 1 091 - 1095 cm^{-1} characteristic for Si–O normal to the plane stretching vibration. The inner layer vibration of Al–O in aluminosilicates is presented at 796 cm^{-1}. The peak at 539 cm^{-1} corresponds to Si–O–Al deformation vibration. Peaks at approx. 469 cm^{-1} can be attributed to the O–Si–O bond vibration. In spectral line of palm was there are two dominant peaks at 2916 and 2848 cm^{-1} that can be attributed to the symmetric and antisymetric stretching vibration of –(C)–CH$_2$. These peaks are dominant also in a spectral line of the developed composite. At 1471 cm^{-1}, there is clearly visible ester double bond stretching. Peak at 1294 cm^{-1} corresponds to the wagging vibration of –(C)–CH$_2$–. These peaks were identified in palm wax as well as in DPWC. Peak at 719 cm^{-1} belongs to the out-of-plane vibration of aliphatic chain –(CH$_2$)$_n$. Shifts in peaks of DPWC prove that palm wax molecules are bonded by the capillary and surface tension forces which exclude

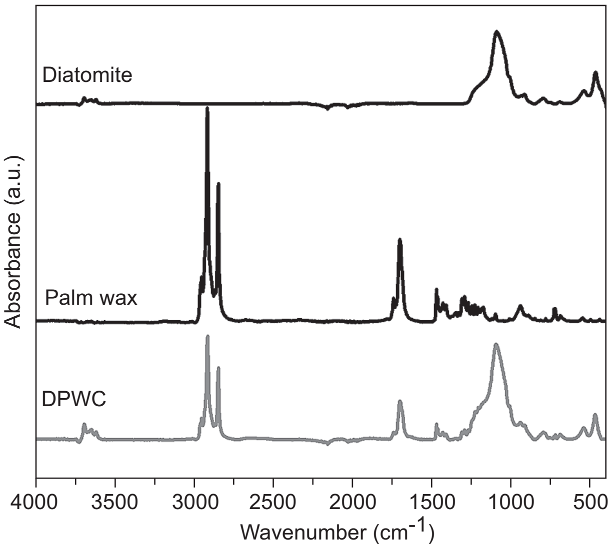


Figure 3. FT-IR spectra of palm wax, diatomite and DPWC.

leakage during phase change process. The presented spectral lines clearly document the rate of diatomite impregnation by palm wax.

Diatomite, due to its pozzolanic activity found use as mineral microfiller and alternative for Portland cement or hydrated lime replacement in blended binders [37]. Results of Frattini test presented in Figure 4 proved the pozzolanic activity of diatomite as well as of DPWC. This finding is highly promising for stable implementation of the developed DPWC into the matrix of cement and lime-based composites. Here, the pozzolanic activity of the developed DPWC will enable its incorporation into the C–S–H, C–S–A–H and C–H hydrates.

Based on DSC analysis, phase transition temperature intervals were determined. In case of cooling, the DPWC solidification started at 55.3°C and this process was finished at ~ 49.6°C. On the hand, the melting process started at 50.5°C and continued up to 62.4°C. The differences in phase change temperatures within cooling and heating as well as in the corresponding temperature intervals are caused by several kinetic effects, e.g., supercooling phenomena during the solidification. It is quite apparent that the heating and cooling rate applied for DSC tests affects its results. Feng at al. [38] introduced that heating/cooling rate 5°C min^{-1} is the common choice applied in DSC tests of PCMs. It complies with the typical standards used in DSC analysis, but it did not follow the advices of Lazaro and Dumas [39] who recommended a slow heating rate for the PCM sample to be able to reach phase equilibrium in both thermal and chemical aspects. Nevertheless, the heating and cooling rate applied in the presented work can be considered as adequate for the tested materials. Summary of DSC data is presented in Table 3.

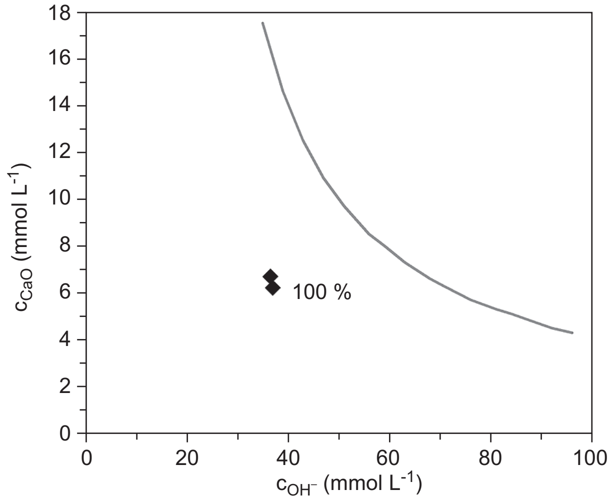


Figure 4. Pozzolanic activity of diatomite and DPWC.

Comparison of the specific heat capacities of the developed DPWC and pure palm wax measured by DSC is given in Figure 5. Looking at measured specific heat capacity curves, one can see their significant increase as a result of palm wax melting. Within the melting of palm wax in DPWC, enthalpy of 44.3 J·g^{-1} is consumed, i.e. stored as latent heat of fusion. This heat is accommodated by the temperature induced phase change and within the cooling can be reversibly released based on the temperature conditions of material. Comparing the enthalpies of pure palm wax and developed DPWC, one can assume the amount of palm wax embedded in composite. In our case, the amount of palm wax embedded in diatomite porous structure was ~50 mass. %. Similar results attained for example Karaipekli and Sari [18] who reported on decrease of the latent heat of fusion directly proportional to the amount of PCM in vermiculite.

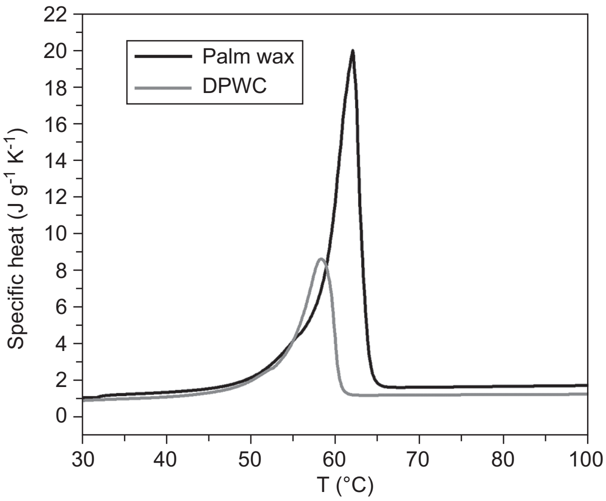


Figure 5. Specific heat capacity in dependence on temperature – heating →.

CONCLUSION

In this paper, two components composite based on diatomite and palm wax (DPWC) was prepared using vacuum impregnation method as optimal preparation technique for shape stabilized PCM. The deve-

Table 3. Phase change temperature and enthalpy.

Material	Phase transition temperature [°C]				Enthalpy [J·g^{-1}]	
	Heating		Cooling		Heating	Cooling
	Onset	Endset	Onset	Endset		
Palm wax	50.1	64.2	56.1	46.5	87.48	87.04
Composite	50.5	62.4	55.3	49.6	44.29	44.19

loped DPWC was studied in respect to its potential application in cement and lime-based composites for latent heat storage. The incorporation of palm wax into the diatomite particles affected the particle size distribution to a limited extent only what gave evidence that no agglomeration of the particles took place within the vacuum impregnation process. This finding was supported by SEM analysis. The SEM images exhibited that the structural differences in diatomite and prepared DPWC were very small and the highly porous structure of diatomite particles was partially filled by palm wax. Therefore, the diatomite properties enabling its stable incorporation into the matrix of cement and hydrate lime-based composites were not significantly affected what was verified by pozzolanic activity test. The prepared composite was found to be pozzolana active and able to form hydrated products in alkali environment of materials based on cement or lime binder. This is the main benefit of the prepared material in comparison with commercial products based on microencapsulation of PCM in inert polymer shell. Because of the pozzolanic activity, the mechanical properties of composites with incorporated prepared shape stable PCM will remain unaffected. Based on FT-IR analysis it was found out that the bands of the pure PCM are still visible in the developed DPWC due to the physical bonds between the diatomite and palm wax and the incorporated palm wax is stable in the porous structure of diatomite even after the phase change cycles. The ability of the developed composite to store and release thermal energy during the temperature induced phase change was proved by DSC analysis. Based on the performed tests and summarizing the experimentally accessed data, the developed DPWC represents promising material for cement and lime-based composites possessing latent heat storage and release that can find used e.g., in roof panels, insulators of heat exchangers, heat supplies or technological processes at elevated temperatures.

Acknowledgment

The authors gratefully acknowledge the financial support received from the Czech Science Foundation under project No. 14-22909S.

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