

THERMAL EFFICIENCY EVALUATION OF SILICA FUME/PHASE CHANGE MATERIAL COMPOSITE FOR APPLICATION TO CONCRETE

Su-Gwang Jeong¹, Seulgi Yu¹, Jae-Han Lim² and Sumin Kim^{1*}

^{1*}Author for correspondence

¹Building Environment & Materials Lab,

¹School of Architecture, ²Department of Architectural Engineering

¹Soongsil University, ²Ewha womans University

¹Seoul, 156-743, ²Seoul, 120-750

^{1,2}Republic of Korea,

E-mail: skim@ssu.ac.kr

ABSTRACT

Silica fume has been used as a replacement for cement, due to its high early compressive strength, high tensile and flexural strength, high bond strength, and enhanced durability of concrete. In this study, enhanced thermal performances of silica fume by incorporating organic PCMs were examined, for applying to concrete. Three kinds of organic PCMs were incorporated into the silica fume. The silica fume/PCM composites were prepared by the vacuum impregnation method. Because the silica fume has a high porous structure compared to the cement, it is useful to incorporate the PCM, to enhance its thermal storage performance. The characteristics of the composites were determined by using SEM, DSC, FTIR and TGA. SEM morphology showed the micro structure of silica fume/PCM. Also, thermal properties were examined by DSC and TGA analyses; and the chemical bonding of the composite was determined by FTIR analysis.

INTRODUCTION

Recently, the use of thermal energy storage with phase change material (PCM) is considered to be one of the most important advanced technologies, and a lot of attention has been paid to utilization of the essential techniques for thermal applications, ranging from heating to cooling in buildings. Using thermal energy storage system in a building can smooth temperature fluctuation, and it can be implemented by sensible heat, or latent heat [1]. Latent heat storage enables the passive control of temperature in buildings. The latent heat storage method provides a much higher heat storage density, with a smaller temperature difference between storage and release of heat [2]. Organic PCMs have been widely used in thermal energy storage applications, due to their large latent heat, and proper thermal characteristics, such as little or no super cooling,

low vapor pressure, good thermal and chemical stability, and self-nucleating behavior [3-9]. However, the application of PCMs to various fields is difficult, due to their phase instability in the liquid state. Therefore, PCMs need shape stabilization. To solve these problems, some investigators have studied the possibility of a container that can prevent the leaking of liquid PCMs, by using shape-stabilized PCM (SSPCM), microencapsulated PCM (MPCM), and incorporated PCM techniques [10-15]. Actually, PCM should be incorporated into building construction materials, such as gypsum wallboard, plaster, concrete, clay minerals, and other wall covering material [16,17]. Therefore this paper has used silica fume as a container of PCM. Silica fume has been used as a replacement of cement, due to its high early compressive strength, high tensile and flexural strength, high bond strength, and enhanced durability of concrete. Silica fume is a by-product from electric furnaces, used in the manufacture of silicon metal or silicon alloys. These advantages of silica fume derive from a high specific surface, and the pozzolanic activity of silica fume particles [18-22]. Considering all those features mentioned above, silica fume is one of the feasible candidates as an economical and light-weight building material, to incorporate PCM for thermal energy storage in buildings. Therefore in this study, enhanced thermal performances of silica fume were examined for applying to concrete, by incorporating organic PCMs. In order to increase the impregnation amount of PCM in porous silica fume, the vacuum impregnation technology is applied during the fabrication process [23]. The vacuum impregnation method guarantees heat storage of PCM after the incorporation process. Therefore this paper addresses the enhancing of thermal properties of the silica fume. Also, we evaluated the applicability of PCM/silica fume composites for applying to concrete using silica fume, which replaces the

cement. This paper analyzed the microstructure, chemical bonding, heat capacity and thermal durability of PCM/silica fume composites, from the results of SEM, FTIR, DSC and TGA analysis.

EXPERIMENTAL

Materials

In this experiment, we used three types of PCMs to incorporate the silica fume. Hexadecane, octadecane and paraffin were used for the experiment as heat storage materials. Those PCMs have different phase change ranges, which are 20.84°C, 30.4°C and 57.09°C, respectively. Also, the latent heat capacities are 254.7J/g, 247.6J/g and 144.6J/g, respectively. The typical bulk density of silica fume is 200-350kg/m³, and the silica fume contains over 85% SiO₂. The silica fume was placed in a container, and the sample was dried at 80°C for 5h, before the experiment. Silica fume has a good structure for incorporating PCM into itself, compared to cement.

Preparation

The PCM/silica fume composite was prepared using vacuum impregnation. A schematic of the vacuum impregnation system is shown in Fig. 1. The dried silica fume sample was put in a flask, which was connected to a round bottom flask to evacuate air from the porous structure of silica fume. Then, the valve between the flask and the container with liquid PCM was opened, to let PCM into the flask to impregnate the silica fume. The vacuum process was continued for 90 min, and then air was allowed to enter the flask again, to force the liquid PCM to penetrate into the porous structure of the silica fume. Then we carried out the filtering process, to remove the extra PCM in the PCM/silica fume composite. The colloidal state was filtered by 1µm filter paper, until a granular sample appeared, which was dried in a vacuum drier at 80°C for 24h, 48h and 72h, for hexadecane, octadecane, and paraffin, respectively.

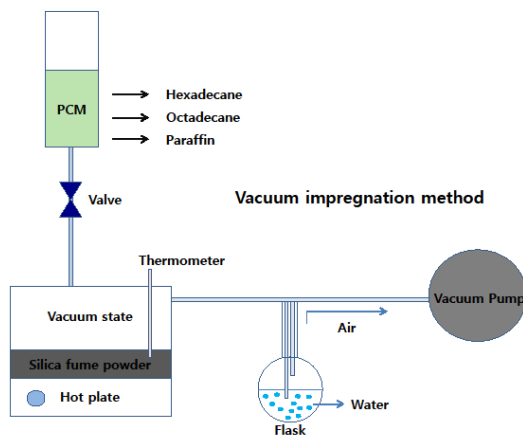


Figure 1 DSC analysis of PCM/silica fume composites.

Characterization techniques

We carried out scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR: 300EJasco), differential scanning calorimetry (DSC:Q1000) and thermo gravimetric analysis (TGA: TA Instruments, TGA Q5000). To confirm the morphology and micro structure of composites, we performed the SEM analysis at room temperature. A SEM with an accelerating voltage of 12kV and working distance of 12mm was used to collect the SEM images. The samples were coated with a gold coating of a few nano meters in thickness [24]. FTIR was also utilized, to monitor the changes of chemical groups upon curing. Clear potassium bromide discs were molded from powder, and used as back-grounds. The samples were analyzed over the range of 525 – 4000cm⁻¹, with a spectrum resolution of 4cm⁻¹. All spectra were averaged over 32 scans. This analysis of the composites was performed by point-to-point contact with a pressure device [25]. Thermal properties, such as the melting temperature and latent heat capacity of pure PCMs and composite PCMs, were measured using a DSC apparatus. The melting temperature was measured by drawing a line at the point of maximum slope of the leading edge of the peak, and extrapolating to the baseline [10]. The latent heat of the samples was determined by numerical integration of the area under the peaks that represent the solid–solid and solid–liquid phase transitions. Thermo gravimetric analysis measurements of the samples were carried out, using a TGA on approximately 2-4mg samples over the temperature range 25°C-600°C, at a heating rate of 10°C/min under a nitrogen flow of 20ml/min. TGA was measured, with the composites placed in a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere, to prevent unwanted oxidation.

RESULTS AND DISCUSSION

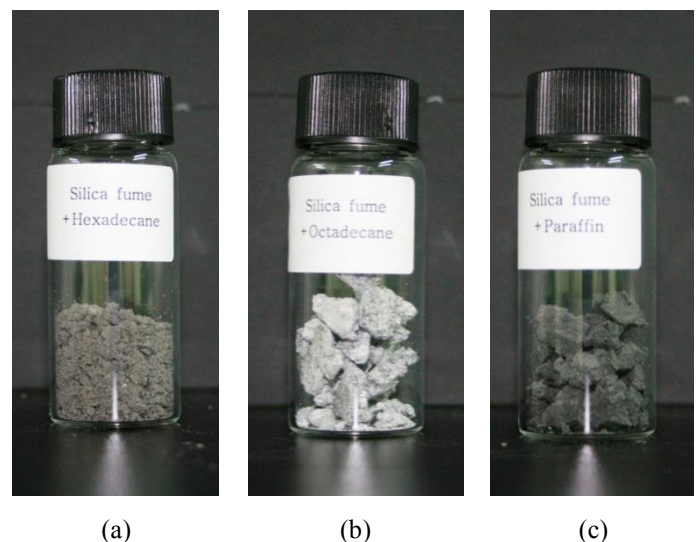


Figure 2 Sample images of PCM/silica fume composites: (a) hexadecane/silica fume composite, (b) octadecane/silica fume composite, and (c) paraffin/silica fume composite.

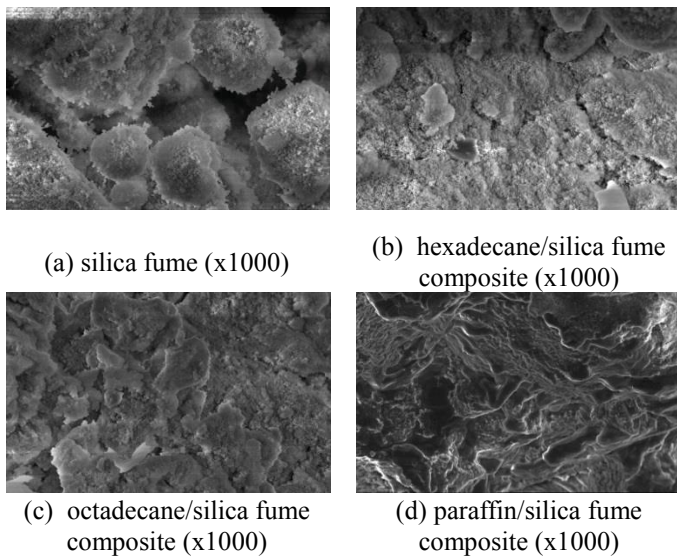


Figure 3 SEM analysis of PCM/silica fume composites: (a) silica fume, (b) hexadecane/silica fume composite, (c) octadecane/silica fume composite, and (d) paraffin/silica fume composite.

Morphology and Microstructures of silica fume with impregnated PCM

Fig. 2 shows the morphology of the PCM composites, which were included in the container. When we see the PCM composites with the naked eye, these seem to be well dispersed into the silica fume's structure. In this study, we confirmed that the minimum mixture ratio of PCM was secured in the structure of silica fume. Each PCM composite is shown, as these samples have different morphologies. In the case of hexadecane composite, this was prepared as a powder type after the manufacturing process, compared to the other PCM composites. The octadecane composite and paraffin composite were made with a granule type. However, although they had different types of shape, leakage phenomenon due to the liquid PCM did not occur in the container under the high temperature condition. This result showed that the PCM was well incorporated into the structure of silica fume. Also, no leakage properties of PCM composite were revealed by SEM analysis, as shown as Fig. 3. Fig. 3 (a) shows a micro structure of natural silica fume. Silica fume is more porous than cement; and we found from the BET (Brunauer - Emmett - Teller equation) analysis that the specific surface area is larger than that of cement. As mentioned above, the silica fume has a good structure for incorporating PCM, compared to the cement. As can be seen in Figs. 3 (b), (c) and (d), we found that many porous parts of the silica fume have disappeared. This means that each PCM was incorporated well into the structure of the silica fume. In the case of the paraffin, the micro structure image is not similar to the other PCM/silica fume composites. This shows the unique characteristics of paraffin. As a result, from the micro structure analysis, silica fume could contain the PCM, and PCM maintained its thermal properties, after the incorporation process.

Latent heat storage analysis

The DSC curves of PCM/silica fume composites during heating and subsequent cooling are presented in Fig. 4. As clearly seen in the figure, the hexadecane/silica fume, octadecane/silica fume and paraffin/silica fume melt at 22.32, 33.61 and 58.39°C, respectively; also they freeze at 12.85, 22.48 and 49.04°C, respectively. Three types of phase change temperature range are shown. This graph shows the melting peaks of composite PCMs have a high temperature range, because the PCMs were influenced by supercooling. The latent heat peak and peak temperature, regarding the melting and freezing of the composite PCMs, are also given in Table 1. The latent heat capacities are obtained by numerical integration of the total area under the peaks of the solid-liquid transition curves of the PCMs in the composite. The latent heat capacities of each PCM are indicated at 86.16, 90.72 and 56.19J/g during the melting process; also they release 86.32, 91.76 and 57.40J/g of latent heat during the freezing process. As shown in the paraffin peak line, it can be seen that paraffin has two phase change peaks. The sharp or main peak near 58°C represents the solid-liquid phase change of paraffin, and the minor peak on the left side of the main peak corresponds to the solid-solid phase transition of paraffin. The first peak of the paraffin/silica fume indicates 11.97 and 9.15J/g, during the melting and

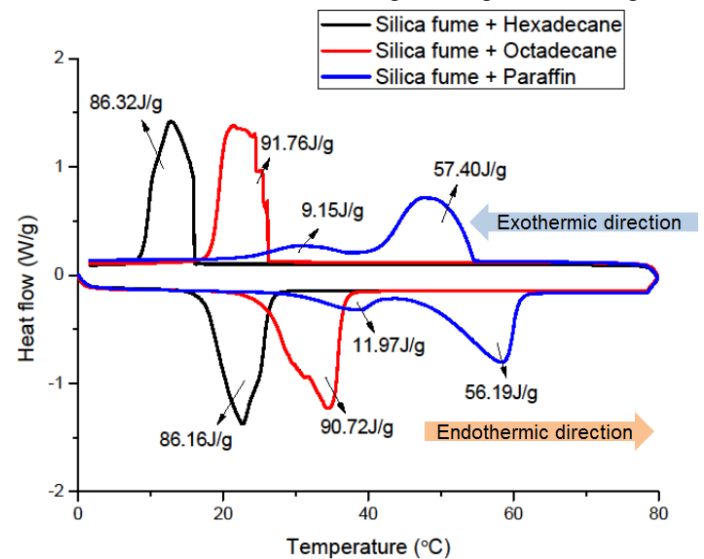


Figure 4 DSC analysis of PCM/silica fume composites.

Table 1 Heat storage properties of PCM/silica fume composites.

PCM Samples	Melting point (°C)	Freezing point (°C)	Latent heat (J/g)	
			solid-liquid melting	liquid-solid freezing
Hexadecane/silica fume	22.32 ± 5	12.85 ± 5	86.16 ± 3	86.32 ± 3
Octadecane/silica fume	33.61 ± 5	22.48 ± 5	90.72 ± 3	91.76 ± 3
Paraffin/silica fume	58.39 ± 5	49.04 ± 5	56.19 ± 3	57.40 ± 3

freezing processes. However, its latent heat capacity is small. Also, it is not difficult to find that the latent heat peaks of PCM still exist in the PCM/silica fume composites. The thermal characteristics of the PCM/silica fume composites, such as the melting and freezing temperatures, approach those of pure PCMs. This is because the PCMs are composed of silica fume, and there are no chemical reactions among PCM and silica fume during the impregnating process. Also, the incorporation rate of each PCM is 33.8, 36.6 and 38.8% of value for the pure PCMs. Although the latent heat capacity of the PCM/silica fume shows a slight decrease, compared to the pure PCMs, it is still enough to apply to a building material, such as concrete. Therefore, considering applications in building materials, the PCM/silica fume can still act to prevent the leakage of paraffin occurring, during the phase change from solid to liquid. As a result, we confirmed that the latent heat properties of PCM remained in the pores of the silica fume, and we expect that the PCM/silica fume composites can be used as thermal energy storage material, to apply to building material.

Thermal durability of PCM/silica fume composites

TGA is frequently used to analyze the thermal-durable property of PCMs. This property is important, because processes to manufacture various PCM products are subject to high temperature. The thermal durability property is one of the most important parameters for a composite PCM used in thermal energy storage applications, because it should be durable over its working temperatures. The thermal durability limits of the prepared composite PCMs were investigated by TGA analysis. TGA curves of PCM/silica fume composites are shown in Fig. 5. As shown in the graph, the weight loss processes of the PCM/silica fume composites were carried out in one step. In the case of the hexadecane/silica fume composite, the initial degradation step started at around 150°C, and finished at around 200°C. This degradation means oxidation of hexadecane, and also octadecane/silica composite, showed similar behavior. However, the thermal degradation curve of paraffin/silica fume composite started at around 200°C, which is higher than the other composite PMCs. This means paraffin has a high thermal durability property. For the hexadecane/silica fume, 50% of weight loss occurred between

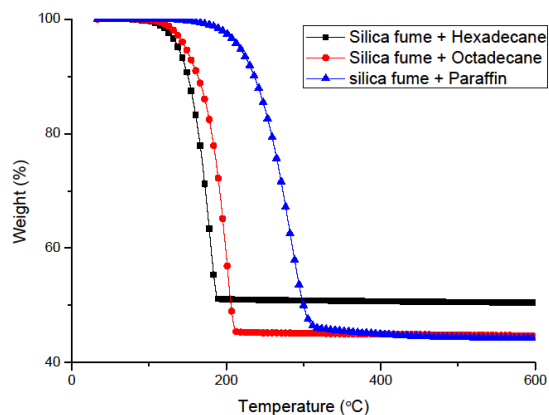


Figure 5 Thermal gravimetric analysis of PCM/silica fume.

150-200°C. As also seen from the octadecane/silica fume and paraffin/silica fume, composites lost composites, 55% of their weight in the range of 150-200°C and 200-300°C, respectively. Generally, PCM/silica fume composites show 50-55% degradation of weight. This means that the weight degradation of PCM/silica fume is attributed to the oxidation of PCM. Also, we determined that the silica fume remained after the oxidizing process. This shows that the PCM incorporated into the structure of silica fume, and the high thermally durable properties of silica fume, led to enhance the thermal durability of the PCM/silica fume composite. As a result, we determined that silica fume supplied not only the porous space to incorporate the PCM, but also its thermal retardant properties.

Chemical combination analysis

The FTIR absorption spectra of the PCM/Silica fume composites are shown in Fig. 6. This experiment was carried out to check whether or not there was the characteristic of chemical bonding. As can be seen in Table 2, the silica fume is composed of more than 85% silica. So, the silica peak showed in the FTIR graph. The most intense band at 1085 cm^{-1} is due to asymmetric stretching of the Si-O-Si bonding. This band usually appears between 1200 and 1000 cm^{-1} . Not only is this band very intense, but it has an asymmetric shape, which can be used as a diagnostic marker for the presence of silica in a sample. These stretching vibration bands have appeared after the compositing process with PCMs. This means that the chemical properties of silica fume were not changed. Also, the hexadecane, octadecane and paraffin have the same FTIR peaks, because these PCMs have a similar molecular structure, which is $\text{C}_n\text{H}_{(2n+2)}$. So the peaks of these PCMs show the stretching vibration of functional groups of $-\text{CH}_2$ and $-\text{CH}_3$. These FTIR absorption spectra have peaks of 2954, 2955 and 2961 cm^{-1} , which was caused by C-H₃ asymmetric stretch, and of 2870 and 2876 cm^{-1} , which were caused by C-H₃ symmetric stretch. Also, the 2920 and 2860 cm^{-1} peaks were caused by C-H₂ groups. As a result, these peaks of PCMs have not

Table 2 FTIR spectra of the PCM/silica fume composites.

Vibration	Wave number Range (cm^{-1})
Si-O-Si Asymmetric stretch	1200-1000 ± 10
silanol Si-O stretch	944 ± 10
Si-O-Si symmetric stretch	802 ± 10
C-H ₃ Asymmetric stretch	2954, 2955, 2961 ± 10
C-H ₃ Symmetric stretch	2870, 2876 ± 10
C-H ₂ Asymmetric stretch	2920 ± 10
C-H ₂ Symmetric stretch	2860 ± 10

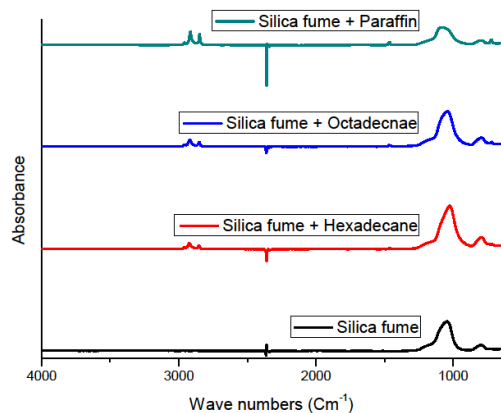


Figure 6 FTIR analysis of PCM/silica fume composites. disappeared from the FTIR graphs. Whole peaks of the silica fume and PCM have not changed, and have not disappeared. Therefore, this means that these composites are composed of the PCM and silica fume, by mechanical bonding. So the thermal properties of PCM were maintained in the structure of the silica fume; and its latent heat storage performance would be revealed, after applying mortar or concrete.

CONCLUSION

Recently, many studies have been carried out on the reduction of energy consumption. Therefore, we prepared PCM/silica fume composites for the reduction of energy, by improving thermal efficiency through latent heat storage. We manufactured these samples to apply to a building material, such as concrete. PCM/silica fume composites designed to produce high thermal performance were prepared through vacuum impregnation. Impregnation of PCM is one way to prevent leakage of liquid state PCM, and vacuum treatment is effective in conserving the thermal properties of pure PCM. We carried out experiments to confirm the characteristics of the PCM/silica fume composites, by SEM, FTIR, DSC and TGA analyses. SEM analysis showed that each PCM was completely incorporated into the pores of the silica fume. The peaks of pure PCM and silica fume are still shown in the PCM/silica fume composites peaks from the TGA analysis, because PCM/silica fume composites are composed of mechanical bonding between the pure PCMs and the silica fume. From the latent heat storage analysis, we confirmed that the PCM/silica fume composites have high latent heat storages, since each PCM was well incorporated into the structure of silica. Also, we found that the high thermally durable properties of silica fume led to an enhancement of the thermal durability of the PCM/silica fume composites. Consequently, we expect the PCM/silica fume composites to be useful for applying to building materials, such as concrete, due to the shape stability characteristics and high thermal performance of PCM/silica fume composite. In future research, this experiment has to be expanded, in order to obtain high heat storage properties and thermal durability.

ACKNOWLEDGEMENT

This research was supported by a Grant 13CHUD-C061954-02 from Construction & Transportation Technology Advancement Research Program funded by Ministry of Land, Infrastructure and Transport of Korean Government.

REFERENCES

- [1] L.F. Cabeza, A. Castell, C. Barreneche, A. de Gracia, A.I. Fernández, Materials used as PCM in thermal energy storage in buildings: A review, *Renewable and Sustainable Energy Reviews* 15 (2011) 1675-1695.
- [2] X. Zhang, P. Deng, R. Feng, J. Song, Novel gelatinous shape-stabilized phase change materials with high heat storage density, *Solar Energy Materials and Solar Cells* 95 (2011) 1213-1218.
- [3] A. Abhat, Low temperature latent heat thermal energy storage: Heat storage materials, *Solar Energy* 30 (1983) 313-332.
- [4] B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Applied Thermal Engineering* 23 (2003) 251-283.
- [5] S.D. Sharma, K. Sagara, Latent heat storage materials and systems: a review, *International Journal of Green Energy* 2 (2005) 1-56.
- [6] A. Sari, Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: preparation and thermal properties, *Energy Conversion and Management* 45 (2004) 2033-2042.
- [7] Z. Zhang, X. Fang, Study on paraffin/expanded graphite composite phase change thermal energy storage material, *Energy Conversion and Management* 47 (2006) 303-310.
- [8] Y. Zhang, J. Ding, X. Wang, R. Yang, K. Lin, Influence of additives on thermal conductivity of shape-stabilized phase change material, *Solar Energy Materials and Solar Cells* 90 (2006) 1692-1702.
- [9] X. Liu, H. Liu, S. Wang, L. Zhang, H. Cheng, Preparation and thermal properties of form stable paraffin phase change material encapsulation, *Energy Conversion and Management* 47 (2006) 2515-2522.
- [10] S. Jeong, J. Jeon, J. Seo, J. Lee, S. Kim, Performance evaluation of the microencapsulated PCM for wood-based flooring application, *Energy Conversion and Management* 64 (2012) 516-521.
- [11] X. Wang, J. Niu, A.H.C. van Paassen, Raising evaporative cooling potentials using combined cooled ceiling and MPCM slurry storage, *Energy and Buildings* 40 (2008) 1691-1698.
- [12] X. Xu, Y. Zhang, K. Lin, H. Di, R. Yang, Modeling and simulation on the thermal performance of shape-stabilized phase change material floor used in passive solar buildings, *Energy and Buildings* 37 (2005) 1084-1091.
- [13] B.M. Diaconu, Transient thermal response of a PCS heat storage system, *Energy and Buildings* 41 (2009) 212-219.
- [14] P. Zhang, Y. Hu, L. Song, J. Ni, W. Xing, J. Wang, Effect of expanded graphite on properties of high-density polyethylene/paraffin composite with intumescent flame retardant as a shape-stabilized phase change material, *Solar Energy Materials and Solar Cells* 94 (2010) 360-365.
- [15] Y. Wang, T.D. Xia, H. Zheng, H.X. Feng, Stearic acid/silica fume composite as form-stable phase change material for thermal energy storage, *Energy and Buildings* 43 (2011) 2365-2370.
- [16] P. Schossig, H.-. Henning, S. Gschwander, T. Haussmann, Micro-encapsulated phase-change materials integrated into construction materials, *Solar Energy Mater. Solar Cells*. 89 (2005) 297-306.

- [17] A. Karaipekli, A. Sari, Capric–myristic acid/expanded perlite composite as form-stable phase change material for latent heat thermal energy storage, *Renewable Energy*. 33 (2008) 2599-2605.
- [18] W. Wongkeo, A. Chaipanich, Compressive strength, microstructure and thermal analysis of autoclaved and air cured structural lightweight concrete made with coal bottom ash and silica fume, *Materials Science and Engineering: A*. 527 (2010) 3676-3684.
- [19] M.S. Amin, F.S. Hashem, Hydration characteristics of hydrothermal treated cement kiln dust–sludge–silica fume pastes, *Constr. Build. Mater.* 25 (2011) 1870-1876.
- [20] M. Mazloom, A.A. Ramezaniapour, J.J. Brooks, Effect of silica fume on mechanical properties of high-strength concrete, *Cement and Concrete Composites*. 26 (2004) 347-357.
- [21] H. Song, S. Pack, S. Nam, J. Jang, V. Saraswathy, Estimation of the permeability of silica fume cement concrete, *Constr. Build. Mater.* 24 (2010) 315-321.
- [22] G. İnan Sezer, Compressive strength and sulfate resistance of limestone and/or silica fume mortars, *Constr. Build. Mater* 26 (2012) 613-618.
- [23] A. Sari, A. Karaipekli, Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable PCM for thermal energy storage, *Solar Energy Mater. Solar Cells* 93 (2009) 571-576.
- [24] S. Kim, L.T. Drzal, High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets, *Solar Energy Mater. Solar Cells* 93 (2009) 136-142.
- [25] H. Kim, B. Lee, S. Choi, S. Kim, H. Kim, The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites, *Composites Part A: Applied Science and Manufacturing* 38 (2007) 1473-1482.