Mahmoud M. Reda Taha *Editor*

International Congress on Polymers in Concrete (ICPIC 2018)

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Chapter 23

Mortars with Phase Change Materials (PCM) and Stone Waste to Improve Energy Efficiency in Buildings

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The main objective of this contribution is the study of mortars with the incorporation of polymer-based phase change materials (PCM) for the improvement of energy efficiency in buildings. The mortars are intended for an indoor thermal comfort in the typical climatic conditions of the Southern European countries. Production waste, such as stone powder from quarry, will also be incorporated in the mortars. The finer powder is proposed as mortar aggregate and, at the same time, as support for the PCM. Firstly, different procedures aimed at effectively introducing the selected polymeric material (PEG) into the Lecce Stone have been performed. The chemical and thermal characterization of these compounds has been carried out. The LS/PEG composites have been, then, added to a mortar. Experiments are in progress in order to characterize from chemical, physical, and thermal point of view the mortars with and without PCM, following the recommendations of the international standards in this field. In addition, the studied materials will be used to build laboratory-scale prototypes that will be tested in real environmental conditions.

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1 Introduction

The world consumes a huge amount of fossil fuels and energy for heating and cooling buildings. This represents a serious global problem because a large use of fossil fuels increases climate change. Furthermore, these materials have high costs and the oil fields are running out rapidly [1]. For this reason, in the last two decades, research has been concentrated to find a possible way to reduce the negative environmental impacts through the study of environmentally friendly and renewable energy technologies [2].

The energy efficiency of buildings is one of the main objectives of international policy, because buildings are one of the largest energy consumers for heating and cooling necessities. Systems that can reduce the cooling/heating energy demand to maintain the internal thermal comfort are, then, constantly explored. The use of phase change materials (PCM) in building applications has been found as a suitable method to stabilize the indoor temperature [3]. The operating principle of PCM consists of a change in their status, according to the environment temperature [4]. During daytime, when the temperature is higher, the PCM melts and retains part of the heat involved in the melting process; then, this material possesses the capability to release the previously stored energy when the temperature decreases, changing its status from liquid to solid [5]. A wide variety of materials with different melting point ranges is employed as PCM. Based on their chemical composition, these materials are classified as organic, inorganic, and eutectic [2, 6].

Suitable phase change materials for thermal energy storage of buildings must have, above all, melting temperature lying in the practical range of operation, large latent heat of fusion/crystallization, and high thermal conductivity. Chemical stability, small volume variation during solidification/melting, low toxicity, and low costs are also required [3]. The recent research in this field depicts a rising interest on the use of PCM in mortars [7]. Different methods of PCM incorporation in mortars make it possible to obtain systems with different characteristics and different energy efficiency [8].

Starting from previous experiences [9], a research aimed at incorporating a polymer-based phase change material in a mortar has been undertaken. Materials intended for indoor thermal comfort in climatic conditions typical of the Southern European countries have been considered. Stone powder from waste production was adopted as support for the PCM, and the same powder will be used as mortar aggregate. The use of natural stone waste represents an element of novelty. This choice allows exploiting the waste materials, pursuing the environmental protection strategies. The chemical and thermal characterization of both the PCM and the stone material was first performed. The same investigations were repeated on the PCM-stone composites obtained after mixing under vacuum for different time spans.

Fig. 23.1 Lecce Stone in flakes (a) and sieved Lecce Stone (b)

Table 23.1 Sample of PCM-stone composites

Sample	LS [g]	PEG 1000 (g)	Vacuum time (min)	Impregnation time (min)
LS/PEG-10	10.0	1.0	30	10
LS/PEG-30	10.0	1.0	30	30
LS/PEG-60	10.0	1.0	30	60

2 Materials and Methods

Lecce Stone (LS) was used as supporting matrix. This is a typical stone of South Italy (quarries located near Lecce, in the Apulia region), composed of CaCO_3 (92–95%) and in a smaller percentage of glauconite, quartz, feldspar, muscovite, phosphate, and clay materials. The material provided by a local company was in the form of flakes (Fig. 23.1a), and it was sieved to obtain little granules (Fig. 23.1b) with granulometry between $1.0 \text{ mm} > x > 2.0 \text{ mm}$.

Polyethylene glycol 1000 (PEG1000) selected as PCM was purchased from Sigma-Aldrich company (Germany). PEG1000 was chosen since its melting temperature is in the range $37\text{--}40^\circ\text{C}$ and it is non-toxic and eco-friendly.

PEG1000 was incorporated into the stone granules using a shape-stabilization principle, due to its lower costs of production. The chosen amount (i.e., 10 g) of Lecce Stone was placed in a flask. Air removal was performed at the vacuum pressure of 0.1 MPa for 30 min. Then, PEG1000, previously heated in oven at 80°C , was added to the stone, in order to obtain LS/PEG composites, using different mixing times (from 10 to 60 min).

Composition and details of production for each system are reported in Table 23.1.

A FT-IR Thermo Nicolet Nexus spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector, was used for the chemical characterization of the produced systems as well as the pristine materials. The samples, mixed with KBr, were analyzed in transmission mode. The spectra were acquired in the range of $4000\text{--}400 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} and 32 scans per measurement; the background spectrum was collected on a pellet made of KBr only.

Fig. 23.2 (a) FT-IR spectra of LS, pure PEG and PCM-stone composite. (b) TGA curves of pure PEG and PCM-stone composites

Table 23.2 TGA analysis: degradation temperatures and percentage composition of pure PEG and PCM-stone composites

Sample	Onset (°C)	Endset (°C)	Residual mass (%)	Amount of PEG (%)
PEG1000	289.3	401.1	1.7	100
LS/PEG-10	219.1	286.0	80.5	19.5
LS/PEG-30	218.2	296.1	78.0	22.0
LS/PEG-60	219.1	292.6	77.0	23.0

The thermal properties were measured by a DSC1, and the thermal degradation temperature was measured by a TGA/DSC1, both instruments by Mettler Toledo.

3 Results and Discussion

The FT-IR spectra of the composite materials are very similar to one another, irrespective of the impregnation time. The absorbance bands of PEG are the main peaks (Fig. 23.2). The absence of new signal proves that no chemical interaction occurred between PEG and the stone material. In fact, slight shifts (e.g., the peak at 1114 cm^{-1} shifted to 1104 cm^{-1}), observed in the spectra of the composites, indicate some physical attractions, including hydrogen bonds [10, 11], between the two components. The hydrogen bonds occurring in the composite can contribute to the stability of the PCM material because the PEG molecules are tied to the stone and lose their freedom of motion.

To evaluate thermal resistance and the degradation temperature, TGA analysis was used. The related results are shown in Fig. 23.2b and briefly summarized in Table 23.2.

Thermal resistance is one of the most important properties for a selected PCM for a thermal energy storage (TES) application. In this case, the selected PCM and the

Fig. 23.3 DSC curves of the pure PEG and PCM-stone composites

Table 23.3 LHTES properties of PCM and of PCM-stone composites

Sample	Heating		Cooling	
	T _m (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)
PEG1000	42.8	129.3	23.6	129.8
LS/PEG-10	38.4	28.2	18.5	28.7
LS/PEG-30	38.2	31.1	20.4	31.3
LS/PEG-60	39.3	27.7	19.4	26.2

produced PCM-stone composites were characterized between 25 and 450 °C. The same range of temperatures was used to test the PCM-stone composites, to ensure the complete degradation of PEG inside. As shown in Fig. 23.2b, PEG1000 begins to lose weight at 290 °C, and the degradation process is complete just above 400 °C. For this reason, the selected PCM can be regarded as a material with high thermal resistance and good thermal stability, as reported in literature [11].

The complete degradation of PEG in the PCM-stone composites occurs at a lower temperature than the pure PEG, irrespective of the amount of PCM into the stone.

TGA analysis was also employed to evaluate the amount of PEG truly absorbed by the granules of LS. The percentage of PEG contained in each PCM-stone composite is around 20% by weight. It was, then, concluded that the granules of stone were effectively impregnated by PEG1000 using the procedure under vacuum, increasing the amount of PEG by increasing the impregnation time.

To evaluate latent heat thermal energy storage (LHTES) properties of PCM-stone composites, the melting temperature and latent heat capacity were measured. Figure 23.3 shows the DSC thermograms of pure PEG1000 and of PCM-stone composites, including heating and cooling cycles. Table 23.3 summarizes melting (T_m) and crystallization (T_c) temperatures with the relative latent heat of melting (ΔH_m) and crystallization (ΔH_c) for each system.

As seen in Fig. 23.3 and in Table 23.3, PEG1000 and PCM-stone composites show endothermic (melting) peaks at around 38–40 °C during the heating stage and crystallization peaks at about 20–25 °C during cooling. The reduced values of melting and crystallization enthalpies found for LS/PEG samples are related to the lower amount of PEG into the PCM-stone composites.

4 Conclusions

The production of LS/PEG composites under vacuum has proved to be successful in effectively impregnating the granules of stone. All the obtained materials exhibit high thermal resistance and good stability. No significant differences in properties are observed changing the impregnation time. However, LS/PEG-60 can be judged more favorable than others, since the longer impregnation time can insure a deeper penetration of PEG and, in turn, a further increased stability.

The measured properties confirm that these materials can be regarded as promising candidates for building applications. Starting from this characterization, tests of addition of LS/PEG to mortars are in progress in order to evaluate the behavior of the obtained materials as PCM. The developed mortars, in fact, should present adequate characteristics in fresh and hardened states.

Acknowledgments The authors wish to thank Ing. L. Pascali and staff of S.I.PRE. S.r.l. (Cutrofiano, Lecce, Italy) for the technical support and Pitardi Cavamonti Company (Melpignano, Lecce, Italy) for supplying the Lecce Stone flakes.

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