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Development of calcium silicate-coated expanded clay based form-stable phase change materials for enhancing thermal and mechanical properties of cement-based composite

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ABSTRACT

In this study, the thermal energy storage cement mortar (TESCM) was developed by incorporating calcium silicate-coated paraffin/expanded clay based form-stable PCMs (CS-ECPCM). The thermophysical properties, microstructure and spectroscopic characterization of CS-ECPCM and the thermal and mechanical properties of the TESCM were investigated. MIP and SEM results show that the paraffin mixture consisted of 52# paraffin and liquid paraffin can be well impregnated into expanded clay (EC) pores. The thermal-cycling test results indicate the good thermal stability of CS-ECPCM by the cladding of three-layer calcium silicate. And DSC results reveal that the CS-ECPCM has the phase change temperature and latent heat of 23.67 °C and 24.43 J/g, respectively, and the lower phase change temperature of CS-ECPCM compared with pure paraffin mixture can be supported by FT-IR and Raman spectra results. Furthermore, the CS-ECPCM was incorporated in cement mortar at 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100%, by weight of sand. However, the interfacial zone structures between CS-ECPCM and cement has been enhanced by secondary encapsulation of calcium silicate, relieving the decrease in the compressive strength of TESCM. In addition, the thermal conductivities of the TESCMs decrease with the increase of mixing amount of CS-ECPCM, which are positive to their thermal insulation performance. And the excellent thermal energy storage performance of TESCMs is clearly suggested by the results of specific heat capacity test and heating test.

1. Introduction

The building energy consumption has occupied a considerable proportion in the global energy consumption. Thus, the building energy conservation design has become an effective way of alleviating the energy shortage, promoting the national economic development (Memon, 2014; Pérez-Lombard et al., 2008). A promising technique is to utilize the abundant solar energy resources in the form of thermal energy storage in buildings. By means of the endothermic and exothermic characteristics, solar energy storage in buildings can be achieved with the incorporation of PCMs (Baetens et al., 2010; Ramakrishnan et al., 2017). As a prospective solid-liquid PCM, paraffin is one type of organic PCMs and has been extensively used in solar energy storage applications due to its high energy storage density, little or no sub-cooling and smaller volume change(Das et al., 2012; Kheradmand et al., 2015; Xu et al., 2015). Moreover, of the common paraffin PCMs, 52# paraffin with the phase change temperature about 50–55 °C, is popularly used as a PCM because of its moderate price. It is known that the phase change temperature within the range of around 22 and 28 °C can be used in the applications of building thermal comfort for solar energy storage (Cabeza et al., 2011). Thus, the 52# paraffin cannot meet the requirement for the adjustment of building thermal comfort. However, benefiting from the eutectic phenomena that the phase change temperatures of many PCMs can be adjusted by mixing with other PCM (Liu and Yang, 2017; Yuan et al., 2011), a paraffin mixture PCM consisted of 52# paraffin and liquid paraffin is designed, and the appropriate phase change temperature is expected.

Of the most commonly used building materials, cement-based materials have been widely used for building components and are considered to be suitable for incorporation of PCMs (Cui et al., 2015a; Sharifi and Sakulich, 2015; Zhang et al., 2013). Two methods are mainly proposed to incorporate PCMs into cement-based materials.

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Nomenclature

I (t)	pulse heating current
T(x, t)	temperature response
K	heat transfer coefficient
λ	thermal conductivity
δ	thickness of sample

Direct immersion method is simple and low cost, but more vulnerable for the leakage of PCMs from cement-based materials after several heating-cooling cycles (Lee et al., 2000); PCMs can also be impregnated in cement-based materials in the form of form-stable PCMs (Konuklu et al., 2015; Liu et al., 2018). Considering the cost reduction and the simplification of procedure, the form-stable PCMs can be prepared by incorporating PCMs into inorganic porous materials, which are abundant and readily available, such as diatomite (Lorwanishpaisarn et al., 2016), vermiculite (Deng et al., 2016), attapulgite (Liang et al., 2014) and expanded graphite(Liu and Yang, 2018), etc. Expanded clay (EC), also named as ceramsite sand, is screened from the ceramsite with the size less than 5 mm. EC is mainly used to replace natural sand for the preparation of lightweight aggregate concrete and light mortar to reduce the building weight. Meanwhile, it can also be used as the fine aggregate for acid and heat-resistant concrete due to the good chemical and thermal stability. As a type of porous support materials, EC can not only prevent the leakage of PCM, but also improve the mechanical properties for the PCM. Therefore, the EC is taken as the inorganic porous materials for the encapsulation of the paraffin mixture PCM.

However, the solid-liquid PCMs still prone to leak from EC after a great deal of heating-cooling cycles, which is the prevalent problem of inorganic porous building materials based form-stable PCMs. To settle this problem, a method of secondary encapsulation has been proposed recently to prevent the further leakage of form-stable PCMs. Li et al. (Li et al., 2016; Li et al., 2014) presented a new method to prevent the leakage of expanded perlite/paraffin and diatomite/paraffin phase change material by using hydrophobic nanosilica as surface coating material. Memon et al. (Cui et al., 2015b; Memon et al., 2015a; Memon et al., 2015b) prepared PCM composites by absorbing paraffin into different types of porous support materials and used epoxy coatings to encapsulate the surface of PCM composite for leakage prevention. In the work reported by Yuan et al. (2018), in order to obtain a more stable composite PCM, a polymer-coated $CaCl_2{\cdot}6H_2O$/EG composite PCM has been synthesized by adsorbing $CaCl_2{\cdot}6H_2O$ into EG, followed by coating with the photo-cured polymer. Unfortunately, the incorporation of hydrophobic nanosilica, epoxy coatings and photo-cured polymer was disadvantageous to the compressive strength of cement-based composites because of the hydrophobic characteristic of surface. Wang et al. (Wu and Wang, 2015) produced a hydrated salt/expanded graphite composite PCM by direct impregnation method. And paraffin was used as a coated shell material to further improve the stability of composite PCM. In the work reported by Chen et al. (2014), a novel PCM capsules with SiO_2 on their surface was prepared by incorporating paraffin into PVC hollow capsules and by the polycondensation reaction of TEOS in different conditions. Subsequently, in order to further improve the seal of the PCM capsules, the secondary SiO_2 layer was synthesized out of the first SiO_2 layer (Chen et al., 2017). However, the paraffin and SiO_2 shells are easily broken during the mixing process when incorporated into cement substrate, leading to the leakage of PCMs. Furthermore, the interface compatibility of paraffin and cement substrate is poor, which causes the strength reduction of thermal energy storage mortar. Therefore, it is urgent to develop a coating material for secondary encapsulation with the advantages of easy fabrication, higher strength and good compatibility with cement substrate. To solve this problem, a novel coating material, calcium silicate, is proposed as a shell structure to clad the EC incorporated with PCMs, for the purpose of leakage preventing. Moreover, the good compatibility between calcium silicate and cement substrate has a positive effect on the combination and interfacial defects reduction of form-stable PCMs and cement substrate.

In this study, a novel binary paraffin mixture with 52# paraffin and liquid paraffin was developed as PCM, which supplies a suitable application temperature with higher latent heat. The expanded clay based form-stable PCM (ECPCM) was prepared by adsorbing the binary paraffin mixture PCMs into the pores of expanded clay (EC). Meanwhile, an encapsulation process of three-layer calcium silicate coated shell was designed to prepare the calcium silicate-coated expanded clay based form-stable PCMs (CS-ECPCM). And the thermal stability and the thermophysical properties were examined as well. Then the CS-ECPCM was added into cement mortar by mechanical blending to prepare the thermal energy storage cement mortar (TESCM). The microstructure, spectroscopic characterization and thermophysical properties of CS-ECPCM were discussed in detail, and the mechanical properties, thermal conductivity and specific heat capacity of the TESCM samples with different contents of CS-ECPCM were investigated. The thermal energy storage performances of the TESCM boards containing different contents of CS-ECPCM were evaluated as well.

2. Materials and experimental methods

2.1. Raw materials

Liquid paraffin and 52# paraffin were supplied by the Beijing Reagent Company and used to prepare the paraffin mixture. The phase change temperatures of liquid paraffin and 52# paraffin are −82 °C and 54.1 °C, respectively; the latent heats of liquid paraffin and 52# paraffin are 62.8 J/g and 140.5 J/g, respectively. The properties of expanded clay are shown in Table 1. The pore size distribution of expanded clay is measured by mercury intrusion measurement (MIP), and the obtained result is demonstrated in Fig. 1. It can be observed the pore size of EC is mainly distributed in 100–1000 nm. Calcium chloride ($CaCl_2$, AR) was purchased from Harbin Xinchun Chemical Factory. The properties of potassium silicate solution used in this work are shown in Table 2. The P·O 42.5 ordinary Portland cement was purchased from Yatai Co. Ltd (Tianepai Cement, China, Harbin) complied with GB175-1999. Table 3 shows the physical properties of sand; Grade I fly ash used in this study was produced in the Harbin No. 3 Generating Station.

2.2. Preparation of binary paraffin mixture PCMs

The binary paraffin mixture PCMs were prepared by the replacement of liquid paraffin with 5, 10, 15 and 20 wt% 52# paraffin, respectively. The paraffin mixture PCMs were filled into a small beaker, melting completely at 100 °C in high temperature oven for 30 min, and then the molten paraffin mixture were stirred until uniform. Then the prepared paraffin mixture PCMs were cooled down to the room temperature. The mass ratio, melting temperature and latent heat of binary paraffin mixture PCM were determined by DSC.

2.3. Preparation and characterization of CS-ECPCM

The binary paraffin mixture was impregnated into expanded clay (EC) directly without vacuum treatment as a result of the trivial latent

Table 1
Properties of expanded clay.

Particle size (mm)	Sphericity	Volume density (kg/m^3)	Crushing value index (%)		
			52 MPa	69 MPa	86 MPa
≤ 5	0.9	748.6	6.0	8.5	29.4