Applications of graphite-enabled phase change material composites to improve thermal performance of cementitious materials

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Abstract. Enhancing the thermal efficiency to decrease the energy consumption of structures has been the topic of much research. In this study, a graphite-enabled microencapsulated phase change material (GE-MEPCM) was used in the production of a novel thermal energy storage engineered cementitious composite feathering high heat storage capacity and enhanced thermal conductivity. The surface morphology and particle size of the microencapsulated phase change material (MEPCM) were investigated by scanning electron microscopy (SEM). Thermal properties of MEPCM was determined using differential scanning calorimetry (DSC). In addition, thermal and mechanical properties of the cementitious mortar with different admixtures were explored and compared with those of a cementitious composite. It was shown that the latent heat of MEPCM was 162 J/g, offering much better thermal energy storage capacity to the cementitious composite. However, MEPCM was found to decrease the thermal conductivity of the composite, which can be effectively solved by adding natural graphite (NG). Moreover, the incorporation of MEPCM has a certain decrease in the compressive strength, mainly due to the weak interfaces between MEPCM and cement matrix.

1. Introduction
In recent years, building structures consume enormous amounts of energy due to population growth, the increasing demand for thermal comfort and the fact that more and more people spend their time indoor [1-3]. Decreasing the energy consumption of structures by enhancing their energy efficiency has become significant research topic worldwide during the last two decades [4, 5]. Incorporation of thermal energy storage systems in buildings is regarded as a feasible way of enhancing energy efficiency [6]. Compared to the other two thermal energy storage types, which are sensible heat storage and chemical reaction heat storage, latent heat storage with PCMs has remarkable advantages like high-energy storage density and the isothermal nature during the energy storage process, rendering it an attractive material for saving energy and improving occupant comfort of buildings [7-9].
Cementitious materials are considered suitable for incorporation of PCMs because it is one of the most extensively used construction material around the world. The large thermal mass of concrete walls, ceilings, and floors with PCMs can be well used to store energy during the day time and release it during night time. To effectively enhance the thermal storage capacity of concrete, much research [10-12] has been conducted by using phase change materials (PCMs) during recent decades. Xu et al. [3] presented their study on incorporating a paraffin/diatomite composite phase change material to concrete for improving the thermal performance. Their results revealed that the PCMs effectively enhance the ductile performance and heat energy storage capacity. Sharifi and Sakulich [13] stated that adding PCM in mortar increases the thermal mass and delays temperature changes. However, a compressive strength loss was found in both researches. It is caused by significant disparity between the cementitious material and the microencapsules. In addition, partially leakage caused by the damage of the microencapsules during the mixing process and subsequent interference with the surrounding materials is another reason resulting in the compressive strength loss.

Among different types of PCMs, microencapsulated PCM (MEPCM) turns out a promising candidate due to its non-leakage property and relatively high heat of fusion. It is composed of n-octacosane as core PCM and a polymer shell for keeping liquid PCM from leaking during the phase change process. However, both the PCM inside and the polymer shell have an even lower thermal conductivity than cement matrix, so the incorporation will cause temperature gradient when a temperature difference exists, further resulting in thermal cracks of the cementitious composite. Several studies have been directed to the improvement of concrete thermal conductivity [14-16]. Lie et al. [14] investigated the use of steel fiber in the concrete mixture to improve thermal properties. Fu et al. [16] reported their tests on the use of different additives, including silica fume, latex, methylcellulose and carbon fibers, on the thermal conductivity of cement paste. Clearly, the literature review shows that although there are studies that addressed either of two aspects (i.e., the low thermal conductivity and low thermal storage capacity), very limited information is available to consider both in the design of the building materials. This study is to investigate the feasibility of using graphite-enabled PCM composite for the enhanced thermal management of cementitious material. A series of laboratory tests such as SEM and DSC were performed to characterize the morphology and thermal behavior of different mixtures. In addition, heat transfer and compressive strength test were conducted to examine the thermal and mechanical properties of the composite.

2. Experimental program

2.1 Specimen Preparation

Technical-grade MEPCM purchased from Microtek Laboratories, Inc. were used as the PCMs. They are very small bi-component particles consisting of a core material—octadecane—and an outer shell or capsule wall. The melting point of MEPCM is 109.4 °F (43°C). NG (Grade 3772) donated by Asbury Carbon, Inc. was selected as a heat exchanger to enhance the thermal conductivity of the composite, which has an average particle size of 300 µm. In order to reduce the number of influence factors and focus the research on the thermal property, conventional mortar consisting of water, Type I Portland cement, and natural sand was prepared, excluding the effect of coarse aggregate. To achieve more homogeneous mortar mixtures, viscosity modifying admixture (VMA) and water reducer were used at a weight ratio of 7.95:1000 to cement. In this test, seven mix proportions were used with the same water/cement ratio of 0.35 (Table 1). The specimen of heat transfer test and compressive strength test was prepared by casting a 50×50×50 mm3 (2×2×2 in3) cuboid mold. The samples were compacted by tempers in two layers.
Table 1. Mix proportion of mortar with different admixtures

| Groups          | Cement (kg/m³) | Water (kg/m³) | Natural Sand (kg/m³) | VMA (kg/m³) | Water Reducer (kg/m³) | NG (m³/m³) | MEPCM (m³/m³) |
|-----------------|---------------|---------------|----------------------|-------------|-----------------------|------------|---------------|
| Reference       | 1000          | 350           | 857                  | 7.95        | 7.95                  | 0          | 0             |
| 10% NG          | 900           | 315           | 771.4                | 7.16        | 7.16                  | 0.1        | 0             |
| 20% NG          | 800           | 280           | 685.71               | 6.36        | 6.36                  | 0.2        | 0             |
| 15% MEPCM       | 850           | 297.5         | 728.57               | 6.76        | 6.76                  | 0          | 0.15          |
| 30% MEPCM       | 700           | 245           | 600                  | 5.57        | 5.57                  | 0          | 0.3           |
| 10%NG +15%      | 750           | 262.5         | 642.86               | 5.96        | 5.96                  | 0.1        | 0.15          |
| 20%NG +15%      | 650           | 227.5         | 557.14               | 5.17        | 5.17                  | 0.2        | 0.15          |

2.2 Sample characterization
The morphology of MEPCM and its interface with cement matrix was explored using a scanning electron microscope (SEM). DSC measurements of MEPCM were carried out on a Differential scanning calorimeter (DSC2910, TA Instrument Inc., USA) under N2 atmosphere. The typical mass of the sample was about 4mg, and the scanning rate was 5°C/min.

2.3 Heat Transfer and Compressive Strength Tests
In the thermocouple heat transfer test, the operating principle is based on the association of a heating device with temperature sensors. A data logger was connected to the thermocouples (type T) to record the temperature increase on the top surface of the specimen during a predetermined temperature range. The hot plate was used as a heating device to provide a constant temperature (80 °C) for the bottom of the specimen.

ASTM C109/109M was followed for the compressive strength test of the mortars. After mixing, mortar was placed in 50mm (2 in) cube plastic molds for 24h. Then they were demolded and cured at room temperature (22 °C) with relative humidity of 16% till the day of testing (3, 7, and 28 days). For each mix, the compressive strength is calculated as the average value of three repeated samples.

3. Results and discussions

3.1 Morphology and Thermal Energy Storage Capacity Investigation
Surface morphology of obtained MEPCM was studied by SEM. Figure 1(a) shows that the particles size of MEPCM is 5-15 µm. During phase change process, the capsule wall can effectively maintain liquid materials and avoid the PCM from leaking. Figure 1(b) indicates that the heat of fusion of MEPCM is 162.0 J/g, which make it a promising material for thermal energy storage application. In addition, the material starts to melt at 41.67 °C, which is very close to the nominal melting point of 43°C.
3.2 Heat Transfer Speed

Heat transfer test aims at investigating the effect of MEPCM and NG on the thermal conductivity of mortar paste. The heat transfer speed was calculated as the average temperature of three samples cured for 28 days. Figure 2(a) shows that the addition of MEPCM results in an obvious reduction of thermal conductivity. This can be explained by the enhanced air content and the low thermal conductivity of MEPCM. Moreover, the temperature increasing tendency of the sample with 30% MEPCM indicates that phase transition from solid to liquid lasts from 64.7min (38.75°C) to 108.5 min (45°C), which centers on the melting point of MEPCM. During this period, a large amount of latent heat was stored in the composite, which can be released when the ambient temperature drops. Figure 2(b) reveals that NG significantly increases the heat transfer speed of the mortars, rendering it an attractive candidate as a heat exchanger.

The effect of a combination of MEPCM and NG on thermal conductivity of the mortar was presented in Figure 3. It can be observed that NG contributed a lot to the heat transfer speed enhancement of the composite with 15% MEPCM. When 20% NG is added, the heat transfer rate of the composite with 15% MEPCM is even higher than the reference mortar. The addition of a combination of MEPCM and NG can introduce the mortar thermal energy storage capacity without decreasing the thermal conductivity of the cementitious composite.

Figure 1. Characterization of MEPCM

Figure 2. Heat transfer speed comparison of mortars with different additives
3.3 Compressive strength

The Compressive strength of the mortars was measured in accordance with ASTM C109/C109M. Figure 4(a) shows the compressive strength development of the mortars (cured for 28 days) with different amount of MEPCM and NG. It can be observed that the corporation of different admixtures reduces the compressive strength of mortar in different levels. The reduction effect on compressive strength can be listed as follows: NG together with PCM > NG > MEPCM. This can be explained by the hydrophobic property of the graphite product and MEPCM, which results in a bonding strength reduction of the cement paste. It can be found in Figure 4(b) that there are some gaps between the cement matrix and NG (position 1) as well as MEPCM (position 2), which can result in the compressive strength loss of the composite. Moreover, some PCM capsules can be damaged (see position 3 in Figure 4(b)) with the PCM inside filling surrounding cement matrix during the mixing process, resulting in further compressive strength loss of the cementitious composite.

![Figure 3. Heat transfer of mortars with a combination of MEPCM and NG](image)

(a) Compressive strength of different mixtures

(b) SEM image of mortar with 10% NG and 15% MEPCM

Figure 4. Compressive strength of mortars with different additives and the SEM image of one composite

4. Conclusions

This study developed an innovative graphite-enabled phase change material composite that is capable of inducing thermal energy storage capacity and high thermal conductivity to the cementitious composite. The test results demonstrated that MEPCM in the composite can absorb and store a large amount of latent heat during phase transition from solid to liquid. Moreover, the incorporation of NG significantly increased the thermal conductivity of the mortars. The thermal efficiency of cementitious composites was improved a lot by adding both of MEPCM and NG, without decreasing their compressive strength too much. Further work needs to be carried out to enhance the hydrophilic
property of the graphite by surfactant treatment to increase the bond strength of the cement paste and admixtures.

5. References
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