THE EFFECT OF MICROENCAPSULATED PHASE-CHANGE MATERIAL ON THE COMPRESSIVE STRENGTH OF STRUCTURAL CONCRETE

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ABSTRACT

Latent heat energy storage through phase-change materials (PCMs) is one possible strategy to control interior temperatures in buildings, improve thermal comfort, and passively reduce building energy use associated with heating and cooling. While PCMs integrated into building structure elements have been studied since the 1970s, challenges of integrating PCMs into building materials while maintaining their heat storage benefits have limited their application in practice. The recent introduction of microencapsulated phase-change materials provides the energy storage capability of PCMs in micron-scale, chemically-inert capsules that can be easily integrated into composite materials such as gypsum wallboard and concrete. The size and physical properties of microencapsulated PCMs suggest that they will behave similarly to filler materials in concrete. Such filler materials are generally less than 125 μm in diameter and can increase concrete strength when added to a mix. This study uses the compressive strength of hardened concrete mixes with varying amounts of PCM to evaluate the effect of PCM addition on concrete structural integrity.

KEYWORDS

building energy efficiency, phase change materials, green building, concrete, compressive strength

1. INTRODUCTION

As of 2010, 41% of energy consumption in the United States can be attributed to building energy use, and a significant proportion of this energy use is for heating and cooling of buildings (US Department of Energy 2011). As energy supplies dwindle and become more expensive, passive methods of controlling environmental temperature in buildings will become more valuable. In the absence of heating and cooling systems, the daily air temperature in the interior of a building will fluctuate substantially and often be outside the acceptable range for human comfort. Passive methods of maintaining temperatures within desirable comfort limits include the use of latent heat energy storage materials, also known as phase-change materials

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(PCMs). The ability of these materials to absorb heat when the ambient temperature exceeds their melt temperature, and release heat when it declines past the solidification temperature, all by storing the energy as latent heat rather than changing temperature, allow them to significantly reduce peaks and troughs in the diurnal fluctuation of indoor air temperature. This can result in improved thermal comfort, the reduction in energy consumed for heating and cooling, or both.

The ability of PCMs to effectively store and release heat is dependent on the quantity and melting temperature of the PCM, as well as the thermal environment to which it is exposed. Elements of building structure are ideal candidates for PCM integration due to their volume and surface area exposure to the interior environment. Concrete in particular is very favorable due to its extensive use in the building industry and its nature as a composite material that can be custom-mixed for each application. The advent of microencapsulated PCMs (ME-PCMs) has made the energy storage benefits of PCMs more flexible and useful than at any time in the past, and their integration in structural concrete may be a key strategy in passive building energy use reduction.

2. BACKGROUND

2.1. A review of latent heat energy storage

Materials undergoing a phase transition store or release energy according to the enthalpy value of the phase transition for the material. They do this without changing temperature until the phase transition is complete. A common example of this phenomenon is ice melting to form liquid water.

From a thermodynamic point of view, some of the key criteria for the selection of a latent heat energy storage material are a high latent heat of fusion; a melting point within the desired operating temperature range; and high specific heat, density, and thermal conductivity. For practical implementation, other factors are also important, including chemical stability, flammability, toxicity, degradation over many freeze/thaw cycles, and cost. Early research focused on common salt hydrates, which have the advantage of high latent heats of fusion, but which suffer from chemical and thermal instability and recurring issues with uneven cooling preventing full phase transitions (Zalba et al. 2003). Resurgence of research interest in phase-change materials for building applications followed the energy crisis of the 1970s, with a focus on a collection of organic compounds, primarily paraffins, fatty acids, esters, alcohols, and glycols (Zalba et al. 2003). Organic phase-change materials do not have the chemical instability and undercooling problems of inorganic materials, but generally have lower enthalpy and thermal conductivity values. In recent years, research has explored eutectic phase-change materials. The development of PCM technology and the properties of many PCMs are extensively covered by Kenisarin and Mahkamov (2007). Thermophysical properties of some common PCMs and comparison materials are given in Table 1.

For centuries, the sensible heat storage properties of common building materials like stone and concrete have been used to modulate indoor ambient temperatures without the need for mechanical heating or cooling. For example, concrete has a sensible heat capacity of roughly 0.88 kJ/kg °C (each kilogram of concrete can store 0.88 kJ of heat for every one degree C increase in temperature). As sophisticated building methods and efficient materials

TABLE 1. Sample material thermophysical properties (Farid et al. 2004), (Hawes et al. 1993).

Material	Phase-Change Temperature (°C)	Latent Heat Capacity (J/g)
Water	0	334
Potassium fluoride tetrahydrate (a salt hydrate)	18.5	231
Sodium sulphate decahydrate (a salt hydrate)	32.4	254
Butyl stearate (an organic PCM)	19	140
Paraffin (an organic PCM)	20–60	~200

came into use in the 20th century, buildings became significantly less massive, resulting in less sensible heat storage capability. This phenomenon coincided with the development and widespread deployment of mechanical heating and cooling, during a period of relatively inexpensive energy. As current design practice shifts to more of a focus on minimizing energy use in buildings, the prospect of latent heat energy storage within building materials is gaining interest—the large difference in the latent heat capacity of modern PCMs compared to the sensible heat capacity of traditional building materials suggests that the energy storage effects of massive buildings can not only be regained in modern, lightweight buildings, but surpassed.

Pasupathy et al. (2008) published a concise but comprehensive review of methods of integrating PCMs into building structures. Two broad approaches have been used to take advantage of latent heat energy storage in buildings. One of the most studied approaches is the construction of specially designed "PCM walls". These include simple designs that allow PCM to absorb much of the incident solar radiation on the wall. In hot climates, this can shift the cooling load to off-peak electricity rate periods. A similar but more sophisticated approach can be used in cool climates by designing the wall with a glass layer to trap solar gain, absorb it into an interior PCM layer, then release it to the interior of the building, providing free heating. In areas subject to large ambient temperature fluctuations, free cooling can be achieved by "storing" nighttime coolness in the PCM. These approaches typically rely on cavities in building structure to house the PCM, which increases construction cost, presents the risk of leaking when damaged, and in general has been shown to lead to uneven cooling, which has a significant negative effect on the heat transfer ability of the PCM.

A second approach has been the incorporation of PCMs into the interior building structure material, primarily in gypsum wallboard and in concrete. Gypsum wallboard designs generally include 20 to 25% by volume of paraffin-based PCM added to the gypsum plaster mix. Commercial PCM wallboard products are starting to become available on the market in some countries. Despite the large quantity of concrete used in building construction, particularly in commercial and industrial buildings, relatively little attention has been given to the integration of phase-change material into concrete and the bulk of the research in this area has focused on manufactured concrete blocks (Hawes et al. 1989; 1990; 1992; 1993). The primary hurdle to direct incorporation of PCMs into wet concrete has been the effect of the PCMs on the concrete curing process. Research has demonstrated that thermally effective PCM concrete blocks can be manufactured, but that there remain significant limitations with respect to composition and cost.

2.2. Microencapsulated phase-change materials

In general, microencapsulated phase-change materials (ME-PCMs) are standard phase-change materials contained in a polymer capsule of a size between 1 and 300 μm. The primary advantages of ME-PCMs are their chemically-inert nature (due to the polymer barrier between the PCM and any other material), the optimized heat transfer due to a high surface area-to-volume ratio, and their ability to be readily mixed into or coated onto other materials. The concept of ME-PCMs and their potential advantages have been known for more than twenty years, but until recently have been prohibitively expensive. Now commercial products are available from companies including BASF and Microtek in dry powder and liquid dispersion forms and in a variety of phase-change melt temperatures.

Very few studies have been published involving ME-PCMs in building applications. In one of the early studies, Schlossig et al. (2005) modeled a building with lightweight walls coated with a mixture of ME-PCM and gypsum plaster. The results indicated a consistent smoothing of temperature peaks throughout the day. Further tests were conducted in a full-size physical testing facility with similar results. Cabeza. et al. (2007) tested the thermal performance of concrete mixed with ME-PCM. Two small, outdoor concrete structures were built, one with a standard concrete mix and the second mixed with 5% by weight of ME-PCM. Sensors monitored temperature and heat flux at points throughout the structures for several weeks at a time. Consistent smoothing of temperature peaks was observed. These results, together with the inherent advantages of ME-PCM over other PCM options, suggests that ME-PCM has significant promise as a component of passive building energy reduction. This is particularly true for applications involving concrete due to its central role in large building construction. The limited evidence at hand suggests that ME-PCM integrated in concrete can offer thermal benefits under the right conditions. What is currently unknown is the effect of ME-PCM integration on the structural integrity of concrete.

2.3. The effect of fine particles in concrete

The particle sizes of solid concrete components fall into well-defined ranges—aggregates are generally greater than 150 μm in diameter, and cement particles range between 1 and 50 μm. Cement reacts chemically with water to form a paste that binds aggregate particles together. However, non-cement particles less than 125 μm can have unique effects on the concrete. The primary physical effect is increased packing density due to addition of fine particles, which has been shown to reduce porosity in hydrated cement paste and to promote its homogeneity. The result is an increase in the strength of the bond between the cement and the aggregates. In this way, fine particles added to a concrete mix can increase the concrete's strength.

Moosberg-Bustnes et al. (2004) demonstrated that the addition of quartz filler in concrete can improve the concrete's strength. They added fillers with a wide range of particle sizes to concrete in varying proportions. They found that while replacing cement with filler tends to reduce strength, replacing aggregate with filler or adding filler without changing the cement and aggregate quantities tended to increase strength. They also found that average particle size plays an important role, with particle sizes of 4 μm and 2.2 μm (both finer than the average cement particle) being significantly more effective than 125 μm and 14 μm particles (larger than and roughly equal to cement particle sizes, respectively). Çelik and Marar (1996) examined the effects of incorporating crusher dust with an average particle size of 75 μm into concrete, and found that replacing up to 10% of the fine aggregate with crusher dust increased compressive and flexural strength.

In summary, prior research has shown that the addition of fine particles to concrete has the potential to either increase or decrease the strength of a given concrete mix depending on the size distribution of the particles, the method of addition or replacement in the concrete mix, and the volume fraction of the fine particles. Because the size of ME-PCM particles falls into this same range, they may have a similar effect on concrete strength.

2.4. Purpose of the present study

Incorporation of ME-PCM in structural concrete has the potential to add significant thermal storage capacity to modern, lightweight construction. An understanding of the effect of ME-PCM on the structural integrity of concrete is critical to determining whether its incorporation into concrete is economical and safe. Data on the effect of ME-PCM incorporation in concrete can provide an estimate of the effect of the ME-PCM on concrete strength. It is standard in practice for concrete strength tests to be conducted prior to project construction to ensure expected strength values in the mix design, whether a novel material is being added to the concrete or not. However, general-purpose results that indicate the systemic effect of ME-PCM on concrete can provide an indication of the applicability of ME-PCM in concrete to a building project much earlier in the design phase than project-specific mix testing.

The particle size and chemically-inert nature of ME-PCM means that the concrete component it most closely resembles is filler. If it can be demonstrated that ME-PCM has an effect similar to previously-tested filler materials, then in addition to the results of this study, the results of more basic studies on filler materials will provide valuable insight into the behavior of ME-PCM in concrete and its effect on concrete strength. On the other hand, if it is found that ME-PCM behaves much differently than filler materials, this will provide evidence that there are other physical factors in play in the behavior of very fine particles in concrete, and the results of this study will provide some guide to the behavior of ME-PCMs in particular.

3. EXPERIMENTAL STUDY

3.1. Materials and methods

In general, strength testing is performed on cured concrete mixes for structural applications. However, because the effects of ME-PCM on concrete occur at the cement or fine aggregate level, the contribution of coarse aggregate is not relevant to the general-purpose results sought in this study. On the other hand, because creating pure cement-paste samples to a consistent specification is particularly challenging, tests of such samples tend to have high variability and provide little predictive value. Thus the standard procedure for testing the strength of cement is via cement-sand mortars, as described in ASTM C109-08. This procedure allows an examination of the effect of ME-PCM either as a component of the cement paste or as a fine aggregate.

As specified in ASTM C109-08, cement mortar cube samples of 50 mm dimensions were formed from Type I Portland cement and standard-graded sand at a ratio of 1:2.75, with a water/cement ratio of 0.485. The volume of water added to each mix was altered as necessary to account for the water content of the sand. The ME-PCM incorporated into samples was BASF Micronal®, which is composed of a proprietary PCM wax mixture contained within a spherical polymer shells with an average diameter of 5 μm. For each series of samples, the dry materials were mixed separately, then mixed with water before being added to molds. Samples were removed from molds after 24 hours and allowed to cure submerged in lime

water for a period of 7 days. Samples were then subjected to unconfined compressive strength tests to determine failure stress.

3.2. Test parameters

Three different incorporation methods were tested, each with an associated series of samples. The first method was to simply add ME-PCM to the base mortar mix without altering the cement-sand ratio or water-cement ratio at 10%, 20%, 30%, 40%, and 50% of the total cement-sand volume (series A). The second method was to replace the cement in the mix with ME-PCM by the same set of percentages based on volume of cement, leaving sand content and water-cement ratio the same (series B). The last method is identical to the second, except that sand was replaced by ME-PCM and cement content and water-cement ratio were held constant (series C). Summary test sample compositions for the 3 series of tests are given in Table 2.

Due to the number of unique samples, testing was done with three samples at 7 days rather than the common practice of testing at 7, 14, and 28 days. Since the relative strength difference between the modified samples and the control is the key result, absolute strength values for fully-developed, 28-day concrete were not tested. An assumption inherent in this testing methodology is that the PCM-modified concrete samples exhibit the same development characteristics as the control.

TABLE 2. Cement-mortar cube compositions by mass proportion (0 to 50%).

	ME-PCM (%)*	Mix proportions on unit mass basis			
		Cement	Sand	ME-PCM	Water
Control	0%	1.000	2.750	0.000	0.485
Series A (add ME-PCM in proportion to dry materials)	10%	1.000	2.750	0.375	0.485
	20%	1.000	2.750	0.750	0.485
	30%	1.000	2.750	1.125	0.485
	40%	1.000	2.750	1.500	0.485
	50%	1.000	2.750	1.875	0.485
Series B (replace cement with ME-PCM)	10%	0.900	2.750	0.100	0.437
	20%	0.800	2.750	0.200	0.388
	30%	0.700	2.750	0.300	0.340
	40%	0.600	2.750	0.400	0.291
	50%	0.500	2.750	0.500	0.243
Series C (replace sand with ME-PCM)	10%	1.000	2.475	0.275	0.485
	20%	1.000	2.200	0.550	0.485
	30%	1.000	1.925	0.825	0.485
	40%	1.000	1.650	1.100	0.485
	50%	1.000	1.375	1.375	0.485

*Percent ME-PCM based on dry materials (cement + sand) for Series A, based on percent cement removed from mix for Series B, and based on percent sand removed from mix for Series C.

4. RESULTS AND DISCUSSION

The results of the cement-mortar cube tests are plotted in Figure 1. In all cases, the PCM-modified cement samples exhibited average compressive strengths less than the control sample, with diminishing strength as the quantity of PCM was increased. The series A samples, which have PCM added to the base cement-sand mix, show the highest strength, consistent with expectations since the sand to cement ratio remains the same, allowing complete cementation of the voids between the sand particles. Series C, which had PCM replacing cement, resulted in the lowest strength performance, again consistent with expectations—removing cement from the mix should lead to incomplete cementation of the voids between the sand particles. Series B results appear to be bounded by Series A and C. All sample strength values fell outside of the standard error range of the control samples, suggesting that the effect of integrating ME-PCM into the samples is significant. The variability of failure stress within each sample series is generally small enough to suggest that the trend in the data is indeed a result of the different mix designs.

Observations of the specimens' failure surfaces revealed no apparent release of the PCM wax from the microcapsules, ruling out the possibility of the mechanical destruction of the PCM capsules as a cause of specimen failure. This suggests that the reduced strength of the samples with integrated ME-PCM is not due to the structural properties of the ME-PCM material itself, but from its effect on the properties of the hardened mortar mix.

Qualitative observations may explain some of these results. During the mixing process, it was noticed that the ME-PCM has a high affinity for water. It readily soaks water, creating what appears to be a colloidal mixture. The cement hydration process relies on the chemical reaction between water and cement, but if ME-PCM is more hygroscopic than cement, water can be effectively denied from the cement, preventing full hydration.

Observations of workability during the mixing process reinforce this explanation. Even small amounts of ME-PCM added to the mix had a very large effect on workability since water content was left constant in all samples. This is indicative of a lack of free water in the concrete mix. Two possible scenarios can result—either the water affinity of the ME-PCM sequesters a certain amount of the free water, severely reducing workability, or the ME-PCM

FIGURE 1. Cement-mortar cube average failure strengths with standard error for the three series of samples.
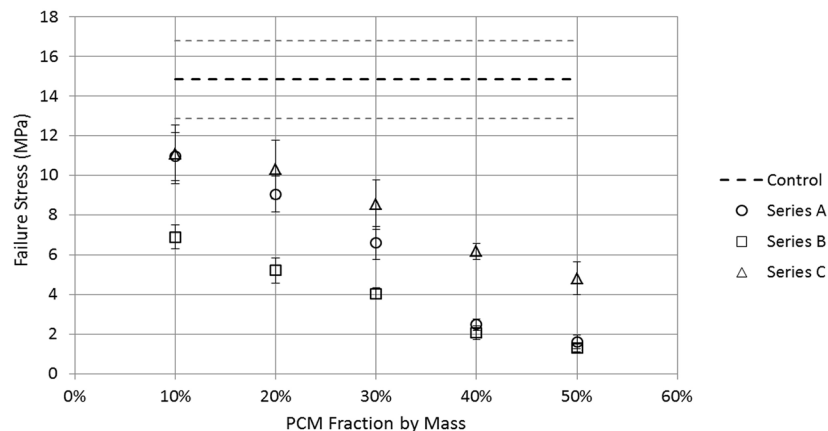
sequesters all of the free water as well as some of the water necessary for full hydration of the cement. In both cases, practical applications will require an increase in water content to get a workability adequate for forming and/or placing, thus further reducing the strength of the concrete below values reported here.

So, the experimental results suggest that the significant decrease in strength at high ME-PCM levels could be due to lack of complete cement hydration as a consequence of the ME-PCM sequestering a large proportion of the water. This is most dramatic in Series B. In Series C, ever decreasing amounts of cement are mixed with ever increasing amounts of ME-PCM, at the same water content, leading to consistently low strength values. Series A has the best chance of retaining strength, but even at moderate ME-PCM contents the strength of the mix is compromised. An alternate or additional possibility is that the test methodology assumption of equal strength gain for the control mix and the modified mixes is false—if the addition of ME-PCM causes a significant delay in strength gain, abnormally low strength values will be found in 7-day tests that may not appear or may appear to a lesser degree in 28-day tests. In particular, because the samples were water-cured per ASTM C109-08, a curing period longer than 7 days may allow any water potentially sequestered by the ME-PCM to be replaced by water in the curing environment.

In an effort to minimize member sizes, high concrete strengths are often preferred in structural design. Given the degree to which even moderate amounts of ME-PCM integrated into concrete reduce the concrete's strength, the use of ME-PCM appears to constrain the ability to increase concrete strength to save on material cost and reduce building space occupied by the structure. Small amounts of PCM, less than 5%, may yield workability and strength values suitable for structural concrete, but the added latent heat storage capacity of that concrete may offer limited thermal benefit. Nevertheless, one of the few empirical studies of the effect on interior temperature of a structure made of concrete with ME-PCM (5% by weight) demonstrated reductions in peak temperature between 1 and 3°C. (Cabeza, 2007). Because variables aside from ME-PCM proportion have a large impact on the ability of a concrete structure with ME-PCM to regulate internal temperature, including site conditions, building geometry and configuration, and usage, there is not enough data at present to judge whether ME-PCM included atproportions adequate for strength and workability can have a substantive effect on building heating and cooling energy use or thermal comfort.

5. CONCLUSIONS

This study began with the question of whether ME-PCM, due to its physical similarities to other fine particles shown to increase concrete strength, could also increase concrete strength while providing it with enhanced thermal energy storage. The test results reported herein suggest that ME-PCM has physical properties that differ from the other fine materials studied to date. Specifically, its water affinity appears to be much higher. As a result, strength values for concrete with ME-PCM are not consistent with those in studies testing concrete integrating other fine materials at the same proportions. One explanation for this difference is that the water affinity of the ME-PCM may deny water from the cement, partially preventing the cement hydration reaction that gives concrete its strength. Alternatively, rather than reducing the final strength of the concrete, ME-PCM may have a large impact on strength development, requiring longer curing times under conditions with sufficient moisture to replace water sequestered by the ME-PCM. Further investigation of the water content of ME-PCM

concrete mixes as well as curing times and conditions is necessary to better understand the effect of ME-PCM on the strength of concrete.

While phase-change materials remain a promising tool for reducing building energy use, more research is required on ways to effectively integrate them into the building structure. Further investigation of the physical properties of ME-PCM could lead to mitigation strategies allowing larger proportions to be included in concrete that meets building code strength requirements. Continued empirical studies and modeling of ME-PCM concrete structures' thermal performance can lead to estimates of energy savings that can be gained through the incorporation of ME-PCM. Together, these data can provide tools to make informed decisions about the feasibility of using ME-PCM in the building industry.

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