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微胶囊相变材料对砂浆热性能和力学性能的影响

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摘要:将微胶囊相变材料(MPCM)加入水泥砂浆中制成建筑储能砂浆,研究了储能砂浆的微观形貌、相变特性、热稳定性、导热系数、储热性能和力学性能.结果表明:储能砂浆的导热系数随MPCM含量的增加而降低;储能砂浆的MPCM芯材为固态时的导热系数大于其为液态时的导热系数;当MPCM含量为20%时,储能砂浆的内表面峰值温度较水泥砂浆降低3.1℃,达到峰值温度的时间比水泥砂浆延迟20.5 min,其28 d龄期硬化浆体的抗压强度为9.3 MPa;储能砂浆具有足够的抗压强度和良好的储能调温能力,可用于建筑围护结构.

关键词:微胶囊相变材料;储能砂浆;热性能;力学性能

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Effect of Microencapsulated Phase Change Material on Thermal and Mechanical Properties of Mortar

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Abstract: The energy storage mortar for buildings was developed by incorporating microencapsulated phase change material(MPCM) into cement mortar. The microscopic morphology, phase change characteristics, thermal stability, thermal conductivity, thermal and mechanical properties of energy storage mortar were investigated. The results show that the thermal conductivity of energy storage mortar decreases with the increase of the content of MPCM. The thermal conductivity of the energy storage mortar with solid MPCM is greater than that of the energy storage mortar with liquid MPCM. The peak temperature of the inner surface of the energy storage mortar with 20% MPCM is 3.1 °C lower than that of the cement mortar, the time to reach the peak temperature is 20.5 min later than that of the cement mortar, and the compressive strength of which at the age of 28 d is 9.3 MPa. The energy storage mortar can be used in the building envelope due to its sufficient compressive strength and good ability of energy storage and temperature regulation.

Key words: microencapsulated phase change material(MPCM); energy storage mortar; thermal property; mechanical property

建筑围护结构中添加相变材料不仅能减小室外温度波动对室内热环境的影响,还能提高围护结构的保温隔热性能^[1-4].微胶囊相变材料(microencapsulated phase change material, MPCM)能很好地集成到包括水泥砂浆^[5]、混凝土^[6-7]和石膏^[8]等在内的建筑围护结构的支撑材料中.在广泛使用

的抹灰砂浆中加入MPCM,不仅可以提高新建建筑围护结构的储热能力,还可以对既有建筑进行节能改造.Kheradmand等^[9]提出,可在水泥砂浆中掺入3种不同相变温度的MPCM以适应不同季节的需求.Frazzica等^[10]通过数值计算,确定西西里气候条件下水泥砂浆中添加MPCM的最佳熔化温度为27℃.Wi

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等^[11]发现,添加10% MPCM的外抹灰水泥表现出优异的蓄热性能.多数研究结果表明,加入MPCM后,水泥砂浆的储热能力有所提高,但其力学性能有所下降^[12-14].因此,有必要进一步研究MPCM与水泥砂浆的配合比对储能砂浆热性能和力学性能的综合影响,在保证储能砂浆强度符合相关规范要求的前提下,使其发挥出理想的储能调温效果.本文将商用正十八烷/密胺树脂MPCM加入水泥砂浆制备成储能砂浆,对其微观形貌、相变特性、热稳定性、导热系数、储热性能和力学性能进行研究,以确定MPCM与水泥砂浆的合理配合比.

1 试验

1.1 原材料

正十八烷/密胺树脂MPCM来自上海儒熳新能源科技有限公司,为白色粉末,其芯壳比为9:1,密度为 0.9 g/cm^3 ,粒径分布范围为 $5\sim 15\ \mu\text{m}$,熔化过程的相变峰值温度和相变潜热分别为 $29.2\text{ }^\circ\text{C}$ 和 78.8 J/g ,凝固过程的相变峰值温度和相变潜热分别为 $21.8\text{ }^\circ\text{C}$ 和 76.1 J/g .水泥为P·O 42.5普通硅酸盐水泥,28 d抗压强度和抗折强度分别为 54.3 MPa 和 7.8 MPa ,表1为水泥的化学组成.细骨料为来自厦门艾思欧标准砂有限公司的中国ISO标准砂,其 SiO_2 含量(质量分数,文中涉及的含量、掺量等除特别指明外均为质量分数)大于98%.

表1 水泥的化学组成

Table 1 Chemical composition of cement

w/%						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3
19.91	4.35	3.50	64.10	2.25	0.15	2.93

1.2 试样制备

根据GB/T 17671—1999《水泥胶砂强度检验方法(ISO法)》制备储能砂浆,其配合比见表2,其中MPCM的掺量分别为水泥质量的5%,10%,15%和20%.编号C-M的试件为未掺MPCM的水泥砂浆,编号MPCM5的试件为MPCM掺量为水泥质量5%的储能砂浆,其他试件编号含义以此类推.

取规格为 $40\text{ mm}\times 40\text{ mm}\times 20\text{ mm}$ 、 $70.7\text{ mm}\times 70.7\text{ mm}\times 70.7\text{ mm}$ 和 $300\text{ mm}\times 300\text{ mm}\times 20\text{ mm}$ 的铸铁水泥模具,对模具内壁及表面进行清理并涂油,将搅拌均匀的材料分别装入铸铁水泥模具内,反复振实填平,静置24 h后脱模,置于 $20\text{ }^\circ\text{C}$,湿度为90%的养护室内养护28 d. $40\text{ mm}\times 40\text{ mm}\times 20\text{ mm}$ 的试件用于导热系数测试; $70.7\text{ mm}\times 70.7\text{ mm}\times 70.7\text{ mm}$ 的试件用于抗压强度测试; $300\text{ mm}\times 300\text{ mm}\times 20\text{ mm}$ 的试件用于储热/放热性能测试.

表2 储能砂浆的配合比

Table 2 Mix proportions of energy storage mortars

Sample	Cement	Standard sand	Water	MPCM
C-M	450	1 350	225	0
MPCM5	450	1 350	225	22.5
MPCM10	450	1 350	225	45.0
MPCM15	450	1 350	225	67.5
MPCM20	450	1 350	225	90.0

1.3 试验方法

用S-3400N型扫描电子显微镜(SEM)观察MPCM和储能砂浆的微观形貌;用3500 Sirius型差示扫描量热(DSC)仪在氮气气氛测试环境下以 10 K/min 的升/降温速率在 $-10\sim 60\text{ }^\circ\text{C}$ 温度范围内测试MPCM和储能砂浆的相变温度和相变潜热;用209 F3型热重(TG)分析仪以 10 K/min 的升/降温速率在 $25\sim 500\text{ }^\circ\text{C}$ 温度范围内测试MPCM和储能砂浆的热稳定性;用DRE-III型导热系数测试仪测试储能砂浆的导热系数;用DYH-300B型水泥压力试验机测试储能砂浆的抗压强度,加载速率为 $(50\pm 10)\text{ N/s}$.

图1为自制的储热/放热性能测试试验箱示意图^[15-17],箱体材料为保温板.由图1可见:试验箱内部尺寸为 $300\text{ mm}\times 300\text{ mm}\times 500\text{ mm}$;热源采用FGW-620型加热器,加热器与试件外表面距离为 500 mm ,通过热辐射方式加热试件;试件内、外表面各布置2个T型热电偶进行温度测试.进行储热/放热性能测试时,开启加热器,使试件外表面温度在33 min内由 $25.5\text{ }^\circ\text{C}$ 逐步升高到 $43.8\text{ }^\circ\text{C}$,然后关闭加热器,通过自然降温,使试件外表面温度由 $43.8\text{ }^\circ\text{C}$ 逐步降低到 $25.5\text{ }^\circ\text{C}$,测试升温/降温过程中试件内表面温度的变化情况.每隔5 min,用FLIR T200型红外热像仪拍摄升温过程中试件内表面的温度分布情况.

2 结果与分析

2.1 微观形貌

图2为MPCM和储能砂浆的SEM图片.由图2可见:MPCM外观呈光滑的球形,密胺树脂壳材将相变材料正十八烷封装在球体内;储能砂浆中的MPCM保持完整的球形,且在砂浆中均匀分布,没有出现明显的团聚现象,表明MPCM与水泥砂浆相容性较好,在储能砂浆制备过程中混合较为均匀.

2.2 相变特性

图3为储能砂浆的DSC曲线.由图3可见:由于MPCM的存在,储能砂浆的DSC曲线出现明显的吸热峰和放热峰,为MPCM的相变过程;MPCM含量为5%、10%、15%和20%的储能砂浆在熔化过程中

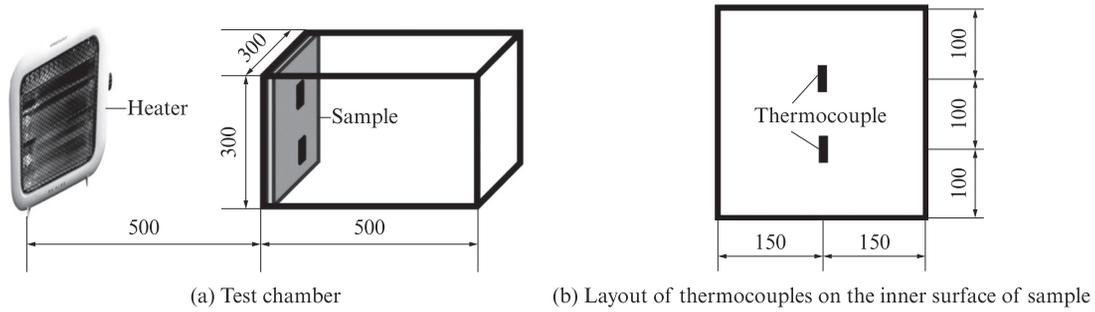


图1 储热/放热性能测试试验箱示意图
Fig. 1 Schematic diagram of thermal energy storage/ release property test chamber (size: mm)

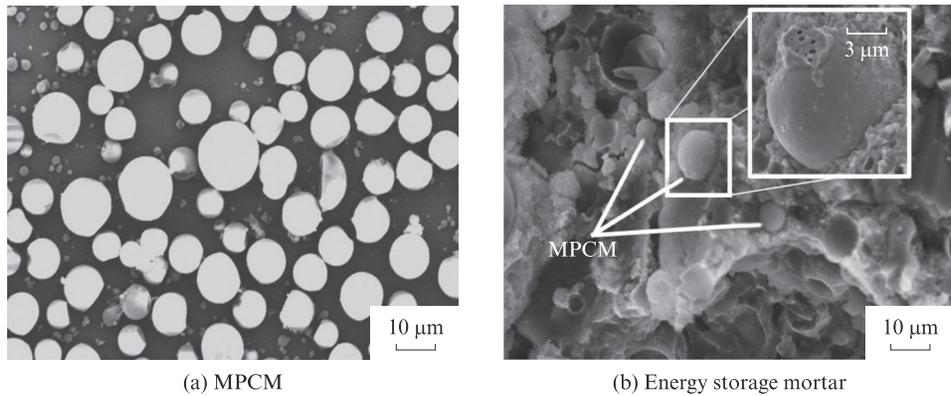


图2 MPCM和储能砂浆的SEM图片
Fig. 2 SEM images of MPCM and energy storage mortar

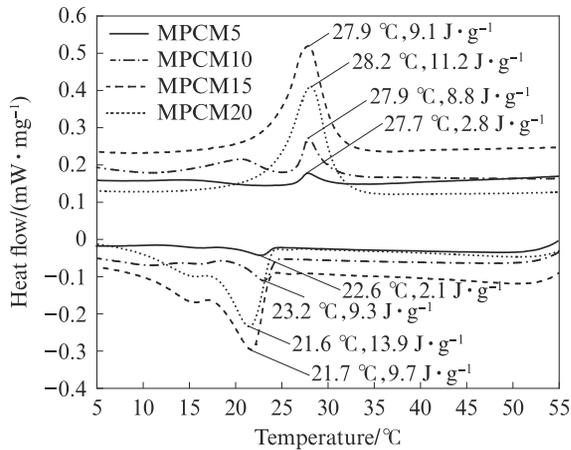


图3 储能砂浆的DSC曲线
Fig. 3 DSC curves of energy storage mortars

的相变潜热分别为2.8、8.8、9.1、11.2 J/g,在凝固过程中的相变潜热分别为2.1、9.3、9.7、13.9 J/g;随着MPCM含量的增加,储能砂浆的相变潜热逐渐增大.因此,MPCM的掺入提高了水泥砂浆的储热能力.

2.3 热稳定性

图4为MPCM、水泥砂浆和储能砂浆的热重曲线.由图4可见:MPCM在200 °C左右开始产生明显的失重现象,500 °C时其质量剩余约为初始质量的5%;水泥砂浆的热稳定性最好,热失重很小,500 °C

时其质量剩余约为初始质量的95%;温度低于100 °C时,储能砂浆的热重曲线与水泥砂浆的热重曲线重合,热稳定性非常好,100 °C时仅有部分水分的散失,其质量剩余约为初始质量的99%;在100~500 °C温度范围内,随着温度的升高,由于部分MPCM发生热分解,储能砂浆的热稳定性逐渐下降,500 °C时其质量剩余约为初始质量的94%.

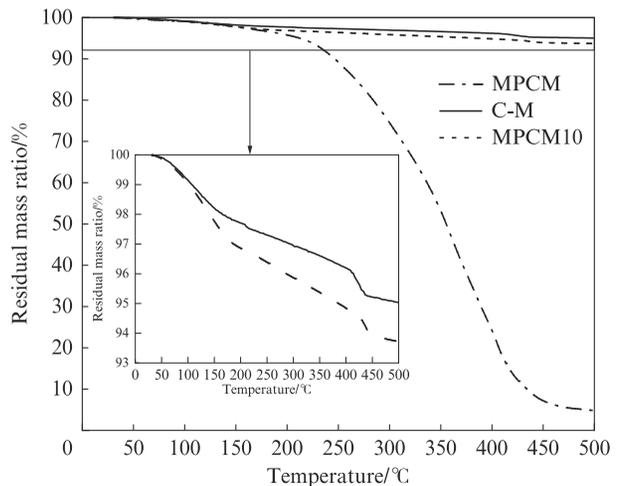


图4 MPCM、水泥砂浆和储能砂浆的热重曲线
Fig. 4 TG curves of MPCM, cement mortar and energy storage mortar

2.4 导热系数

图5为不同温度下MPCM含量对储能砂浆导热系数的影响,其中20℃时MPCM为固态,40℃时MPCM为液态.由图5可见:相同温度条件下,储能砂浆的导热系数随着MPCM含量的增加而降低,这主要是由于固态MPCM和液态MPCM的导热系数分别为0.314 W/(m·K)和0.206 W/(m·K),水泥砂浆的导热系数为0.912 W/(m·K),前者远低于后者,当MPCM含量不断增加时,储能砂浆的导热系数逐渐降低,且储能砂浆表观密度降低和孔隙率增加也可能导致其导热系数降低^[18];由于MPCM由固态变为液态时导热系数降低^[19-20],储能砂浆芯材为固态时的导热系数大于其为液态时的导热系数;当MPCM含量由5%增加到20%时,储能砂浆芯材为固态和液态时,它们之间导热系数的差异从0.03 W/(m·K)逐渐增大到0.09 W/(m·K).

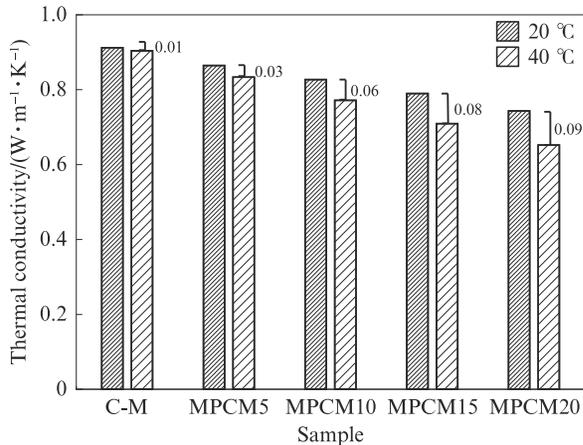


图5 不同温度下MPCM含量对储能砂浆导热系数的影响
Fig. 5 Effect of MPCM content on thermal conductivities of energy storage mortars at various temperatures

2.5 储热/放热性能

图6为水泥砂浆和储能砂浆内表面温度随时间的变化曲线,A点表示水泥砂浆的内表面峰值温度与对应的时间,B点、C点、D点和E点分别表示MPCM含量为5%、10%、15%和20%的储能砂浆的内表面峰值温度与对应的时间.由图6可见:储能砂浆的升温/降温速率比水泥砂浆小,且随MPCM含量的增加逐渐减小,表明MPCM可提高砂浆的热惯性,因而对储能砂浆的储热/放热能力有显著影响;MPCM含量为5%、10%、15%和20%的储能砂浆的内表面峰值温度分别为37.5、37.2、36.5、35.7℃,较水泥砂浆的内表面峰值温度(38.8℃)依次降低1.3、1.6、2.3、3.1℃,这是由于储能砂浆中的MPCM在相变过程中

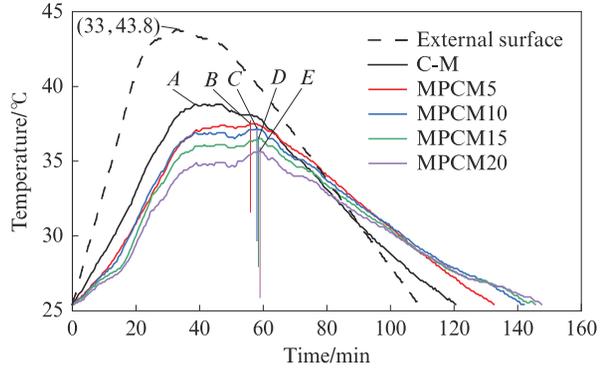


图6 水泥砂浆和储能砂浆内表面温度随时间的变化
Fig. 6 Variations of temperatures of inner surface of cement mortar and energy storage mortars with time

吸收相变潜热,MPCM含量越大的储能砂浆吸收的相变潜热越多,其表面峰值温度降低越明显,表明MPCM具有储热和调温能力;MPCM含量为5%、10%、15%和20%的储能砂浆达到峰值温度的时间比水泥砂浆(38.5 min)分别滞后17.5、19.5、20.0、20.5 min,即储能砂浆的温度延迟时间随着MPCM含量的增加而增加;降温过程中,MPCM逐渐释放出升温过程中所储存的热量,因而储能砂浆的温度下降速率比水泥砂浆缓慢,MPCM比例越大的储能砂浆,其温度下降速率的减缓程度越明显.

图7为升温过程中水泥砂浆和储能砂浆内表面的红外热像图.由图7可见:与水泥砂浆相比,储能砂浆的内表面温度始终较低,温升慢,温度变化有所延迟;与水泥砂浆相比,储能砂浆的温升不明显,这是由于水泥砂浆的温度变化仅取决于其显热,而储能砂浆的温度变化除了取决于水泥砂浆的显热外,还与MPCM达到其熔点发生相变的相变潜热相关;储能砂浆内表面的终温随着MPCM含量的增加而降低,表明其热惯性变大,具有良好的储能调温能力.

2.6 力学性能

图8为不同温度下MPCM含量对储能砂浆抗压强度的影响.由图8可见:相同温度条件下,储能砂浆的抗压强度低于水泥砂浆的抗压强度,且随MPCM含量的增加而降低;MPCM的抗压强度仅为3.0 MPa,当其分布在水泥砂浆内部时会弱化骨料的支撑作用,同时MPCM与水泥砂浆基体结合面之间的孔隙以及MPCM的受力破坏都可能导致储能砂浆抗压强度的降低;储能砂浆的抗压强度在不同温度条件下保持不变,表明MPCM芯材在固态和液态之间的相变对其没有影响.

28 d龄期时,MPCM15和MPCM20储能砂浆的抗压强度分别为11.2 MPa和9.3 MPa,根据GB50574—2010《墙体材料应用统一技术规范》和

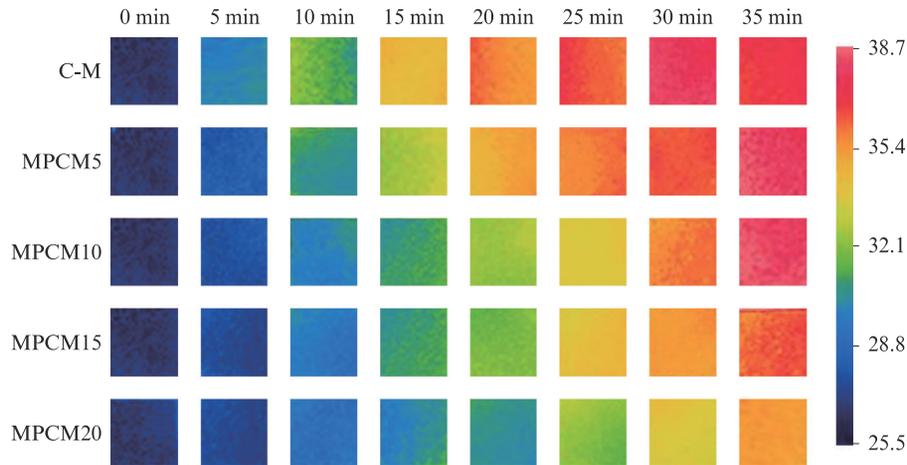


图7 升温过程中水泥砂浆和储能砂浆内表面的红外热像图

Fig. 7 Infrared thermography images of inner surface of cement mortar and energy storage mortars during heating process

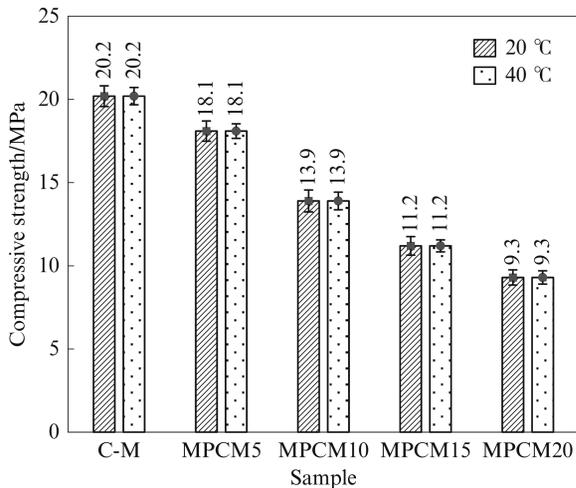


图8 不同温度下 MPCM 含量对储能砂浆抗压强度的影响

Fig. 8 Effect of MPCM content on the compressive strengths of energy storage mortars at various temperatures

JC/T 2338—2015《建筑储能调温砂浆》的规定, MPCM15用作采暖地区外墙抹灰砂浆, MPCM20用作内墙抹灰砂浆和非采暖地区外墙抹灰砂浆,完全满足建筑应用的强度性能要求。

3 结论

(1) 储能砂浆的导热系数随着 MPCM 含量的增加而降低。储能砂浆芯材为固态时的导热系数大于其为液态时的导热系数。

(2) 储能砂浆的储热性能随着 MPCM 含量的增加而增加。MPCM5、MPCM10、MPCM15 和 MPCM20 储能砂浆内表面峰值温度较水泥砂浆依次降低 1.3、1.6、2.3、3.1 °C, 达到峰值温度的时间比水泥砂浆分别延迟 17.5、19.5、20.0、20.5 min。

(3) 储能砂浆的抗压强度随 MPCM 含量的增加

而降低。MPCM15 和 MPCM20 储能砂浆的抗压强度分别为 11.2 MPa 和 9.3 MPa, MPCM15 用作采暖地区外墙抹灰砂浆, MPCM20 用作内墙抹灰砂浆和非采暖地区外墙抹灰砂浆, 完全满足建筑应用的强度性能要求。

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