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Novel metal-organic framework (MOF) based phase change material composite and its impact on building energy consumption

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Abstract: Space cooling (including dehumidification) is the fastest-growing use of energy in buildings. Materials that have high thermal and moisture buffer capacities can passively mitigate indoor temperature and humidity fluctuations, thus reducing the demand for air conditioning and improving building energy efficiency. Here, we report a novel metal-organic framework (MOF) based microencapsulated phase change material (MPCM) composite. The new MOF-MPCM is a dual-function material that can simultaneously absorb/release heat and moisture from surrounding air and passively regulate the indoor hygrothermal environment. MIL-160(Al), a novel green and biomass-derived MOF material with excellent sorption performance and large-scale production potential, was prepared for moisture buffering. MPCM containing an n-octadecane core and polymethylmetracrylate shells were synthesized for temperature control. Physicochemical and hygrothermal properties of MOF-MPCM composite were characterized by SEM, XRD, DVS, DSC, and TGA techniques, etc. A HAM-Enthalpy model was developed to study the impact of MOF-MPCM on the indoor hygrothermal environment and building energy performance in different climates. Seven cities around the world (i.e., Singapore, Hong Kong, Phoenix, Denver, Barcelona, London, and Beijing) were selected as the representative climate locations. The simulation indicates that MOF-MPCM can effectively mitigate indoor temperature and moisture variations and cut down the energy consumption of air conditioning systems, especially in hot-dry, temperate, and continental climates with large diurnal air temperature and humidity variations. The maximum energy-saving potential could reach 35.2% in Phoenix. The study provides guidance for the further improvement and application of dual-function MOF-MPCM composite in different climates.

Keywords Metal-organic framework; Phase change material; Hygrothermal environment; Building energy conservation

1. Introduction

The fast-growing use of air-conditioning systems in buildings worldwide has become one of the main drivers of global energy demand. An estimated 3.3 billion room air-conditioners (A.C.) will be installed globally between now and 2050 [1]. The majority of this growth will come from emerging economies with hot climates and growing populations. Using air conditioners for cooling and dehumidification already accounts for more than 30% of the total building electricity consumption [2]. Drastic transformation of cooling technology by using new materials and new physical-chemical processes can significantly cut down the energy demand of AC systems, improving indoor hygrothermal comfort and minimizing the negative impacts on the environment and climate. One promising approach is developing and applying novel dual-function materials to passively regulate both indoor temperature and moisture conditions [3, 4].

A conventional air conditioning system typically performs two functions at once: cooling and dehumidification. Most previous studies using passive materials for indoor environment control mainly focus on a single function, i.e., either temperature or moisture regulation [5, 6, 7]. The latent load and sensible load are handled separately by different materials. Phase change material (PCM) with high thermal inertia can absorb/release a significant amount of thermal energy during the phase change process while its temperature remains constant. Many researchers have studied the use of PCMs in buildings to moderate the variations of the thermal indoor environment and improve building energy performance [5, 7, 8, 9]. The direct application of PCMs in building materials or structures has some limitations, such as the mobility of some PCMs in the solid-to-liquid phase change, and some PCMs have a high degree of super-cooling, etc. In order to enhance the performance of PCMs and better integrate with building materials, different encapsulation methods were developed. Microencapsulation techniques [10, 11] have been proven to be an economical and effective method. However, PCMs have little effect on indoor humidity conditions, which also significantly impact building energy consumption and occupants' comfort. Latent load (moisture) accounts for around one-third of the total cooling load of AC systems, and its proportion is even higher in many hot/humid and semi-humid climates [12]. Hygroscopic materials with large moisture buffer capacity can autonomously moderate indoor humidity variations and cut down the latent cooling load for AC systems [4, 12].

Normally, it is challenging to find one single material that can achieve a dual-function of ad/desorption of both heat and humidity at the same time. Some researchers have tried to mix MPCMs with conventional hygroscopic materials, such as diatomite, sepiolite, zeolite, hemp concrete, etc. [3, 13, 14, 15], to prepare new phase change humidity control materials (PCHCMs) [16] for the passive control of indoor hygrothermal conditions. The PCHCMs exhibit a promising potential for moderating both temperature and humidity fluctuations and reducing building energy consumption. However, the conventional hygroscopic building materials have distinct drawbacks, e.g., the water vapor adsorption and moisture buffering capacity are low, and the energy demand for regeneration is high [17]. To make the PCHCMs have a satisfactory ability of moisture buffering, the proportion of porous sorbent materials in the composite is relatively high, which will significantly reduce the enthalpy and thermal inertia of the whole composite materials.

Metal-organic frameworks (MOFs), a new class of cutting-edge crystalline porous materials, have become one of the most promising functional materials for indoor moisture regulation due to the high specific surface areas, high porosity and pore volume, and the tunable and flexible crystalline structure [18, 19, 20, 21]. Some MOFs have much higher water vapor uptake and moisture buffer capacity, and milder regeneration conditions than traditional or conventional hygroscopic materials [21, 22, 23]. Feng et al.'s research shows the moisture buffer value (MBV) of a Fe-MOF (MIL-100(Fe)) is more than 30 times larger than wood and 45 times larger than diatomite [17]. The key barriers and considerations in large-scale applications of MOFs in buildings are: cost, scalability, long-term stability, and safety [23].

More recently, a green and biomass-derived Al-MOF (MIL-160) has been developed for sorption-based applications [24]. The new MOF performs excellently in heat transformation, moisture adsorption, energy storage, and stability [25, 26]. The primary constituent element iron atom of MIL-160 is Al, which is non-toxic, widely available, and inexpensive. The ligand of MIL-160 (2,5-Furandicarboxylic acid) is derived from a biomass source (fructose). The synthesis process is green and environmentally friendly. We have recently optimized the green synthesis approach, making it possible for mass production for building applications.

The aim of this study consists of: (1) preparing a series of MIL-160(Al)-MPCM materials for indoor hygrothermal regulation; (2) characterizing the physico-chemical and hygrothermal properties of the new materials by XRD, SEM, DVS, MBV, DSC and TGA techniques; (3) developing a numerical model to investigate the impact of MOF-MPCM composites on the indoor hygrothermal environment; and (4) calculating the energy-saving potential of using MOF-MPCMs in different cities/climates.

2. Materials

2.1 Raw materials

Aluminum acetate (Al(O.H.)($CH_3COO)_2$) (Reagent grade, Sigma-Aldrich) and 2,5-Furandicarboxylic acid (FDCA) (Reagent grade, Sigma-Aldrich) were used to prepare MIL-160(Al). N-octadecane (Reagent grade, Sigma-Aldrich) was used as the phase change material (PCM). Methyl methacrylate ($CH_2=C(CH_3)COOCH_3$) (Reagent grade, Sigma-Aldrich) was used to prepare the polymethylmetracrylate shells. The Sodium dodecylbenzene sulfonate (SDBS) and ammonium persulfate (APS) were purchased from Sinopharm chemical. All chemicals were used as received without further purification.

2.2 Preparation of MIL-160(Al)

MIL-160(Al) was prepared by the solvothermal synthesis method [25]. First, 0.6 mol (93.7 g) Aluminum acetate and 0.6 mol (97.3 g) FDCA were mixed in a round bottom flask filled with 600 mL of deionized water. Second, the mixture was heated and stirred under the reflux condition at 100 °C for 24h. Third, the mixture was filtered and washed with deionized water and ethanol at 20 °C for 3h. Finally, the grey-white solid in powder form was dried in a vacuum oven at 100 °C to yield activated MIL-160(Al).

2.3 Preparation of MPCM

First, 21 grams n-octadecane and 9 grams methyl methacrylate were mixed in beaker A and stirred by ultrasonic for 10 mins. It is the oil phase. Second, 3% sodium dodecylbenzene sulfonate and 30 mL distilled water were mixed in beaker B and stirred at 60 °C for 10 mins. It is the water phase. Third, the oil phase (in beaker A) was added to the water phase (beaker B) to prepare the oil/water emulsion. The temperature was maintained at 80 °C. The oil/water emulsion was stirred for 30 mins. Finally, 1% APS solution (0.13g/mL) of methyl methacrylate was added dropwise into the oil/water emulsion and continued to stir the emulsion for two hours until the end of the polymerization. The synthesized MPCM was filtered and washed with distilled water three times. The white MPCM powder was obtained after vacuum drying (50 °C) for twelve hours.

2.4 Preparation of MOF-MPCM

A series of MOF-MPCM materials with different MOF/MPCM ratios were prepared by gridding. First, both MIL-160(Al) and microencapsulated PCM were put in a vacuum dryer (50 °C) for 24 hours. Second, different proportions of MIL-160(Al) and MPCM were mixed and ground in a controlled environment (20 °C and 15 % RH) for 10 mins until they were fully homogeneous. Finally, the MOF-MPCM composite materials with different MOF contents of 25%, 50%, and 75% were obtained.

3. Characterization

The Nova NanoSEM scanning electron microscope (SEM) and the Tecnai F30 transmission electron microscopy (TEM) were used to investigate the microscopic morphology and detailed structures of MIL-160(Al) and MPCM. The high-resolution X-ray diffractometer (Rigaku Smartlab) was used to measure the powder XRD pattens of the synthesized materails. The thermal properties of the new MOF-MPCM composites were measured by a differential scanning calorimeter (DSC, TA Q200). The rate of heating temperature was 5 °C/min under a constant stream of N_2. The thermal gravimetric analyzer (TGA, TA Q50) was used to measure the thermal stability of the new composite material. The temperature range is from 20 °C to 600 °C with the heating rate of 20 °C/min under a constant stream of N_2. Water vapor sorption isotherms of MIL-160(Al), MPCM and MOF-MPCMs were measured using a dynamic vapor sorption (DVS, DVSAdventure from Surface Measurement Systems) instrument.

3.1 Micromorphology

Figs. 1(a) and 1(b) show the SEM and TEM images of the microencapsulated PCM, respectively. The SEM image shows the sizes of the prepared MPCMs are relatively uniform (around hundreds of nanometers). The TEM image indicates that the MPCM exhibits a clear core-shell structure. The inner core is n-octadecane, and the outside shell is PMMA. Figs. 2 presents the SEM images of MIL-160(Al), showing the crystals are in a pillar shape. The connected voids between crystals further enhance the vapor diffusion. The pore diameter of MIL-160(Al) is 0.5 nm, the pore volume is 0.42 $cm^3\ g^{-1}$, and the BET (Brunauer, Emmett and Teller) surface area is around 1200 $m^2\ g^{-1}$.

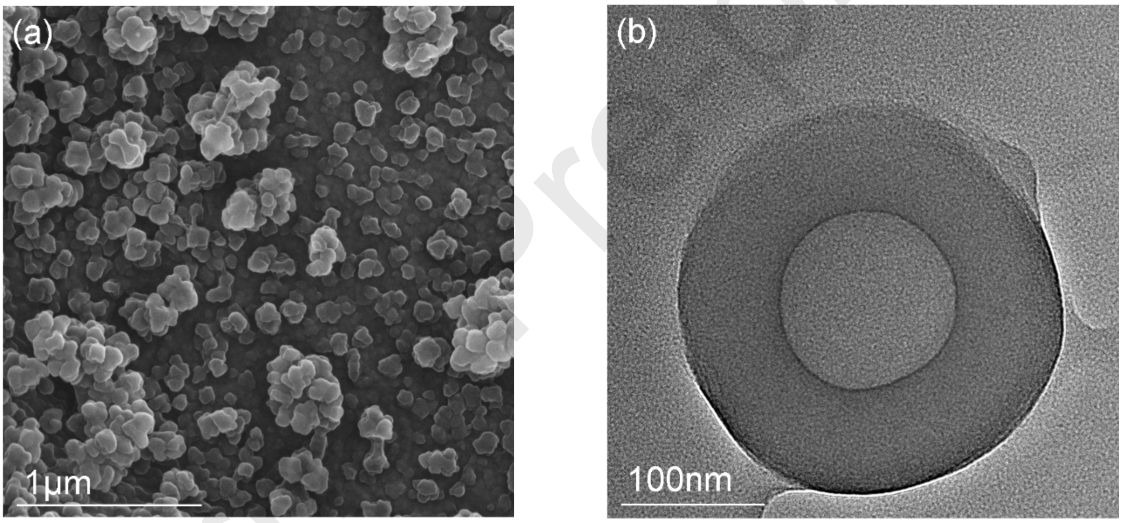

Fig. 1. (a) SEM image of MPCM, (b) TEM image of MPCM

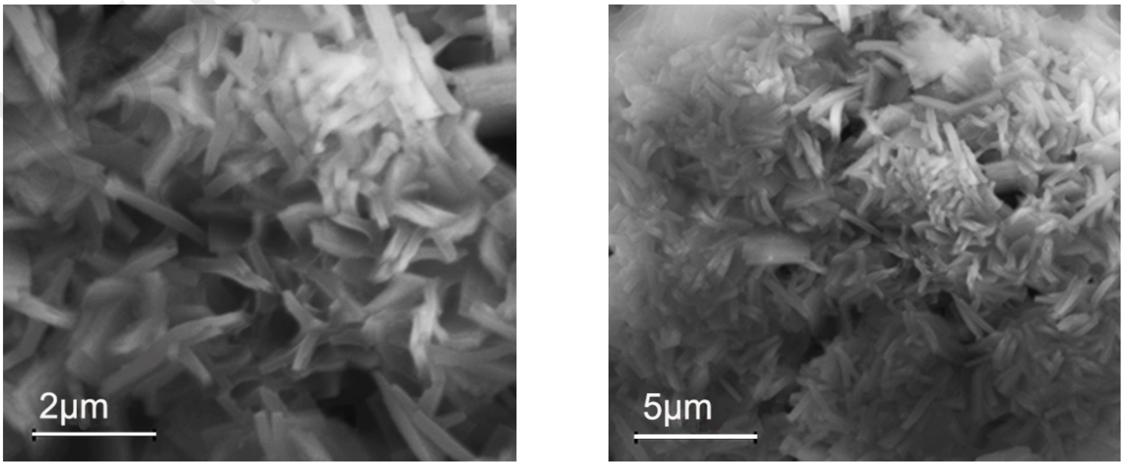

Fig. 2. SEM images of MIL-160(Al)

3.2 XRD patterns

Fig. 3(a) shows the XRD patterns of MOF MIL-160(Al), the microencapsulated PCM, and MOF-MPCM composite material. The diffraction peaks of MIL-160(Al) prepared in this work at 2θ values of 8.4°, 9.3°, 12.5°, 15.1°, 18.6°, 22.7°, 24.5°, and 27.1° are consistent with the samples prepared with small-scale process reported in previous study [24]. In the XRD pattern of MPCM, the diffraction peaks at 2θ values of 19.3°, 19.8°, and 23.3° are assigned to (010), (011), and (105) planes that are related to the crystal of n-octadecane. The XRD analysis confirms the existence and a good crystallinity of n-octadecane inside the microcapsules. Furthermore, it can be observed that the diffraction peaks of the MOF-MPCM curve correspond to the peaks in MIL-160(Al) and MPCM curves despite the fact that the intensities of the peaks of MOF-MPCM attenuated a lot. It indicates that both MOF and MPCM still remain good crystallinity after grinding mixing.

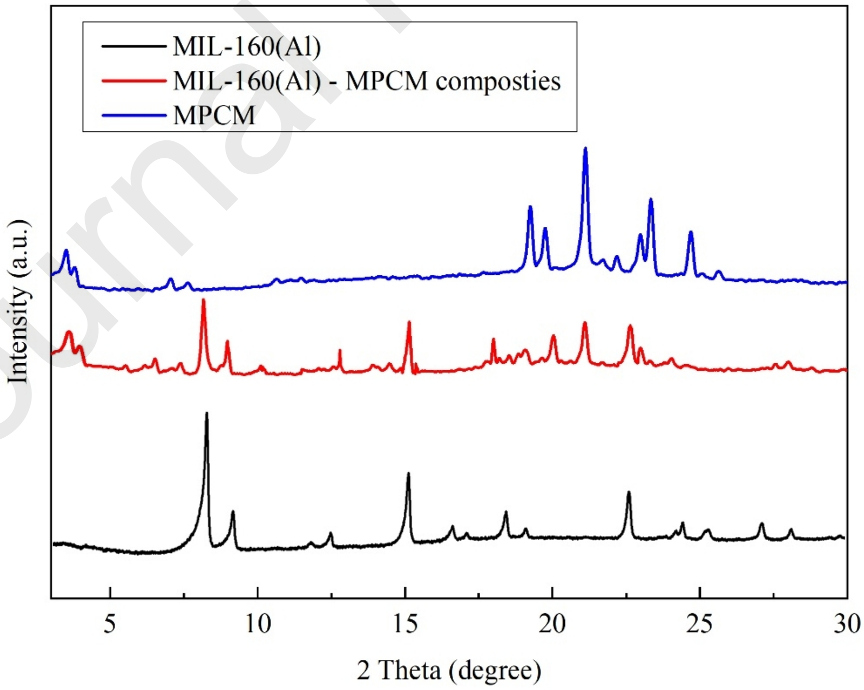

Fig.3. XRD Patterns of MIL-160(Al), MPCM and MOF-MPCM composites

3.3 Thermal properties

Differential scanning calorimeter (DSC) curves of MIL-160(Al), MPCM, and MOF-MPCM composites are presented in Fig. 4. The DSC results first indicate that the pure MIL-160(Al) has no phase change during the heating process, while MPCM and all MOF-MPCM composites have one endothermic peak. The melting latent heat (enthalpy) of MPCM is 147.52 kJ kg^{-1}. The crystallization form of the MPCM in the MOF-MPCM composites hasn't been changed by adding MIL-160(Al). The melting latent heat (enthalpy) of MOF-MPCM decreases as the content of MIL-160(Al) increases. It is ranged from 92.31 kJ kg^{-1} (25% MOF) to 19.63 kJ kg^{-1} (75% MOF). The detailed thermal properties of different samples are shown in Table 1.

Both the peak temperature and the melting temperature of the MOF-MPCM composite materials were decreased by certain degrees compared to the pure Microencapsulated PCM. One possible reason is that MOF crystals and PMMA as impurities will destroy the lattice arrangement of the pure phase change material and thus reduce the lattice energy that may lead to the reduction of the melting point of the composites. The nanoparticles' surface tension and intermolecular force may also affect the melting points and lattice energy.

Table 1. DSC data of MIL-160(Al), MPCM, and MOF-MPCM composites

Samples	Temperature (°C)		Latent heat/Enthalpy (kJ/kg)
	Melting	Peak	
MPCM	24.08	28.86	147.52
MOF-MPCM (75%)	23.15	27.03	92.31
MOF-MPCM (50%)	23.97	26.81	45.98
MOF-MPCM (25%)	24.58	26.02	19.63
MIL-160(Al)	-	-	0

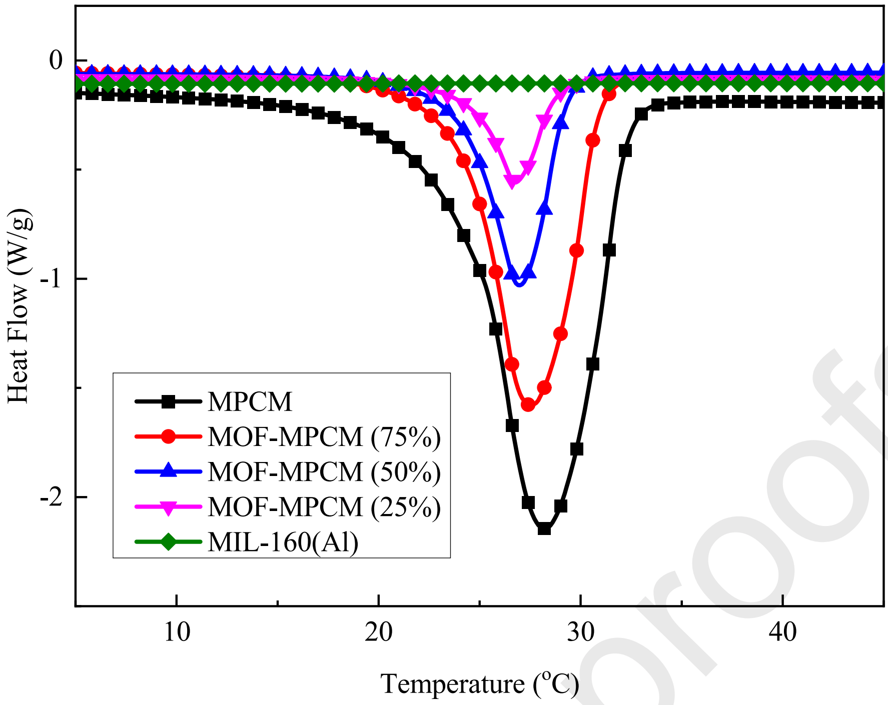

Fig. 4. DSC curves of MPCM, MIL-160(Al), and MOF-MPCM composites containing 75%, 50%, and 25% MPCM.

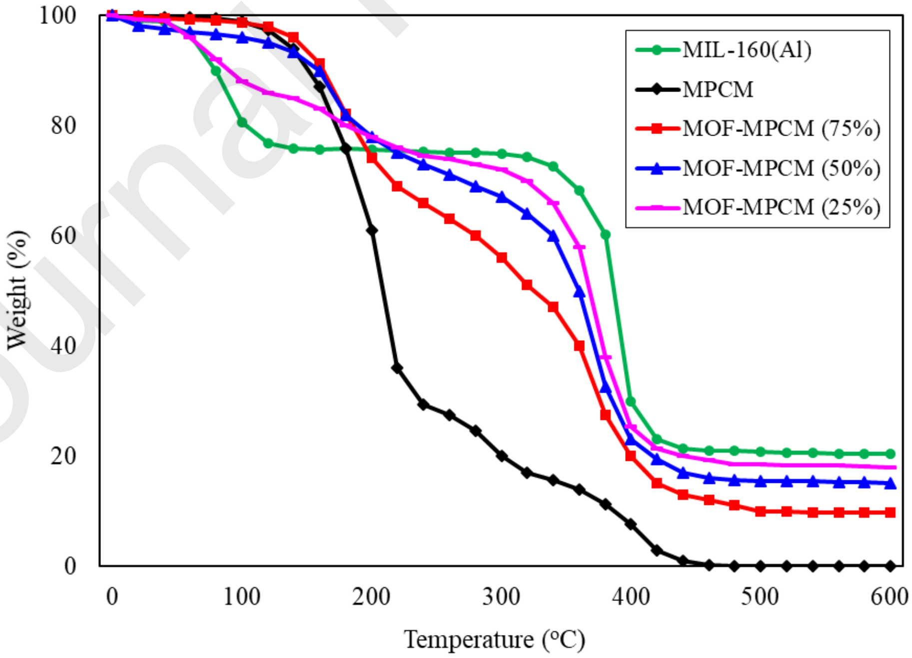

Fig. 5 TGA curves of MPCM, MIL-160(Al), and MOF-MPCM composites containing 75%, 50%, and 25% MPCM.

The thermal stability of MIL-160(Al), MPCM, and the MOF-MPCM composites containing different ratios of MPCM was investigated by using a thermal-gravimetric analyzer (TGA). The TGA data of all samples are presented in Fig. 5. The residual mass at 600 °C and the starting temperature of decomposition of MIL-160(Al), MPCM, and different MOF-MPCM composites are listed in Table 2.

It can be observed that MIL-160(Al) has a two-step weight loss process. The first step occurs between 60 °C and 120 °C. The weight loss is about 25 wt%, which is mainly because of the desorption/evaporation of free water and bonded water. The second step occurs between 350 °C and 450 °C. The weight loss of the second step is about 54 wt%, which is mainly due to the thermal degradation of the organic ligand. The degradation of MPCM begins at around 110 °C and completes at around 470 °C, consisting of two main steps. The first step corresponds to the degradation of octadecane, and the second step mainly corresponds to the degradation of the PMMA shell. The TGA curves of MOF-MPCM composites are generally between the curves of MIL-160(Al) and MPCM and can be divided into two stages. In the first stage (from 0 to 200 °C), the rate of weight loss of MOF-MPCM composites increases with the increasing ratio of MIL-160(Al) in the composites. However, in the second stage (from 200 °C to 600 °C), the TGA curves show a reverse trend. The MOF-MPCM composites with higher MPCM content lose their weight faster than those with lower MPCM ratios. At the end of the thermal degradation process (600 °C), the MPCM has 0 residual mass, and MIL-160(Al) has 20.8% residual mass. The residual mass of different MOF-MPCM composites is between 0 and 20.8%. The higher MIL-160(Al) content leads to a higher residual mass.

Table 2. TGA data of MIL-160(Al), MPCM, and MOF-MPCM composites containing 75%, 50%, 25% MPCM.

Samples	Temperature of initial decomposition (°C)	Residual amount (%) (600 °C)
MPCM	192.2	0
MOF-MPCM (75%)	173.5	9.78
MOF-MPCM (50%)	172.3	15.7
MOF-MPCM (25%)	51.5	18.3
MIL-160(Al)	51.0	20.8

3.4 Water vapor sorption isotherms

Dynamic vapor sorption (DVS) instrument was used to measure the water vapor sorption isotherms of MIL-160(Al), MPCM, and the MOF-MPCM composites. The test results are presented in Fig. 6 and show that MIL-160(Al) has S-shaped isotherms during the ad/desorption process. It is mainly due to the uniform pore size in the crystals. It fits the Langmurian sorption isotherm model well. The max. water vapor uptake can be up to 0.45 g g^{-1} (30°C, 80% RH) with small hysteresis between adsorption and desorption, which indicates that MIL-160 (Al) has a great potential in moisture buffering over traditional building materials. The water vapor isotherms of MPCM are almost linear. The maximum water vapor uptake of MPCM is 0.055 g g^{-1}, which again confirms its hydrophobicity. We also measured the adsorption isotherms of MOF-MPCM composites. Since MPCM is almost hydrophobic, the water uptake of MOF-MPCM decreases with increasing the MPCM content in the composites. The max. water vapor uptake of MOF-MPCM with 25%, 50%, and 75% MPCM decreased to 0.36 g g^{-1}, 0.26 g $g^{-1,}$ and 0.15 g $g^{-1,}$ respectively.

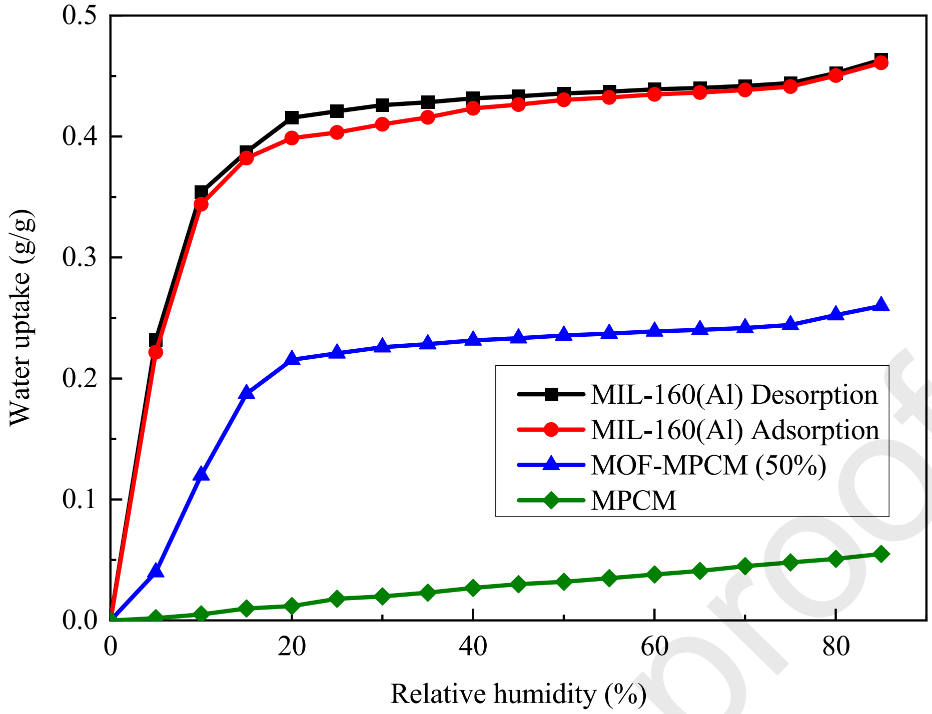

Fig. 6. Vapor sorption isotherms of MIL-160(Al), MPCM, and MOF-MPCM (50%)

3.5 Moisture buffer value

Hygroscopic building materials have the ability to adsorb moisture from surrounding air when the indoor RH increases, and desorbing moisture to the surrounding air when the indoor RH decreases. This ability is defined as the moisture buffering capacity, which is an important approach to passively regulating indoor moisture conditions [27, 28, 29]. NORDTEST [30] project has proposed a standardized method to characterize the moisture buffering capacity of different porous building materials. The core of the NORDTEST method is the measurement of Moisture Buffer Value (MBV), representing the weight change of specimens when subjected to cyclic RH variations under a given temperature. The test method developed by NORDTEST was adopted in this study. The test samples were placed in a climatic chamber (see Fig. 7) and exposed to the cyclic step-changes in RH of the inner air between the high humidity level (75%, 8 hours) and the low humidity level (33%, 16 hours). The MBV value (kg $m^{-2}(\% \text{ RH})^{-1}$) is a direct measure of the amount of moisture adsorbed or desorbed by the sample per exposed surface area (m^2) and per RH change (%) in a certain period. The MBVs of MIL-160(Al) and MOF-MPCM composites were measured using the small climatic chambers at DTU. The experimental setup is shown in Fig. 7. The test results are presented in Table 3. The MBVs of some conventional hygroscopic building materials are also listed in Table 4 for reference. The MBV results show that MIL-160(Al) and MOF-MPCM (containing 50% and 25% MPCM) have an excellent moisture buffer ability compared to traditional and conventional porous building materials. The MOF-MPCM composites with high MBV values have an excellent potential to reduce the latent cooling load by moisture buffering.

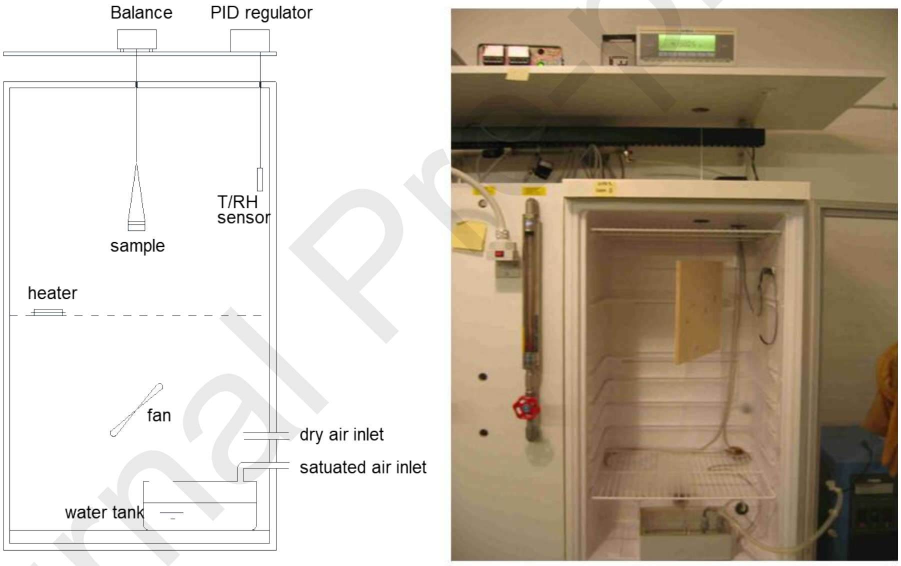

Fig. 7. Climatic chamber and experimental setup for MBV test

Table 3 MBV of MIL-160(Al), MPCM, and MOF-MPCM composites

Samples	MBV ($g \cdot m^{-2} \cdot \%RH^{-1}$)
MPCM	0.08
MOF-MPCM (75%)	0.65
MOF-MPCM (50%)	1.72
MOF-MPCM (25%)	2.13
MIL-160(Al)	2.75

Table 4. MBV of some hygroscopic building materials [13, 30]

Samples	MBV ($g \cdot m^{-2} \cdot \%RH^{-1}$)
Gypsum board	0.26
Brick	0.41
Birch panels	0.61
Concrete	0.38
Laminated Wood	0.45
Diatomite	0.33
Sepiolite	0.54
Vesuvianite	0.79

4. Modelling

Numerical modeling was carried out to study the combined hygrothermal transfer and phase change process in the MOF-MPCM composite materials. The basic phenomenon of heat, air, and moisture (HAM) transfer in porous media has been widely investigated, and many numerical models have been proposed [31, 32, 33]. However, few of them take into account the phase change process inside the materials. Therefore, this section will present a combined model of hygrothermal transfer with the phase transition process.

4.1 HAM-Enthalpy model

First, the classic HAM model from Künzel [31] was adopted, which represents the simultaneous heat and moisture transfer in porous materials. Eq. (1) is the governing equation for the heat balance, and Eq. (2) is the governing equation for moisture balance. These two equations are highly coupled. The moisture content of the material significantly affects the total enthalpy, the heat conductivity, and the heat sources/sinks due to the moisture condensation/evaporation in

Eq. (1). The temperature of the material will also affect the vapor and liquid transfer considerably, as shown in Eq. (2).

$$\frac{\partial H_m}{\partial T}\cdot\frac{\partial T}{\partial t}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+h_v\frac{\partial}{\partial x}\left(\delta_p\frac{\partial \varphi P_{sat}}{\partial x}\right) \tag{1}$$

$$\frac{\partial w}{\partial \varphi}\cdot\frac{\partial \varphi}{\partial t}=\frac{\partial}{\partial x}\left(D_w\frac{\partial \varphi}{\partial x}\right)+\frac{\partial}{\partial x}\left(\delta_p\frac{\partial \varphi P_{sat}}{\partial x}\right) \tag{2}$$

Where, $\frac{\partial H_m}{\partial T}$ is the volumetric heat storage capacity (kJ m^{-3} K^{-1}), $\frac{\partial w}{\partial \varphi}$ is the volumetric moisture storage capacity (kg m^{-3}), H_m is the volumetric enthalpy of the moist material (kJ m^{-3}), w is the moisture content (kg m^{-3}), T is the temperature (K), φ is relative humidity (%), λ is the thermal conductivity (W $(m\cdot K)^{-1}$), h_v is the latent heat of water evaporation (kJ kg^{-1}), δ_p is the permeability of water vapor (kg $(m\cdot s\cdot Pa)^{-1}$), P_{sat} is the saturated pressure of water vapor (Pa), D_w is the coefficient of liquid transport (kg $(m\cdot s)^{-1}$), t is the time (s), x is the thickness (m).

The total enthalpy of a porous building material consists of the dry material's enthalpy and the enthalpy of the moisture adsorbed in the material. Therefore, the total specific enthalpy of the moist material can be expressed as follows:

$$\frac{\partial H_m}{\partial T}=\frac{\partial H_d}{\partial T}+wc_{p,vapor} \tag{3}$$

Where, H_d is the enthalpy of the dry material (kJ m^{-3}), $c_{p,vapor}$ is the specific heat capacity of water vapor (kJ $(kg\ K)^{-1}$).

Secondly, The enthalpy model was introduced to calculate the thermal performance of MPCMs [34, 35]. The total enthalpy (H_d) of dry MPCM material consists of sensible heat and latent heat.

A melting fraction f_l (Eq. 3) was introduced to describe latent heat in the one-dimensional transient heat transfer.

$$H_d = h_s + L\rho \cdot f_l \tag{4}$$

where H_d is the total volumetric enthalpy of dry material (kJ m^{-3}), h_s is the sensible volumetric enthalpy (kJ m^{-3}), L is the latent heat/enthalpy of PCM (kJ kg^{-1}), ρ is the density (kg m^{-3}), f_1 is the liquid fraction, and can be defined as follows:

$$f_1 = \begin{cases} 0 \quad \text{if} \quad T < T_\mathrm{m}, \ \text{(Solid)} \\ 1 \quad \text{if} \quad T \geq T_\mathrm{m}, \ \text{(Liquid)} \end{cases} \tag{5}$$

Where, T_m is the melting temperature of PCM (K).

Combining Eqs. (1), (3), and (4), we can get the heat balance equation for hygroscopic materials with the phase change process.

$$\frac{\partial H_d}{\partial t} + wc_{p,vapor}\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) + h_v\frac{\partial}{\partial x}\left(\delta_p\frac{\partial \varphi P_{sat}}{\partial x}\right) \tag{6}$$

In summary, the HAM-Enthalpy model consists of the moisture balance equation Eq. (2) and the heat balance equation Eq. (6). The coupled effects of heat, air, and moisture transfer, as well as the phase change process, are calculated simultaneously. The HAM-Enthalpy model will be used for calculating the impact of MOF-MPCM on the indoor hygrothermal environment.

4.2 Validation

Since the HAM model [31, 32, 36] and the enthalpy model [34, 37, 38] have already been validated by many studies separately, this section mainly focuses on the validation of the combined HAM-Enthalpy model. The full-scale test facilities at DTU were used to carry out the experimental validation. Fig. 8 shows the picture of the test cells and the internal structure.

The floor area of the test room is 13.8 m^2, and the height is 2.75 m (volume: 38.0 m^3). All walls, ceilings, and floor were well insulated with 0.40 m of mineral wool. Steel sheets were installed on both interior and exterior wall surfaces (except the south facade) to prevent moisture transfer. The south façade is changeable and is composed of a wooden cladding facing the outside, 0.30 m of mineral wool, 0.11 m of a brick wall, and a vapor retarder facing the inside [39]. The test room is very air-tight. The interior wall surfaces were covered by 10 mm-thick MOF-MPCM composites containing 50% MPCM in the experiments. The total surface area of the MOF-MPCM materials is about 20 m^2. The air change rate during the tests was 0.5 h^{-1}. There is an internal heat source of 200 W working from 9:00 to 17:00 every day. There are no window on the wall.

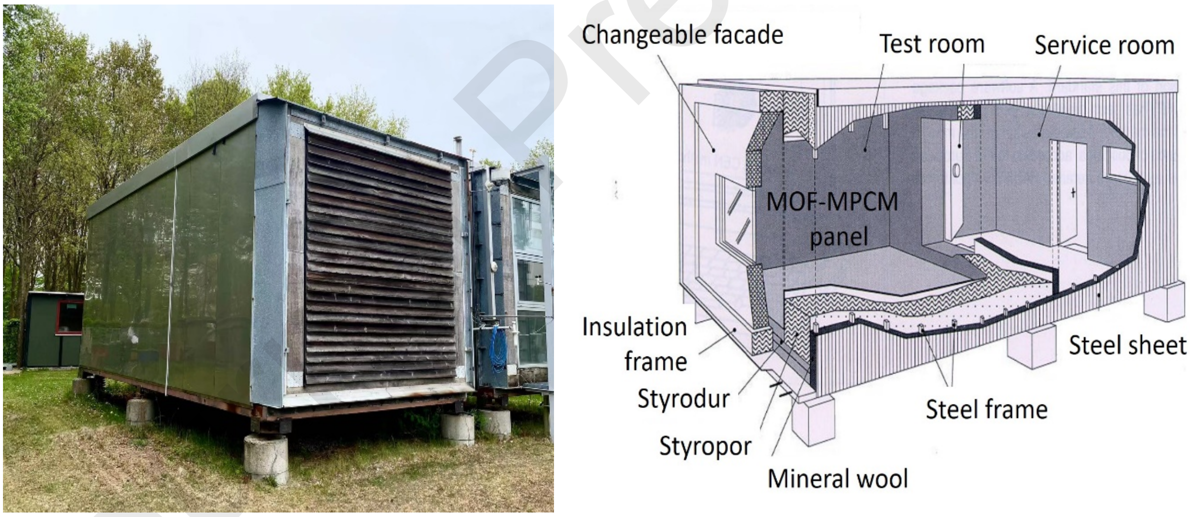

Fig. 8 Picture of the test cells (left) and the internal structure (right)

The temperature and relative humidity inside and outside the test room were measured. The measured outdoor climatic conditions (one week in July) were used as the external boundary conditions for the HAM-Enthalpy model. Figs. 9 and 10 compare the experiment and simulations. The simulated indoor temperature fits well with the measured data. The measured indoor RH has a slightly larger fluctuation than the simulation results. The minor differences in

RH values are probably due to non-uniform indoor humidity distribution in the actual test conditions. It is assumed in the simulation that the room air is well mixed. However, there were some small stratifications in the real test, while the sensor was located in the center of the room. The mean relative error (MRE) for temperature simulation is 0.38%, and the MRE for relative humidity simulation is 1.06%. Nevertheless, the agreement between the simulated and measured data is quite good, which shows that the HAMT-Enthalpy model is reliable for calculating the coupled heat and moisture transfer with phase change processes in buildings.

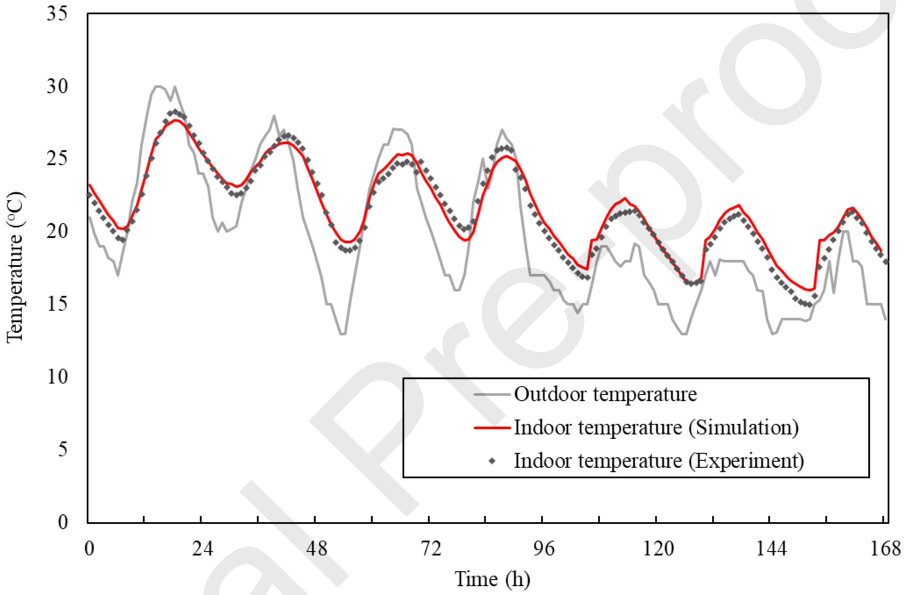

Fig. 9. Comparison of simulated and measured indoor temperature (July)

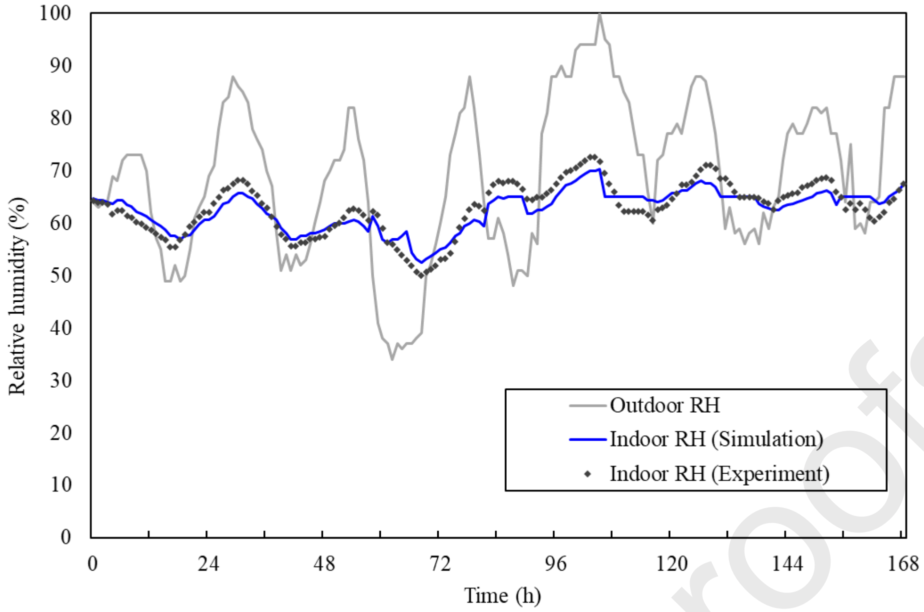

Fig. 10. Comparison of simulated and measured indoor relative humidity (July)

5. Indoor hygrothermal simulation

5.1 Hygrothermal buffering behavior of MOF-MPCM

The HAM-Enthalpy model was used to evaluate the impact of MOF-MPCM on indoor temperature and humidity conditions and the total load of the AC system. Hygrothermal buffering behavior of the MOF-MPCM composites containing different MIL-160(Al) ratios was analyzed by numerical simulation. The test room was assumed to be in Rome, Italy, with a Mediterranean climate. Other settings are the same as the experiments in Section 4.

The calculated indoor temperature and RH of the cases with the MOF-MPCM composites (25%, 50%, 75%) are presented in Figs. 11 and 12, respectively. The simulated results of a reference room with standard plasterboard are also presented in the figures. Compared with the reference room, Fig. 11 indicates that MOF-MPCM can considerably mitigate the periodic indoor temperature variations because of the thermal storage of MPCM.

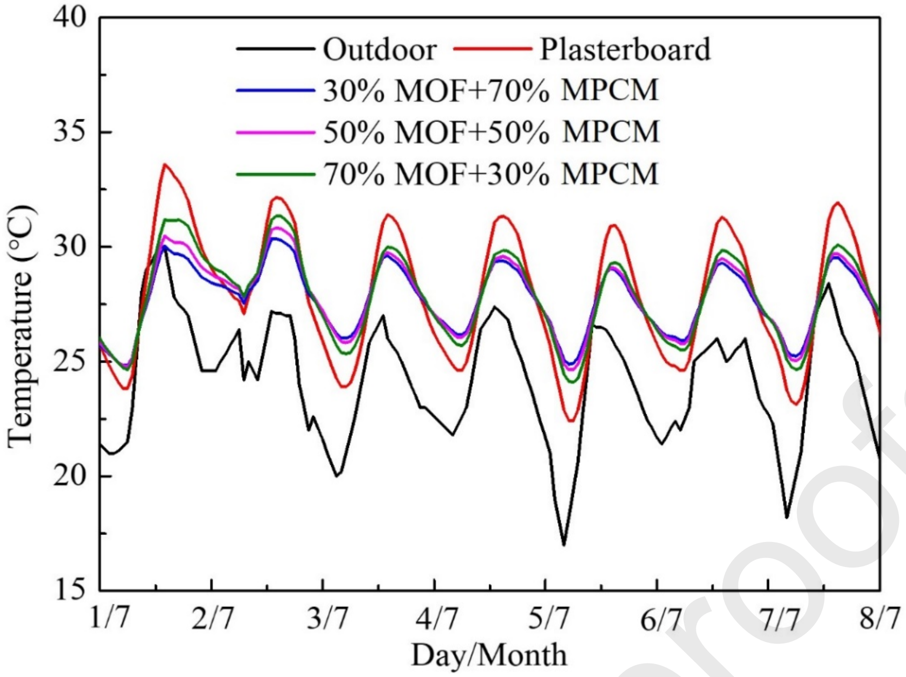

Fig. 11. Indoor temperature of cases with and without MOF-MPCM composites

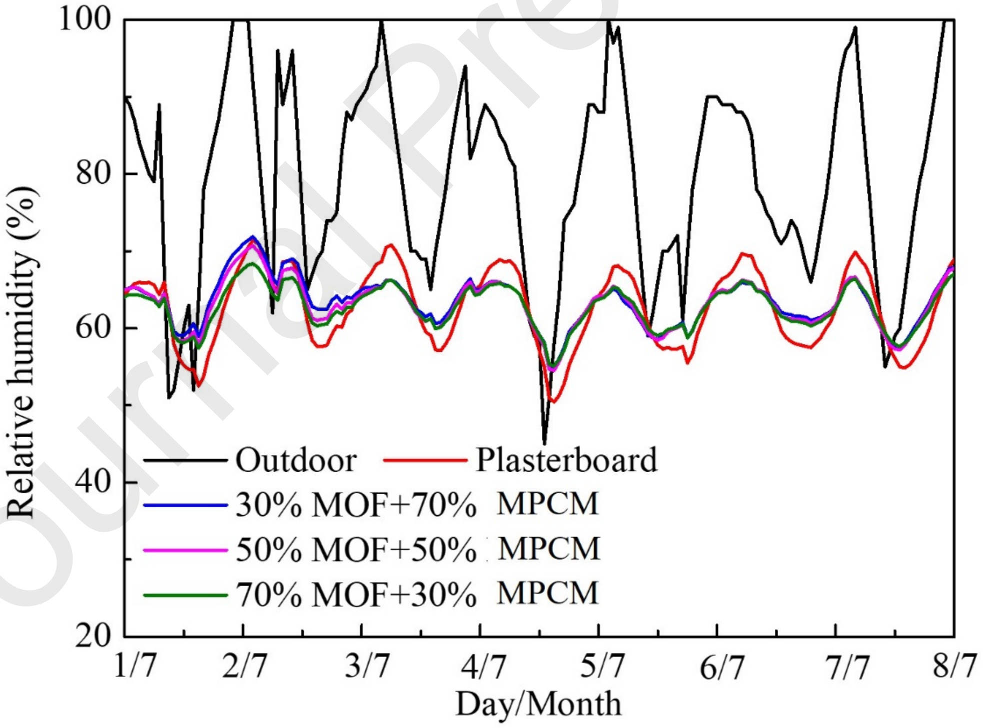

Fig. 12. Indoor RH of cases with and without MOF-MPCM composites

Fig. 12 indicates that the indoor RH has smaller amplitudes in the case with MOF-MPCM composites, proving that MOF-MPCM composites have an excellent buffering capacity that can adsorb a great amount of moisture. Further study reveals that the larger diurnal air temperature and humidity variations, the greater performance of MOF-MPCM composites for indoor hygrothermal management. The MOF-MPCM composites can fully use the day/night temperature and RH difference and moderate the peak temperature and humidity levels during the daytime. The simulation results also show that with the increase of the content of MPCM in the MOF-MPCM composites, the fluctuation of indoor temperature descends, while the RH fluctuation increases. However, it is difficult to determine which ratio is optimal only based on temperature and humidity attenuation. Considering the general balance of thermal and moisture buffering efficiency, we choose MOF-MPCM with 50% MPCM for further discussions about the energy-saving potential in the next section.

5.2 Impact on building energy consumption

Both the experimental measurements and simulations show that the MOF-MPCM composite materials have an extraordinary hygrothermal buffering capacity and can effectively mitigate indoor temperature and RH variations. This section will investigate the effect of MOF-MPCM on the energy performance of office buildings in different cities/climates.

5.2.1 Climates and test building

Outdoor climatic conditions greatly affect the indoor hygrothermal environment and the performance of the phase change humidity control materials. According to the Köppen climate classification, the climates worldwide can be divided into five main climate groups. They are Group A (tropical), Group B (dry), Group C (temperate), Group D (continental), and Group E (polar). To investigate the energy impact of MOF-MPCM on building performance under different weather conditions, seven representative cities around the world were selected from

Group A, B, C, and D. They are, Group A: Singapore (humid tropical climate), and Hong Kong, China (humid subtropical climate); Group B: Phoenix, USA (hot dry climate), and Denver, USA (hot semi-arid climate); Group C: Barcelona, Spain (temperate Mediterranean climate), and London, UK (temperate oceanic climate); Group D: Beijing, China (humid continental climate). These seven selected climates represent the most populated areas worldwide. Since the MOF-MPCM is mainly designed for reducing the energy consumption for air-conditioning, cold climates (Group E) that require heating most of the time are not discussed in this paper.

The test room at DTU was assumed to be an office in the above seven cities/climates. Three simulation cases: Reference case (no MOF-MPCM), Case I (interior walls painted with 38.2 m^2 MOF-MPCM), and Case II (interior walls, floor and ceiling painted with 65.8 m^2 MOF-MPCM) were investigated. The thickness of the MOF-MPCM layer is 20 mm in the simulation. The detailed settings of the simulation are presented in Table 5.

Table 5. Settings of simulation cases.

	Reference	Case 1	Case 2
MOF-MPCM area (m^2)	0	38.2	65.8
Heat power ($W\ m^{-2}$)	15 (occupied period)		
Moisture releasing rate ($g\ m^{-3}h^{-1}$)	3 (occupied period)		
Permissible room temperature range (°C)	18-26 (occupied period)		
Permissible max indoor RH (%)	≤65% (occupied period)		
Air change rate (h^{-1})	0.5 (occupied period)/1(Unoccupied period)		
Air infiltration	No		
Occupied period (h)	09:00-17:00		

Unoccupied period	The rest of the day

5.2.2 Results and discussion

The simulated energy consumption of the test room and the potential energy-saving rate of MOF-MPCM in different cases and climates are summarized in Table 6. It is evident that MOF-MPCM can effectively reduce the energy use of the air conditioning system and achieve a considerable energy-saving potential in all climates. The potential energy-saving rate and building energy efficiency rise with the increase of MOF-MPCM and highly depend on the local climates.

According to the maximum energy-saving potential (Case 2), the seven cities can be classified into three categories. Category I (excellent performance, the energy-saving potential > 25%) consists of Phoenix (hot dry climate), Denver (hot semi-arid climate), and Barcelona (temperate Mediterranean climate). Their energy-saving potentials (Case 2) are 35.19%, 28.92%, and 27.30%, respectively. The MOF-MPCM composite materials have significantly reduced the total energy consumption for air-conditioning. The common climatic features of these three cities are hot and dry summer with large daily temperature and humidity differences. The MOF-MPCM material adsorbs heat and moisture from indoor air in the daytime and maintains indoor hygrothermal conditions. During the night (the unoccupied period), the cool and dry outdoor air can regenerate MOF-MPCM. The composite material will release heat and humidity adsorbed during the daytime (the occupied period), and the regenerated MOF-MPCM will be ready for the next day (next cycle).

Category II (good performance, the energy-saving potential between 10% and 25%) consists of London (temperate maritime climate) and Beijing (continental monsoon climate). The max. energy-saving potentials of these two cities are 23.12% and 14.55%, respectively. London has a temperate oceanic climate with mild summers and winters. The annual and diurnal air temperature ranges are relatively narrow, with a few temperature extremes. Beijing has a monsoon-influenced continental climate featuring hot-humid summers and cold-dry winters. There are remarkable temperature differences between night and day in Beijing. The cities in Category II have milder summer (i.e., cooler, more humid, and less day/night temperature fluctuations) than those in Category I. Therefore, the energy impact of MOF-MPCM in temperate and continental climates is smaller than that in hot and dry climates. This is because the mild and humid outdoor air in the evening is not conducive to the complete regeneration of MOF-MPCM, which affects the adsorption capacity of the MOF-MPCM material on the morning of the next day/cycle. Nevertheless, both the simulation and experiments prove that the MOF-MPCM materials can considerably reduce the energy demand for air-conditioning systems in temperate climates in a purely passive manner.

Category III (fair performance, the energy-saving potential < 10%) consists of Hong Kong (humid subtropical climate) and Singapore (humid tropical climate). Hong Kong has a hot, rainy, and humid summer (May to September) and very mild winter (December to February). The daily high-low air temperature differences are small (about 4 °C). The humidity is high throughout the day. Singapore has a typical tropical climate. The outdoor temperature and RH are relatively high and uniform throughout the year. The annual average daily temperature is about 27.5 °C, and the annual average RH is 84%. The common climatic features of Hong Kong and Singapore are hot and humid with small day/night temperature and humidity differences. This will significantly affect the performance of MOF-MPCM. The max. energy-saving potentials of these two cities are 9.26% and 8.37%, respectively. The hot and humid outdoor air at night restrains the exothermic process of solidification of MPCM and curbs the desorption of MIL-160(Al). The MOF-MPCM cannot efficiently release and discharge the heat and moisture adsorbed during the occupied period by night ventilation, which will limit its ability to moderate indoor heat and moisture variations during the next day/cycle. Therefore, the potential energy-saving of using MOF-MPCM in a purely passive manner in these climates is fair.

Table 6 Simulated energy consumption and energy-saving of using MOF-MPCM in different cases/climates

City	Load and energy-saving	Area of MOF-MPCM		
		$0\ m^2$ (Reference)	$38.2\ m^2$ (Case 1)	$65.8\ m^2$ (Case 2)
Phoenix (hot dry climate)	Total load ($kWh\ m^{-2}a^{-1}$)	100.35	81.77	65.03
	Energy-saving potential (%)	-	18.52	35.19
Denver (hot semi-arid climate)	Total load ($kWh\ m^{-2}a^{-1}$)	90.23	75.47	64.13
	Energy-saving potential (%)	-	16.35	28.92
Barcelona (Mediterranean climate)	Total load ($kWh\ m^{-2}a^{-1}$)	71.56	60.80	52.02
	Energy-saving potential (%)	-	15.03	27.30

London (temperate oceanic climate)	Total load (kWh m^{-2}a^{-1})	70.29	60.91	54.03
	Energy-saving potential (%)	-	13.35	23.12
Beijing (continental monsoon climate)	Total load (kWh m^{-2}a^{-1})	75.12	68.68	64.19
	Energy-saving potential (%)	-	8.57	14.55
Hong Kong (humid subtropical climate)	Total load (kWh m^{-2}a^{-1})	103.63	98.32	94.03
	Energy-saving potential (%)	-	5.12	9.26
Singapore (humid tropical climate)	Total load (kWh m^{-2}a^{-1})	130.21	123.66	119.31
	Energy-saving potential (%)	-	5.03	8.37

In summary, the study shows that MOF-MPCM has a significant effect on the energy performance of building in most climates with large diurnal temperature and humidity differences, especially in Group B (hot/dry climates) and Group C (temperate climates). The energy-saving potential could achieve 35.19% in Phoenix and 27.30% in Barcelona. These values are obtained by using 50% MPCM in the MOF-MPCM composites. The energy-saving potential can be further improved by optimizing the ratio of MOF/MPCM content in the composites. For example, we can increase the MPCM content to enhance the thermal inertia for hot and dry climates; or increase the MIL-160(Al) content to improve the moisture buffer capacity for temperate and semi-humid climates. It will further enhance the overall hygrothermal performance of the MOF-MPCM composites. Moreover, the synergistic effect between MOFs and MPCM is also favorable to the combined hygrothermal buffering. During the daytime, the endothermic process of PCM melting will absorb the heat of adsorption released by MOF during moisture adsorption. It will avoid the temperature increase of the composite and maintain the performance of MOFs. During the nighttime, the exothermic process of PCM solidification will release heat to accelerate the regeneration of MOF. More detailed studies on these topics will be carried out in future studies.

For hot and humid climates with small daily temperature and humidity differences (e.g. Hong Kong and Singapore), the current MOF-MPCM composite has a relatively small energy-saving potential (< 10%) in a purely passive approach. In that case, the MOF-MPCM composite material needs to be integrated with an appropriate mechanical regeneration system, such as heating/cooling systems powered by low-grade or renewable energy. Once the MOF-MPCM material has been completely regenerated during the unoccupied period, it can still be used to passively control the indoor temperature and humidity during the occupied period. However, the current paper mainly discusses the synthesis, characterization, and passive application of the new MOF-MPCM material. We will report a detailed investigation of the integration of MOF-MPCM with different mechanical regeneration systems in future projects.

6. Conclusion

This paper proposes a new metal-organic framework (MOF) based microencapsulated phase change material composite (MOF-MPCM) for the passive regulation of indoor hygrothermal conditions. The synthesized MOF-MPCM material has a dual-function of ad/desorption of both heat and humidity and can simultaneously mitigate the fluctuations of indoor temperature and humidity. MIL-160 (Al), a newly developed green and biomass-based MOF, was prepared as the moisture buffer material. Microencapsulated PCM with n-octadecane core and PMMA shell was synthesized for thermal buffering. Physico-chemical and hygrothermal properties of the new composite materials were measured by various techniques (e.g., SEM, XRD, DVS, DSC, TGA, etc.) The study shows that the novel MOF-MPCM composite holds an excellent hygrothermal buffering capacity. The PMMA shell improves the stability of PCM, while the addition of MIL-160(Al) significantly increases the moisture buffer capacity of the composite. The synergistic effect between MOFs and MPCM has further improved the combined hygrothermal buffering. The ratio of MOF/MPCM content in the composite can be optimized according to the latent/sensible load ratio in different climates.

A numerical model (HAM-Enthalpy model) was developed to calculate the combined hygrothermal transport with the phase transition process in MPCM. The HAM-Enthalpy model was validated by experimental tests conducted at DTU. Numerical simulations were carried out to study the energy impact of MOF-MPCM on an office building in seven cities worldwide. The simulation results indicate the new MOF-MPCM composite material can passively regulate indoor hygrothermal control and cut down the energy consumption of air conditioning systems in all climates. However, the potential energy-saving rate varies in different climates. The MOF-MPCM has the best performance in hot-dry climates with a large amplitude of daily hygrothermal difference. The max. energy-saving potential could be up to 35.19% in Phoenix. The MOF-MPCM composite also has a good hygrothermal buffer capacity in temperate and continental climates (e.g., London and Beijing). The energy-saving potential could reach 23.12% in London. For hot and humid climates, the value of energy-saving potential is relatively low (< 10%). However, since the total energy use is high, the absolute value of energy-saving is still considerable. Higher energy-saving potential can be achieved by integrating MOF-MPCM with a proper HVAC system.

To sum up, the new MOF-MPCM composite material is a promising material for passive management of the indoor hygrothermal environment, reducing building energy consumption and improving occupants' comfort in different climates. MIL-160(Al) synthesized in the paper is a green and biomass-derived MOF. It is non-toxic, low-cost, and environmentally friendly, which is suitable for large-scale applications in the building industry. Further studies will focus on optimizing the MOF/MPCM ratio for different climates to maximize the energy-saving potential of the MOF-MPCM composite.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- A novel MOF-MPCM composite was prepared for indoor hygrothermal control.
- Biomass-derived green MOF MIL-160(Al) was synthesized for moisture buffering.
- The MOF-MPCM composite can moderate both heat and moisture simultaneously.

- The MOF-MPCM has a significant impact on the energy performance of buildings.
- The potential energy saving by using MOF-MPCM could be up to 35.2%.