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Research on the preparation of reversibly thermochromic cement based materials at normal temperature

Yiping Ma *, Beirong Zhu

Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China

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A B S T R A C T

In this paper, reversibly thermochromic cement at normal temperature was prepared by adding reversibly thermochromic microcapsules in white Portland cement. The research results showed that the color of the reversibly thermochromic cement added with a kind of blue reversibly thermochromic microcapsule with 30 °C switching temperature (B30, in which B is for the blue color, 30 is for the switching temperature, and the similar way is used in the following of the paper) could be changed reversibly from blue at lower temperature to white at higher temperature, and the switching temperature was about 42 °C. When added with a kind of red reversibly thermochromic microcapsule with 30 °C switching temperature (R30) or a kind of green reversibly thermochromic microcapsule with 30 °C switching temperature (G30), the color could be reversibly changed from red or green to white, and the switching temperature was about 58 °C. The kind of red reversibly thermochromic microcapsule could thus meet the needs of warm tone in winter and cool tone in summer in buildings. When the thermochromic microcapsule B30 was added in white Portland cement, the water content of the standard consistence of cement slurry increased by about 13%, and the mechanical properties, such as flexural strength and compressive strength, decreased by 20%–40%, but the setting time and the soundness of cement were not affected. All the research results indicate that the prepared material could meet the demand for creation of thermally comfortable environment of buildings. Through changing the solvent, the thermochromic microcapsule R5, G5 and B5 etc. were prepared further. Then by mixed 10% R5, G5 and B5 with white Portland cement, the switching temperatures could be lowered down to 26 °C, 26 °C and 17 °C respectively. The thermal effect of improved reversibly thermochromic cement based material (white cement mixed with 10% black microcapsule, and its switching temperature was about 24 °C) showed that it could warm buildings in winter and avoid buildings over-heated in summer.

1. Introduction

Since there are different seasons in nature, the solar energy absorbed by buildings varies largely in winter and summer [1]. Therefore building thermal environment is not always comfortable for living and working. To create a thermally comfortable building environment, a lot of measures have been taken for buildings, in which porous insulating materials are used widely. Although they can contribute essentially to the reduction of the fossil fuel consumption, the problems of fossil fuel consumption and environmental protection can't be resolved thoroughly by use of these materials. Reasonable usage and disposal of solar energy may be the final resolving method, which includes various solar walls and other solar devices, but the above material and devices may be complex and expensive for buildings. The author and his colleagues have developed the so-called reversibly thermochromic building coatings [2] to meet with the needs, whose color can be changed from red, blue etc. below a switching temperature to white above the switching temperature. During this process, solar energy is mainly absorbed below the switching temperature, and much of it is reflected above the switching temperature. The reversible transforming effects between energy-absorbing and energy-reflecting of the coatings and the reversible transforming mechanism between energy-absorbing and energy-reflecting properties of the coatings are also researched [3,4]. Considering the reversible transforming effects between energy-absorbing and energy-reflecting are taking place at the surfaces of materials, cement based materials consist of main surface of buildings, and up to now there are no any reports to be found about the so-called reversibly thermochromic cement based materials at normal temperature, the authors tried to prepare the materials to meet the needs in the paper.

* Corresponding author.
E-mail address: ypma1239@sina.com (Y. Ma).

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2. Experiment

2.1. Preparation of reversibly thermochromic microcapsules

2.1.1. Searching for thermochromic pigments

At present, the phenomena causing reversible changing of color include conversion of crystalline type with temperature, variation of pH value with temperature, loss of crystalline water of some crystal substance by heating, equilibrium movement of electrons between an electron-donor and an electron-acceptor with temperature, ring-opening reaction of molecules by heating etc.[5]. Based on the above thermochromic effects, a lot of materials were investigated in searching for thermochromic pigments, the authors selected crystal violet lactone and its analogues as thermochromic materials, 4,4′-dihydroxydiphenyl propane as the color-developing agent and phenol, alcohol etc. as solvents. In proportion of lactone:dihydroxydiphenyl:solvent to be equal to 1:5:30, the above materials were used to prepare thermochromic pigments at normal temperatures. Table 1 shows the results.

2.1.2. Microencapsulation of thermochromic pigments

After identifying thermochromic pigments, the authors tried to mix the pigments with ordinary white Portland cement, but it was found that the thermochromic properties of the pigments would be lost after the thermochromic pigments were mixed with white cement. Hence, it was necessary to microencapsulate the thermochromic pigments with a certain substance. Although microencapsulation method had been used in waste disposal [6,7], they are not suitable for the liquid thermochromic pigments. In the present study, two methods, interface polymerization and in site polymerization, were used to microencapsulate the thermochromic pigments. In the process, commercial chemicals were used as reagents and the microencapsulation was carried out according to the following examples:

Preparation of core solution: 10 – 20% by weight lactone compound was mixed with 80 – 90% color-developing agent in about five times volume solvent. When the method of interface polymerization was used for the microencapsulation, 0.2 g terephthaloyl chloride was added to 25 g core solution.

Emulsification of core solution: since the prepared core solution was an oily solution and its hydrophile lyophile balance (HLB) value was about 14, two types of emulsifying agents, oπ-10(polyoxyethylene alkylphenol ether, HLB = 14.5) and a mixing emulsifying agent (HLB = 14.1) (a mixture of OPE-4 (polyoxyethylene nonyl phenyl ether, HLB = 5) and OPE-30(polyoxyethylene nonyl phenyl ether, HLB = 17.1) in proportion 1:3), were used to emulsify the core solution to water by addition of 4.4% (by weight of solution).

Microencapsulation of core solution: 25 g core solution was emulsified in 200 ml water containing 1 g NaHCO3 and 10 g mixing emulsifying agent while keeping the temperature at 40 °C by use of a super thermostat. Then 50 ml 10% ethylene glycol solution was added into the above system under stirring (about 800 rpm). The encapsulation reaction was as following:

$$\mathrm{ClOC{-}C_6H_4{-}COCl + HO{-}CH_2{-}CH_2{-}OH \rightarrow {-}[{-}OOC{-}C_6H_4{-}COO(CH_2)_2{-}]{-}_n}$$

The interface reaction time was about 45 min. Subsequently, the solution was filtered in a centrifugal subsiding machine at 7000 rpm and the resulting microencapsulated pigments were washed with distilled water. Since during the forming of polyamide, hydrochloric acid was released, which would affect the thermochromic property of the pigment, another method, in site polymerization, was used further. In the in-site-polymerization method, reagent was not added to the core solution. Firstly, 9.5 g urea–formaldehyde prepolymer was dissolved in 160 ml water, then 9 g core solution (containing 5% oπ-10 emulsifying agent) was emulsified to water under stirring (about 800 rpm). 10% acetic acid solution was added to the above system while keeping the temperature at 45 °C under stirring for 4 h. During the process, prepolymer was converted into a crosslinked, network state and non-soluble sediment, which would encapsulate the core solution to form microcapsules. At the end of the process, the solution was filtered and washed with distilled water. After drying in room, the reversibly thermochromic microcapsules powder could be obtained. Fig. 1 was the photo of the microcapsule R30.

Table 1
Thermochromic pigments at normal temperatures

No.	Composition (by weight)	Color-changing temperature, °C	Changing of color
R30	Lactone 1: dihydroxydiphenyl: solvent 1 = 1:5:30	30	Red ⇔ colorless
G30	Lactone 2: dihydroxydiphenyl: solvent 1 = 1:5:30	30	Green ⇔ colorless
B30	Lactone 3: dihydroxydiphenyl: solvent 1 = 1:5:30	30	Blue ⇔ colorless

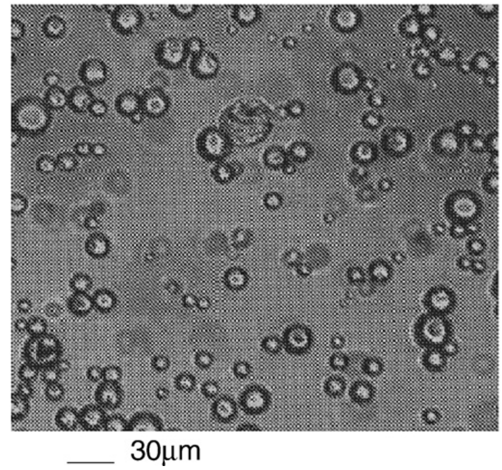

Fig. 1. Micrograph of microencapsulated R30.

2.2. Preparation of reversibly thermochromic cement based materials

In present research, grade 425# white Portland cement made by Shanghai White Cement Company Ltd. was used, whose chemical composition, mineral composition and physical and mechanical properties were showed respectively in Tables 2–4. Through mixing for about 15 min in a mixer, the reversibly thermochromic cement based material could be prepared out by adding a certain amount of reversibly thermochromic microcapsules powder in ordinary white Portland cement. Considering color, strength and economy, the minimum amount of reversibly thermochromic microcapsules powder in ordinary white Portland cement was about 10% by weight.

Table 2
Chemical composition of white Portland cement

Chemical component	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	SO_2	$CaCO_3$	Loss
Content (%)	20–22	63–65	4–4.5	0.5	0.3–0.5	1.42	20	11–12

Table 3
Mineral composition of white Portland cement

Mineral component	C_3S	C_2S	C_3A	C_4AF	f-CaO	Other
Content (%)	60	20	12	1	3	4

Table 4
Properties of white Portland cement

Whiteness (%)	Initial setting time (h:min)	Final setting time (h:min)	Soundness	Flexural strength (MPa)			Compressive strength (MPa)		
				3d	7d	28d	3d	7d	28d
81.7	2:07	2:52	Pass	5.0	6.3	8.1	28.9	37.7	51.9

3. Results and discussion

3.1. Ordinary properties of reversibly thermochromic cement based material

The ordinary properties of reversibly thermochromic cement based materials, such as water content of the standard consistence of cement slurry, fineness, setting time, soundness, strength, were tested according to or referring to Chinese Standard GB1345, GB1346 and GB17671. In GB1345, the fineness of cement was tested by a 80 μm sieve. In GB1346, the water content of the standard consistence of cement slurry and the setting time are tested by the Vicat apparatus. The soundness of cement is tested by the boiled method according to Chinese Standard GB1346, in which the cement sample is formed into a round cake with a diameter about 80 mm and a thickness about 5 mm. At 24 hours age, the cement cake sample is boiled in water for about 4 h. If the boiled cement cake is observed with no cracks and no any deformations, the soundness of cement is considered to be good. Since the amount of the reversibly thermochromic microcapsules powder was very limited, the strengths of cement were tested by use of 10 mm×10 mm×40 mm samples by reference to Chinese Standard GB17671.

Table 5 shows the test results of fineness of cements added with 10% B30. From the table it can be seen that the fineness of cement with 10% B30 is finer than that of pure white cement, which meets the need of Chinese standard less than 10%. The reason may be due to the smaller particle size of B30 (about 7 μm). Table 6 shows the test results of water content of the standard consistence, setting time, soundness of cements added with 10% B30. From the table it can be seen that the water content of the standard consistence is bigger than that of pure white cement by about 13%, which may be caused by the higher surface of B30. From the table it can also be seen that the setting time and the soundness of the mixed cement are not much be affected, which all can meet the needs of Chinese standard. Table 7 shows the test results of strengths of cements added with 10% B30. From the table it can be seen that the compressive strengths of the mixed cements decrease by about 43%, 35% and 39% respectively for 3 d, 7 d and 28 d specimens, the flexural strengths of the mixed cements decrease by about 22%, 19% and 19% respectively for 3 d, 7 d and 28 d specimens. The reasons may be due to the following two aspects. One is that the water to cement ratio of the mixed cement is higher than that of pure white cement by about 15% since the standard consistence reason. Another is that the strength of the microcapsules is much lower than that of cement. The drops of strengths due to the first reason can be reduced by use of plasticizer at the condition of the same workability. Considering the reversibly thermochromic cement based material is used mainly at the surface of buildings as a thin coating for functional usage, the drops in strengths seem tolerable in engineering. Fig. 2 shows the microstructure of the mixed cement paste after compressive failure.

Table 5
Test results of fineness of cement

No.	Composition of cement (g)	Amount retained after sieving (g)	Percentage retained after sieving (%)
1	B30 (5g)+White cement (45 g)	1.06	2.1
2	B30 (5 g)+White cement (45 g)	1.32	2.6
3	B30 (5 g)+White cement (45 g)	1.51	3.0
4	B30 (5 g)+White cement (45 g)	1.08	2.2
5	White cement (50 g)	2.20	4.4
6	White cement (50 g)	1.87	3.7
7	White cement (50 g)	2.06	4.1
8	White cement (50 g)	1.83	3.7

Table 6
Test results of physical properties of cement

Samples	Water used in standard consistence slurry (ml)	Initial setting time (h:min)	Final setting time (h:min)	Soundness
White cement	135.6	2:00	3:02	Pass
White cement with 10% B30	153.0	2:05	3:10	Pass

Table 7
Mechanical properties of cement pastes

Kind of cement paste	Age (d)	Flexural strength (MPa)	Compressive s trength (MPa)
White cement	3	18.4	40.4
	7	21.7	64.7
	28	24.7	89.9
White cement with 10% B30	3	14.4	23.2
	7	17.5	42.1
	28	19.9	55.3

3.2. Thermochromic properties of reversibly thermochromic cement based material

The thermochromic properties of reversibly thermochromic cement based materials were tested with a WGD5-0.2 experimental box made in China, in which the temperature could be kept stably below or above the switch temperature. Fig. 3 shows the test results of color change of the cement materials above and below the switch temperature, in which the specimens no. 1, 2 and 5 are the white cement specimens respectively with R30, G30 and B30, the specimens no. 3 and 7 are respectively the ordinary white paper and pure white cement paste for reference of color, the specimens no. 4 and 6 are the white cement pastes with B30 but treated respectively with boiled water for 3 h and alcohol for 3 d. From Fig. 3 it can be seen that the colors of specimens no. 1, 2 and 5 can be changed respectively from red, green and blue below their switch temperatures to white above their switch temperature, and the switch temperatures for the specimens are respectively 58 °C, 58 °C and 42 °C. When temperature goes down, all the colors of the specimens can be recovered. But the specimens no. 4 and 6 lose their thermochromic properties, which may be due to their destruction of molecular constructions. The reasons of the switch temperatures of the thermochromic cement materials (specimens no. 1, 2 and 5) much higher than that of the thermochromic microcapsules themselves (R30, G30 and B30) may be due to higher thermal capability of cement paste and lower thermal conductivity of cement paste.

From all above research, it can be seen that the colors of the prepared materials can be changed from red, blue, green etc. below the switch temperatures to white above the switch temperature reversibly, the prepared materials seem to help buildings to create a thermally comfortable environment by absorbing solar energy to warm the buildings in winter and reflecting solar energy to avoid the building over-heated in summer without fossil fuel consumption, which indicate that the

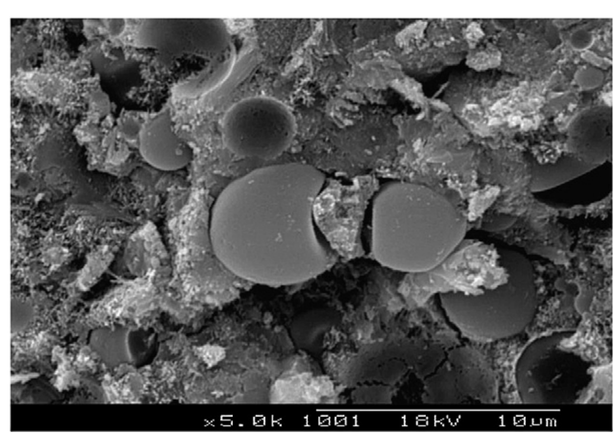

Fig. 2. The microstructure of the mixed cement paste after compressive failure.

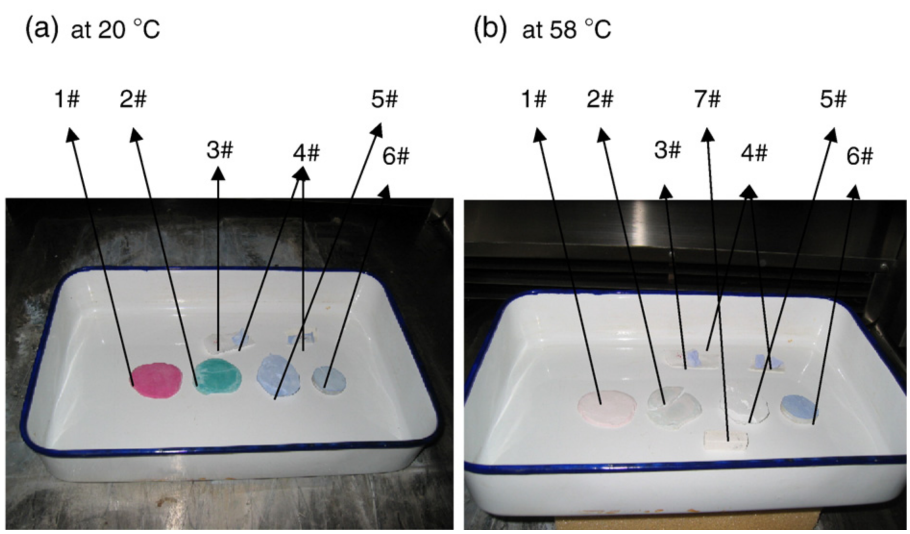

Fig. 3. Color change states of reversibly thermochromic cement paste at normal temperature.

prepared material could meet the demand for creation of thermally comfortable environment of buildings. Since the switch temperatures of the prepared materials are too high to be used for buildings immediately, the authors focus their research to lower the switch temperature to about 20 °C and to measure their thermal effects for buildings. All the research results are reported in the following.

3.3. Thermal effect of improved reversibly thermochromic cement based material

Firstly through changing the solvent, the authors prepared the thermochromic microcapsule R5, G5 and B5 etc. Then by mixed 10% R5, G5 and B5 with white Portland cement, the authors prepared the improved reversibly thermochromic cement based materials whose switching temperatures were respectively 26 °C, 26 °C and 17 °C.

In order to test the thermal effect of improved reversibly thermochromic cement based material, the authors designed an insulating box (see Fig. 4), in which there were two chambers in it, one was opened in one side and the another was closed. Between the two chambers there was a glass plank with 2 mm thickness to be used as a movable drawing plank, which was coated respectively with normal white Portland cement (as a reference), improved reversibly thermochromic cement based material (white cement mixed with 10% black microcapsule, and its switching temperature was about 24 °C) and normal black paint (as a reference). Put the insulating box in the WGD5-0.2 experimental box, set temperatures of the WGD5-0.2 experimental box as 10 °C and 30 °C

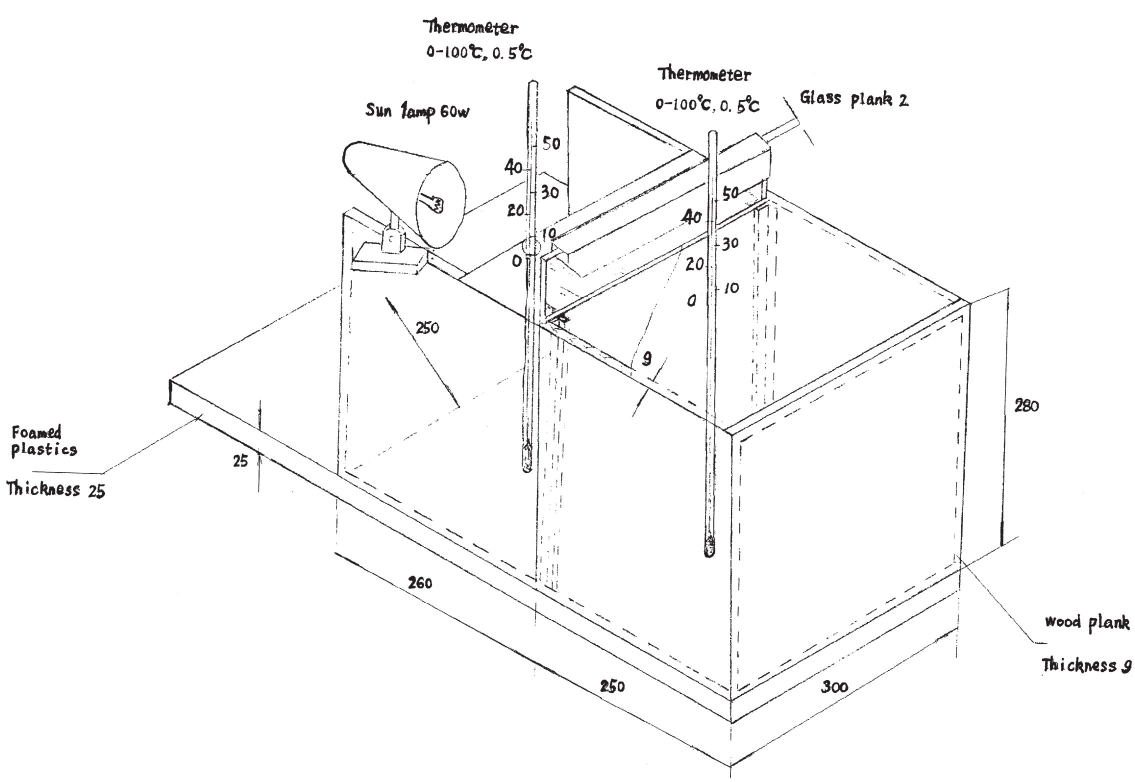

Fig. 4. Sketch of self-made insulating box (mm).

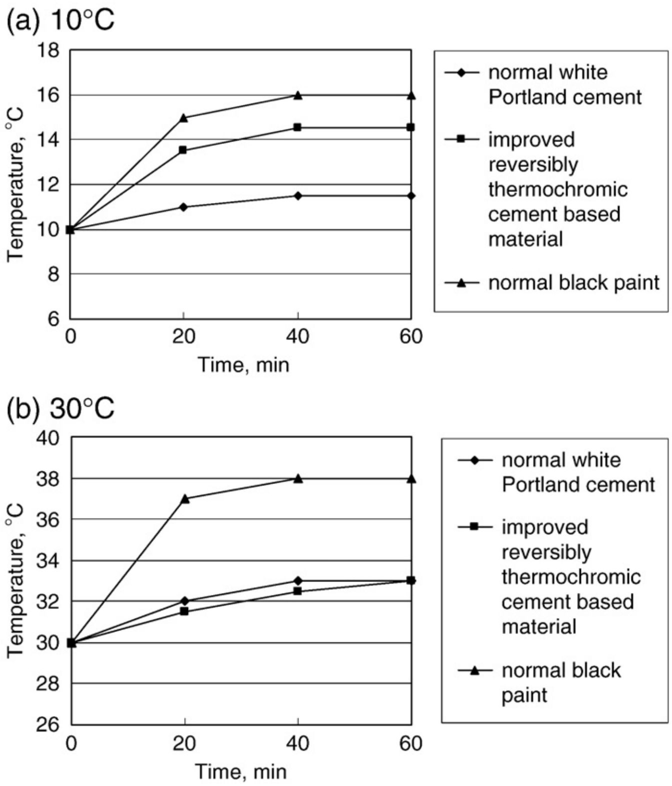

Fig. 5. Test result of thermal effect of improved reversibly thermochromic cement based material.

respectively. After about 5 h, open a 60 W sun lamp and shine light onto the surface of glass plank, read the temperature of the closed chamber every 20 min. The test results were shown in Fig. 5. From Fig. 5(a), it can be seen that at the lower temperature (10 °C), the color of the improved reversibly thermochromic cement based material is black, it can absorb light and after 1 h light shining, the temperature is higher than that of normal white Portland cement by 3 °C, which means the material can help to warm buildings in winter without consumption of fossil fuel. From Fig. 5(b), it can be seen that at the higher temperature (30 °C), the color of the improved reversibly thermochromic cement based material is changed to white, it can reflect light and after 1 h light shining, the temperature is the same as that of normal white Portland cement, which is much lower than that of normal black paint. All the results mean that the prepared reversibly thermochromic cement based materials at normal temperature can meet the demand for creating thermally comfortable building environment.

4. Conclusion

In the present paper, reversible thermochromic pigments at normal temperatures were identified, and an emulsion polymerization process was used to microencapsulate the pigments. By blending the microencapsulated thermochromic pigments with ordinary white cement, the reversibly thermochromic cement at normal temperature was prepared. The research results showed that the color of the reversibly thermochromic cement added with B30 could be changed reversibly from blue at lower temperature to white at higher temperature, and the switching temperature was about 42 °C. When added with R30 or G30, the color could be reversibly changed from red or green to white, and the switching temperature was about 58 °C, in which the R30 microcapsules could meet the needs of warm tone in winter and cool tone in summer in buildings. When B30 was added in white Portland cement, the water content of the standard consistence of cement slurry increased by about 13%, and the mechanical properties, such as flexural strength and compressive strength, decreased by 20%–40%, but the setting time and the soundness of cement were not be affected. All the research results indicate that the prepared material could meet the demand for creation of thermally comfortable environment of buildings.

Through changing the solvent, the thermochromic microcapsule R5, G5 and B5 etc. were prepared further. Then by mixed 10% R5, G5 and B5 with white Portland cement, the switching temperatures could be lowered down to 26 °C, 26 °C and 17 °C respectively. The thermal effect of improved reversibly thermochromic cement based material (white cement mixed with 10% black microcapsule, and its switching temperature was about 24 °C) was tested. At the lower temperature (10 °C), the material could absorb light and make the temperature higher than that of normal white Portland cement by 3 °C, which mean that it could heat buildings in winter. At the higher temperature (30 °C), the material could reflect light and make the temperature as the same as that of normal white Portland cement, which mean that it could help buildings to avoid over-heated in summer.

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