Construction and Building Materials 91 (2015) 133–137

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Preparation and characterization of high porosity cement-based foam material

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HIGHLIGHTS

- A physical air-entraining method has been reported.
- The properties of high porosity cement-based foam materials have been investigated.
- Influence of water–cement ratio and HPMC on material properties has been analyzed.
- Pore structure formation mechanism has been clarified.

ARTICLE INFO

Article history:
Received 18 October 2014
Received in revised form 2 April 2015
Accepted 1 May 2015
Available online 16 May 2015

Keywords:
Cement-based foams
Mechanical air-entraining method
Pore structure
Porosity
Thermal conductivity

ABSTRACT

High porosity cement-based foam materials were prepared through physical air-entraining method and the pore structure and the properties of materials were characterized. The results show that water–cement ratio and Hydroxypropyl Methyl Cellulose (HPMC) content have crucial influence on material properties. When the water–cement ratio was 0.9 and the content of HPMC was 0.4%, the cement-based foam material with the porosity of 94.33% and thermal conductivity value of 0.049 W/(m K) could be obtained. The formation mechanism of pore structure was analyzed that water–cement ratio and HPMC content affect the bubble film toughness which influence on material properties.

1. Introduction

Cement-based foam material is more attractive than polymer foam materials for its unique a set of properties: they have high heat capacity, excellent fire resistance and low cost [1,2]. In field of building energy efficiency, cement-based foam material could substitute the combustible organic thermal insulation materials so as to reduce the occurrence of fire disasters effectively [3]. But compared with organic thermal insulation materials, the thermal conductivity of conventional cement-based foam materials is higher. The opinion of Lysenko and Raed [4,5] is that the materials could obtain the extremely low thermal conductivity value when the pore diameters of porous thermal insulation materials drop to nanometer grade. However, achieving nano-grade pore is greatly difficult for cement-based thermal insulation material. The methods usually adopted to improve the mechanical property, meanwhile thermal performances of cement-based foam materials not only are raising porosity but also optimizing pore structure [6]. The conventional methods for preparing cement-based foam materials mainly include chemical foaming method and physical preparation foam method [7]. Chemical foaming method is to mix foaming agents such as aluminum powders, hydrogen peroxide solution and modified cement paste to stir evenly for preparing material paste to be poured into mold, in which foams are produced via chemical reactions. Foam materials prepared by this method could get a porosity reaching as high as 50–90%. Physical method for preparing foam material is to inject preformed foam into cement paste. Tony and Gibson [9] have used this method to prepare foam materials with the density of 160–1600 kg/m^3. Akthar and Evans [8] prepared a high porosity (92%) cement-based foam by using the similar foaming method for high temperature ceramics [10]. Researchers have been exploring a variety of methods to improve the properties of cement-based foam materials. Verdolotti et al. [11] prepared the composite cement–polyurethane foams by mixing the inorganic cement powder to the polyurethane precursors. Polystyrene granules were used as the filler in a light-weight thermal-insulation foam cement

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http://dx.doi.org/10.1016/j.conbuildmat.2015.05.032
0950-0618/

composite and the density in the region of 150–170 kg/m^3 [12]. The methods above mentioned are considerably complicated. Foam collaboration is easy to appear if these methods are employed to prepare high porosity cement-based foam material [13,14].

A simple mechanical air-entraining method is adopted to prepare cement-based foam material, which is using mechanical stirring to bring a great quantity of air into a modified cement paste with foaming admixture. After the setting and hardening of cement paste, foams solidified gradually. Some correlated researches on adopting mechanical mixing air-entraining method to prepare high porosity cement-based foam material are still under the exploratory stage so that few research achievements have been reported. In this research, the porosity, strength, water absorption, thermal conductivity and other relevant properties of foam materials were tested. Microstructure of pore was also observed by electronic microscopy. Some relevant effective factors on the properties of cement-based foam materials were investigated in this paper.

2. Experimental

2.1. Materials

Grade 42.5 rapid-hardening sulfate aluminate cement was used and its performance is shown in Table 1. When mechanical mixing air-entraining method was used to prepare cement-based foam material, cement type had some influences on the pore structure. The rapid-hardening sulfate aluminate cement is characterized by fast setting, hardening and micro-expansion. Compared with Portland cement, these characteristics are more helpful to shorten solidification time and form small and uniform cells in cement matrix [15]. Modified sodium alcohol ether sulfate was used as foaming agent. The addition of superplasticizer was necessary to ensure foaming cement paste with a low water volume. The pore structure of the hardened foam material was optimized by using additive Hydroxypropyl Methyl Cellulose (HPMC) with viscosity value of 400 mPa S. Foaming agent to cement ratio by weight was 6% and superplasticizer was 0.2%.

2.2. Preparation of high porosity cement-based foam material

The procedure of sample preparation is described as follows. (1) Cement and other dry powder materials were weighed accurately and poured into a mixer. (2) Making the mixer run to stir the materials for 3 min at the speed of 140 ± 5 r/min to obtain the dry powder mixture, where the weighed water with foaming agent was then added into. (3) After stirring the mixed material paste evenly for 10 s at the speed of 140 ± 5 r/min, and then continually stirring the mixed material paste for 5 min at the speed of 285 ± 10 r/min, the mixed material paste was full foamed, and then poured into molds which were removed after curing at room temperature for 8 h. (4) The materials were further cured for 3 days in the standard curing condition. According to the Chinese Standard [15], the 3 days age compressive strength of this kind of cement exceeds the 28 days age compressive strength 90%.

2.3. Porosity test

Before testing, the samples should be dried until the constant weight was obtained under the temperature of 100–110 °C. The porosity of cement-based foam material was calculated using $P = \left(1 - \frac{\rho_{\text{apparent}}}{\rho_{\text{th}}}\right) \times 100\%$ with apparent density derived from weighing a known volume of dried foam material, and theoretical density $\rho_{\text{th}} = \sum_{i=1}^{n} v_i \rho_i$ (v_i = volume fraction of component i, ρ_i = density of component i) [16].

Table 1
Physical performances of grade 42.5 rapid-hardening sulfate aluminate cement.

Setting time (min)		Compressive strength (MPa)			Flexural strength (MPa)		
Initial setting time	Final setting time	1d	3d	28d	1d	3d	28d
29	48	35.2	46.5	48.8	6.7	7.1	8.0

2.4. Test of compressive strength and water absorption

Pressure testing machine was adopted to estimate the compressive strength. The load was added to cubic dried samples with the side length of 70.7 mm at the speed of (10 ± 1) mm/min till the testing sample was damaged.

Water absorption was measured as follows: weighed the mass of the cubic dried sample with side length of 70.7 mm, and then soaked the sample into water for 2 h under the room temperature. Water surface must be higher 25 mm than the surface of testing sample. When soaked process finished, the residual water of the samples taken out of water was absorbed by sponge. The water absorption can be calculated in terms of Eq. (1) as follows:

$$W_v = \frac{m_1 - m_0}{V_0 \cdot \rho_w} \cdot 100\% \tag{1}$$

where, W_v – water absorption, %; m_0 – the mass of dried testing sample, g; m_1 – the mass of sample saturated with water, g; V_0 – the sample volume, cm^3; ρ_w – water density, taking 1 g/cm^3.

2.5. Thermal conductivity test

Samples of specification with size of 300 × 300 × 30mm^3 were dried to constant weight at the temperature of 100–110 °C and cooled to the room temperature for thermal conductivity measuring. Thermal conductivity was measured using TPMBE-300 flat plate thermal conductivity meter and the steady-state guarded hot plate method according to the Chinese Standard [17]. A JEOL JSM-6700F scanning electronic microscope (SEM) was utilized to observe the microstructure of the samples after hydration for 3 days. The samples were dried to reach constant weight at the temperature of 100–110 °C. Fracture surfaces were sputter coated with gold.

3. Results and discussion

3.1. Influence of water–cement ratio upon material properties

When mechanical mixing air-entraining method was used to prepare cement-based foam material, water–cement ratio has crucial influence on the material pore structure and properties, due to the variable water–cement ratio was taken to prepare the cement-based foams material. The physical and mechanical properties of samples are shown in Table 2.

It can be seen from Table 2 that the porosity of each group is higher than 80% and the porosity increase with the water–cement ratio increase. When water–cement ratio is 0.95, porosity can reach as high as 93.3%, while the water absorption increased gradually, inversely the apparent density, compressive strength and thermal conductivity values decreased gradually. The water absorption to porosity can reflect the pore connectivity of foam material [18].

It can be seen from Fig. 1 that the ratio of water absorption to porosity changes little when water–cement ratio is between 0.75 and 0.85. The ratio of water absorption to porosity increases when water–cement ratio is over 0.85. Connected pores can be filled with water when sample is soaked into water. The numerical value of water absorption is equal to the numerical value of connected porosity. The ratio of water absorption to porosity means the ratio of connected porosity to the total porosity. The curve in Fig. 1 indicates that pore connectivity increases with the increasing of water–cement ratio.

From Fig. 2 the relation curve of strength-apparent density rate and water–cement rate is obtained. It can be seen that the decrease rate of strength is larger than that of apparent density and the decreasing rate of strength is aggravated when water–cement ratio is over 0.85. The above mentioned results show a high pore connectivity which could aggravate the stress concentration when foam material was subjected to loads.

3.2. Influence of cellulose ether on material properties

When mechanical mixing air-entraining method was used to prepare cement-based foam materials, the stability of air bubbles

Table 2
The mix proportion and testing results at different water–cement ratios.

Nos.	Experiment matching rates			Testing results				
	Water–cement ratios	Cement (g)	Foaming agent (g)	Porosity (%)	Water absorption (%)	Apparent density (kg/m^3)	3d com. strength (kPa)	Thermal conductivity (W/(m K))
1	0.75	500	3.0	84.78	14.87	409	682	0.078
2	0.80			88.67	15.30	306	485	0.072
3	0.85			90.37	13.57	260	401	0.069
4	0.90			92.56	42.99	201	304	0.058
5	0.95			93.30	56.49	181	223	0.059

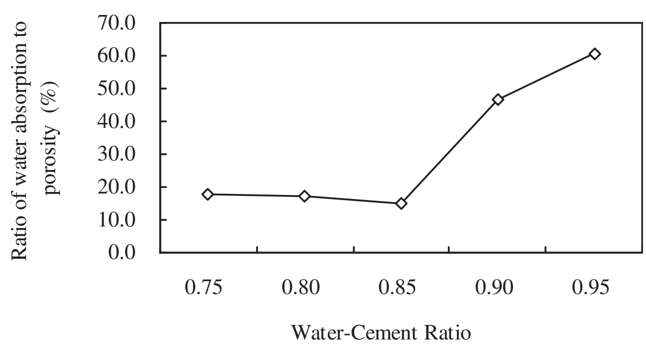

Fig. 1. Ratio of water absorption to porosity changes with water–cement ratio variation.

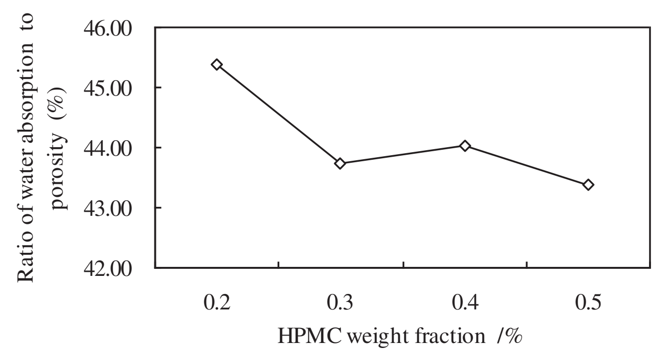

Fig. 3. Ratio of water absorption to porosity changes with HPMC weight fraction.

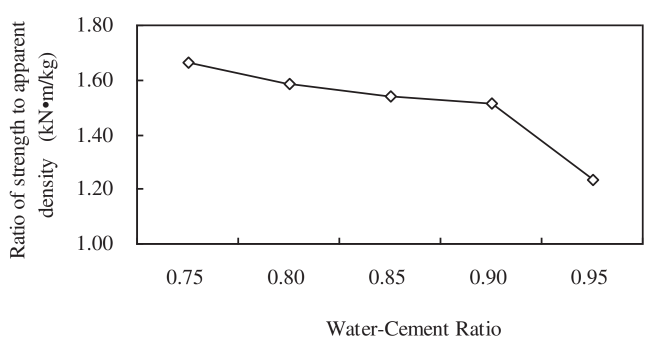

Fig. 2. Ratio of strength to apparent density changes with water–cement ratio.

depended on the ability of cement paste inhibiting foam breakage and escaping [19]. Cellulose ether is a polymer containing polar groups and surface active groups which are widely applied in cement-based materials [20–22]. Cellulose ether (HPMC) was employed in this experiment to improve the flexibility and mechanical strength of the cement paste liquid film, which are favorable for reducing air bubble breakage and escaping.

Based on Table 2 tests results, HPMC was used to modify cement paste at 0.9 water–cement rate. The mix proportion and test results are shown in Table 3.

It can be seen from Table 3 that, with the increase of HPMC weight fraction, apparent density decreases, while porosity increases. The addition of HPMC improved the ability of cement paste containing entrained air. The data in the Table 3 shows that the of HPMC weight fraction increasing from 0.2% to 0.3%, 0.4% and 0.5% causes the porosity increase from 93.48% to 94.11%, 94.33% and 94.41%, respectively. It is worthwhile to note that the variation of water absorption and compressive strength are not consistent with the change of the porosity and apparent density, respectively. Fig. 3 shows the ratio of water absorption to porosity decrease gradually although there is no great variation in water absorption. Fig. 4 shows the ratio of compressive strength to apparent density enlarge when HPMC weight fraction increases.

Cellulose ether (HPMC) is widely used as water-retention agents, thickeners, and film formers in cement-based materials [23–26]. Controlling the porosity of cement-based material is important, since the matrix porosity is fundamental for thermal conductivity and strength. Due to accumulation of HPMC at the air-void interfaces, air voids are stabilized in a fresh cement-based foam paste [27]. In addition to the entrained air pores, HPMC may impact the microstructure of the matrix by affecting the hydration process of cement in different ways. Foamed paste is underwent the most severe moisture loss conditions when it is poured into molds in the preparation of cement-based foam material. HPMC agent can reduce the rate of water evaporation for its water-retention property, therefore, the

Table 3
Mix proportion and testing results with HPMC admixture.

Nos.	Mix proportion			Testing Results				
	Cement (g)	Foaming agent (g)	HPMC mixture (%)	Apparent density (kg/m^3)	3d com. strength (kPa)	Porosity (%)	Water absorption (%)	Thermal conductivity values (W/(m·K))
1	500	3.0	0.2	180	262	93.48	42.42	0.055
2			0.3	159	243	94.11	41.15	0.051
3			0.4	153	232	94.33	41.53	0.049
4			0.5	151	230	94.41	40.96	0.050

Note: HPMC mixture refers to HPMC mass percentage of cement mass.

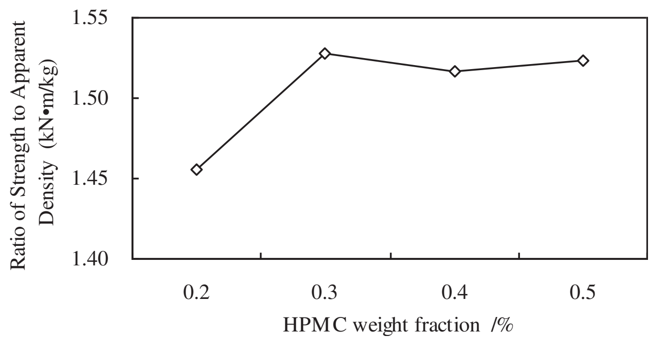

Fig. 4. Ratio of strength to apparent density changes with HPMC weight fraction.

shrinkage and cracking in hardening foam material is controlled [28]. Furthermore, during evaporation, a polymer-enriched layer may form at the cement–air interface. The cracks and holes in the modified high porosity cement-based foam material could be repaired and reinforced through the formation of flexible polymer film which could improve the micro tensile strength and macro compressive strength. As expected, an increase in total porosity and the ratio of strength to apparent density was evident when HPMC was added (see Fig. 4). Moreover, the ratio of water absorption to porosity decrease slightly with increasing HPMC dosage (see Fig. 3). The testing results show that the addition of HPMC agent can improve the foam structure and properties of high porosity cement-based foam material.

3.3. Influence of porosity and pore structure on thermal conductivity

Thermal conductivity is an important property for cement-based foam material. Water–cement ratio and HPMC can apparently affect the material porosity and pore structure, whereby affecting thermal conductivity value of material. The correlation among thermal conductivity, porosity and foam connectivity are illustrated in Fig. 5.

Fig. 5 shows that porosity affects cement-based foam material thermal conductivity greatly. Thermal conductivity value decreases with increase of porosity, but thermal conductivity value is not in agreement with porosity varying law when cement paste without HPMC modification. When porosity increases from 92.56% to 93.30%, the thermal conductivity value does not further decrease but increase slightly. This change may be caused by the intensifying of pore connection. The increase of pore connection can be reflected by the change of the ratio of water absorption to porosity. The ratio of water absorption to porosity increase significantly from 13.57% to 56.49%, when porosity increases from 90.37% to 93.30% by reflecting from Tables 2, 3 and Fig. 5.

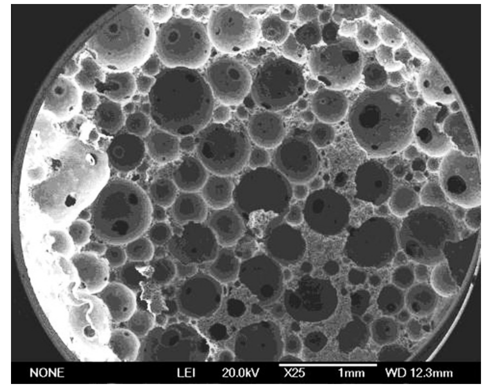

Fig. 6. SEM image of fracture surface of pores at water–cement ratio of 0.8.

The curves in Fig. 5 show that the porosity and foam structure are improved by HPMC modification. When HPMC mixture increase from 0% to 0.4%, the porosity increases from 93.30% to 94.33% and the thermal conductivity value decreases from 0.059 to 0.049 W/(m K). Nevertheless, with the further increase of HPMC from 0.4% to 0.5%, porosity and thermal conductivity value all increase slightly. It is possible that ultra-high porosity degrades foam structure.

3.4. Formation mechanism of pore structure

The formation of foam in cement paste is just the process of balancing the paste pressure, that is foam internal pressure and cement paste surface tensile force of three interactions with each other. Based on Young–Laplace formula [29] (Eq. (2)), that is,

$$P_1 - P_2 = \frac{2\sigma}{R} \tag{2}$$

where, P_1, P_2 – the foam internal and external pressures; R – radius of curvature; σ – cement paste surface tensile force coefficient.

The pressure difference between two neighboring air bubbles is as follows (they can be viewed as locating in the same depth in cement paste):

$$\Delta P = 2\sigma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \tag{3}$$

In an assumed ideal model, the cement paste surface tensile force coefficient is a fixed value and the radius of curvature of two neighboring air bubbles is R_1 and R_2, respectively. Due to the

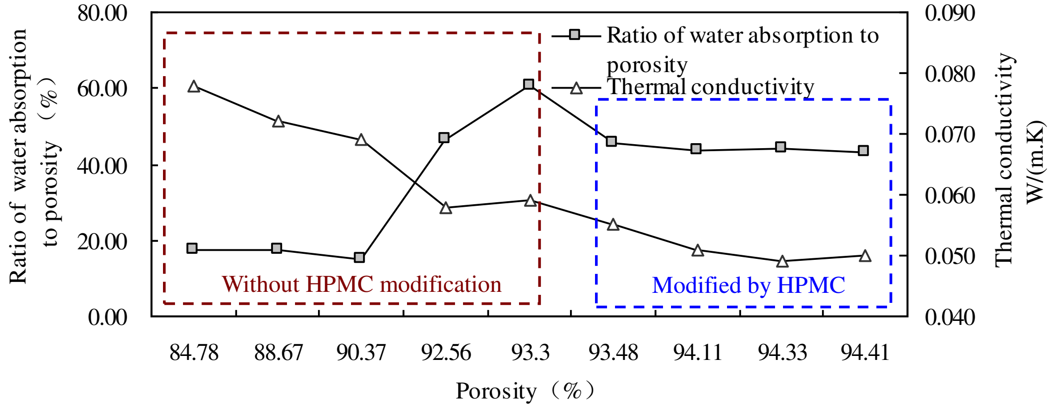

Fig. 5. Ratio of water absorption to porosity and thermal conductivity changes with porosity.

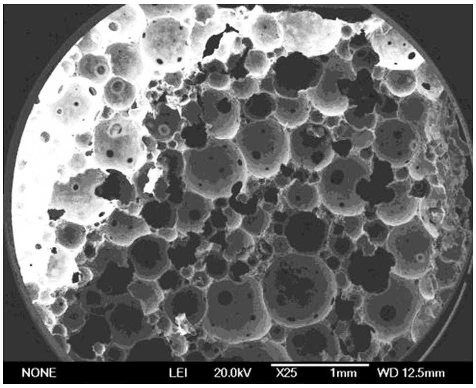

Fig. 7. SEM image of fracture surface of pores at water–cement ratio of 0.9.

difference of radius of curvature, there is a pressure difference between the two neighboring air bubbles. The pressure difference promotes the radius of curvature of two neighboring air bubbles tends to be the same. If the pressure difference is large enough to overcome the surface tensile force of cement paste, the air bubbles breakage will occur. The sample of 0.8 and 0.9 water–cement ratios were observed using scanning electronic microscope (Figs. 6 and 7).

It can be found from the contrast between Figs. 6 and 7 that water–cement ratio has a crucial influence on pore structure. With the increase of water–cement ratio, the surface tensile force of cement paste decreases so that pores are damaged seriously. Comparison of Figs. 6 and 7, when the water–cement ratio increased from 0.8 to 0.90, the pores are damaged obviously and the uniformity of pore size also decreased significantly. The pore structure is a key factor to affect the properties of cement-based foam material, including pore sizes, pore shape and pore connection, etc. The analysis shows that pore structure is influenced by the setting time of the cement paste and the stability of foam in cement paste. The variation in water–cement ratio has changed the consistence of cement paste, whereby affecting the cement paste setting time and foam curing speed. HPMC admixture could improve the flexibility and mechanical strength of the cement paste liquid film so that it is favorable for improving pore structure too.

4. Conclusions

With rapid-hardening sulfate aluminate cement taken as matrix, mechanical mixing air-entraining method was successfully applied to prepare the high porosity cement-based foam material with porosity being over 90%. When the water–cement ratio was 0.9 and the content of HPMC was 0.4%, the cement-based foam material with the porosity of 94.33% and thermal conductivity value of 0.049 W/(m K) could be obtained. Water–cement ratio has a crucial influence on the apparent density, compressive strength, porosity and water absorption of cement-based foam material. Especially, when the water–cement ratio exceeds 0.85, the damage of pores marked increase and the properties of compressive strength and water absorption worsen significantly. The characterization of modified cement-based foam material by HPMC admixture was investigated. Consequently, research results showed HPMC admixture could improve the pore structure, porosity and thermal conductivity value.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51278419), the Science & Technology Research and Development Program of Shaanxi Provincial (2011K07-33), Scientific Research Program Funded by Shaanxi Provincial Education Department (2013JK0945).

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