Construction and Building Materials 171 (2018) 404–413

Contents lists available at ScienceDirect

Construction and Building Materials

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

Preparation and characterization of fire retardant straw/magnesium cement composites with an organic-inorganic network structure

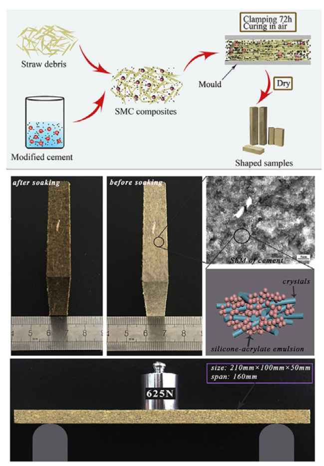
Yingfeng Zuo, Junhua Xiao, Jian Wang, Wenjie Liu, Xingong Li, Yiqiang Wu *

College of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, PR China

HIGHLIGHTS

- The straw/magnesium cement composites prepared by Mg-based adhesive and straw debris.
- The organic-inorganic network structure increased bonding performance and integrity.
- The coverage and blocking effect of emulsion suppressed the phase transition in the water.
- Straw/Magnesium cement composites fully meet the requirements of building materials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 July 2017
Received in revised form 7 March 2018
Accepted 13 March 2018

Keywords:
Straw
Magnesium cement
Silicone-acrylate emulsion
Mechanical property
Water resistance
Fire-retardant
Organic-inorganic network structure

ABSTRACT

Magnesium cement product is an excellent fire-retardant material that has been extensively used in the building materials industry. But their strength and ability to withstand humid conditions still yet to be improved. The silicone-acrylate emulsion was utilized in this study to improve the water resistance and mechanical strength of the straw-magnesium cement (SMC) composites. The properties improvement mechanism and fire-retardant performances was also analyzed. For the SMC composites containing 6% silicone-acrylate emulsion, the modulus of rupture, internal bond strength and the strength retention coefficient after immersion have all increased significantly. In contrast, the thickness swelling, water absorption decreased dramatically. The analysis results showed that an organic-inorganic network structure was formed in the novel magnesium cement, which enhanced the integrity of the material and played a role in protecting the crystals against hydrolysis. With the enhanced water resistance and mechanical strength, the novel SMC composites broadened the use in humid environments and increased the service life. Their excellent fire-resistant properties make the novel SMC composites an ideal candidate for use in public venues.

1. Introduction

Magnesium cement was synthesised by combining light-burned magnesium oxide, magnesium chloride hexahydrate and

* Corresponding author.
E-mail address: wuyq0506@126.com (Y. Wu).

https://doi.org/10.1016/j.conbuildmat.2018.03.111
0950-0618/

magnesium sulphate heptahydrate [1,2]. Magnesium oxide, the main component of magnesium cement, is the first commonly used refractory oxide with a refractoriness of 2800 °C. Therefore, magnesium cement products generally possess good fire and temperature retardant characteristics and are often compounded with combustible materials such as plant fiber, which has been found to withstand high temperatures above 500 °C [3]. Moreover, magnesium cement can bond well with rice, corn, wheat and other crop straw [4]. Traditional polymer adhesives are difficult to bond with crop straw because of the high ash content and inorganic cuticle layer of crop straw [5]. All this makes magnesium cement as emerging cement in the wood-based panel industry and building materials industry to produce straw-magnesium cement (SMC) composites. Nowadays, SMC composites have been widely used in wall panels, fire doors, light flooring, furniture panels, construction, decorations and packaging materials [6,7].

Magnesium cement can be cured at normal temperature and pressure [8]. The cured product is largely comprised by the xMg$(OH)_2 \cdot yMgCl_2 \cdot zH_2O$, $xMg(OH)_2 \cdot yMgSO_4 \cdot zH_2O$, and with a small amount of $Mg(OH)_2$ gels. But the $3\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 3) and $5\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 5) serve as the main crystalline phases [9,10], and the needle-like phase 5 is the strength phase, which means that the bonding strength of magnesium cement increases with increasing proportion of this phase [11]. However, if magnesium cement coagulate too fast, most of the heat of hydration is released within a short time, thus, the reaction heat is too concentrated during the hardening process, resulting in a low proportion of the phase 5 [12]. Moreover, the phase 3 and phase 5 crystallites would slowly hydrolyse and transform into loose, layered $Mg(OH)_2$ crystals in a wet environment, finally forming $MgCl_2$ and other water-soluble salts [13]. The hydrolysis reaction will irreversibly occur as follows [14].

$$[Mg_3(OH)_5(H_2O)_x]^+ \cdot Cl^- \cdot (4-x)H_2O(\text{phase } 5) + H_2O \rightarrow 3Mg(OH)_2 \downarrow + H^+ + Cl^- + 4H_2O \quad (1)$$

$$[Mg_3(OH)_5(H_2O)_x]^+ \cdot Cl^- \cdot (4-x)H_2O(\text{phase } 3) + H_2O \rightarrow 2Mg(OH)_2 \downarrow + H^+ + Cl^- + 4H_2O \quad (2)$$

$$2HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2H_2O \quad (3)$$

This process severely reduces the strength of the cements and products, and causing brine-back and pan-cream, thus affecting the decorative quality of the composites, limiting their application's range and shortening their service life. In order to improve the strength and water resistance of magnesium cement products, silica fume, fly ash, phosphoric acid, phosphate and other similar materials have been widely used to improve the performance [15–17]. However, the reported thus far has not been satisfactory. In this paper, a silicone-acrylic emulsion (SAE) was selected because of its high temperature resistance, environmentally friendly, good hydrophobicity, low temperature of film formation, high adhesion and similar pH to magnesium cement [18]. The properties improvement mechanism of silicone-acrylic emulsion was also analysed.

2. Materials and methods

2.1. Materials

The raw material photos of SMC composites were shown in Fig. 1. Light burnt magnesium oxide (MgO) (Fada Mines Co., Ltd. Liaoning, China), hexahydrate magnesium chloride ($MgCl_2 \cdot 6H_2O$) (Yufeng Chemical Co., Ltd. Shandong, China) and heptahydrate magnesium sulphate ($MgSO_4 \cdot 7H_2O$) (Tongchuan Chemical Co., Ltd. zibo, China) were used to prepare the magnesia cement. Light burnt magnesium oxide, supplied as an industrial raw material, was calcined magnesite powder with 85.2% MgO, 1.4% CaO, 3.8% SiO_2, 0.3% Al_2O_3, 0.2% Fe_2O_3, and 9.1% loss on ignition. Magnesium chloride crystal and magnesium sulphate crystal were also an industrial-grade chemical with the purity of 98.8%. A silicone-acrylate emulsion with a solids content of 42% and a viscosity of 36 mPa•s was obtained from Coating Dev. New Materials Co., Ltd., Guangdong, China. Rice straw was approximately 1 m in height at harvest and was cut above the water line; remove panicle, leaves, weeds, dirt and other impurities. The straw was broken down in a hammer mill and then filtered through a vibrating screen. The debris was about 3–5 mm long (accounted for 85%) by 0.4–1.5 mm wide and 0.2–0.5 mm thick. Commercial straw composites were used as a control, purchased from Wanhua Eco-Board Industry Co., Ltd., which employed polyurethane resin as binder.

2.2. Preparation of straw/magnesium cement composites

The preparation route of SMC composites was shown in Fig. 2. Magnesium cement was prepared by mixing MgO, $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$ and deionized water with a molar ratio of 8: 1: 0.35: 22.5 and then blended with silicone-acrylic emulsion. On the basis of a large number of experiments on the previous period, the different addition amounts of emulsion including 2%, 4%, 6%, 8% and 10%, were calculated as a mass percentage of MgO, and respectively marked as S-2, S-3, S-4, S-5 and S-6. The control group did not add emulsion, marked as S-1. The cement and straw debris were fully stirred in a periodical mixing machine (BS180, Huade Mechanical Equipment Co., Ltd. Guilin, China). The mixture was spread onto a wooden frame with dimensions of 325 mm × 300 mm × 10 mm and then clamped in a mould, and further cured in air for 28 days. The shaped samples were dried in an oven at 80 °C to a moisture content of approximately 10%. The density of the SMC composites was 1.0 g/cm^3, the thickness was 10 mm, and the filler content was 30% of the total mass.

2.3. Properties and characterization

2.3.1. Evaluation of mechanical properties

The modulus of rupture (MOR), and internal bond strength (IB) of composites were determined in accordance with Chinese national standard (GB/T 24312-2009). The MOR was measured by conducting three-point static bending tests (using an Universal Testing Machine (MWW-100, Naier testing machine Co., Ltd. Ji'nan, China)) on specimens with dimensions of 210 mm × 100 mm × 10 mm at a loading speed of 10 mm/min. The IB was measured by pulling the specimen (50 mm × 50 mm × 10 mm) apart in a perpendicular direction. The steel fixtures were bonded on each side of the specimen using hot melt glue. A tensile load with a crosshead speed of 5 mm/min was applied to each steel fixture until failure occurred in the specimen. Each measurement presented herein is the average for six specimens cut from two different composites.

2.3.2. Water resistance test

The water resistance of the SMC composites was evaluated by thickness swelling (TS), water absorption (WA) and strength retention coefficient (R), which also measured according to Chinese national standard (GB/T 24312-2009). The TS was the ratio of the increment in thickness after water absorption to the thickness before water absorption. The WA was the ratio of the difference in mass after water absorption to the mass before water absorption. They were measured after 24 h immersions in deionized water at 25 °C, with specimen size 50 mm × 50 mm × 10 mm. The strength retention coefficient was the ratio of the mechanical