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Investigations into the function of sticky rice on the microstructures of hydrated lime putties

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HIGHLIGHTS

- The effect of the sticky rice on the lime mortar during carbonation was investigated.
- 1–3 wt.% sticky rice regulated the growth of calcite particles while doesn't change the phase composition after carbonation.
- A conservation practice on Guoansi pagoda using 3 wt.% sticky rice lime mortar has been performed.

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ABSTRACT

Sticky rice lime mortar has a long history as the building materials for many historic masonry buildings in ancient China. However, the motivation for the addition of sticky rice into the inorganic lime is not very clear. In this article, lime mortars with 1–3 wt.% sticky rice additions were studied and compared in terms of specific area, microstructures and phase evolutions during the carbonation process. The specific surface area of the $Ca(OH)_2$ particles was found to increase with the addition of sticky rice. Also, during the carbonation of the lime mortars, the sticky rice took a role in regulating the growth of the $CaCO_3$ crystals. Among the three crystalline polymorphs of calcium carbonate-calcite, aragonite and vaterite, only calcite was found after the complete carbonation of the lime. Finally, one conservation application using 3 wt.% sticky rice lime mortar on the restoration of Guoansi pagoda in Zhejiang Province of China was discussed in detail.

1. Introduction

Lime mortar is a type of mortar, composed of lime and aggregates such as sand or marble dusts, mixed with water. During the carbonation process, the portlandite particles reacts with atmosphere CO_2 to transform into calcium carbonate. The morphology and microstructure of the calcium carbonate crystals will be critical in determining the properties and performance of the lime mortars or plasters. Thus, the morphological control of the calcium carbonate crystals is important.

Calcium carbonate has three crystalline polymorphs-calcite, aragonite and vaterite. Thermodynamically, calcite is the most stable phase among the three while vaterite is the least stable [1]. However, the three polymorphs could be synthesized via precipitation reaction. Many parameters have been varied to control the phase and morphology of $CaCO_3$ crystals, including solution pH [2–5], temperature [1,6–12], relative humidity [13–15], Mg^{2+} concentration [16–21], SO_4^{2-} concentration [22], as well as additions of a series of functional surfactants or additives, such as polysorbate 20 [23], disodium salt of EDTA [6], aspartic acid, serine and glucose [19] and microcrystalline cellulose [24], etc. The three polymorphs of $CaCO_3$ could be distinguished by Raman spectroscopy, X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) [1,2,6,25–28].

Functional admixtures were often added into the mortar, in order to improve the working properties as well as the long-term performance. For instance, polycarboxylate-based plasticizer gained great popularity during the preparation of lime mortars [29–33]. Typically 0.5–1 wt.% addition of such plasticizers would enable the slaked lime putty to achieve about the same consistence, with only 70% of the original water/lime ratio [29]. This would lead to a reduction in shrinkage and thus an increase in the mechanical strength of the mortars.

Mortars obtained by mixing sticky rice, slaked lime putty and calcareous aggregates were found to be employed when building

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up city walls, ship locks, monuments and tombs in ancient China [34–38]. The sticky rice starch paste were intentionally added to improve the overall performances of the lime mortars, especially mechanical strength after carbonation [35,39]. The existence of sticky rice starch in ancient mortars could be confirmed through the starch-iodine test. An addition of 3–5 wt.% sticky rice starch was suggested, to obtain a lime mortar with desired properties for the restoration of the ancient masonry buildings [34,37,40].

The rice usually consists of two types of starch: amylopectin and amylose. Amylopectin is a highly branched starch molecule that's responsible for making rice gelatinous and sticky. In general, for normal rice, amylopectin was found to take up over 70 wt.% of the starch [41]. The content and the structure of amylopectin have a great influence on the gelatinization temperature, swelling behavior, light transmittance as well as retrogradation tendency of the starch paste [42–48]. On the other hand, the other starch-amylose, is a long, straight starch molecule consisting of long chains with hundreds to thousands of glucose units connected with α-1,4-glucans. The amylose content is usually less than 5 wt.% of the sticky rice starch and doesn't gelatinize during cooking [41,43,44].

Besides amylopectin and amylose, protein was also found to be present within the rice, of which the content ranged from 6.8 wt.% to 9.6 wt.% [49]. The protein could play an important role in regulating the carbonation of the $Ca(OH)_2$ within the lime putty [49–53]. Typically, in a neutral environment, protein works as biomacromolecular polypeptides to direct and control the formation of calcium carbonate crystals [50,53,54]. However, during the preparation of the sticky rice starch paste for lime mortars, the rice starch would be heated in boiling water for hours. Then the rice protein will undergo thermal denaturation and finally coagulate. Thus the possible influence of the protein on the calcium carbonate crystals could be excluded.

A lot of efforts have been put into developing sticky rice lime mortars for conservation applications [34,36,40,55]. However, the influence of the sticky rice starch paste on the morphology and the microstructures of the $CaCO_3$ crystals was not well studied. The specific area of the freeze-dried lime putties with 1 wt.% and 3 wt.% sticky rice starch as well as 3 wt.% pregelatinized sticky rice starch will be compared. Meanwhile, in the presence of different sticky rice starch, the phases, morphology and microstructures of the carbonated $CaCO_3$ crystals would also be monitored and compared. Finally, one conservation application using 3 wt.% sticky rice lime mortar on Guoansi pagoda in Zhejiang Province of China would be discussed in detail.

In summary, the objective of this work was to explore the effects of sticky rice starch paste on the lime putty at different carbonation stages, as well as provide a way for studying lime based mortars with organic additives for conservation or restoration purposes.

2. Materials and methods

2.1. Raw materials

Commercial dry hydrated lime powders were purchased from Jianghu Titanium White Chemical Co. Ltd. (Shanghai, China). The food-grade additive powders have a purity over 95% and an average particle size of 6.98 μm.

The plasticizer C-SP, a polycarboxylate ether type polymer, was purchased from SNF Floerger (France).

Pulverized sticky rice (*Indica* type, Enuo 6 variety) used in this study was purchased from the local market in Jingzhou city of Hubei province, China. The amylose content in the rice starch ranges from 0.9 wt.% to 1.1 wt.% with a protein content of around 8.6 wt.%. Pregelatinized sticky rice (*Indica* type, Yangfunuo variety) was purchased from Yuanguan Food Materials Co. Ltd. (Nantong, China) with an amylose content of 1.7–3.2 wt.%.

Analytical grade I_2, KI, KBr and CH_3COOH were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used as received. Purified water with an electric conductivity less than 10 μS/cm was used throughout this work.

2.2. Sample preparations

In order to compare the amylose content within the pulverized sticky rice and the pre-gelatinized sticky rice, both samples were prepared following a modified iodine-binding method [42]. In this modified method, 0.1 g of the sticky rice flour was suspended in 10 ml saturated $Ca(OH)_2$ solution at room temperature, followed by heating at 80–90 °C for 10 min under stirring. Afterwards, the suspension was cooled to room temperature and then diluted to 50 ml using pure water. 2.5 ml of the dispersions was transferred to a 50 ml beaker followed by the addition of 25 ml pure water. The PH value of the solution was adjusted to 3.0 using 0.1 mol/l acetic acid, followed by addition of 0.5 ml I_2-KI solution, and again diluted to a total volume of 50 ml using pure water. The dispersions were then subject to spectrophotometric examinations.

A common approach was followed to prepare the sticky rice starch paste [48]. First, water disinfection was performed by boiling the pure water for at least 10 mins and then the water was cooled to room temperature. Afterwards, 2.5 g of the pulverized sticky rice was added into 50 ml disinfected water and left to soak for an hour. The rice starch was gradually heated and stirred in the boiling water until it got gelatinized. Afterwards the starch paste was left to cool to room temperature and vigorously stirred for 10 min. A 5 wt.% paste of sticky rice starch was then obtained.

Once the 5 wt.% sticky rice starch was ready, five groups of samples were prepared, including pure lime putty, lime putty with C-SP plasticizer, lime putty with both C-SP and 1 wt.% sticky rice starch, lime putty with both C-SP and 3 wt.% sticky rice starch as well as lime putty with both C-SP and 3 wt.% pregelatinized sticky rice starch. A total weight of 20 g was prepared for each of the samples with a water to lime ratio of 1:1. Except the group of pure lime putty, 0.05 g of C-SP plasticizer were used in all the other lime putties, in order to reduce the particle agglomerations and increase the flowability of the lime putties.

Immediately after the samples were prepared, they were transferred to a freeze drier for the BET test. One drop of each lime putty was deposited onto the glass slide and left for carbonation in the air, under a room temperature of 20 ± 5 °C and relative humidity of 65 ± 10%. XRD, SEM, FTIR were preformed to examine the phase evolutions during the lime carbonation after a period of 5 days and 45 days. The first 5-day carbonation was chosen because it's in the process of partial carbonation while the water loss of the putty was adequate for the samples to undergo FTIR, XRD and SEM examinations. A final 45-day carbonation time was chosen because a full carbonation was expected considering the thinness of the lime putty layer on the slide (around 250 μm).

2.3. Instrumentation and operating conditions

The thermal analysis of pulverized sticky rice and pregelatinized sticky rice was performed on a thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC) using a NETZSCH STA 409 PC/PG thermo-gravimeter in a flowing air environment. Temperatures were scanned in the range between 30 °C and 900 °C with a heating rate of 20 °C/min.

Light absorption of the iodine complex mainly formed during the reaction between rice starch and the iodine was measured from 400 to 800 nm with a resolution of 1 nm, using a double-wavelength UV–Vis simultaneous spectrophotometer (UV-1800, Mapada Company, Shanghai, China).

The lime putties were freeze-dried using a VirTis Advantage EL-85 (Gardiner, New York, USA) benchtop freeze dryer with an initial shelf temperature of 25 °C, condenser temperature of −80 °C and an ultimate pressure of 10^{-6} bar.

N_2 adsorption and desorption isotherms of the five lime putties were measured at N_2 boiling point (77 K) of using a Quantachrome Autosorb-1-C chemisorption-physisorption analyzer. Prior to test, each dry hydrated lime powder was degassed by heating up to 200 °C for 2 h. The specific surface areas were calculated from the isotherm data in the relative pressure range of 0.05–0.25 using the BET (Brunauer–Emmett–Teller) method. A value of 0.162 nm^2 was taken for the cross-section area of N_2 molecule in the liquid nitrogen bath. A density value of 1.251×10^{-3} g/ml was taken for the N_2 gas under standard temperature and pressure (STP).

Microstructural examinations on calcium carbonate crystals carbonated from the lime putty were carried out using a FEI SIRION-100 field emission scanning electron microscope (SEM). Samples were gold coated before examination.

X-ray diffraction (XRD) measurements on the lime putties that were left for carbonation for 5 days were performed on a Rigaku Ultima IV diffractometer with the following measurement parameters: Cu Kα radiation $\lambda = 1.54056$ Å, 40 kV, 30 mA, 15–50° 2θ exploration range with a step size of 0.02° 2θ and scan speed of 15°/min. Mineral phases were identified by using the JCPDS (Joint Committee on Powder Diffraction Standards).

FTIR was also performed on the four lime putties that has been carbonated for 5 days and 45 days on a Nicolet iS10 FTIR spectrophotometer (Thermo Fisher Scientific, USA). The samples were grinded with KBr powders and pressed into solid pellets. The spectra were collected at 16 scans in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.