minerals

Communication

Bending Improvement of CO_2-Activated Materials through Crosslinking of Oligomers

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Abstract: Calcium carbonate is the main carbonation product of most CO_2-activated materials (CAMs); however, its brittle nature usually leads to low bending, which represents the major drawback of CAM in its application as a construction material. Herein, the bending of CAM was greatly improved by the addition of triethylamine (TEA) in the carbonation process. Both the grain size of the carbonation product, i.e., calcite, and the intensity ratio of the crystal planes from (104) to (113) obviously increased with the addition of TEA, as shown by the scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements, suggesting the crosslinking of oligomers. Compared with the CAM without TEA, the flexural strength of CAM was significantly improved under optimized curing conditions, which was attributed to the crosslinking of oligomers formed with TEA addition. The present work may provide a promising strategy for improving the bending of CAM materials.

Keywords: CO_2-activated materials; microstructure; toughness; crosslinking oligomers; triethylamine

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1. Introduction

CO_2-activated materials (CAMs) are a kind of novel low-carbon binder prepared with pure calcium/magnesium alkaline minerals or calcium/magnesium-bearing alkaline industrial wastes (steel slag, magnesium slag, carbide slag, etc.) under the curing condition of accelerated carbonation [1]. Along with the process of CO_2 sequestration, CAM can develop excellent mechanical properties in a few hours. Until now, the effect of the partial pressure of CO_2, temperature, curing time, molding pressure and characteristics of the minerals on the carbonation reactivity of CAM has been studied widely [2].

Calcium carbonate is the primary product of most CAMs, which acts as a cementation and creates the strength of the matrix [3]. However, calcium carbonate is a typical brittle material, which leads to a low bending of CAM [4]. In order to improve the bending of CAM, chitosan [5] and amino acids [6] have been introduced to the CAM to enhance its flexural strengths by regulating the relative proportions of the various crystal types (vaterite, aragonite, calcite) of calcium carbonate and to reduce the critical pore size in the matrix.

Recently, a small-size calcite inorganic polymer has been prepared with calcium hydroxide via crosslinking ionic oligomers stabilized by triethylamine (TEA) in an aqueous solution, in which a hydrogen bond was formed by the protonated carbonate through its tertiary amine group [7]. However, the main synthetic steps of stirring, centrifuging and re-dispersion are unrealizable in the preparation of large-size structural materials with ionic oligomers. Nevertheless, the chemical binding of part of oligomers generated between particles would be much better than the mechanical interlocking of particles in terms of reducing crack development, thus hypothetically improving the flexural strengths of CAM. Therefore, the crosslinking oligomers of calcites formed on the surface of carbonation products would be vital to the bending of CAM.

In this work, the CAM was prepared with $Ca(OH)_2$ via accelerated carbonation, and the TEA was introduced to form crosslinking oligomers on the surface of carbonation products to increase the flexural strength of the CAM. The effect of TEA concentration ranging from 0% to 9% on its mechanical properties and CO_2 uptake were investigated, the phase composition and microstructure of the carbonation products were characterized, and the microstructure formation mechanism of carbonation products was discussed. It was confirmed that the bending of CAM was significantly improved via the formation of crosslinking oligomers with TEA.

2. Materials and Methods

2.1. Specimen Fabrication of CAM

$Ca(OH)_2$ powder (purity: 99%, Sinopharm, Shanghai, China) and TEA (purity: 99%, Sinopharm, Shanghai, China were used as received, and deionized water was used throughout the study. The particle size of calcium hydroxide powders is shown in Figure 1. Aqueous solutions of various TEA concentrations ranging from 0% to 9% were freshly prepared before use. Compact samples were prepared with TEA solution and $Ca(OH)_2$ at a water–solid ratio (w/s) of 0.125 and a pressure of 30 MPa for 2 min. Prismatic samples with a size of 40 mm × 10 mm × 10 mm and cylindrical samples with a diameter of 15 mm and a height of about 15 mm were compacted for the tests of flexural strength and compressive strength, respectively.

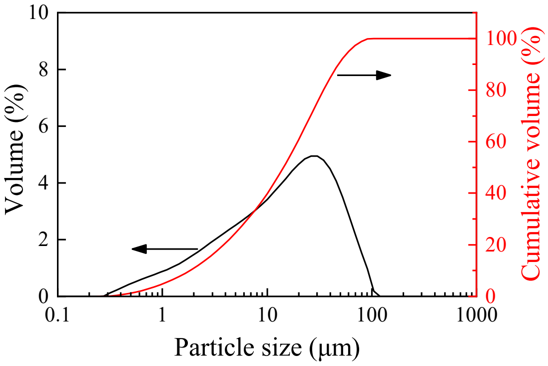

Figure 1. The particle size of calcium hydroxide powders.

The samples were placed in an enclosed carbonation chamber, which was purged with 99.9% CO_2 for 1 min before the carbonation at an atmospheric pressure. The samples were carbonated for 4 h in the carbonation chamber at room temperature and then heated for 24 h in an oven at 60 °C. During the curing, the relative humidity (RH) and temperature was adjusted using temperature and humidity sensor of curing box.

Two novel curing regimes were designed to improve the crosslinking of particles through oligomers. In regime I, the samples were carbonated for 2 h at room temperature in the carbonation chamber before being heated for 20 min at 65 °C in an oven without $CO_{2,}$ followed by carbonation for another 2 h. In regime II with earlier evaporation, the samples were carbonated for 30 min before being heated for 5 min at 65 °C, and then carbonated for 1 h followed by being heated for 5 min at 65 °C for three cycles, after which they were further carbonated for 30 min. In the two curing regimes, the total carbonation times were both 4 h, and the total evaporation times were both 20 min. The evaporation of TEA took place when the samples were heated to 65 °C. In regime II, the evaporation of TEA started after carbonation for only 30 min, which was much earlier than in regime I (after carbonation for 2 h), causing the different crosslinking degrees of calcite oligomers.

2.2. Testing Procedures of CAM

The degree of carbonation (DOC) of CAM was calculated using the method reported elsewhere [8]. The compressive strength and three-point flexural strength of CAM were evaluated via the MTS testing system (Criterion Model 43) at a loading rate of 0.2 mm/min and 0.05 mm/min, respectively. In regard to the flexural strength, the sample was tested at a 30 mm support span.

The whole sample was ground to less than 75 µm in particle size, and its mineral phase was analyzed by an X-ray diffractometer with Cu Kα source (XRD, PANalytical X'Pert PRO, Almelo, Netherlands) at a scanning rate of 5°/min. The fracture morphology on the specimen in the bending test was observed by scanning electron microscopy (SEM, Quanta FEG 450, FEI, Hillsboro, OR, USA).

The Scherrer Formula (1) was used to calculate the grain size D of the carbonated product.

$$D = 0.89\,\lambda/(\beta \times \cos\theta) \tag{1}$$

where λ is the wavelength of X-ray, nm; β is the width of diffraction peak at half height, rad; θ is the Bragg angle of diffraction, °.

3. Results and Discussion

3.1. Carbonation Properties of CAM

As shown in Figure 2a, after carbonation for 4 h without heating, the flexural strength of CAM increased substantially with the increase in TEA concentration. At 7% TEA, a maximum flexural strength of 7.3 MPa was reached, which accounted for a 31.5% improvement compared with that of the CAM without TEA, while a further increase in TEA concentration caused a decrease in flexural strength. However, in the same procedure, the DOC and compressive strength of CAM only increased slightly, by less than 2% and 1 MPa, respectively. The ratio of flexural strength to compressive strength changed from 0.14 to 0.20, which indicated that the bending was significantly improved by the addition of TEA.

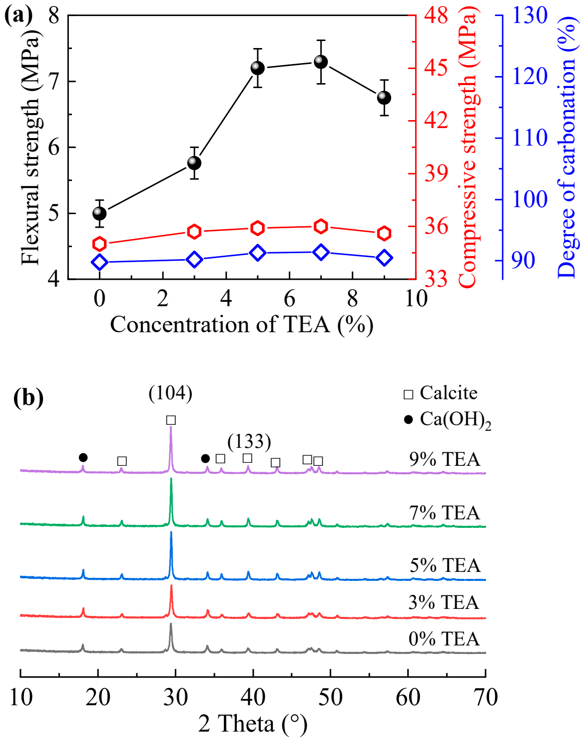

Figure 2. Flexural strength, compressive strength and DOC of CAM (**a**) and XRD patterns of CAM at different TEA concentrations (**b**).

Figure 2b showed diffractive peaks (at 2θ degree of 23.0°, 29.4°, 35.9°, 39.4°, 43.1°and 48.5°) after carbonation, in good accordance with the diffraction patterns of calcite (PDF#47-1743) with crystal planes of (012), (104), (110), (113), (202) and (018), respectively, confirming that the calcite was the carbonation product. The diffractive peaks (at 2θ degree of 18.2°and

34.2°) indicated the presence of the unreacted hydrated lime (PDF#84-1266). According to Liu [7], the yield of oligomers can be determined by comparing the diffraction intensities of crystal plane (104) with other crystal planes. As shown in Table 1, the ratio of the diffraction peak intensity of crystal planes (104) to (113) obviously increased first and then decreased slightly with the increase in the concentration of TEA, and the grain size showed the same tendency. As shown in Figure 3, upon the addition of TEA, the calcite particle size increased from approximately 500 to 1500 nm, and the connection between particles was more obvious.

Table 1. Ratios of diffraction peak intensity of crystal plane from (104) to (113) and grain size of calcite.

Concentration of TEA, %	0	3	5	7	9
Ratios of Diffraction Peak Intensity	5.2	5.5	6.1	6.2	5.7
Grain Size, nm	27.1	33.8	38.7	40.6	35.3

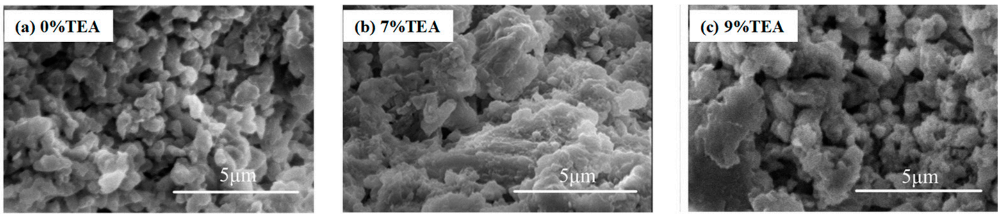

Figure 3. SEM of carbonated matrix with 0% TEA (**a**), 7%TEA (**b**) and 9%TEA (**c**).

Through a comparative analysis of composition and microstructure, it could be found that the TEA promoted the crosslinking of oligomers between calcite particles, which hindered the crack development under tension and thus improved the bending of CAM. Nevertheless, the increase in compressive strength was inconspicuous compared with flexural strength for the limited contribution of crosslinking to the shearing force, which was the principal form under compressive pressure [9]. However, the excess TEA (9%) was not conducive to further increases in bending; therefore, excessive TEA could serve as a capping agent of oligomers, preventing the crosslinking between calcite particles [7], which was corroborated by the reduction in grain size in Table 1 and Figure 3c.

Through the above analysis of the toughness improvement of CAM and the changes in composition and structure, the mechanism of microstructure formation of CAM with TEA can be proposed. As shown in Figure 4, calcium ions leach from calcium hydroxide and are caught by TEA to form a complex compound before carbonation. With the dissolution of CO_2 into water, the concentration of carbonate ions increases. The complexes dissociate when the solubility product of calcium ions and carbonate ions exceeds the solubility product equilibrium constant of calcium carbonate. Additionally, then, the calcium carbonate continues to form. By means of forming a hydrogen bond, TEA retards the polymerization of calcium carbonate, and stable calcium carbonate oligomers form.

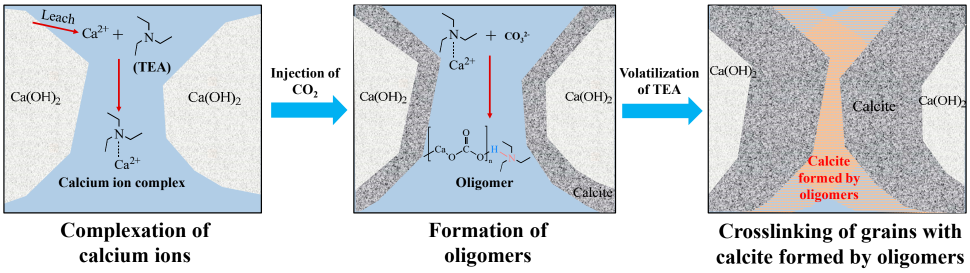

Figure 4. Mechanism of microstructure formation of CAM with TEA.

TEA volatilizes during the carbonation reaction or heating, and calcite is produced by the crosslinking oligomers of calcium carbonate coats on the surface of normal carbonation products, binding them together. This kind of calcite exhibits excellent compatibility with calcium carbonate grains. The crosslinking between grains hinders the crack development under tension, improving the bending of CAM. However, excessive TEA yields excessive complex compounds, which retards the formation rate of the calcium carbonate, resulting in a reduction in its mechanical properties.

3.2. Further Improvement of the CAM Bending

Two novel curing regimes (curing regime I and II) were adopted to further promote the bending of CAM, in which the flexural strength of CAM improved substantially, as shown in Figure 5. Compared with the CAM with neither TEA addition nor heating, the flexural strength of CAM with 7% TEA under curing regime II maximized 9.6 MPa, increasing by 96%, while the compressive strength increased to 38.1 MPa. Therefore, the ratio of flexural strength to compressive strength of CAM reached 0.25, improving by 79%. Moreover, the ratio of the diffraction peak intensity of the crystal planes from (104) to (113) increased to 6.5, and the grain size of calcite grew to 43.3 nm, exceeding the largest grain size of the CAM without heating, which indicated the improved extent of the crosslinking of oligomers.

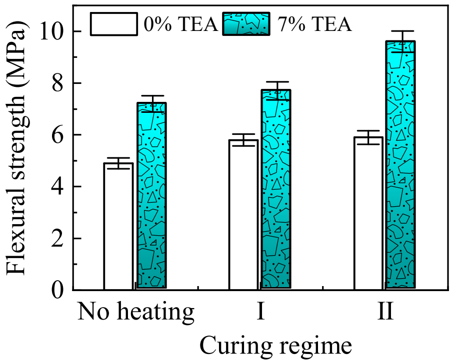

Figure 5. Flexural strength of CAM at different curing regimes.

Meanwhile, the flexural strength of CAM without TEA also increased because the high temperature facilitated the reaction rate of carbonation. Moreover, the heating accelerated the volatilization of TEA, thus facilitating the crosslinking of oligomers. The earlier the TEA volatilized, the larger the extent of the crosslinking of oligomers was reached. Hence, the flexural strength of CAM increased, especially in curing regime II, which was more conducive to the evaporation of TEA.

4. Conclusions

(1) With the increase in TEA concentration ranging from 0% to 9%, the flexural strength of CAM increased obviously, reaching a maximum at 7% TEA, and then reducing gradually while the increases in the compressive strength and DOC of CAM were inconspicuous.

(2) The early evaporation of TEA (curing regime II) was beneficial to the improvements in CAM bending. Compared with CAM with neither TEA addition nor heating, the ratio of flexural strength to compressive strength of CAM with 7% TEA improved by 79%.

(3) With the addition of TEA, the grain size of calcite increased due to the crosslinking of oligomers, and the interconnection of the larger particles resulted in improvements in the bending properties of CAM.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lippiatt, N.; Ling, T.-C.; Pan, S.-Y. Towards carbon-neutral construction materials: Carbonation of cement-based materials and the future perspective. *J. Build. Eng.* **2020**, *28*, 101062. [CrossRef]
2. Zhang, D.; Ghouleh, Z.; Shao, Y. Review on carbonation curing of cement-based materials. *J. CO2 Util.* **2017**, *21*, 119–131. [CrossRef]
3. Wang, D.; Xiong, C.; Li, W.; Chang, J. Growth of Calcium Carbonate Induced by Accelerated Carbonation of Tricalcium Silicate. *ACS Sustain. Chem. Eng.* **2020**, *8*, 14718–14731. [CrossRef]
4. Ashraf, W.; Olek, J. Carbonation activated binders from pure calcium silicates: Reaction kinetics and performance controlling factors. *Cem. Concr. Compos.* **2018**, *93*, 85–98. [CrossRef]
5. Zhao, S.; Liu, Z.; Mu, Y.; Wang, F.; He, Y. Effect of chitosan on the carbonation behavior of γ-C2S. *Cem. Concr. Compos.* **2020**, *111*, 103637. [CrossRef]
6. Khan, R.I.; Ashraf, W.; Olek, J. Amino acids as performance-controlling additives in carbonation-activated cementitious materials. *Cem. Concr. Res.* **2021**, *147*, 106501. [CrossRef]
7. Liu, Z.; Shao, C.; Jin, B.; Zhang, Z.; Zhao, Y.; Xu, X.; Tang, R. Crosslinking ionic oligomers as conformable precursors to calcium carbonate. *Nature* **2019**, *574*, 394–398. [CrossRef] [PubMed]
8. Zhang, Y.; Wang, R.; Liu, Z.; Zhang, Z. A novel carbonate binder from waste hydrated cement paste for utilization of CO_2. *J. CO2 Util.* **2019**, *32*, 276–280. [CrossRef]
9. Li, L.; Cao, M.; Yin, H. Comparative roles between aragonite and calcite calcium carbonate whiskers in the hydration and strength of cement paste. *Cem. Concr. Compos.* **2019**, *104*, 103350. [CrossRef]