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Characterization of mechanical behavior and mechanism of calcium carbonate whisker-reinforced cement mortar

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HIGHLIGHTS

- $CaCO_3$ whisker was incorporated into cement mortar.
- Mechanical behavior and reinforcing mechanism were presented.
- $CaCO_3$ whisker-reinforced mortar showed satisfied properties.
- An appropriate weak matrix is very beneficial to $CaCO_3$ whiskers to play their roles.

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ABSTRACT

In order to reinforce cement mortar, a new kind of micro-fibrous material, calcium carbonate whisker ($CaCO_3$ whisker), was incorporated in this study. Microstructure, mechanical properties and reinforcing mechanism of this composite were characterized. It was found that the addition of $CaCO_3$ whisker improved not only the compressive and flexural strength of cement mortar, but also the load–deflection curves and work of fracture. Further work using mercury intrusion porosimetry tests confirmed the filler effect and the refining of the pore distribution of whiskers in cement mortar. Scanning electron microscopy showed that the microscopic mechanism primarily consists of whisker pullout, crack deflection, whisker-cement coalition pullout, whisker bridging and whisker breakage. These mechanisms are related to the matrix strength. As compared to the strong matrix, the weak matrix that was modified with $CaCO_3$ whisker achieved the highest increase in strength and toughness of the cement mortar. This is likely attributed to the crack deflection mechanism, which is weakened by the strong interfacial bonding between the $CaCO_3$ whisker and cement matrix in the stronger mortar matrix.

1. Introduction

Cement based composites are very brittle, and, therefore, are typically reinforced with fibrous materials. A variety of fibrous materials are available commercially and their feasibility in cement based composites has been well documented [1–3]. Recently, there has been considerable interest in the development of nano- and micro-fibrous materials reinforced cement based composites [4]. Extensive research has been conducted in the field of processing technology and towards understanding of the mechanical behavior of the composite. It has been shown that the strength and toughness of brittle cementitious composites can be significantly improved by incorporating nano- or microfibers, which restrict and delay the propagation and coalescence of cracks at the microscopic level. Carbon nanotubes and carbon nanofibers have also recently been used in cement based composites, and they have been found to improve not only the mechanical properties but also the intelligentization [5–10]. However, these carbon materials are expensive, which limits their application in cement based composites.

In this study, a new type of inexpensive micro-fibrous material, $CaCO_3$ whisker, was incorporated in order to improve the mechanical properties of cement mortar. $CaCO_3$ whisker is a type of inorganic single crystal with a diameter of 0.5–2 μm and an aspect ratio of 20–60. It has excellent mechanical properties as demonstrated by the elastic modulus and the tensile strength being 410–710 GPa and 3–6 GPa, respectively. These basic properties make it suitable to serve as microfibers in cement based composites. Importantly, the production cost of $CaCO_3$ whisker is very low, only about $230 per ton, which is very beneficial to decrease the production cost of microfiber reinforced cement

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based composites. The object of this study was to assess the mechanical properties as well as thoroughly understand the reinforcing mechanisms of $CaCO_3$ whisker reinforced cement mortar. It is thought a better understanding of these materials will lead to significant progress in the characterization and utilization of this new cement based composite. Furthermore, a decrease in the production cost of micro-fibrous material reinforced cement based composites would lead to an increase in their use in large scale construction project.

2. Materials and methods

Cement (PC 32.5 and P·O 42.5R), ISO 679 standard sand, silica fume (specific surface 17.33 m^2/g), fly ash (specific surface 0.41 m^2/g, 45 μm sieve residue 23.6%) and $CaCO_3$ whisker (length 20–30 μm, diameter 0.5–2 μm) were the raw materials used in this study. Their chemical components are shown in Table 1. The morphology and XRD pattern of $CaCO_3$ whisker are shown in Fig. 1a–c, along with the TEM image of silica fume used in this study (Fig. 1d).

Three types of mortar matrix were designed that had compressive strengths of 30, 40, and 60 MPa. The mix proportion is given in Table 2. Mass fraction (proportion of cement) of 5% (M5), 10% (M10), 15% (M15), and 20% (M20) $CaCO_3$ whisker were employed. The amount of the water reducer (polycarboxylic acid type, ASTM C494 type F, water reducing ratio 24.1%) varied from 0 to 0.5 wt.% of binder content to ensure the mixtures had a similar flow and can be cast easily. Furthermore, an increased mixing time was employed to the mixtures with low water/binder ratio in this study according to Ref. [19], as illustrated in Fig. 2.

The flow of the fresh mortar mixtures was evaluated according to ASTM C230 and ASTM C1437-07. Briefly, the diameter of the mortar along the four lines scribed in the table top was measured after the removal of the forming cone and dropping the sample 13 mm, 25 times. The resulting increase in average base diameter of the mortar mass was expressed as a percentage of the original base diameter, as shown in Table 3.

The specimens were cast in three lifts, and each was vibrated on a vibration machine for 60 s. After curing for 24 h in a standard curing box of cement, the samples were demoulded and subjected to 20 °C water for 28 days as described by ISO 679-2009.

The compressive strength was determined using 70.7 mm × 70.7 mm × 70.7 mm cubes and a pressure machine at a crosshead speed of 0.5 mm/min according to Chinese standard JGJ/T 70-2009. The loading method for the compression test is shown in Fig. 3a. Samples with a dimension of 40 mm × 40 mm × 160 mm were used to determine the flexural strength and the work of fracture. A computer controlled electro-hydraulic servo universal tester (WDW-300) was used at a cross-head speed of 0.02 mm/min according to ASTM C348 and ASTM C1609. The loading method used in the flexural test is shown in Fig. 3b. The work of fracture was calculated from the area covered underneath the load–deflection curve divided by twice the fracture surface area of the specimen. The microstructures of the composites were examined using a scanning electron microscopy (SEM, QUANTA 450). A matched energy dispersive spectrometer (EDS) was also used to analyze the elemental composition of the designated location. The pore size distribution of the samples was determined using a mercury intrusion porosimetry (MIP, AutoPore IV 9500).

3. Results and discussion

3.1. Compressive strength

The average compressive strength values for all the mortar mixes are shown in Fig. 4. For the composites with a matrix strength of 30 MPa, the compressive strength ranged from 34 MPa to 38 MPa. Additionally, the composites containing 10 wt.% whisker had the highest compressive strength. Similar trends were found for the matrices with a compressive strength of 40 and 60 MPa. The relative increases in compressive strength caused by whisker loading are shown in Fig. 5. It can be seen that as the maximum boost in compressive strength decreased, the matrix strength increased. The composites with 10 wt.% whisker and a 30 MPa matrix strength had a 13% increase, while the composites with 60 MPa matrix strength only achieved an 8.5% increase.

3.2. Flexural strength

The flexural strength of the composites is plotted as a function of the whisker content in Fig. 6. As expected, the flexural strength of all the whisker reinforced mortars was higher than their comparisons. The flexural strength phenotype paralleled that of the compressive strength for the mortars, where it increased gradually and then decreased with an increase in whisker content. The relative increase in flexural strength caused by whisker loading is shown in Fig. 7. For the matrix with 40 MPa compressive strength, the addition of 10% whiskers resulted in the highest level of reinforcement after which the level of reinforcement plateaued. For example, a further increase in matrix strength to 60 MPa did not further enhance the reinforcing effect caused by whisker loading as compared to 40 MPa.

The maximum flexural strength increase was approximately 23% in the 40 MPa matrix strength mortar. When these results are compared to carbon nanotube or other expensive microfiber reinforced cementitious composites, the amount of improvement in the mortar properties caused by whisker loading was satisfactory, as illustrated in Table 4. Unlike carbon nanotube or nanofiber, no special dispersion methods (e.g., chemical dispersant, ultrasonic dispersion, etc.) are needed to generate whisker reinforced cementitious composites.

3.3. Load–deflection curves

The load–deflection curves for the three matrices, 30 MPa, 40 MPa and 60 MPa, are shown in Figs. 8–10, respectively. The addition of whiskers improved both the peak load and peak deflection of the mortars, but failed to change the brittle nature of cement mortar. Specifically, there was a drastic, yet incomplete, drop in the load after fracture, suggesting semi-stable crack propagation during the test. The peak deflection improved with an increase in whisker content, but decreased with the increase of matrix strength, although the peak loads of the mortars with a strong matrix were higher than those with weak matrix. There was little difference in the slope at the linear stage, suggesting that the deformability of the composite reinforced with whiskers was slightly higher than without whiskers. Nevertheless, the addition of whiskers, most likely due to their microscopic size, did not significantly improve the post-peak behavior.

As shown in Table 5, numerous studies have focused on the load–deflection curves of cement based composites reinforced with nano- or micro-fibrous materials. However, within this work, only the peak deflection was compared, because a few other studies failed to obtain the descending or softening branch of the load–deflection curve. This is likely a reflection of a lack in stiffness in the test machine, where more elastic energy is stored in the soft

Table 1
Chemical components of raw materials (wt.%).

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	CO_2	MgO	K_2O	SO_3	Na_2O	P_2O_5	MnO
Cement (PC 32.5)	52.61	3.45	6.95	2.44	–	4.30	1.06	3.45	0.16	0.05	0.08
Cement (PO 42.5R)	61.13	21.45	5.24	2.89	2.37	2.08	0.81	2.50	0.77	0.07	0.06
Silica fume	0.81	93.47	0.16	0.10	–	0.95	2.89	0.84	0.23	0.40	0.04
Fly ash	6.61	50.96	30.61	5.61	–	0.63	0.78	1.02	0.17	–	–
Whisker	54.93	0.29	0.11	0.07	42.07	2.14	–	0.31	–	–	–