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Impact of Nano-$CaCO_3$ and PVA Fiber on Properties of Fresh and Hardened Geopolymer Mortar

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Abstract: Geopolymer is a green substitute for Portland cement but has low tensile strength, high brittleness and easy cracking. Therefore, fibers and nanomaterials are used to strengthen and toughen geopolymer composites. The influence of nano-calcium carbonate and PVA fiber on the properties of fresh and hardened geopolymer mortar were studied herein. The hybrid of long and short fibers with small content (0.8 vol.%) is conducive to flowability, while the hybrid with large content (1.6 vol.%) and nano-calcium carbonate is conducive to flowability. The slump flow and flow rate of geopolymer mortars with low fiber factor (product of fiber volume fraction and length-diameter ratio) decrease with the growth in nano-calcium carbonate content. As the PVA fiber factor reaches 464.8%, the slump flow and flow rate values of mortars with 0, 1 wt.% and 2 wt.% nano-calcium carbonate are close to each other. About 450% is the density packing threshold of PVA fiber in geopolymer composites. The combination of 0.8 vol.% 12 mm + 0.4 vol.% 6 mm fiber + 1 wt.% nano-calcium carbonate presents the highest flexural strength and flexural to compressive strength ratio, with a compressive strength of about 36 MPa. The optimal fiber factor range of PVA fiber in cement and geopolymer mortar is about 400% and higher than 600%, respectively. PVA fibers show more effective enhancement of flexural strength and toughness in geopolymer than cement mortar. The ultrasonic wave velocity and apparent density of geopolymer mortar show a downward trend as a whole with the increase in fiber factor. The intensity rise of the hump between 17° and 38° (2 θ) in the XRD pattern is observed. The SEM indicates that the surface of PVA fiber in geopolymer mortar with nano-calcium carbonate is heavily scratched, and the fiber filaments are rolled up, demonstrating improved bonding between PVA fiber and geopolymer mortar.

Keywords: nano-calcium carbonate; PVA fiber; flowability; strength; compactness; microstructure

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1. Introduction

With the rapid development of construction engineering, the amount of concrete has increased substantially, and the demand for Portland cement has also risen. According to statistics, the annual output of cement in China in 1997 was 5.100 million tons (clinker consumption 3.500 million tons) and as high as 23.300 million tons by 2019 [1]. Each ton of cement produced emits about 1 ton of CO_2. CO_2 emissions from the cement industry account for about 7% of the global total CO_2 emissions [2]. Geopolymers usually refer to polymers made from alkaline solutions (e.g., NaOH, KOH, Na_2SiO_3, etc.) reacted with the vitreous structure of silica-rich aluminous inorganic minerals (such as fly ash, metakaolin, volcanic ash, etc.) to form a 3-dimensional network of inorganic bonding materials [3–12]. Geopolymers can replace cement in the preparation of concrete. Geopolymer significantly reduces the environmental impact of concrete products by reducing greenhouse gas emissions by 73% and energy consumption by 43% compared to Portland cement [13].

As a kind of reinforcement material, fiber is incorporated into cement-based materials, which can prevent the generation and propagation of cracks, improve the strength and toughness of cement-based materials [14], prevent their fatigue, improve impact resistance [15] and heat resistance [16–25], etc., which is one of the main means to improve the performance of cement-based materials and extend their service life. At present, there are many varieties of fiber, often used in concrete, such as steel fiber [26,27], glass fiber, basalt fiber [28], polyvinyl alcohol fiber [29–32], polypropylene fiber [33] and hybrid fiber [34–38]. Fibers are also used to reinforce geopolymer concrete. Hu et al. [6] used polyethylene fiber to reinforce geopolymer paste. For flexural strength, the optimal fiber factor was 600. While for compressive strength, the optimal fiber factor was 350. Pu et al. [11] used polypropylene fiber to reinforce geopolymer paste. For flexural strength and compressive strength of 0.35 w/b geopolymer, the optimal fiber factors were both 350. Wang et al. [39] studied the mechanical and fracture properties of basalt fiber-reinforced fly ash geopolymer concrete with 3–18 mm lengths. For compressive, splitting tensile strength, peak load, fracture toughness and fracture energy, 6 mm was always the best length for basalt fiber.

The commonly used nanotechnology for Portland cement-based cementitious materials is mixing nano-ultrafine particles, carbon nanotubes, graphene and other nano-components. Nano ultrafine particles have high surface energy and many surface bond breaks, so they have chemical activity. Its particles are small, filling ability is strong, but it also has the physical filling effect [40]. It can accelerate hydration, improve strength, refine pore structure, inhibit calcium loss and improve durability. Therefore, the addition of nano-ultrafine particles and other nano-components has become one of the means to prepare high-performance cement-based materials. Research on the effect of nano-clays, carbon nanotubes, graphene, nano-TiO_2, nano-metakaolin and other nano-components on the coagulation and hardening process, workability, mechanical properties and durability of geopolymers has been gradually carried out. In general, the above nano-components can improve geopolymer materials' mechanical properties and permeability resistance.

There is a positive hybrid effect between nano-materials and fibers to improve the mechanical properties of cementitious and geopolymer materials [41]. But the addition of nanoparticles and fibers worsens the flowability of cementitious composites. Poor flowability of cementitious materials may result in balling of fibers and flaws rise in the matrix, which may ultimately decline mechanical properties [42]. Nevertheless, to the author's best knowledge, there is no research focused on the hybrid effect between nano-calcium carbonate and fiber in geopolymer materials. To bridge this gap, a systematic study is carried out on the workability and mechanical properties of nano-calcium carbonate and PVA fibers of different lengths of reinforced geopolymer composites. The hybrid effect between nano-calcium carbonate and PVA fibers of different lengths is discussed in detail based on experimental results.

2. Raw Materials and Experiments

2.1. Materials

Silica-aluminum material precursors employed herein are fly ash, granulated blast furnace slag powder and silica fume. The alkali activators are Na_2SiO_3 solution and NaOH powder. The water was municipal tap water. The size of PVA fibers is 6 mm and 12 mm long, with the same diameter of 40 μm. The direct tensile strength and modulus of elasticity of PVA fibers are 1500 MPa and 36.7 GPa, respectively. The particle size of nano-calcium carbonate is 50 nm.

2.2. Mix Procedure and Test Specimens

In this paper, the water-binder ratio (the mass of water to the sum of the mass of fly ash, slag and silica fume) is 0.44. The ratio of fly ash, slag and silica fume is 7:1:2. The sand-binder ratio (the mass of sand to the sum of the mass of fly ash, slag, and silica fume) is 0.2. The alkali activator is sodium silicate combined with solid sodium hydroxide with a modulus of 1.5. By changing the volume dosage, length of PVA fiber, and nano-calcium carbonate dosage, a total of 19 experimental groups were set up. The volume fraction of

PVA fiber was 0, 0.4%, 0.8%, 1.2%, and 1.6%. The proportion of nano-calcium carbonate in the mass of cementitious material is 0, 1% and 2%.

The mixing process of geopolymer mortar is presented in Figure 1. After mixing, the geopolymer mortars were cast into plastic molds and vibrated for 60 s. Then the geopolymer mortar specimens were covered by a polymer plastic film. Finally, 24 h later, the hardened PVA fiber-reinforced geopolymer mortars were de-molded and cured in a 20 °C water tanker in terms of ISO 679-2009.

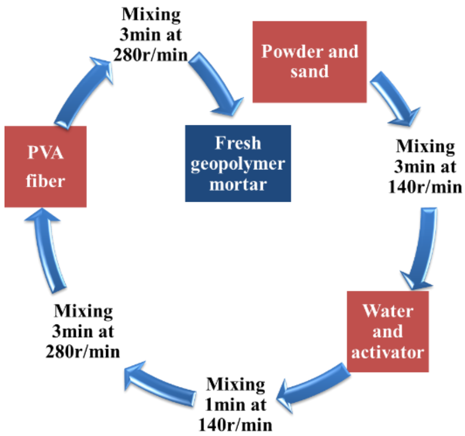


Figure 1. Mixing process of mortar.

2.3. Fresh Properties of Geopolymer Mortar

A minor steel V-funnel was employed to evaluate the flow rate of fresh geopolymer mortar. The V-funnel flow rate was obtained by the volume of the steel V-funnel (1134 mL) divided by the flow time (unit: s). The flow time was tested from turning on the bottom switch to the light observed through the bottom opening. A minor steel slump cylinder was employed to evaluate the slump flow.

2.4. Mechanical Properties Test of Hardened Geopolymer Mortar

Four-point bending experiment was done using a 40 mm × 40 mm × 160 mm prism with a span of 120 mm to assess the flexural strength and toughness. The compressive experiment was conducted using a cube with a side length of 40 mm.

2.5. Compactness Properties of Hardened Geopolymer Mortar

The velocity of ultrasonic pulse was tested by a HC-U91 concrete ultrasonic detector based on Chinese standard CECS 21:2000. The apparent density was obtained by dividing mass by test block volume. The mass was weighed by an electronic scale.

2.6. Microstructure Test of Hardened Mortar

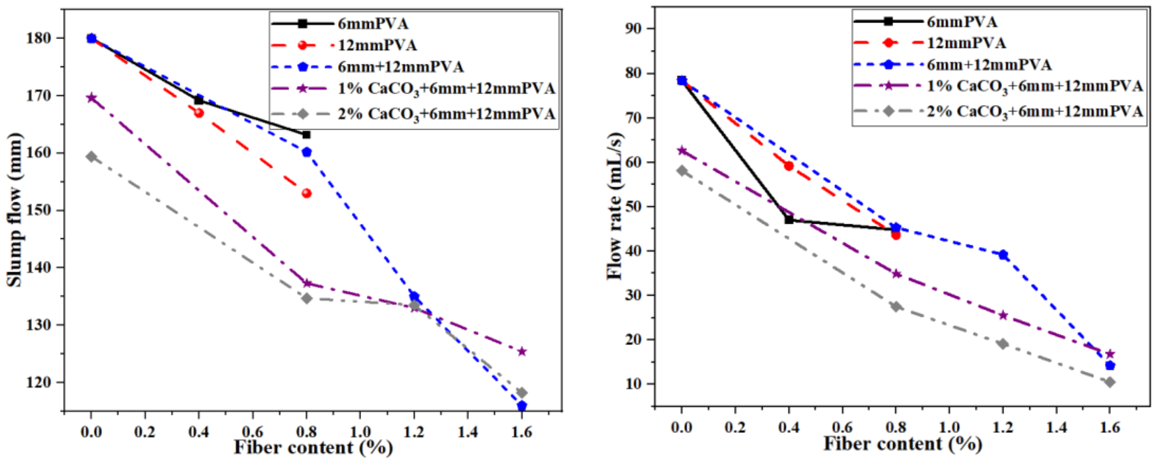
After the mechanical test, the specimen pieces were used for a scanning electron microscope (SEM) test. In addition, the reaction products in geopolymer mortar were studied by X-ray diffraction (XRD).

3. Results and Analyses

3.1. Flowability

3.1.1. Influence of Fiber Volume Fraction on Flowability

The influence of PVA fiber volume fraction and fiber nano-calcium carbonate mix ratio on slump flow is shown in Figure 2a. As expected, the slump flow decreases with the increase in fiber numbers. Specifically, without nano-calcium carbonate, the slump flow of geopolymer mortar declined by 9.3% from 180 mm to 163 mm as short PVA fiber content grew from 0 to 0.8%. The main reason for this phenomenon is that with the addition of PVA fiber, the distance among particles is decreased, increasing the viscosity and volume fraction of the suspension [6]. The further increase in fiber amount in the slurry bonds with each other and even produces an obvious clumping phenomenon. This hinders the free flow of the slurry. The slump flow of geopolymer mortar decreases, while long fibers tend to bond and clump more easily, resulting in a more significant decline range [31].



(**a**) (**b**)

Figure 2. Influence of fiber content on flowability. (**a**) Slump flow; (**b**) Flow rate.

Figure 2b shows the relationship between flow rate and fiber content. Increased fiber numbers also decrease the flow rate of geopolymer mortar. Specifically, without nano-calcium carbonate, as the fiber content increased from 0 to 0.8%, the flow rate of mortar with 6 mm PVA fiber decreased by 42.90% from 78.41 mL/s to 44.77 mL/s. But unlike slump spread, the decreasing amplitude of the flow rate of mortar with short fiber (6 mm) is not much different from that of mortar with long fiber (12 mm). The reason is that in the V-shaped funnel test, there are constraints on both sides of the mortar, so even if the fibers are shorter, there are obvious fibers lapping each other [43]. Therefore, when the volume and content of fibers are equal, the number of short fibers is bigger, and the probability of 6 mm fiber clumping is greater than 12 mm fiber.

The hybrid of 12 mm and 6 mm PVA fibers improves the flowability of geopolymer mortar, shown as the blue lines in Figure 2. Specifically, when 0.4% short PVA fiber is mixed with 0.4% long PVA fiber, slump flow is increased by 4%, compared with that when only 0.8% 12 mm fiber is used. The flow rate of mortar with 0.4% short and 0.4% long PVA fiber is higher than that of 0.8% long fiber or 0.8% short fiber alone. The reason is that when using a hybrid of long and short fibers, the short fibers can be dispersed in the gaps between the long fibers. This reduces the probability of fibers overlapping and improves flowability [26].

When the fiber content is lower than 1.6%, the slump spread and flow rate of the geopolymer mortar are significantly reduced by nano-calcium carbonate due to the increased viscosity with the addition of nano-calcium carbonate with a large specific surface area [44]. On the other hand, when the fiber content reaches 1.6%, the slump flow and flow rate are increased by 8.06% and 17.85%, respectively, by adding 1% nano-calcium carbonate. This is because the nano-calcium carbonate with small particles and a smooth and round surface can play a "ball effect" to lubricate the fibers so as to improve the fluidity of the mortar with a large amount of PVA fibers.

3.1.2. Influence of Fiber Factor on Flowability

The length-to-diameter ratio of synthetic fibers is very important due to their minuscule diameter [45]. Consequently, the fiber factor is a suitable index for assessing the joint influences of fiber volume fraction and the length-to-diameter ratio of PVA fibers. Such an index is the product of fiber volume fraction divided by its length-to-diameter ratio. The effect of the PVA fiber factor and nano-calcium carbonate content on flowability is shown in Figure 3. When the fiber factor value rises, the slump flow and flow rate are reduced significantly. The relationship between these features seems linear, with an intrinsic correlation coefficient higher than 0.90. Therefore, the linear relationship in Figure 3 can be used to predict the flowability of fiber-reinforced geopolymer mortar.

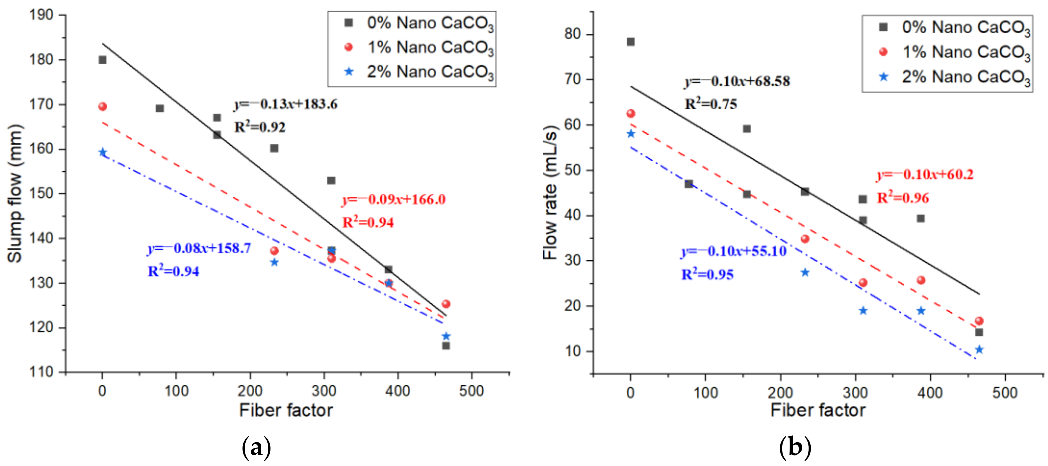


Figure 3. Influence of fiber factor on flowability. (**a**) Slump flow; (**b**) Flow rate.

As shown in Figure 3a, when the nano-calcium carbonate content is 0, 1% and 2%, the intercept of the straight lines is 183.6, 166.0 and 158.7, respectively. That is, the initial slump flow of geopolymer mortar decreases with the increase in nano-calcium carbonate content. The fine particle sizes of nano-calcium carbonate are accountable for this result. Nano-calcium carbonate has much higher surface areas than the other mineral admixtures to be wetted by mixing water, thus leaving less free water and contributing to the flowability of mortar [46]. As the PVA fiber factor increases from 0 to 464.8%, the slump flow is decreased by 35.5%, 26.5% and 25.8%, respectively, for mortar with 0, 1% and 2% nano-calcium carbonate. When the content of nano-calcium carbonate is 0, 1% and 2%, the slopes of the relationship between slump flow and fiber factor are −0.13, −0.09 and −0.08, respectively. That is, the absolute slope value decreases gradually, and the rate of decline slows down gradually. With the increase in fiber content, the workability of fiber-reinforced geopolymer slurry is gradually controlled by fiber contact and balling. In addition, the influence of nano-calcium carbonate in the matrix is gradually weakened. Hence, as the PVA fiber factor reaches 464.8%, the slump flow values of mortars with 0, 1% and 2% nano-calcium carbonate are close to each other. This is consistent with the conclusion from Wang et al. [47] that about 450% is the density packing threshold of PVA fiber in geopolymer composites. While in Portland cement mortar, the density packing threshold of PVA fiber is about 400%, as reported by Si et al. [31].

Presented in Figure 3b, different from slump flow, the flow rate decline is basically unchanged for mortar with different nano-calcium carbonate content. Specifically, when the content of nano-calcium carbonate is 0, 1% and 2%, the slope of the linear relationship between the flow rate and the fiber factor is −0.10. The reason is that mortar is restricted on both sides of a V-shaped funnel, and it is easy to generate friction with the side wall even if the fiber content is low [48]. Therefore, the overall effect of calcium carbonate in the slurry is small; that is, the change in flow rate is mainly controlled by fibers. Similar to slump flow, as the PVA fiber factor reaches 464.8%, the slump flow value of mortars with 0, 1% and 2% nano-calcium carbonate are close to each other.

3.2. Strength

3.2.1. Influence of Fiber Volume Fraction on Strength

As shown in Figure 4a, by raising the PVA fiber volume fraction, the improvement in the flexural strength of geopolymer mortar can be reached irrespective of the fiber and nano-calcium carbonate mix ratio. Specifically, when the fiber content of short PVA fiber increases from 0% to 0.4%, the flexure strength is improved from 3.92 MPa to 4.23 MPa, with an increase of 7.8%. Nevertheless, when the fiber content increased from 0.4% to 0.8%, the flexural strength declined from 4.23 MPa to 5.56 MPa, which was 41.9% higher than that of the control group without fiber. In addition, the 12 mm fiber with a larger aspect ratio has a more obvious improvement effect on the flexural strength of geopolymer mortar. Because the fiber with a larger aspect ratio is bonded longer in the matrix, absorbing more energy in the pulling-out process [35]. The hybrid use of 0.4% short and 0.8% long PVA fiber makes the flexural strength of geopolymer mortar achieve 10.65 MPa, which is increased by 1.72 times compared with the control group. Mixing long and short fibers has a more significant effect on the improvement of flexural strength because long and short fibers can "resist cracking step by step" under loading, i.e., long fibers can still bridge cracks after short fibers are pulled out or broken [49]. In addition, the hybrid use of 1% nano-calcium carbonate, 0.4% short and 0.8% long PVA fiber further improves the flexural strength of geopolymer mortar, reaching the highest flexural strength (11.8 MPa) in this research. This indicates the positive hybrid effect between PVA fiber and nano-calcium carbonate, improving the tensile strength of geopolymer mortar. But the addition of 2% nano-calcium carbonate creates a loss of flexural strength due to excessive defects resulting from the uneven dispersion of nano-calcium carbonate. The reduced flowability discussed in Section 3.1 further aggravates the matrix defects, resulting in a decline in strength.

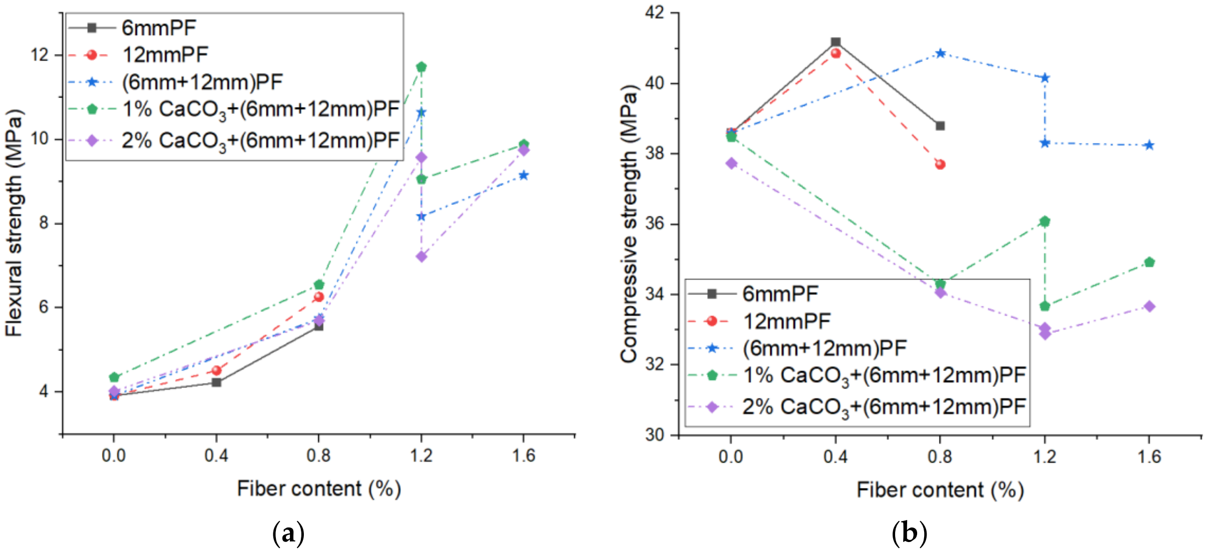


Figure 4. Influence of fiber content on strength. (**a**) Flexural strength; (**b**) Compressive strength.

Unlike the flexural strength, the compressive strength of geopolymer mortar increases little or decreases with the increase in fiber content. As shown in Figure 4b, an increase in fiber content of 12 mm from 0 to 0.4% and 0.8% results in a loss in compressive strength of about −5.86% and 2.3%, respectively. The increase in 6 mm fiber content from 0 to 0.4% and 0.8% presents a loss in compressive strength of about 6.7% and 2.3%, respectively. The compressive strength variation of long-short hybrid PVA fiber is similar to that of one-size fiber. When 0.4% short and 0.4% long PVA fiber is hybrid, the compressive strength of geopolymer mortar is 40.86 MPa, which is 5.36% and 9.19% higher than that of 0.8% short and 0.8% long PVA fiber, respectively. Since the elastic modulus of PVA fiber is significantly lower than that of geopolymer mortar, the increase in compressive strength of PVA fiber is limited [45]. In addition, steel fiber with a higher elastic modulus can significantly improve the compressive strength in the literature [49]. When the fiber content is large, it will dramatically increase the geopolymer mortar's pores and reduce the density of the material. Unlike flexural strength, nano-calcium carbonate significantly reduced compressive strength. This corresponds to the reduced flowability discussed in Section 3.1. The reason is that compressive strength is directly related to the compactness of the matrix.

Flexural to compressive strength ratio (F/C), as shown in Figure 5, is generally employed to evaluate the toughness of concrete. The greater the F/C, the greater the toughness of the concrete [34,50]. In general, the variation trend of F/C is basically the same as that of flexural strength. In other words, fiber content improves the F/C, and 1% nano-calcium carbonate is also beneficial to the F/C. The difference is that the fiber content increases the F/C more than the flexural strength. Therefore, in general, PVA fiber is more effective in toughening than strengthening geopolymer material.

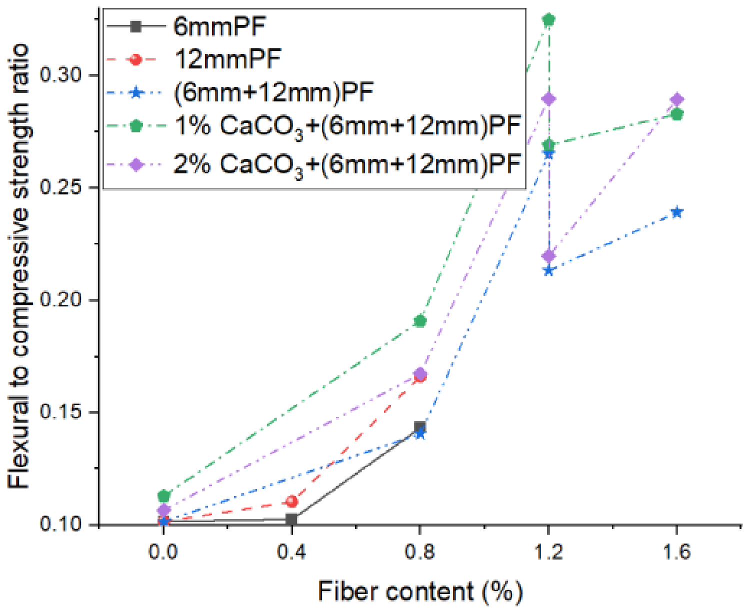
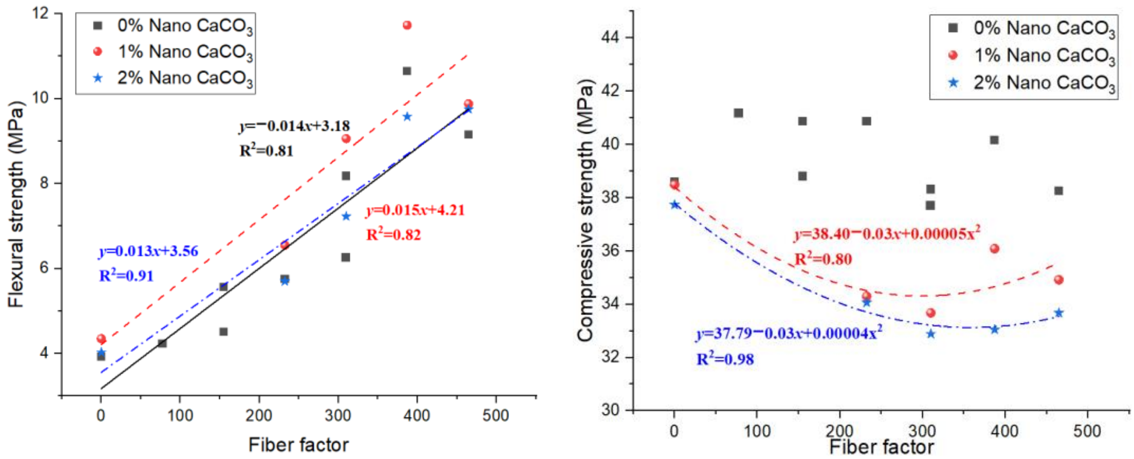


Figure 5. Influence of fiber content on flexural to compressive strength ratio.

3.2.2. Influence of Fiber Factor on Strength

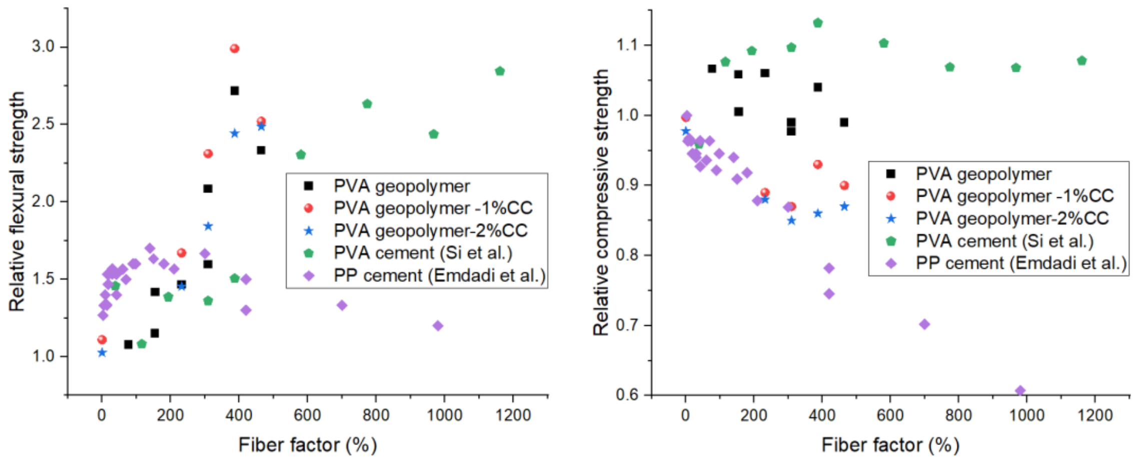
As shown in Figure 6a, regardless of the content of nano-calcium carbonate, with the increase in the fiber factor, the flexural strength of nano-calcium carbonate PVA fiber-reinforced geopolymer mortar increases. The flexural strength and fiber factor shows a good linear relationship. The correlation coefficient of regression analysis in Figure 6a is above 0.80. Therefore, the linear relationship in Figure 6a can be used to predict the flexural strength of fiber-reinforced geopolymer materials. As shown in Figure 6a, as the PVA fiber factor increases from 0 to 464.8%, the flexural strength is improved by 133%, 141% and 145%, respectively, for mortar with 0, 1% and 2% nano-calcium carbonate. As the content of nano-calcium carbonate is 0, 1% and 2%, the slope of the relationship between flexural strength and fiber factor is 0.014, 0.015 and 0.013, respectively, which increases first and then decreases. When the nano-calcium carbonate content is 0, 1% and 2%, the intercepts of the lines are 3.18, 4.21 and 3.56, respectively. In other words, the flexural strength of fiber-free geopolymer mortar increases first and then decreases with the increase in nano-calcium carbonate content. The flexural strength of fiber-reinforced geopolymer mortar with 1% nano-calcium carbonate increases most quickly.



(**a**) (**b**)

Figure 6. Influence of fiber factor on strength. (**a**) Flexural strength; (**b**) Compressive strength.

Figure 7a compares the fiber reinforcement effects on flexural strength in this paper and the literature [31,43]. In the fiber factor range lower than 200%, the reinforcing effect of PP fiber is better than PVA fiber. In the fiber factor range of 200–450%, PVA fiber in cement mortar presents slightly lower relative strength than PP fiber. However, the PVA fiber in geopolymer mortar presents much higher relative strength than PP fiber. In the fiber factor range greater than 450%, PVA fiber in both Portland cement and geopolymers improves flexural strength better than PP fiber. However, the optimal fiber factor ranges for PVA and PP fiber are completely different. The optimal fiber factor range of PP fiber is 50–200%. The optimal fiber factor range of PVA fiber in cement mortar and geopolymer mortar is about 400% and higher than 600%, respectively. PVA fibers showed more effective enhancement of flexural strength in geopolymers due to the higher bonding strength of geopolymer fiber than cement fiber [51].



(**a**) (**b**)

Figure 7. Comparison of fiber reinforcing effects on strength in this paper and the literature. (**a**) Relative flexural strength; (**b**) Relative compressive strength.

Unlike flexural strength, fiber factor growth leads to the decline of compressive strength. Specifically, as the fiber factor increases from 0 to 464.8, the compressive strengths of 0, 1% and 2% nano-calcium carbonate PVA fiber-reinforced geopolymer mortar are reduced by 1%, 9.3% and 10%, respectively. With the increase in the fiber factor, the flexural strength increased significantly, while the compressive strength only increased slightly and showed an overall downward trend. However, the decrease rate of compressive strength is generally low, indicating the descending relation of a quadratic function.

Figure 7b compares the fiber-reinforcing effects on compressive strength in this paper and the literature [31,43]. All the relative compressive strengths were less than 1.15. In Portland cement mortar and geopolymer mortar, whether the fiber is PVA or PP fiber, the enhancement effect on compressive strength is limited or deteriorates. As shown in Figure 7a,b, the strengthening effect of PP fiber is inferior to that of PVA fiber in both flexural and compressive strength. The reason is that PVA fiber is hydrophilic and PP fiber is hydrophobic, leading to a higher bonding strength of the PVA fiber matrix than the PP fiber matrix [52]. In terms of compressive strength, PVA fiber in geopolymer mortar is not as effective as Portland cement mortar. The main reason is that geopolymer mortar is more viscous than cement mortar, so the fiber can easily disperse unevenly, leading to defects in the matrix [53].

As presented in Figure 8, with the growth in the fiber factor, the F/C is improved. The correlation coefficient of regression analysis in Figure 7 is above 0.90. As the fiber factor increases from 0 to 464.8, the flexural to compressive strength ratios of geopolymer mortar with 0, 1% and 2% nano-calcium carbonate increase by 236%, 167% and 170%, respectively. When the content of nano-calcium carbonate is 0, 1% and 2%, the slope of the linear relationship between the F/C and the fiber factor is about 0.0004, which is basically consistent. That is, the F/C has little difference with the increase in the fiber factor. The introduction of nanoparticles mainly affects the F/C of fiber-free geopolymer mortar. This suggests that PVA fibers can toughen geopolymer mortar more effectively rather than merely improving tensile strength.

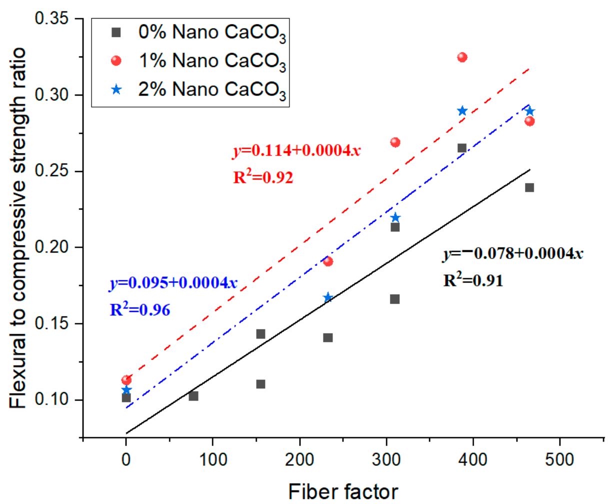


Figure 8. Influence of fiber content on flexural to compressive strength ratio.

Figure 9 compares F/C in this paper and the literature [31,43]. Generally speaking, the toughening effect of PVA and PP fiber is similar in Portland cement mortar. However, as the fiber factor is less than 450, the F/C of PP fiber-reinforced cement mortar is greater than that of PVA fiber-reinforced cement mortar. The result is the opposite when the fiber factor is higher than 450. The toughening effect of PVA fiber in geopolymer mortar is significantly higher than in cement mortar. This once again proves the significant advantage of PVA fiber for geopolymer materials.

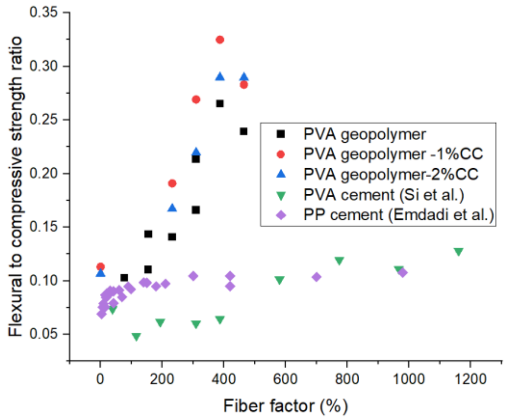


Figure 9. Comparison of flexural to compressive strength ratio in this paper and the literature.

3.3. Compactness

3.3.1. Influence of Fiber Content on Compactness

As presented in Figure 10, with the increase in PVA fiber content, the ultrasonic wave velocity and the apparent density of geopolymer mortar are both decreased. This corresponds to the decline in compressive strength in Section 3.2 and the decrease in flowability in Section 3.1. This indicates that when the fiber content increases, the internal defects in geopolymer mortar are increased. It can be seen that when the fiber content is lower than 0.4%, the ultrasonic wave velocity and apparent density only decrease slightly or even increase slightly. But as the fiber content is higher than 0.4%, the ultrasonic wave velocity and apparent density are reduced significantly. This is because when the fiber content is too large, the fibers have a high probability of overlapping and clumping, which leads to a decrease in the workability of the mortar. The internal defects of the specimen increase after hardening, leading to the decreased compressive strength in Section 3.2.

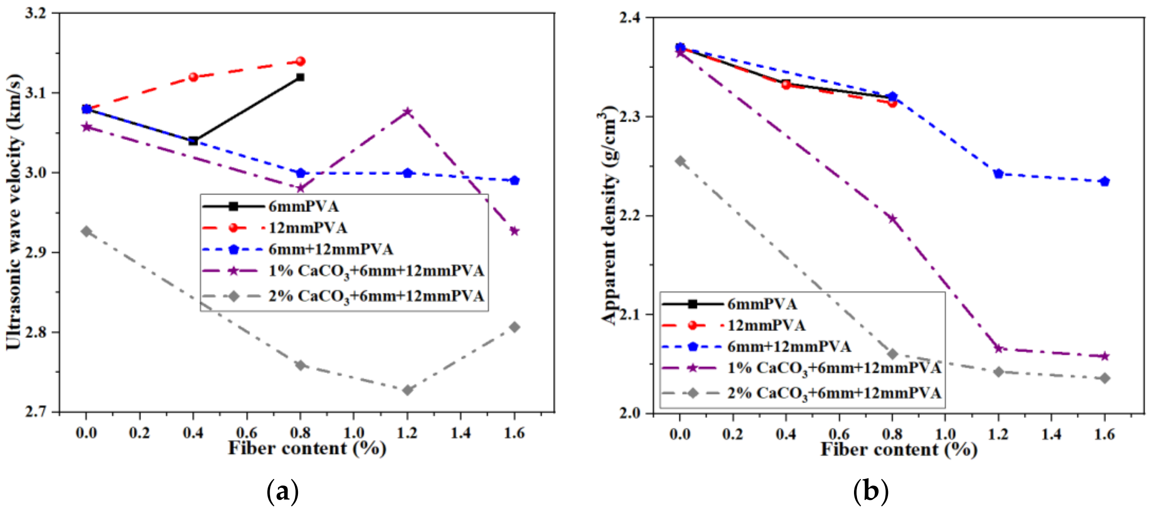


Figure 10. Influence of fiber content on compactness.(**a**) Ultrasonic wave velocity; (**b**) Apparent density.

3.3.2. Influence of Fiber Factor on Compactness

As presented in Figure 11, the ultrasonic wave velocity and apparent density of the specimen show a downward trend as a whole. This is due to the increase in the fiber factor. With the addition of nano-calcium carbonate, the decrease rate of the apparent density of geopolymer mortar (i.e., the linear slope) increases significantly. The reason is that the specific surface area of nano-calcium carbonate is much larger than that of fly ash and other materials, leading to uneven dispersion and defects in the matrix. It is worth noting that there is a good linear relationship between apparent density and fiber factor, and the correlation coefficients of regression analysis are 0.81, 0.92 and 0.83, respectively, as shown in Figure 11a. As for the linear relationship between ultrasonic wave velocity and the fiber factor, the minimum correlation coefficient is only 0.25, as shown in Figure 11b. This suggests that although ultrasonic wave velocity generally decreases with the increase in the fiber factor, it fluctuates greatly. The reason is that the addition of PVA fiber can improve the propagation speed of ultrasonic waves in the geopolymer mortar. This is because it can bridge defects and cracks. Hence, with the growth of the fiber factor, ultrasonic wave velocity can still be improved.

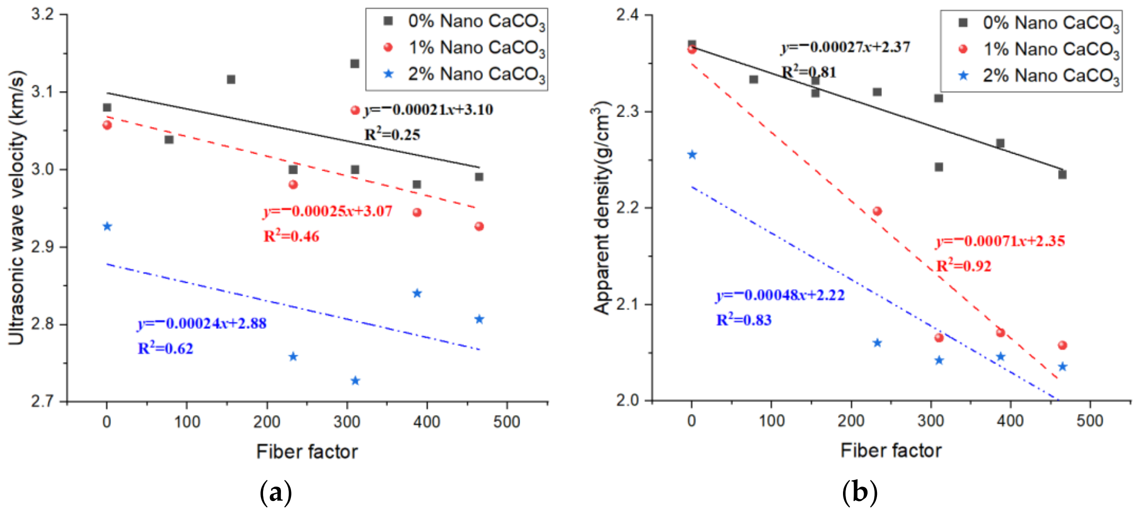


Figure 11. Influence of fiber factor on compactness. (**a**) Ultrasonic wave velocity; (**b**) Apparent density.

As shown in Figure 12, as the ultrasonic wave velocity of geopolymer mortar increases, the flexural strength and compressive strength show different trends. With the growth in ultrasonic wave velocity, the defect of geopolymer mortar decreases, leading to the compressive strength increasing. This indicates that the compressive strength of the geopolymer material is more dependent on the strength of the matrix, namely the compactness of the matrix. On the other hand, the flexural strength depends more on the crack development in geopolymer mortar [23]. The crack development is controlled by the fiber factor in the specimen, that is, with the growth in fiber dosage, the flexural strength of geopolymer mortar is improved significantly, but ultrasonic wave velocity presents a loss somewhat. Therefore, the flexural strength decreases with the increase in ultrasonic wave velocity on the whole.

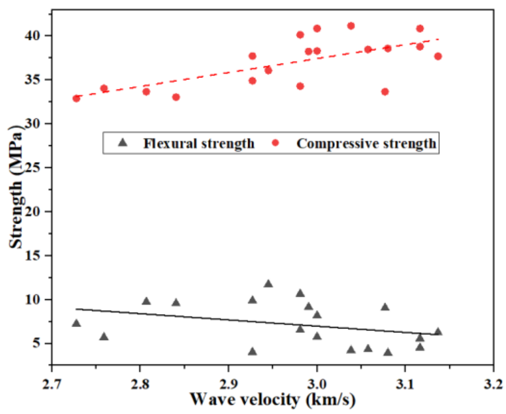


Figure 12. Relationship between ultrasonic wave velocity and strength.

3.4. Microstructure

3.4.1. XRD

Figure 13 shows the mineral phases, both nano-calcium carbonate and various content nano-calcium carbonate reinforced geopolymer. The foremost phases displayed by the XRD pattern of nano-calcium carbonate powder were calcite (PDF # 5-586) and quartz (PDF # 5-349). The diffractogram of geopolymer with 0, 1 and 2% of nano-calcium carbonate is shown in Figure 13, too. The broad hump between 2 θ of 17° and 38° signposted the amorphous geopolymer binder, corresponding to the mechanical strength obtained [54]. In addition, it is observed that special mineralogical phases like quartz, mullite and hematite present in silica fume, fly ash and slag still exist in geopolymers with/without nano-calcium carbonate. This signifies that these mineralogical phases did not participate in the geopolymerization progression. The rise of the intensity of hump situated between 17° and 38° (2 θ) is observed, which could result from the dissolution of partial nano-calcium carbonate leading to the formation of C-S-H gels next to the chief binder like N-A-S-H by outspreading the geopolymer gel.

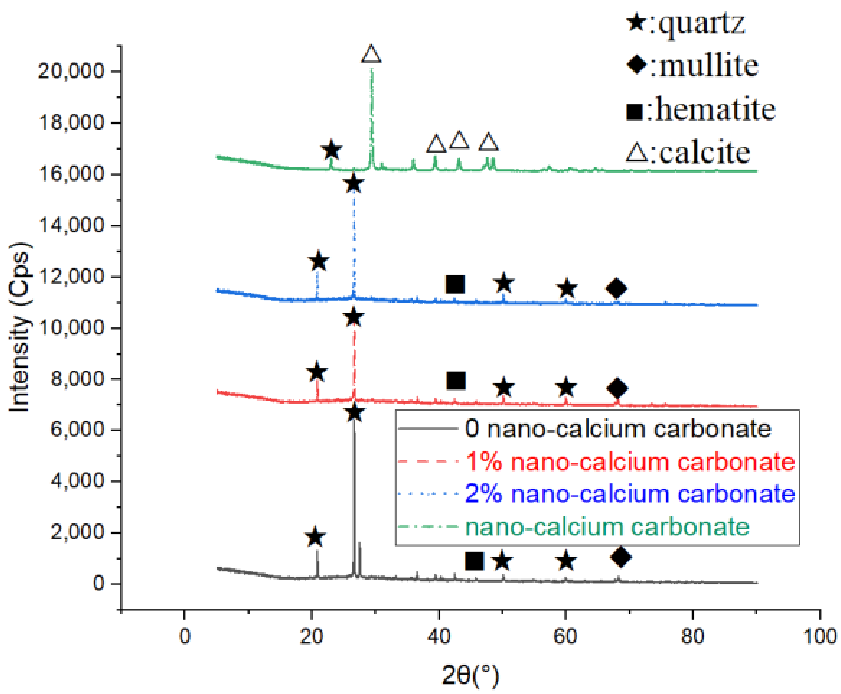
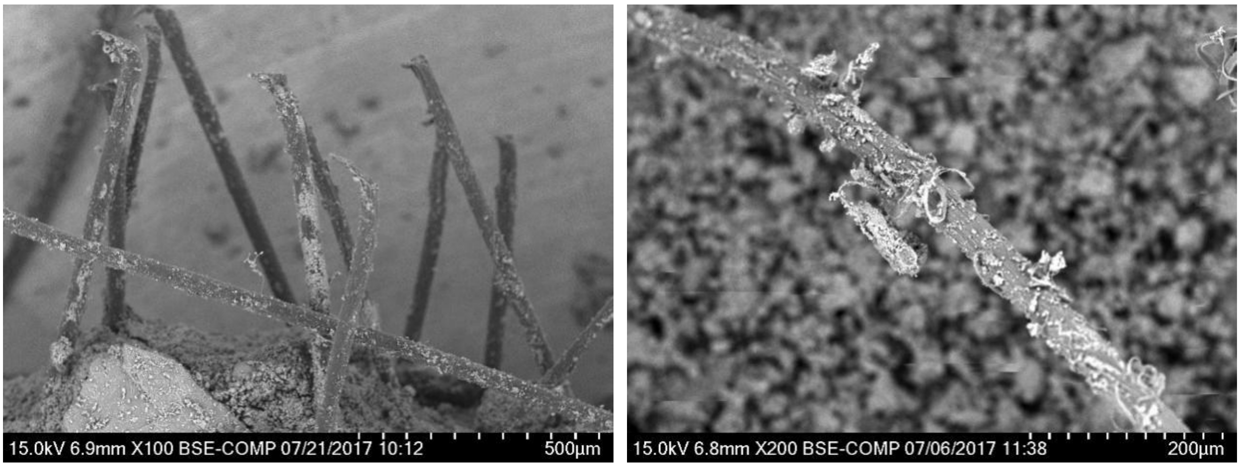


Figure 13. XRD pattern of nano-calcium carbonate reinforced geopolymer.

3.4.2. SEM

Figure 14 presents the micro morphologies of PVA fiber in geopolymer mortar. In geopolymer mortar without nano-calcium carbonate, there was some mortar debris on the surface of the PVA fiber, indicating the good bonding between the PVA fiber and the matrix. Generally, the fiber surface in mortar without nano-calcium carbonate is flat and undamaged, as shown in Figure 14a. However, in geopolymer mortar with 1% nano-calcium carbonate, the surface of PVA fiber is heavily scratched, and the fiber filaments are rolled up, indicating better bonding between PVA fiber and the matrix, as shown in Figure 14b. In addition, it was evidenced that the resistance of the mortar with nano-calcium carbonate is very high, and a lot of energy was consumed during the fiber pulling-out process. Thus the flexural strength of geopolymer mortar was greatly increased.



(**a**) (**b**)

Figure 14. Influence of NC on the surface morphologies of PVA fiber in geopolymer mortar. (**a**) PVA fiber in geopolymer mortar without nano-calcium carbonate; (**b**) PVA fiber in geopolymer mortar with 1% nano-calcium carbonate.

4. Conclusions

This paper studied the influence of nano-calcium carbonate and PVA fiber on the properties of fresh and hardened geopolymer mortar. Based on the investigation of flowability, strength, compactness and microstructure, the following conclusions can be drawn:

(1) The slump flow and flow rate are both reduced with an increase in fiber content. But unlike slump spread, the decreasing amplitude of the flow rate of mortar with short fiber (6 mm) is close to that of mortar with long fiber (12 mm). Therefore, the hybrid of long and short fibers with small content (0.8 vol.%) is conducive to flowability. In comparison, the hybrid of fiber with large content (1.6 vol.%) and nano-calcium carbonate is conducive to flowability.

(2) The slump flow and flow rate of geopolymer mortar with low fiber factor decrease with the growth in nano-calcium carbonate content. As the PVA fiber factor reaches 464.8%, the slump flow and flow rate value of mortars with 0, 1 wt.% and 2 wt.% nano-calcium carbonate are close to each other. This is consistent with conclusions from the literature: about 450% is the density packing threshold of PVA fiber in geopolymer composites.

(3) The combination of 0.8 vol.% 12 mm + 0.4 vol.% 6 mm fiber + 1% nano-$CaCO_3$ obtains the best reinforcing and toughening effect, presenting the highest flexural strength and flexural to compressive strength ratio, with a compressive strength of about 36 MPa. The PVA fiber increases the flexural to compressive strength ratio more than the flexural strength.

(4) The optimal fiber factor range of PP fiber is 50–200%. The optimal fiber factor range of PVA fiber in cement mortar and geopolymer mortar is about 400% and higher than 600%, respectively. PVA fibers showed more effective enhancement of flexural strength and toughness in geopolymer than cement mortar due to the higher bonding strength of geopolymer fiber than cement fiber.

(5) The ultrasonic wave velocity and apparent density of geopolymer mortar show a downward trend as a whole with the increase in the fiber factor. With the increase in ultrasonic wave velocity of the specimen, that is, the defect of the specimen decreases, the compactness increases, and the compressive strength increases on the whole. In contrast, the flexural strength decreases on the whole.

(6) The rise of the intensity of the hump situated between 17° and 38° (2 Theta) in the XRD pattern is observed, which could result from the dissolution of partial nano-calcium carbonate leading to the formation of C-S-H gels next to the chief binder like N-A-S-H

by outspreading the geopolymer gel. Furthermore, the SEM indicates that the surface of PVA fiber in geopolymer mortar with nano-calcium carbonate is heavily scratched, and the fiber filaments are rolled up, indicating better bonding between PVA fiber and the matrix.

At present, a lot of research has been carried out on the basic properties of fiber-reinforced geopolymer materials. However, in the future, the structural properties of fiber-reinforced geopolymer materials should be further studied to expand their engineering applications.

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