

Mechanical properties and durability of fiber reinforced geopolymer composites: A review on recent progress

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Abstract

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Abstract

Geopolymer concrete shares similar mechanical properties with ordinary Portland cement (OPC) concrete, and is even provided with better performances in high temperature and high corrosion circumstances. However, geopolymer binder is still subject to the disadvantages of large shrinkage and high brittleness, which greatly limit its application. Fiber reinforcement is widely used in various geopolymer systems to overcome the brittleness issue, but retains the high strength. Over the past 10 years, a significant advance has been made in the research of fiber reinforced geopolymers in terms of toughening efficiency and durability improvement. This paper, as a mini review, focuses on three types of fibers, i.e., inorganic fiber, natural fiber and synthetic fiber, in geopolymers, and their specific effects on compressive, flexural and tensile strengths, fractural toughness, shear strength and durability including shrinkage, chemical and freezing-thaw resistances. The recent understanding of bonding mechanism and fiber-geopolymer interface are also discussed, and knowledge gaps and future work challenges are correspondingly pointed out.

Key words: geopolymer, fiber reinforcement, interfacial zone, mechanical property, durability

1. Introduction

Geopolymer is considered an alternative cementitious material that alleviates environmental problems, and has the advantages of low CO₂ emission of production and the use of large volume of industrial wastes when compared with Portland cement. The hardened geopolymers contain amorphous and quasi-crystalline three-dimensional network gels by linking of tetrahedrons, such as silicon-oxygen tetrahedron, aluminum-oxygen tetrahedron and phosphorus-oxygen tetrahedron. Considering the special chemical activation process and the resulting three-dimensional network structure, geopolymers usually present the advantages of rapid high strength, excellent corrosion resistance, and high temperature stability, and can be extensively used as suitable binders in building, heavy metal adsorption, traffic repair projects, nuclear waste treatment and other fields.

However, geopolymers with high strength are also highly brittle, and methods overcoming the brittleness of geopolymers can be broadly divided into three categories: (a) adjustment of substrates by chemical or physical means; (b) internal reinforcement; and (c) providing external constraints. Of the three solutions, the latter two are generally more efficient and less costly. One of the ways to improve brittleness is to add fibers to the geopolymer matrix to increase its density and toughness. Zhang et al.[1] introduced the concept of fiber factor that describes the comprehensive influence of fiber content and fiber length. The concept of fiber factor was used to prove that the toughening effect of polyethylene fiber on geopolymer was significantly better than that of steel fiber, polyvinyl alcohol fiber and basalt fiber on cement-based materials. Mohammed et al.[2] found that the toughening effect of geopolymer with 8mm polyvinyl alcohol fiber is better than that of geopolymer with 13mm polyvinyl alcohol fiber, indicating that smaller fibers can better bridge the cracks in grounding polymers, thus providing better performance. Riahi et al.[3] prepared the alumina-coated steel fiber reinforced geopolymer, and found that the flexural strength and compressive strength increases by 17 % and 14 %, respectively compared with the uncoated steel fiber. Rachel et al.[4] found that the addition of bagasse fiber into the geological polymer can reduce the density and increase the sound velocity, thereby improving the sound insulation and thermal insulation properties. However, such an addition will reduce the compressive strength of the matrix, and the permeability increases with the increase of fiber content. Ma et al.[5] added short carbon fibers into geopolymers, which can significantly improve the rheological properties of geopolymers, and found that the flexural strength and compressive strength of the composites are improved and reach the peak in the case of a fiber content of 3 %. When the fiber content increases to 4 %, the fiber agglomerates and reduces the mechanical properties. The geopolymer with short carbon fiber is endowed with the advantages of light weight, high strength and good toughness, which opens up a road for the practical application of fiber reinforced materials. Su et al.[6] prepared geopolymer using fly ash and slag as raw materials of aluminosilicate, and incorporated different fibers and hollow microspheres into the

slurry to improve the properties of the composites. The results show that the improvement effect of fibers on reinforced materials is in turn of polypropylene fiber, alkali-resistant glass fiber and lignin fiber, and that fiber can prevent the separation of hollow microspheres and geopolymer matrix, inhibit the generation and development of cracks, and finally improve the strength whether it is mixed fiber or single fiber. Liu et al.[7] overcame the brittleness of geopolymer matrix using four kinds of steel fibers. When the fiber content and length increase, the fluidity of the mixture decreases and is not affected by the fiber shape. The increase of fiber content and the decrease of the fiber diameter contribute to the improvement of compressive strength, and the bending performance improves with the increase of fiber volume and length. At present, many studies have been conducted on fiber reinforced geopolymers, but there are still few systematic summaries on the addition of inorganic fibers and organic fibers to geopolymers.

To this end, this review focuses on the current status of research on fiber reinforced geopolymer, and attempts to identify the limitations and advances of fiber-reinforced geopolymer. Finally, the knowledge gaps and remaining challenges for future work are discussed.

2.Role of Fibers in Geopolymer Composites

Steel fibers, glass fibers, basalt fibers, polypropylene fibers, and blended fibers are all fibers currently used in concrete. Given that geopolymers and cement are both brittle materials, fibers play similar roles in geopolymers, mainly the following roles in the polymer such as nano filling and crack bridging. The key factors to be considered while selecting fibers for reinforcement modification of cement or geopolymer composites include: (1) compatibility of material properties with application; (2) adequate fiber-matrix interaction to transfer stress; and (3) optimal aspect ratio to ensure effective post-cracking behavior. The addition of fibers affects the fluidity and mechanical properties of viscous carbides, which depends on the surface properties, shape, types and flexibility of the fibers[8].

At present, the fibers used in geopolymers can be roughly divided into the following three categories, i.e., inorganic fiber, natural fiber and synthetic fiber. To be specific, inorganic fiber mainly includes steel fiber, glass fiber and basalt fiber; natural fiber mainly consists of plant fiber, animal fiber and mineral fiber; and synthetic fiber mainly refers to polyethylene, polypropylene, polyvinyl alcohol fiber, etc. Table 1 lists the main characteristics of common fibers added to geopolymer.

- Inorganic fibers. Inorganic fiber can be traced back to the application of ancient asbestos[9]. These fibers consist of a mixture of alumina and silicon dioxide and are often used in high thermal applications such as refractories due to their high melting point. In addition, these fibers also possess the advantages of low cost, high tensile strength, chemical stability and excellent insulation properties[10].
- Natural fibers. Nature fibers are mainly divided into plant fiber, animal fiber and mineral fiber. Plant fibers mainly include fruit fiber, leaf fiber, stem fiber, seed fiber, and bast fiber; animal fiber mainly refers to the silk fiber in animal hair; and iron asbestos, crocidolite, actinite and carlite fibers are the main mineral fibers[11].
- Synthetic fibers. Synthetic fibers refer to the fibers made of synthetic polymer materials, including polyester fiber, polyamide fiber, polypropylene fiber, polyvinyl alcohol fiber, polyvinyl chloride fiber, etc.

Table1 Characteristics of common fibers

Category	Type	Dimension	Specific gravity (gr/cm ³)	Density (kg/m ³)	Young's modulus (GPa)	Tensile strength (MPa)	Ref.
Synthetic fiber	Polypropylene	Length 40-54mm	0.91	-	-	550	Kuranlı et al.[12]

Category	Type	Dimension	Specific gravity (gr/cm ³)	Density (kg/m ³)	Young's modulus (GPa)	Tensile strength (MPa)	Ref.
	Polypropylene	Length 9mm, diameter 0.0074mm	0.9	-	-	774	Bellum et al.[13]
	Polypropylene	Length 3/6/9mm, diameter 20um	-	910	-	-	Wang et al.[14]
	Polypropylene	Length 12mm, diameter 50um	0.91	-	3-3.5	600-700	Aamer et al.[15]
	Polypropylene	Length 65mm, diameter 0.85mm	-	905	3	250	Wang et al.[16]
	Polypropylene	Length 12mm, diameter 40um	0.91	-	42.8	1620	Ghassan et al.[17]
	Polyvinyl alcohol	Length 8mm, diameter 40um	1.30	-	41	1600	Aamer et al.[15]
	Polyvinyl alcohol	Length 12mm, diameter 40um	-	900	-	1560	Wang et al.[18]
	Polyvinyl alcohol	Length 12mm, diameter 39um	1.30	-	5	450	Ghassan et al.[17]
	Polyamide	Length 6.12mm	-	-	-	900	Kuranlı et al.[12]
	Polyolefin	Length 10mm, diameter 63um	0.9	-	-	275	Celik et al.[19]
	Polyester	Length 6mm, diameter 30-40um	1.3-1.4	-	2-4	400-600	Aamer et al.[15]
Inorganic fiber	Steel	Length 6mm, diameter 0.15mm	7.8	-	-	2050	Bellum et al.[13]
	Steel	Length 61mm, diameter 0.75mm	-	6500	200	1350	Wang et al.[16]
	Carbon	Length 150mm, width 100mm, thickness 300mm	-	1570	12.7	190.4	Samal et al.[20]
	Carbon	Length 10mm, diameter 15um	2.0	-	200-220	2930	Aamer et al.[15]

Category	Type	Dimension	Specific gravity (gr/cm ³)	Density (kg/m ³)	Young's modulus (GPa)	Tensile strength (MPa)	Ref.
Natural fiber	E-glass	Length 150mm, width 100mm, thickness 30mm	-	1770	9.7	65.6	Samal et al.[20]
	Glass	Length 3/6/9mm, diameter 18um	-	2540	-	-	Wang et al.[14]
	Glass	Length 12mm, diameter 20um	-	2688	-	-	Ampol et al.[21]
	Basalt	Length 3/6/12/18mm	-	2630	88	1450	Wang et al.[22]
	Basalt	Length 12mm, diameter 20um	2.73	-	-	4100	Celik et al.[19]
	Basalt	Length 3/6/9mm, diameter 20um	-	2630	-	-	Wang et al.[14]
	Kenaf	Length 3-6mm, diameter 19.8mm,	1.20	1310	58	223-930	Wang et al.[22]
	Sisal	Length 35-40mm, diameter 179um	-	1450	-	-	Ampol et al.[21]
	Sisal	Length 10mm, diameter 137um	-	1450	-	-	Silva et al.[23]
	Jute	Length 10, diameter 53um	-	1300-1450	-	-	Silva et al.[23]
	Coconut	Length 35-40mm, diameter 117um	-	1200	-	-	Ampol et al.[21]

Considering the different properties of fiber itself, its microstructure is also rather different. The macroscopic and microscopic morphology of some different fibers are listed below.

The specific density and water absorption of geopolymer composites decrease with the presence of polypropylene fiber, which is mainly attributed to the microstructure enhancement and density increase of the matrix. These effects are directly related to the fiber content, not the fiber type[24]. Natural fibers improve the performance of concrete, cover the similarity between natural fibers and cement matrix, and may reduce the pumpability of shotcrete because they reduce the workability, a key factor in shotcrete's use in construction[25].

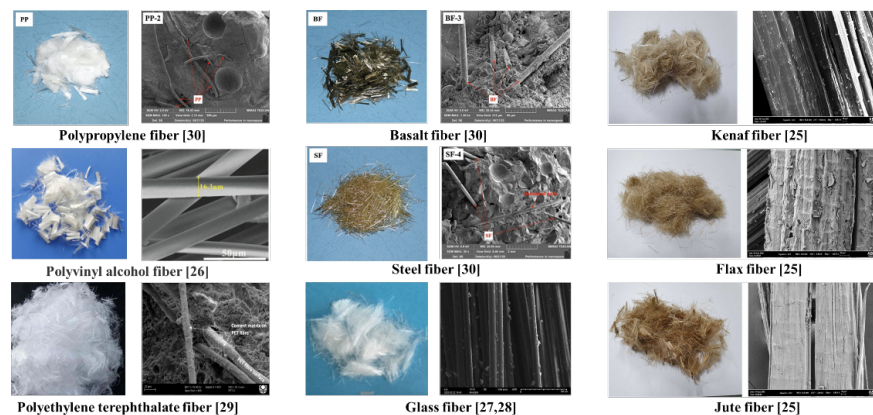


Fig. . Appearance and micromorphology of typical fibers[18, 25-30]

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3. Bonding Between Fibers and Matrix

The properties in fiber reinforced geopolymer depend on the performance of fiber, fiber content, precursor of geopolymer and curing environment. However, the interface between the matrix and the fiber plays a key role in the overall mechanical properties of the composites. If the interface is well bonded and the load can be transferred from the matrix to the fiber with a high carrying capacity, fibers with inert surfaces will also result in weak interface contact[31]. Regarding the interface between fiber and matrix, many scholars have studied the interface bonding zone between fiber and geopolymer by establishing mathematical or physical models.

Fiber fracture and pull-out from the matrix are the two main failure mechanisms of geopolymer. At the same time, the fiber will agglomerate if the fiber content in the matrix is too high, thereby resulting in the decrease of the matrix strength. Fig. 2 depicts the interface bonding between different fibers and geopolymers.

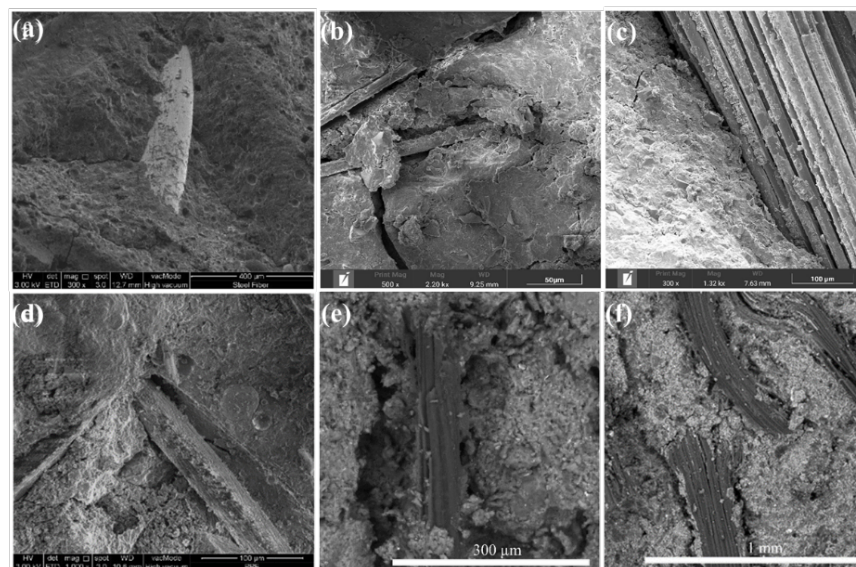


Fig. 2. The interfacial bonding of different fibers with geopolymer

steel fiber[31]; (b) glass fiber[14]; (c) basalt fiber[14]; (d) polypropylene fiber[31]; (e) jute fiber[23]; (f) sisal fiber[23][14, 23, 31]

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Fig. 2(a) shows that the steel fiber and geopolymer matrix contact well, and there is no interface peeling phenomenon. Given that steel fibers are often hydrophilic, they can significantly improve the energy absorption and bending strength of composites[31]. The glass fiber and basalt fiber in Figures 2(b) and 2 (c) present obvious interfacial debonding with geopolymer. The addition of glass fiber increases the compressive strength and flexural strength of the matrix by 32.6 % and 30.35 %, respectively, while the addition of basalt fiber increases the compressive strength and flexural strength of the matrix by 27.3 % and 35.36 %, respectively[14]. Fig. 2(d) describes the interface bonding between polypropylene fiber and geopolymer matrix. Organic fiber also shows the interface peeling phenomenon, and the addition of adding polypropylene fiber increases the compressive strength and flexural strength of the matrix by 27.5 % and 16.07 %, respectively. Fig. 2(e) (f) depicts the interfacial bonding between jute, sisal fiber and geopolymer in natural fibers. The jute with a mass fraction of 1.5 % increases the compressive strength and tensile strength of the matrix by 64 % and 45 %, respectively, while the sisal fiber with a mass fraction of 2.5 % increases the compressive strength and tensile strength of the matrix by 76 % and 112 %, respectively.

The bonding between steel fiber and geopolymer is found the best, and no interface peeling phenomenon is observed. Considering the high strength and rough surface of steel fiber, the mechanical bonding force with geopolymer is formed, and leads to the optimal mechanical properties of geopolymer.

4. Mechanical Properties of Fiber Reinforced Geopolymers

4.1 Compressive strength

Geopolymers are provided with excellent mechanical properties, among which, compressive strength is the most important index. The compressive strength of the specimen depends on the flow resistance of the mixture, while the flow resistance and slump depend on the type, size and weight of the fiber. The proper uniformity and high pressure compaction between the fiber and the cement matrix can improve the compressive strength by the application of fibers. However, for geopolymer, different fibers exercise different effects on the compressive strength[32].

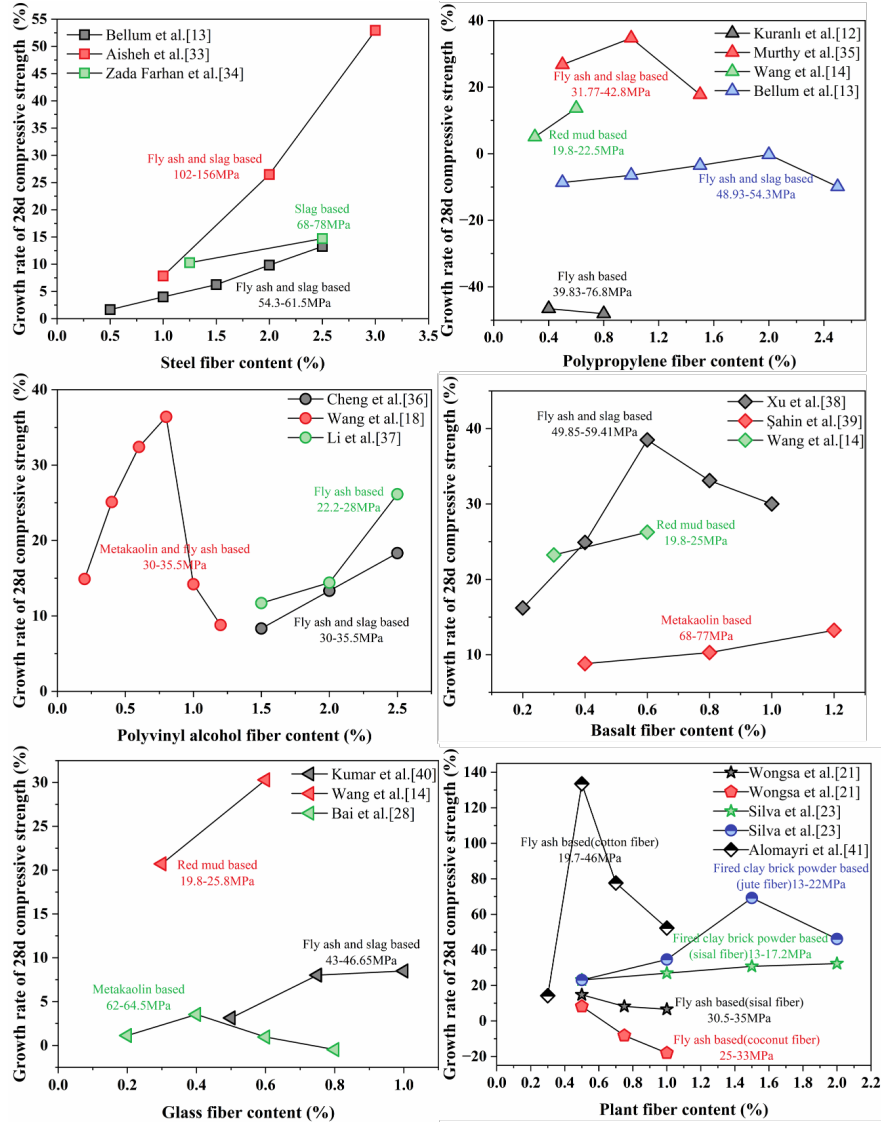


Fig .3. Effect of fiber content on the compressive strength of geopolymer [12-14, 18, 21, 23, 28, 33-41].

The effect of different fiber contents on 28 d compressive strength of geopolymer is listed in Fig. 3.

Due to the high rigidity of steel fibers, its addition improves the compressive strength of geopolymer. The experimental results of Zada Farhan show that 6mm steel fibers improve the compressive strength more efficiently than 12mm steel fibers[34], and that the alumina coating can improve the interfacial bonding strength between steel fiber and geopolymer, which is 151% higher than that of uncoated steel fiber[3]. With the increase of polypropylene fiber content, the decrease in strength is attributed to the formation of interpolymer voids and weak interfacial bonding zone. Murthy's study shows that 1% is the best content for polypropylene fiber to improve the compressive strength of geopolymer[35], while Bellum's research indicates that 2% is the best content for polypropylene fiber to improve the compressive strength of geopolymer[13], and Wang's study considers 0.8% polyvinyl alcohol fiber the best dosage to improve the compressive strength of geopolymer. However, Wang and Li's study indicates that a higher polypropylene fiber content represents

a higher compressive strength[18] [37]. Xu has found that the optimal dosage of basalt fiber to improve the compressive strength of geopolymer is 0.6%, and that the comprehensive performance of 6mm basalt fiber is better than that of 3mm basalt fiber [38]. Wang's study shows that a higher content of basalt fiber indicates a better compressive strength[14], and Bai's study recognizes 0.4% glass fiber as the best dosage to improve the compressive strength of geopolymer. Glass fiber can eliminate the microcrack of polymer and improve the mechanical properties of geopolymer[28]. Silva's research shows that a higher sisal fiber content means a better compressive strength[23]. Wongs's study implies that sisal fibers greater than 0.5% reduces the compressive strength of geopolymers[21], that the jute fiber optimal dosage is 0.5%, and that the cotton fiber optimal dosage is 0.5%[41]. More than 0.5% of coconut fiber decreases the compressive strength of the geopolymer[21].

As shown in Fig.4, internal tensile stress is generated when the fiber reinforced geopolymer is squeezed by external force. The appropriate amount of fiber can play a bridging role and effectively inhibit the crack propagation. The strength growth percentage of cement-based materials caused by fiber inclusions is usually lower than that of geopolymer, which can be explained by the ceramic-like and polymer-like properties of geopolymers and better fiber matrix interface. Geopolymer has finer pore distribution than cement-based materials.

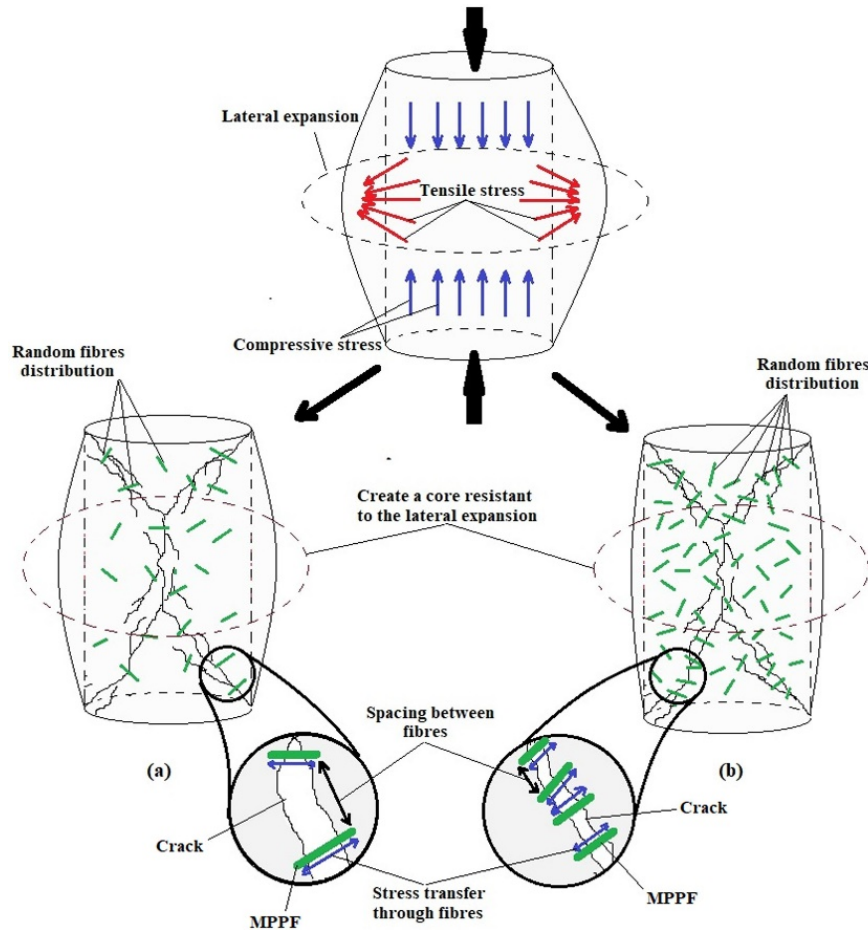


Fig .4. Effect of fiber content on the compressive strength of geopolymer (a) little; and (b) much[42]. Reproduced from [42], with permission from [Publisher]

In short, the strong bond between geopolymer and fiber may be related to the following aspects: (a) different

reaction mechanism and reaction products of geopolymer and cement-based materials; (b) strong adhesion of N-A-S-H to matrix; (c) the formation of an improved interface transition zone (ITZ) in the geopolymer, which is partially attributed to the fact that cement-based materials tend to form low strength silicates at the ITZ, and partially that the fiber matrix interface is affected by higher pH values.

4.2 Flexural strength

Considering the brittleness caused by the internal structure of geopolymer cross-linked each other, adding fiber can significantly enhance the flexural properties of geopolymer, while considering the crack bridging mechanism of fibers, the bending strength of fiber reinforced geopolymer is significantly higher than that of unreinforced geopolymer.

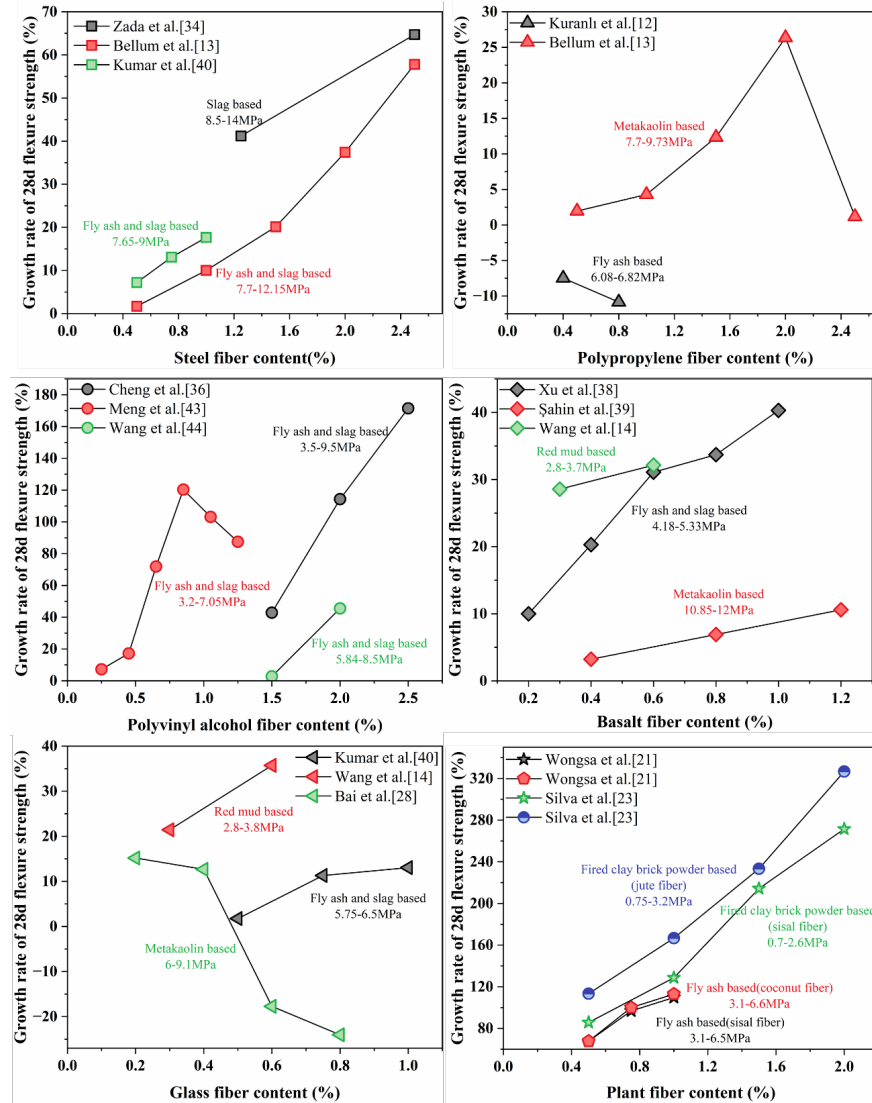


Fig .5. Effect of fiber content on the flexure strength of geopolymer

[12-14, 34, 36, 38-40, 43, 44][14, 21, 23, 28, 40]

The influence of different fiber dosages on the flexural strength of geopolymer is shown in Fig. 5. Steel fiber significantly improves the flexural strength, which is greatly related to the stiffness of steel fiber itself, and the flexural strength increases with the increase of the volume fraction of steel fiber in geopolymer. In the case of a PP fiber dosage of 2%, the flexural strength of the matrix can be greatly improved. Ramamohana[13] found that after adding polypropylene fiber and steel fiber, the bending strength in Day 28 increases by 26.36 % and 57.79 %, respectively, compared with that of pure slurry geopolymer. Chuan Wang[14] found that polypropylene, glass and basalt fiber can increase the flexural strength of pure paste by 16.07 %, 30.35 % and 35.36 %, respectively.

Besides, it has also been found that plant fibers such as sisal fiber, coconut fiber and jute fiber are better than inorganic fiber and organic fiber in improving the flexural strength of geopolymer. For instance, 2% sisal fiber can improve the flexural strength of the matrix by 300%.

Adding fiber in geopolymer can improve the flexural strength of the matrix and greatly improve the bending toughness. The reason why the fiber can enhance the flexural strength of the matrix is as follows: (1) the geopolymer has multiple cracks in the process of bending deformation; (2) fiber bridging plays an important role in crack stability and multi-crack induction; and (3) the existence of fiber changes the stress distribution during the specimen deformation process, and distributes the stress evenly in the specimen, thereby improving the flexural strength.

4.3 Tensile strength

The tensile properties of fiber reinforced composites are greatly affected by the matrix type, fiber type, fiber volume, loading rate, interface bonding strength and even the type of the used impact machine.

The tensile failure process of composites is a progressive damage process: considering the existence of defects, some fibers will fracture first in the initial loading process, and local thermoplastic deformation will occur in the matrix and interface near the fiber fracture. Besides, the redistribution of microscopic stress deformation will occur, accompanied by more fiber failure and local plasticity, considerable fiber instability failure and the final failure of composite materials. It can be found that the tensile strength failure of composites depends on various loss evolutions including fiber fracture and inelastic deformation of the matrix and the interface.

The effects of different fiber dosage or length on the 28-day tensile strength of geopolymers are listed in Fig. 6. Given the brittleness of the geopolymer, the addition of fiber can greatly improve the tensile properties of the matrix, which is not only attributed to the high tensile strength and elastic modulus of the fibers, but also the fact that stress in the sample can be transferred to the fibers through the interface with the geopolymer matrix.

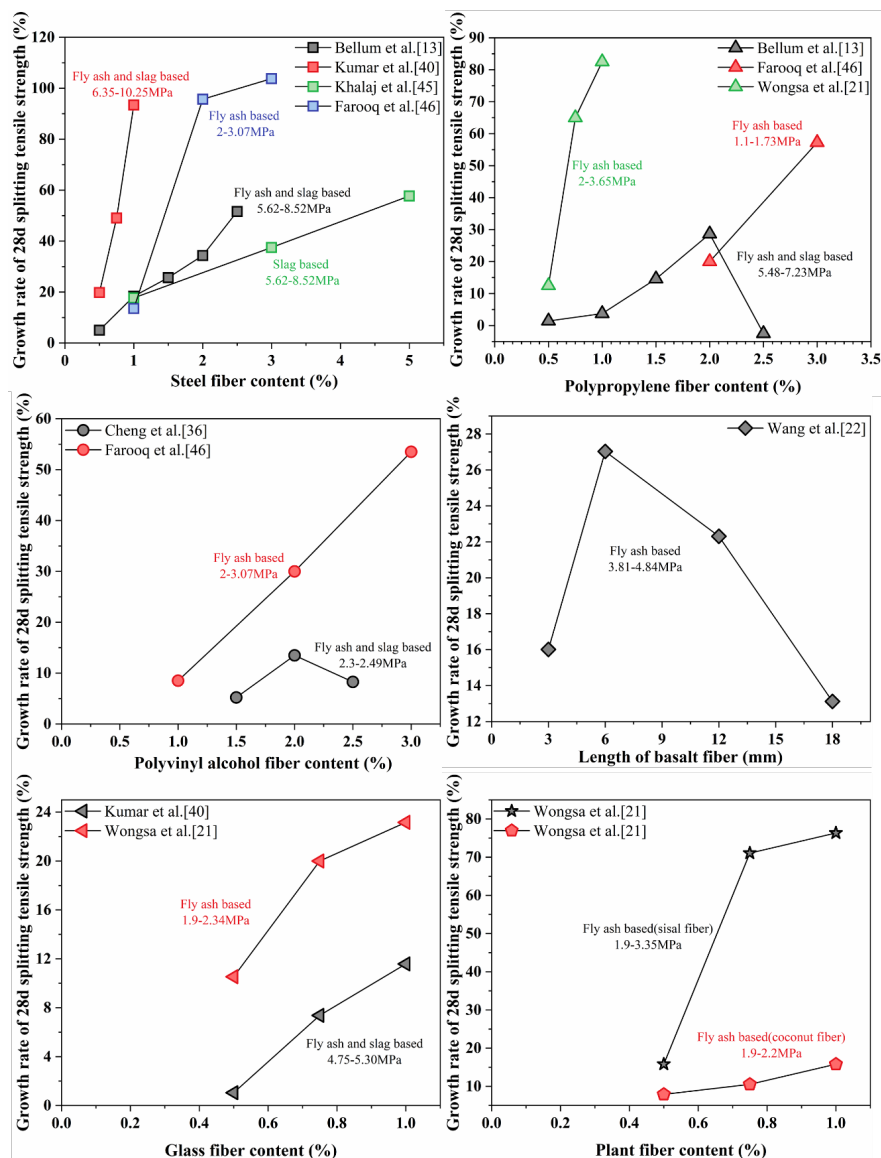


Fig. 6. Effect of fiber content on the tensile strength of geopolymer[13, 21, 22, 36, 40, 45, 46]

The tensile strength of the geopolymer increases with the addition of steel fiber because of its greater rigidity. Bellum's study shows that the best content of polypropylene fiber reinforced geopolymer is 2%, and that the best tensile strength is 7.23MPa. The research conducted by Farooq indicates that the tensile strength of geopolymer increases with the increase of polyvinyl alcohol fiber content. Wang's study presents the maximum splitting tensile strength of 4.84MPa of the 6 mm basalt fiber reinforced geopolymer. The tensile strength of the geopolymer increases with the increase of the glass fiber content. The study of Wongs et al. shows that sisal fiber reinforced geopolymer possesses the greatest tensile strength, while the tensile strength of coconut fiber reinforced geopolymer increases with the increase of coconut fiber. However, Zhang's research shows that the tensile strength increases by 4.6 %, 21.3 %, 4.3 % and 74.3 %, respectively by adding 1 % single fiber PP, PVA, RPP and steel fiber into the geopolymer. Steel fiber is most effective in improving tensile strength because of its high tensile strength and stiffness, but the tensile strength of geopolymer with PVA, PP and RPP increases by 38.2 %, 36 % and 48.9 % by the incorporation of mixed fibers. In this case,

it is more effective to mix PVA, PP, RPP and steel fiber to improve the tensile strength of geopolymer than to use single fiber merely[47].

Considering its own characteristics such as high rigidity and high tensile strength, fiber can obviously improve the splitting tensile strength when added to geopolymer. However, the mixed fiber has a better improvement effect, and the mixture of PP and steel fiber presents the best effect in the case of improving the splitting tensile strength.

4.4 Fracture toughness

Fracture toughness represents the ability of material to prevent against crack propagation and is a quantitative index to measure the toughness of material. The test methods of fracture toughness include direct tensile method, compact tensile method, wedge splitting method and three-point bending beam method. The fracture toughness of the material is larger in the case of a constant crack size, and fracture energy is defined as the energy required for the unit area of fracture propagation in brittle materials, which reflects the energy change during the crack development[48].

Fiber factors can describe the combined effect of fiber content and length: the fracture toughness increases with the increase of the fiber factor in the case of a fiber factor less than 600, indicating that the fiber matters considerably in restricting the cracks at the initial stage of geopolymer cracking. The fracture toughness of geopolymer decreases when the fiber factor exceeds 600.

$$RI = V \cdot L/D$$

Where RI denotes the fiber factor; V, the fiber volume content; and L/D, the fiber length to diameter ratio.

Zhang et al.[1] studied the influence of the ratio of polyethylene fiber to water-binder ratio on the fracture toughness of geopolymers, and found that polyethylene fiber has a good toughening effect on geopolymers. The fracture toughness of the matrix decreases when the fiber content exceeds 1.05%. Due to the high fiber content, the matrix has more pores and interfaces, resulting in more defects. Behzad et al.[49] found that when 2% polyvinyl alcohol fiber is added to fly ash base geopolymer, the fracture toughness can reach 0.436Km. It has also been found that adding 0.5wt% cotton fiber can increase the fracture toughness of geopolymer by $1.12\text{MPa}\cdot\text{m}^{1/2}$. Considering the poor dispersion of cotton fiber in slurry, the fracture toughness decreases with the increase of fiber content. At the same time, the dispersion of cotton fiber in geopolymer has a great influence on the fluidity, adding 0.7 and 1.0wt% cotton fiber will greatly affect the fluidity of the matrix, which must be compensated by increasing the water content of the mixture, and increasing the porosity and microcracks of the matrix. At 0.5wt% cotton fiber, the mechanical and fracture properties of geopolymer composites are optimized. These cotton fiber-reinforced geopolymers can be applied to panels or shingles of siding, roofing, piping and cooling towers[50]. Ghasemzadeh et al. studied the effect of a certain volume of steel and polypropylene fibers on the fracture characteristics of ultra-high performance geopolymer concrete based on abrasive blast furnace slag and silica fume. With the increase of fiber content, the fracture energy increases compared with the control group, and the substitution of polypropylene fibers for steel fibers slightly reduces both types of fracture energy[51].

When the properties of fibers such as the hardness cannot be changed, many scholars improve the fracture toughness of composites by filling admixtures to improve the density of the matrix[52]. The fiber plays a bridging role in the matrix and transmits internal stress in the matrix, thereby improving the ability of resisting crack generation and propagation.

4.5 Shear strength

Shear strength refers to the ultimate strength of the material when it is cut, and reflects the ability of the material to resist against shear sliding.

The influence of different types and volume fractions of fibers on the shear strength of geopolymers is shown in Fig. 7. The optimal dosage of steel fiber (SF) to increase the shear strength of geopolymer is 0.5% and the increment is 56%. However, the shear strength of geopolymer decreases when the dosage is increased to 1%. Given that the geopolymer concrete with high blast furnace slag content has poor workability and fiber dispersion may be affected by the high viscosity of sodium silicate solution, the optimal content of steel fiber in geopolymer decreases compared with that of steel fiber in cement of 2.5%. Besides, the mixed fiber is better to improve the shear performance of polymer. In order to obtain good shear strength with low fiber content, it is recommended to add steel fiber and polypropylene fiber as well as steel fiber and polyvinyl alcohol fiber to the geopolymer.

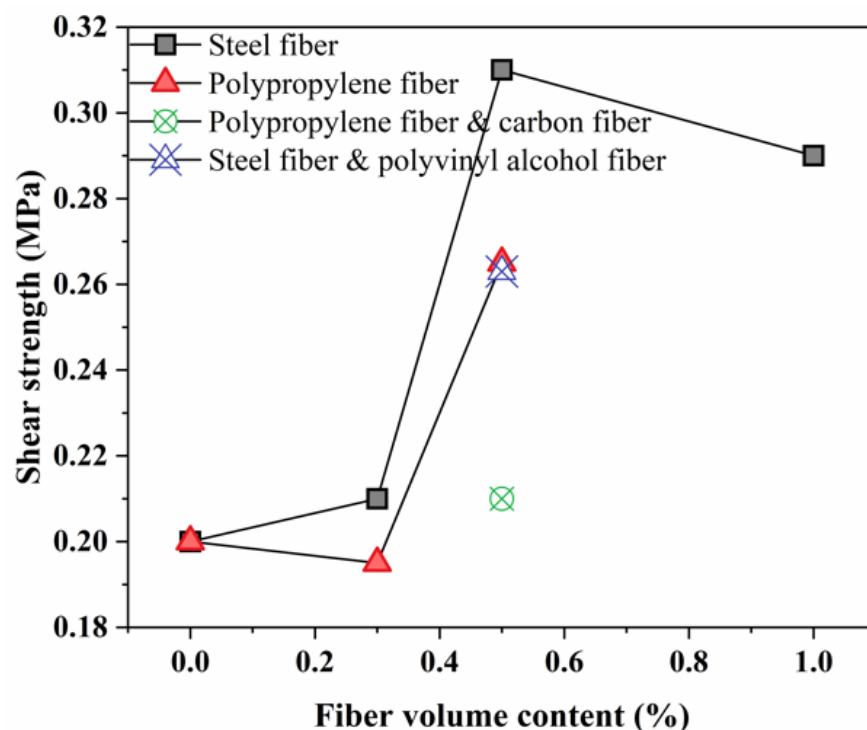


Fig. 7. Effects of different fiber types and dosages on shear strength[53]

SF: steel fiber; PF: polypropylene fiber; CF: carbon fiber; PVF: polyvinyl alcohol fiber

The high shear resistance of fiber-reinforced polymer is more widely used on walls. According to the study of Harry et al.[13], the tested composite polyvinyl alcohol fiber wrapped macroscopic synthetic fiber reinforced concrete wall samples present significantly higher values of interfacial shear strength compared with the test wall samples filled with ordinary concrete. The maximum shear load and interfacial shear strength increases by 93.5%. Tran et al.[54] studied the shear capacity of fiber reinforced geopolymeric concrete beams under impact load, and found that the addition of fibers significantly improves the impact response of geopolymeric beams in terms of maximum and residual displacement and reaction force, and reduces negative cracks and spalling cracks. Lakavath et al.[4] conducted experimental and numerical studies on the shear behavior of large synthetic fiber reinforced prestressed concrete beams, and found that a low fiber volume increase of 0.5% does not significantly improve the shear behavior. However, the test and finite element results of the beams with higher volume fractions (1.0% and 1.5%) significantly improves the post-cracking behavior, ductility and ultimate shear resistance of the beams[55].

5. Durability

5.1 Drying shrinkage

Composites lose their moisture during air drying, resulting in shrinkage and crack formation. Drying shrinkage is an important durability parameter of concrete specimens, indicating the potential cracks formed in hardened cementitious materials[56]. The addition of fiber can offset the stress in the matrix and effectively restrain its drying shrinkage.

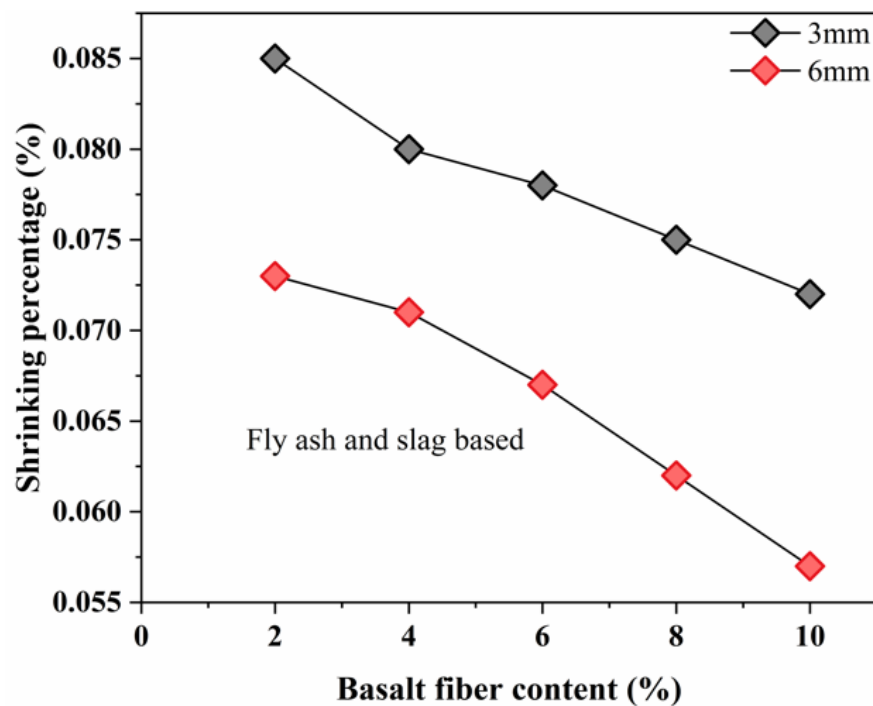


Fig. 8. Effects of basalt fiber content and length on the dry-shrinkage properties of geopolymers[38]

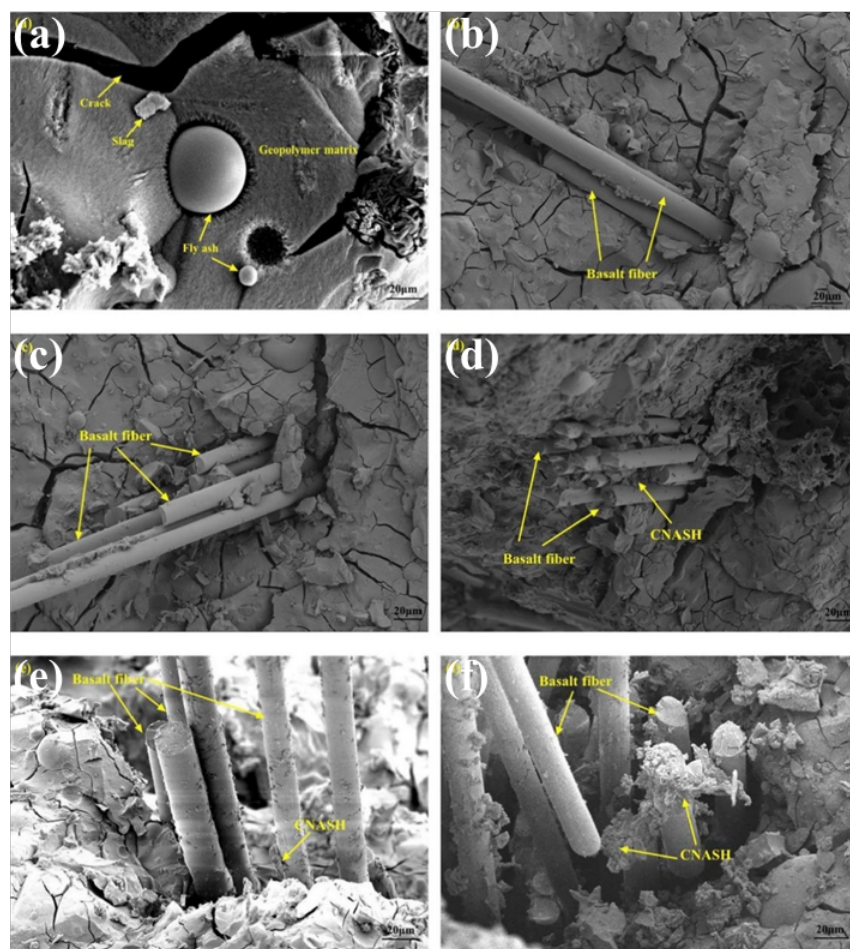


Fig. 9. SEM images of geopolymer with different 3mm basalt fiber contents (a-0%; b-2%; c-4%; d-6%; e-8%; f-10%)[38]. Reproduced from [38], with permission from [Publisher]

The drying shrinkage value of fly ash base geopolymer added with steel fiber is in the range of 264-297 microstrain, that of fly ash base geopolymer added with polypropylene fiber ranges 394-424 microstrain[12], and that of the matrix can be minimized by adding 0.6% polypropylene fiber to the geopolymer[57]. Given that basalt fibers promote the development of C-S-H, the addition of this fiber to the geopolymers can reduce the drying shrinkage of the matrix,. The combination of CASH and NASH leads to the refinement of the pores, and the fiber acts as micropolymer in the matrix, which can well disperse the sample stress [58]. As is shown in Fig. 8, a longer basalt fiber indicates a better shrinkage rate in the case of constant basalt fiber content, and the shrinkage rate of the sample with 6mm basalt fiber is lower than that with 3mm basalt fiber. As is shown in Fig. 9, when the fiber content is constant, a longer fiber indicates fewer roots per unit volume. In this case, the binding energy between fiber and slurry increases with the increase of the fiber length[38]. Adding 0.4% polypropylene fiber and 0.5% expansion agent MgO to the geopolymer can effectively reduce the shrinkage of the matrix[59]. The dry shrinkage rate of fly ash and slag base polymer with 0.3 and 0.6 volume fraction of PVA fiber is 20.53% and 45.69% at Day 7, and 26.92% and 41.18% at Day 28, respectively[60].

The drying shrinkage of the matrix can be reduced when fiber is added to the geopolymer. Since the fiber restrains the extension of micro-cracks in the specimen, it bears part of the stress caused by the shrinkage of the matrix, thus reducing the shrinkage strain of the material[61].

5.2 Chemical resistance

There are many types of chemical erosion, mainly including sulfate erosion and chloride ion erosion. Corrosion is caused by the reaction of sulfate ions and chloride ions from the external environment with hydration products, which results in expansion and cracking, and thereby reduces the matrix properties[62]. It is of great significance to study the effect of fiber-reinforced geopolymers on chemical erosion, since chloride ion and sulfate erosion and freeze-thaw cycle are easy to occur in marine environment. Fig.10(a) describes the breakdown mechanism of chemical erosion (SO_4^{2-} and Cl^- attack) and physical processes (freeze-thaw cycles), and Figures 10(b) and (c) show the SEM before and after Cl^- and SO_4^{2-} attack. The matrix eroded by Cl^- presents cubic crystals (NaCl after drying), indicating that Cl^- invades the internal voids of the geopolymer cementification. However, the matrix changes from a uniform and dense one to a porous one after sulfate erosion[18].

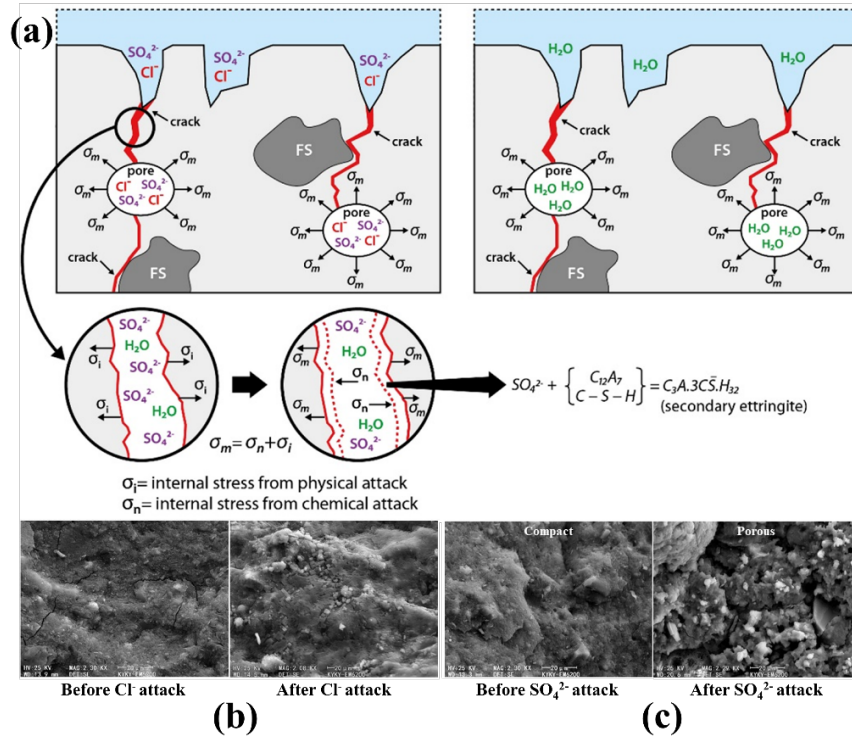


Fig. 10. (a) Chemical erosion and freeze-thaw cycle damage mechanisms;[63]

SEM before and after Cl^- attack; (c) SEM before and after SO_4^{2-} attack[18]

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The resistance to chloride ion erosion can be characterized by resistivity. A sample with a lower total charge passing through is provided with a higher chloride penetration resistance[64]. The local geopolymer possesses high permeability and low resistivity, so the permeability of chloride ion is also high. Adding fiber can reduce chloride ion penetration, and polypropylene fiber is more effective than steel fiber. Considering the conductivity of steel fiber itself and the formation of rust around it, the resistance to chloride ion erosion is not as good as that to polypropylene fiber[65]. Zhu et al.[66] studied the influence of liquid-solid ratio and slag substitution rate on the chloride ion resistance of geopolymer, and found that chloride ion permeability largely depends on the porosity and tortuosity of composites. The porosity of composites decreases with the decrease of the liquid-solid ratio, and the decrease of porosity and increase of tortuosity are beneficial to

the decrease of chloride ion permeability. Banana fiber and coconut shell fiber improve the toughness of the matrix, enhance the durability of the composite against acid erosion, and coconut shell fiber presents a better effect[67]. The mass loss of bamboo fiber composite is about 18% when exposed to an acidic environment, and it possesses good durability[68]. In 10% and 32% hydrochloric acid solutions, the compressive strength of carbon fiber reinforced geopolymer decreases by 66% and 61.3%, and the mass loss decreases by 5.3% and 3.7%, respectively, which can be used for improving the durability of reinforced concrete bridges[69].

The degradation of geopolymers by sulfate erosion mainly focuses on the effect of pores and cracks on the matrix. The porosity and pore size of geopolymers increase with the increase of the sulfate concentration, which will thus reduce the compressive strength. However, a mixture of organic fibers (polypropylene and polyethylene) and inorganic minerals (wollastonite) can improve the sulfate resistance of the composite[26]. After 15 sulfate cycles, the compressive strength of the polymer with 0.2% polypropylene fiber, 0.3% basalt fiber and 0.4% steel fiber reaches 67.9MPa[69]. Besides, it is also found that steel fiber and propylene fiber are acid resistant, while synthetic fiber performs weakly in this aspect[70]. The durability of the geopolymer with a fiber content of 1.2 kg/m³ remains good after soaking 60 times in 5% sodium sulfate solution[71].

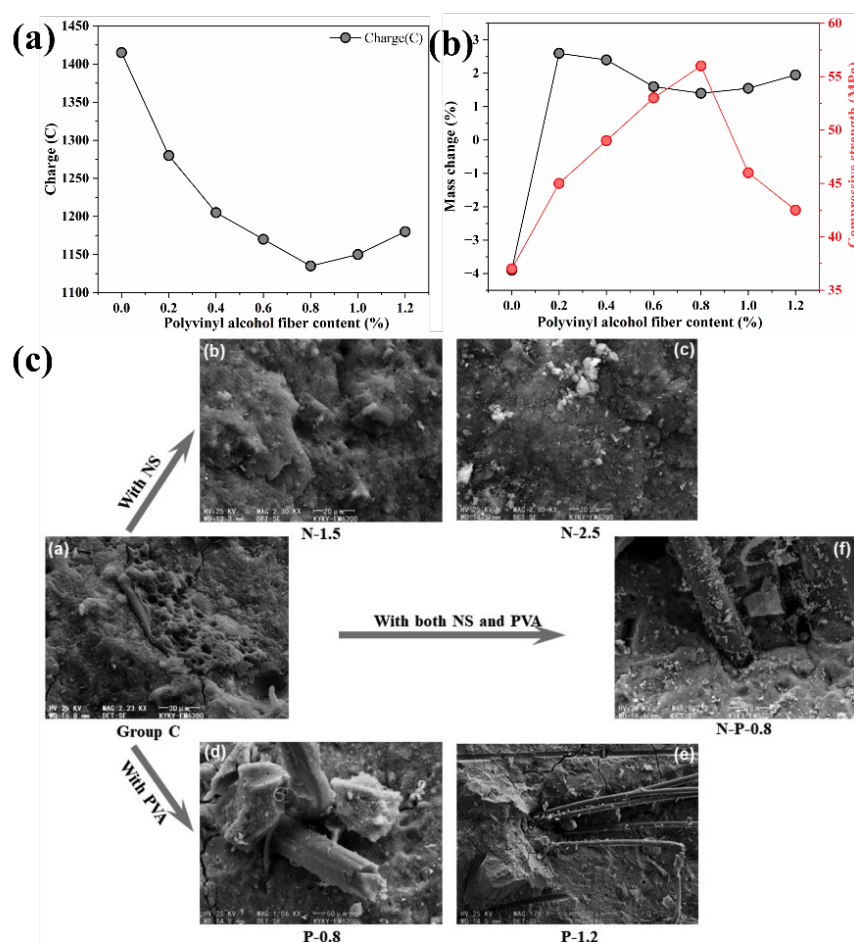


Fig. 11. Corrosion resistance of polyvinyl alcohol fibers (a) erosion by Cl^- (b) erosion by SO_4^{2-} ; (c) coordination of polyvinyl alcohol fiber and Nano-sio₂[18]

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The mixture of mineral particles and fibers can effectively improve the resistance of geopolymers to chemical

erosion. Wang et al.[18] proved that geopolymer mortars with a polyvinyl alcohol fiber content of 0.6 ~ 0.8 v% and a nano-sio₂ content of 1.0 ~ 2.0wt % present better chemical resistance, as shown in Fig. 11. The incorporation of nano-sio₂ and polyvinyl alcohol fiber has a synergistic effect on the durability of geopolymer mortar. The bridging effect of polyvinyl alcohol fibers limits the crack propagation, and nano-sio₂ is found conducive to filling the micropores and improving the microstructure. The addition of wollastonite, tremolite and basalt fibers to metakaolin base polymers can also improve sulfate and chloride ion erosion. The mixture with a ratio of 5% wollastonite, 5% tremolite and 2% basalt fiber sample possesses the highest compressive strength and the strongest erosion resistance[72]. If the polymer is prepared using 0.2% polypropylene fiber and 3% nanoparticles, the durability of the polymer can be increased by 67%[73]. The addition of basalt fiber to geopolymer can reduce weight loss after acid erosion and maintain the compressive strength as much as possible, which indicates the good durability of basalt fiber reinforced geopolymer[74]. The combination of cellulose fiber and fly ash can improve the durability of composite materials under the sulfate dry-wet cycle. In the late cycle, the pore volume increases obviously, the proportion of small holes decreases, and the mesopores increase. In this case, the durability of concrete can be consequently improved by optimizing the ratio to increase the proportion of harmless holes such as micro holes and small holes[75].

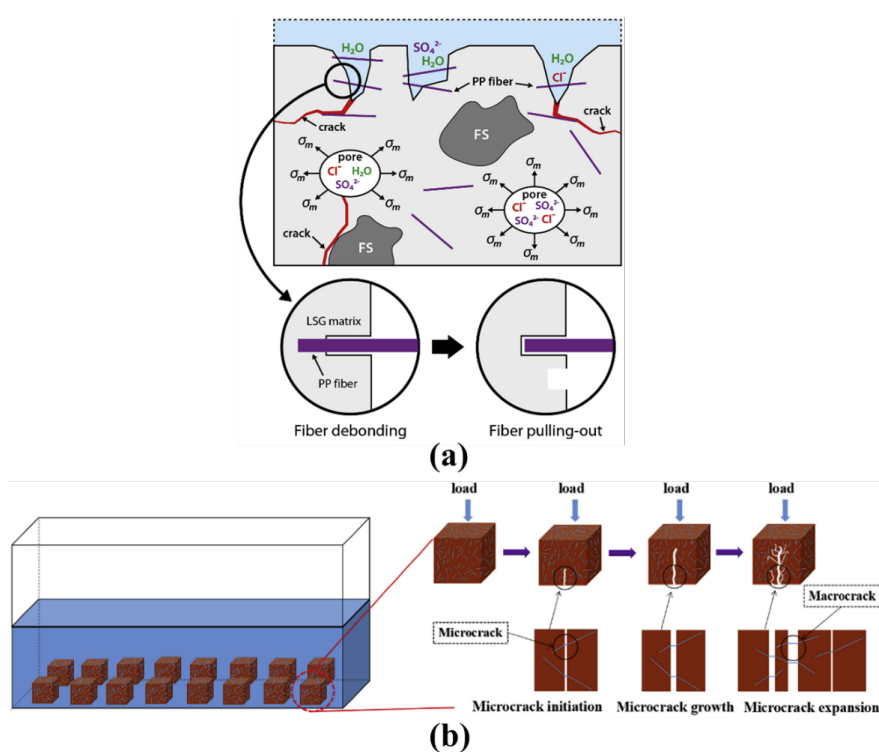


Fig. 12. Mechanism of fiber resistance to SO₄²⁻ and Cl⁻[26]

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In short, fiber-reinforced composites matter considerably in combating against the harsh conditions of the ocean. The bridging effect of randomly distributed fibers inhibits the initiation, development and penetration of cracks in the matrix, delays the diffusion of SO₄²⁻ and Cl⁻ into the base, and prevents against physical (freeze-thaw process) and chemical (SO₄²⁻ and Cl⁻ erosion) attacks[63], which also resists the fatigue load of sulfate crystallization and optimizes the pore structure[73, 76, 77]. When the local geopolymer is subjected to loading pressure, fibers weakly bonded to the matrix will break first, form microcracks and produce elastic deformation afterwards. The mass loss of terpolymer sulfate erosion leads to the formation of porous

structure and sulfate crystal phase, thereby resulting in strength loss[26].

5.3 Freezing-thaw resistance

The freeze-thaw cycle is one of significant indexes to evaluate the durability of the geopolymer[78]. In geopolymer structures, water mainly exists in three forms, i.e., crystal water, gel water and free water. Crystal water and gel water will not be frozen because of its small pore, while only the free water with capillary pores will freeze at a negative temperature. The resistance against geopolymer can be effectively improved by reducing the porosity and improving the compactness of the structure[12].

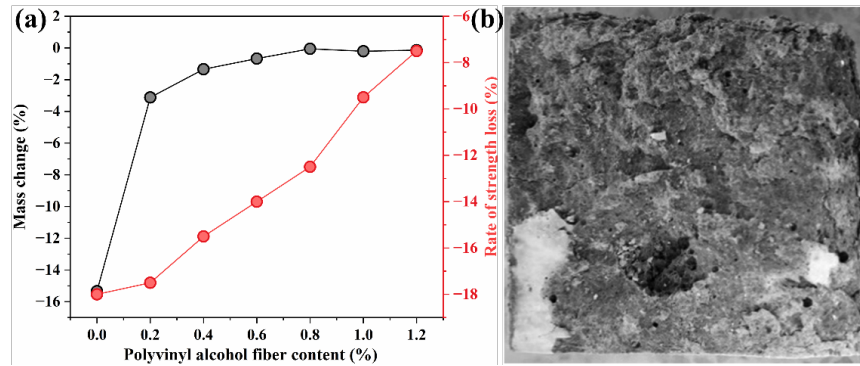


Fig. 13. (a) Effect of polyvinyl alcohol fiber content on sulfate resistance of geopolymer

(b) Appearance of geopolymer after freezing-thawing cycles[18]

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The pure fly ash base polymer is destroyed after 50 freezing-thawing cycles, but the addition of 0.1% carbon nanotubes and 2% polyvinyl alcohol fiber withstands 175 freezing-thawing cycles[78]. Polyamide fiber can also improve the freeze-thaw cycle durability of fly ash base geopolymer[79]. Besides, the compressive strength of polypropylene fiber reinforced geopolymer increases during 56 freeze-thaw cycles, but decreases during 300 freeze-thaw cycles[80]. The durability of polyvinyl alcohol fiber reinforced geopolymer composites decreases with the increase of fly ash and bentonite. When the ratio of fly ash to cement is 1.8, the durability of polyvinyl alcohol fiber reinforced geopolymer composite is the highest in water[81]. After 150 cycles of wetting and drying, the durability behavior of fiber reinforced cement matrix composites in different solutions turns to be: water>MgSO₄>Na₂SO₄(aq) [82]. As shown in Fig.13, the 0.6%-0.8% polyvinyl alcohol fiber and 1.0%-2.0% nano-SiO₂ can enhance the geopolymer durability to the greatest extent, and the residual compressive strength can reach 57.3 Mpa-58.8 MPa after 25 freeze-thaw cycles[18]. The strength of slag fly ash base geopolymer prepared with polypropylene, steel fiber and polyamide fiber does not change significantly after 250 cycles, indicating its excellent durability[12]. The strength loss of basalt fiber reinforced metakaolin base geopolymer is small after 90 freeze-thaw cycles[83], and after 180 freeze-thaw cycles, the compressive strength of the geopolymer with 0.8-1.2% basalt fiber increases while the flexural strength decreases[39].

The addition of fibers can improve the internal structure and macroscopic mechanical properties of geopolymer[81]. Firstly, the fiber is uniformly distributed in the matrix to balance the internal stress caused by water freezing. Secondly, fiber fills the internal pores, and increases the density of the matrix. Therefore, the incorporation of fibers can significantly improve the freeze-thaw cycle resistance of geopolymer[78, 84].

5.4 Other performances

Additionally, the fiber performs excellently in the electric conductivity and high temperature resistance. Carbon fiber and ceramsite can also be used as conductive admixtures in mortar to effectively reduce the resistivity of mortar, but exercise a negative impact on its workability and strength development[85]. Fiber and hollow glass beads are added to geopolymer to prepare heat-insulating composite materials. The improvement effect of fiber on shrinkage resistance of materials is polyvinyl alcohol fiber, glass fiber and lignin fiber in order[6]. The influence of steel fiber, polypropylene fiber and polyvinyl alcohol fiber on the low temperature erosion bending strength and compressive strength of ultra-high performance concrete (UHPC) is also studied, and the results show that the addition of steel fiber and polyvinyl alcohol fiber increases the bending strength and compressive strength of UHPC, and that the bending strength of UHPC increases by 70.06% with the increase of the length-diameter ratio of steel fiber. The compressive strength of UHPC decreases after cryogenic attack. Polyvinyl alcohol fiber and Polypropylene fiber absorb more water, which affects the hydration of cement in UHPC, thereby reducing the strength of UHPC[86]. In order to enhance the adhesion between fiber and matrix, the surface of fiber is modified with chemical reagents such as graphene and silane to enhance the hydrophilicity and roughness of the fiber surface[87].

6. Conclusions and Recommendations

It can be concluded from the present study that fiber-reinforced geopolymer can significantly improve the bending strength of the matrix, which makes the failure mode of the geopolymer change from brittleness to ductility. Fiber acts as a bridge for geopolymer cracks, and transfers stress from cracks to geopolymers, thereby reducing crack propagation. Different fibers have different effects on matrix. Steel fiber is helpful to enhance strength properties, while glass fiber is conducive to eliminating microcracks and the ductility. In order to obtain a composite fiber with comprehensive properties that are endowed with all the benefits of strength, microcrack elimination, ductility, and denser mix, steel and glass fibers can be used in the best proportion of the composite fiber.

At present, the research mainly focuses on the influence of fiber type and content on the performance of geopolymer, but the following factors may also affect the geopolymer performance: the selection of geopolymer matrix, interface strength, fiber extraction method, and fiber treatment. Therefore, the following aspects remain to be further explored:

1. Most geopolymers are prepared by alkali activation, but it is actually feasible to carry out acid activation as well. Studies on fiber reinforced acid activated geopolymers should be taken into consideration.
2. The present research focuses on the influence of fiber type and content on the geopolymer performance. Indeed, more emphasize can be placed on the fiber treatment, extraction method, matrix-fiber interface characteristics and pore structure of composite materials.
3. There are few studies and applications on the influence of unique properties of fibers such as light weight, heat preservation and heat insulation on geopolymer, which requires further exploration.
4. More academic attention should be paid to the special application of geopolymer, such as 3D printing, insulation wall materials, etc.

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Conflicts of Interest

The authors declare that there are no known competing financial interests or personal relationships that may affect the work of this paper.

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