Fiber-reinforced geopolymer composites: A review

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Abstract: There is a burgeoning interest in the development of geopolymers as sustainable construction materials and incombustible inorganic polymers. However, geopolymers show high quasi-brittle behavior. To overcome such weakness, hundreds of research have been focused on development, characterization, and implementation of fiber reinforced geopolymers for a wide range of applications. This paper discusses the rapidly developing state-of-the-art of fiber-reinforced geopolymer composites, focusing on material and geometrical properties of construction fibers, and underlying mechanisms on fiber-binder interaction at fresh and hardened states, mechanical properties, toughening mechanisms, thermal characteristics, and environmental durability. It is intended to build a strong conceptual and technical background for what is currently understood on fiber reinforced geopolymers by tying the subject together with knowns for other similar cementitious composites rather than a historical report of literature.

Keywords: Geopolymer; Fiber; Engineering properties; Strain hardening; Thermal properties; Durability

1 Introduction to geopolymers

The population growth, together with new global standards of modern construction requiring more demanding infrastructures. Statistical trends estimate an increase in global cement production from ~4.3 billion metric tons in 2015 to ~6.1 billion metric tons in 2050. This rate is even higher in developing counties such as China with a production of about half of the global cement in 2019 [1]. The high production of ordinary Portland cement (OPC) is challenged by demolishing reserves of limestone, a huge amount of CO_2 emission (around 7% of global CO_2 emissions), and an energy-consuming process with the average primary energy intensity of about 4.8 GJ/t [2].

Geopolymers, also named "alkali-activated binders", have been introduced as a promising alternative to OPC with less environmental impact. They are produced by mixing waste or natural aluminosilicate sources such as fly ash (FA), volcanic ashes (VA) and metakaolin (MK) with alkali activators such as sodium hydroxide and sodium silicate. After mixing, the alkali activator dissolves the aluminosilicate precursors, and aluminate and silicate monomers are released, which later undergo polycondensation reaction [3]. As a result, the binding gels are produced with potentially low CO₂ footprint, high early strength, and high thermal resistance [4, 5].

Similar to OPC, geopolymers show brittle characteristics and suffer from low tensile strength and cracks under low mechanical loading or shrinkage forces [6]. Fig. 1 compares the relation between tensile, flexural and compressive strengths of different geopolymer compositions with and without aggregates at different ages and curing conditions with those of OPC estimation as per ACI 318-08 and Eurocode 2. The tensile/compressive strength and flexural/compressive strength ratios

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of geopolymers vary in a wide range and are generally higher than the standard code estimations for OPC. However, this tensile strength is still low for several applications.

2 Fibers

Fibers in the different forms of threads, filaments, whiskers and nanoparticles have been used as reinforcement in geopolymer composites to increase the flexural strength and energy absorption. In principle, three main requirements need to be considered in the selection of fiber as reinforcement in cementitious and geopolymer composites, including (1) compatibility of material properties with the application, (2) sufficient fiber-matrix interaction to transmit stresses, and (3) optimum aspect ratio to secure effective post-cracking behavior. Before discussing the composite action of fiber and geopolymer, it is important to have an overview of the material and geometric properties of the fibers used in cementitious materials, which is given below.

2.1 Fiber types

Material properties of fibers are often more dominant in altering the performance of a fiber reinforced geopolymer composite than binders. For example, independent of binder type, geopolymer or cement, polypropylene fiber shows a weak fiber/binder interaction and reduces the compressive strength of the composite [27-32]. To address the importance of material properties, in this study, fibers are categorized into five main groups of steel-, inorganic-, polymeric-, natural- and carbon-based fibers, as listed in Table 1, where the main physical and mechanical properties of the most used fibers in cementitious composites are summarised. The detail of each fiber is explained in the following subsections.

2.1.1 Steel fibers

Steel fibers are commonly used in cementitious composites because of their high mechanical strength, flexibility and availability. ASTM A820-16 specifies five different types of steel fibers for specific purposes, including (1) pieces of smooth or deformed cold-drawn wire, (2) smooth or deformed cut sheet, (3) melt-extracted, (4) mill cut, and (5) modified cold-drawn wire steel fibers, which are sufficiently small to be dispersed randomly in concrete. Depending on the material type and fabrication process, steel fibers may have a wide range of tensile strength and ultimate elongations of about 310-2850 MPa and 0.5-3.5%, respectively [39-41]. It is specified in ASTM A820-16 that the minimum strength of any one of ten specimens should not be less than 310 MPa and the average tensile strength should not be less than 345 MPa. Due to the malleability and manufacturing processes, metallic fibers have a corrugated surface, which results in strong fiber-binder interaction [42, 43].

Despite several practical advantages, the main problem with steel fibers is corrosion [44, 45]. To limit the corrosion, steel fiber is often used in the forms including (1) stainless steel alloys, namely, austenitic, ferritic, martensitic, duplex, and precipitation hardenable steels [46], or (2) sacrificed coating composites such as copper/zinc-coated steels [47, 48].

2.1.2 Inorganic fibers

The application of inorganic fibers such as asbestos backed to ancient times [49]. These fibers consist of mixtures of alumina and silica, and because of high melting points, they are often used in high thermal applications such as refractories. Besides, other key points for these fibers are the low cost, high tensile strength, chemical stability, and excellent insulating properties [33]. Depending on the used material, different processing methods have been performed to produce inorganic fibers, such as (1) rod drawing, e.g. in wire making practices, (2) passage through an orifice, e.g. in melt-spun fiber production, (3) vapor deposition, e.g. in vapor-plating boron on a tungsten core, (4)

crystal growth from a melt solution or by the vapor-liquid-solid technique, e.g. whiskers synthesis, and (5) chemical reactions, as used to produce SiC fibers by the pyrolysis of polycarbosilane precursor fibers [33, 50]. The most important inorganic fibers are discussed below. 2.1.2.1 Silica fibers

Silica fibers are commonly used metal oxide fibers with high purity of SiO₂, which are commercially subclassified into the main E-glass (electrical glass), S-glass (structural glass), C-glass (chemical glass), and AR-glass (alkali-resistant glass). Several types of glass fibers are prone to degradation at the high alkaline environment of cementitious materials [51]. In this regard, the AR-glass fiber has been produced to withstand the alkaline environment of cementitious composites [38, 52].

2.1.2.2 Aluminosilicate and alumina fibers

Aluminosilicate fibers are other types of metal oxide fibers containing almost 45-60% Al_2O_3 , and the rest is silicates. They are often produced through the blown or spun process of molten kaolin or related clays/precursors that contain Al_2O_3 and SiO_2 . The aluminate to silicate ratio of these materials plays an important role in their mechanical properties. For instance, the fibers containing 52% Al_2O_3 can resist 1250 °C and even higher temperatures if the alumina content is increased, and the tensile strength of fibers with higher silica content is higher but their elastic modulus is lower [33]. In addition, the amorphousness of the material influences the tensile strength and thermal shrinkage of these fibers. For instance, when the crystallinity of Al_2O_3 fiber that contains about 4% SiO₂ is increased from 50% to 100%, the 1400 °C shrinkage and tensile strength of the fiber are reduced from 18% to 0% and 1800 MPa to 500 MPa, respectively [53].

2.1.2.3 Basalt fibers

Another widely used inorganic fiber is basalt fiber, which is derived from volcanic rocks based on melting at the temperature of about 1500-1700 °C [54]. Basalt is an inexpensive inert fiber abundantly found with excellent strength, durability, and thermal properties. It is also extremely hard with the Moh's hardness scale of 8 to 9 (diamond = 10) and has superior abrasion resistance [55]. Besides, it was observed that basalt fiber has satisfactory resistance to acid attack while it is corroded at alkaline conditions [56]. The applicability of basalt in terms of temperature ranges from very low (about -200 °C) up to the comparative high (700-800 °C). However, basalt may undergo structural changes at higher temperatures [57].

2.1.2.4 Other inorganic fibers

There are many other inorganic fibers such as boron, boron carbide, boron nitride, zirconia, silicon carbide, silicon nitride, and different whiskers with high mechanical properties and thermal resistance developed for specific applications. Reviewing these fibers is worthy of consideration but is beyond the scope of this study. However, more details can be found in [33, 50, 58].

2.1.3 Carbon fibers

Carbon fibers are known for their highest specific strength and lightness of all reinforcing fibers. The fibers show outstanding tensile strength and modulus at high temperatures, very low thermal expansion, chemical, thermal stability, and high electrical and thermal conductivity compared to other materials [59]. Moreover, carbon fibers are perfectly elastic, which is less affected by fatigue deformation during loading-unloading cycles [60, 61]. Sometimes carbon fibers are categorized according to their tensile modulus to low modulus (less than 200 GPa), standard modulus (~230 GPa), intermediate modulus (~300 GPa), high modulus (more than 350 GPa), and ultra-high modulus (more than 600 GPa). According to geometric characteristics, carbon fibers can be

categorized into two main groups, i.e. fibers that are continuous in length and carbon nanofibers [62].

2.1.3.1 Polymeric carbon fibers

The carbon fibers made through carbonizing precursors are mainly derived from sources such as polyacrylonitrile (PAN), petroleum pitch, and rayon fibers [36]. Among these fibers, 90% of commercially used ones are PAN fibers because of the balance in tensile strength and production cost [63]. Carbon fibers have a 2.5-7 GPa tensile strength and tensile modulus of 250-400 GPa with a low breaking elongation at 0.6-2.5% [36]. Pitch fiber that is a residue of the oil refining industry shows a superior tensile modulus of up to 900 GPa with a lower tensile strength of ~1.5-3.5 GPa in comparison with PAN-based fibers [64]. Rayon-based fibers are less favorable due to the lower modulus of ~35-60 GPa and are mainly used in carbon-carbon applications where low thermal conductivity is favored [65]. These carbon fibers can be categorized according to their tow size too. In this regard, tows of 24,000 or fewer are called regular tows, while tows of 50,000 and higher are considered as large tows [62].

2.1.3.2 Carbon nanofibers

These fibers are made in the form of carbon whiskers, with diameters of about 0.5-1.5 µm or even finer. The performance of carbon fibers is mainly determined by the structure of graphite crystallites in their microstructures [62]. The well-known nanofibers of the fullerene family are carbon nanotubes (CNTs) and consist of rolled-up graphene sheets with high-aspect-ratio tubes over 1000 [66]. They are synthesized in single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) with a tensile strength of 11-63 GPa and extremely high Young's modulus of 1-1.8 TPa [67, 68]. The tensile strength of MWCNTs is usually higher than that of SWCNTs, while SWCNTs are more flexible compared with their multiwalled counterparts [67]. Even though graphene is not a fiber, due to its extremely high aspect ratio, it has been investigated widely as nano reinforcement in cementitious materials. Graphene consists of a monolayer of carbon atoms that are packed densely into a 2D hexagonal honeycomb lattice with a thickness of only ~3 nm (one atomic layer) with a formidable tensile strength of ~130 GPa and Young's modulus of ~1 TPa with a high aspect ratio of up to 2000 [69-73]. Until now, different types of graphene have been successfully produced such as graphene oxide (GO) and reduced graphene oxide. Among these 2D reinforcements, GO shows high performance and flexibility because of its highly oxidized nature, although it has large numbers of surface residual epoxides, hydroxyl, and carboxylic acid group, and therefore, there is a wide range of chemically reactive groups for various functionalization purposes [37]. Although the research and development of the abovementioned inorganic fibers are in its infancy, the unique portfolio of properties that micro/nano-carbon fibers bring to the table is used to produce high-performance cementitious composites with higher energy absorption as well as high electrical and thermal conductivity by incorporation of very small fiber content [74, 75]. 2.1.4 Polymeric fibers

Polymers are fundamentally long chains of repeating monomer units, which are held together through strong intermolecular interactions [76]. The intermolecular interaction varies for different polymers and changes their properties. Depending on the order of chains, polymers are also classified as crystalline (over 80% crystallinity), semi-crystalline (10% < crystallinity < 80%), and amorphous (less than 10% crystallinity) polymers [37, 77]. Increasing the crystallinity of polymers can enhance mechanical properties, rigidity, environmental stability, and surface roughness.

Furthermore, polymeric fibers can be categorized into synthetic and natural fibers based on their source materials and production process.

2.1.4.1 Synthetic polymer fibers

Synthetic polymer fibers are extensively produced from raw materials or recycled from plastic wastes. Usage of the recycled fibers in construction is a formidable solution for disposal of the widely consumed plastics such as polyethylene terephthalate (PET) and polypropylene (PP) worldwide [76]. The most used synthetic fibers in cementitious matrixes are based on PP, polyvinyl alcohol (PVA), polyethylene (PE) and PET. PP is derived from the monomeric C₃H₆ and is a pure hydrocarbon like paraffin wax in a variety of shapes and sizes, and with differing properties [78]. The main advantages of this fiber are inexpensive cost, inert characteristic at high pH of the cementitious environment, controlling plastic shrinkage cracking of the concrete, and easy dispersion [79]. However, it suffers from poor thermal resistance, low modulus of elasticity, and poor interfacial contact with cementitious matrices due to its inherent hydrophobic characteristics [27, 52, 80, 81]. Recently, recycling of PET bottles to produce fiber shows a promising future for construction application. The PET fibers have comparable mechanical properties with PP and nylon fibers, while their production is more cost-effective and environmentally friendly [82]. The PVA fiber has higher tensile strength of ~0.8-2.5 GPa and modulus of elasticity of ~29-42 GPa. Moreover, it shows a strong chemical bonding with cementitious binders due to the presence of the hydroxyl group in its molecular chains [83, 84]. However, PVA is relatively expensive [85]. Also, high chemical bonding compounded with low lateral resistance of the PVA fibers leads to a tendency towards fiber rupture, and thus limits the tensile strain capacity of the composite [83, 86, 87]. The properties of PE fibers are significantly dependent on their molecular mass, polydispersity, and the degree of crystallinity [88]. The tensile strength and elastic modulus of a high-density PE fiber can be as high as ~3.5 GPa and ~110 GPa, respectively [89]. This material also has hydrophobic characteristics [90, 91].

2.1.4.2 Natural polymer fibers

Considering the environmental issues and a requirement for the development of environmentally-friendly and energy-efficient materials, monofilament cellulosic fibers such as jute, hemp, kenaf, bagasse, and sisal are regarded as alternatives to synthetic fibers in cementitious composites [92]. These fibers are widely available and have a low price, low density, reduced thermal conductivity, and acceptable mechanical properties. However, there are four major problems with these fibers, including (1) low durability, (2) efficiency at high fiber content that reduces the workability of the fresh composite, (3) inconsistent material properties, and (4) poor interaction with the matrix [92-94].

2.2 Fiber geometry

Next to the material properties, geometrical parameters such as the cross-section and length of fibers, the surface area of fibers in a unit volume of composite, and the cross-sectional area of fibers across a given plane of the fiber reinforced matrix are other key aspects to consider in the evaluation of the fiber efficiency.

2.2.1 Reinforcement size

Reinforcements can be classified into fibers, whiskers, and particles, as shown in Fig. 2a. The mechanical strength and modulus of fibers decrease as the fiber diameter is increased [33, 95]. This has been observed clearly in glass fiber [96], drawn wires, inorganic whiskers [33], alumina fiber, inorganic materials [95], PVA fibers [83, 97], and polycaprolactone [98], as seen in Fig. 2b. This

can be explained by the fact that the risk of imperfections and faults are increased in large diameter fibers in comparison with single-crystal whiskers or smaller fibers [33, 50]. Interestingly, this effect is higher in stronger materials.

2.2.2 Reinforcement longitudinal geometry and cross-section structures

Individual fibers are produced in an almost limitless variety of geometric forms. It is preferable to pre-deform the fibers where the manufacturing processes are feasible to provide mechanical anchorage contribution to fiber-binder interaction [99, 100]. The deformed section can be placed at the end of fibers through hooks, paddles, and buttons, or through longitudinal deformation by indenting, crimping and twisting of fibers, as seen in Fig. 2c. Similarly, the cross-section of fibers varies in a wide range including prismatic rounded or polygon cross-section with a smooth or corrugated surface, irregular cross-section, variable cross-section along the fiber length, multifilament and monofilament networks (or bundles) that are designed to separate during the mixing process. Besides, the cross-section structure can be classified as solid, coated (e.g. copper-coated steel fibers [101]), shielded fibers (e.g. SiC fibers [102] and SiC coated carbon fibers [103]), and tubular structures (e.g. flax fiber [104] and hemp fiber [105]), as shown in Fig. 2d.

2.2.3 Equivalent diameter

Equivalent diameter is used to represent a prismatic circular cross-section of individual none-circular fibers. This is the diameter of the circle that represents the average cross-sectional area of an actual fiber.

2.2.4 Efficient diameter

The minimum diameter along the fiber length that specifies the maximum load-carrying capacity is the efficient diameter.

2.2.5 Fiber aspect ratio

The fiber aspect ratio represents the slenderness of individual fiber by the division of fiber length over its equivalent fiber diameter. This value for short fiber reinforced composites varies in the range of ~40 to 2000; however, it is usually less than 300.

2.2.6 Fiber denier

The denier or den is a unit of measure for the linear mass density of fibers, in grams, of 9000 meters of fiber. One denier is 1 g/9 km. This is mathematically related to equivalent diameter for individual fiber if the specific gravity of the fiber material is known, as:

$$d = \alpha \sqrt{\frac{D}{\rho}} \tag{1}$$

where, *d* is equivalent diameter, α is 0.0120 or 0.0005 for *d* in millimeters or inches, respectively, *D* is fiber denier, and ρ is fiber specific gravity. This unit is usually used for synthetic fibers [35, 110]. Notably, the denier is still in wide use, but it is replaced by an international unit called "tex" that is 1 g/km [111].

2.2.7 Pre- and post-mix denier

The terms of pre-mix denier and post-mix denier are used for bundled or collected fibers to reflect the fact that the form of fiber may change during the mixing process. In other words, when loosely connected or bundled (pre-mix) fibers are introduced to matrices, the mechanical shear of the mixing process is strong enough to break up the fiber bundles and convert them to individual fibers (post-mix). In this case, the post-mix fiber denier should be used in the calculation of the number and distribution of fibers in a composite.

2.2.8 Fiber count and specific surface

Crack development through or around fibers is an energy-consuming process and depends upon the number of fibers encountered and the surface area of these fibers. For instance, debonding is dependent on the surface area of the affected fibers, while pull-out property is dependent on the cross-sectional area of fibers within the crack plane integrated with the elastic properties and bond characteristics of the fibers. These parameters can be estimated using fiber count (*FC*) and fiber specific surface (*FSS*) as expressed by [35]:

$$FC = \left[\frac{1.27 \times V}{l \times d^2}\right] = \left[\frac{5.08 \times V \times \rho \times 10^6}{l \times PoMD}\right]$$
(2)

$$FSS = FC \times \pi \times d \times l = \left[\frac{4 \times V}{d}\right] = \left[\frac{8 \times V \times \sqrt{\rho} \times 10^3}{\sqrt{PoMD}}\right]$$
(3)

where V is total fiber volume percentage/100, l is fiber length (in inches), d is fiber equivalent diameter (in inches), and *PoMD* is post-mix denier.

3 Fiber reinforced geopolymer composites

3.1 Mixing process

Geopolymers have been developed using different mixing and placing technologies for conventional cementitious and ceramic-like composites including batch mixing and placing, slip forming (moving-form extrusion), extrusion (through a stationary die), 3D printing, slurry infiltration, sheet production with or without vacuum or pressure forming, sintering cold-pressed, and hot-pressing. This wide variation of techniques allows producing different geopolymer composites with almost every fiber type, geometry, and content. However, the order of fiber incorporation during the mixing is important to have a uniform fiber dispersion. The mono fibers (e.g. steel and carbon fibers) are often suggested to gradually mix with the dry precursors and then subjected to alkali activator [112-114]. While multifilament fibers (e.g. multifilament PP fibers) do not separate and disperse homogeneously through the dry mixing process. Therefore, they are suggested to mix with the alkali activator solution in advance to break the fiber bundles and then mixed with dry aluminosilicates and other fillers [6, 115]. This enhances the wetting process of the fiber, and consequently, a higher fiber-matrix interaction. Similar procedures have been used for the dispersion of nanofibers/reinforcement in geopolymers. For instance, graphene nanoplatelets were first sonicated in water to separate boundless of particles into individuals, and then induced to the geopolymer matrix [74, 116]. It is worth noting that the shear force, which is used to distribute the fibers into the geopolymer matrix, is another important factor when a brittle fiber is used. In this line, fracture of basalt fiber during the mixing was studied when either a shear mixer or a centrifugal mixer was used [117].

Next to these approaches, which are usually used for mixing short fibers, a very slurry geopolymer matrix and vacuum system have been used in order to have a proper impregnation of binder through the congested continuous fiber or fabric reinforcements [118]. When the binder cannot easily penetrate through the fiber network, unwanted porosity can be observed, which can be eliminated through using the aluminosilicate particles with a dimension of smaller than a single fiber diameter [118].

3.2 Workability

The positive effects of fibers on hardened mechanical properties of cementitious and geopolymer composites have been the subject of numerous studies focusing on the cracking and toughening mechanisms of the fibers according to their shape, volume fraction, and orientation. Despite the superior mechanical properties, fibers reduce the workability of cementitious composites, which results in excessive void formation and poor compaction. Thus, a compromise between hardened behavior and fresh properties is essential for applicability. As seen in Fig. 3, regardless of the fiber type and geometry, increasing the fiber content reduces the flowability of fiber reinforced geopolymer composites. This can be measured by reduction in conventional slump value (ASTM C143) and flowability test (ASTM C230) [27], increase in VeBe time test [119] and time of passing through V-funnel (EFNARC-2002) [120], or in the form of increase in yield stress and viscosity measured using rheometer [121, 122]. The reduced workability can be explained as a result of an increase in yield stress of the fresh composite due to the contact network between rigid fibers inside the matrix, which is increased with the increase of fibers' content, equivalent diameter, and aspect ratio [35, 123]. The critical concentration value was suggested to be in the range of 0.2% to 2% for the geopolymer and cementitious composites [124, 125]. When the fiber content increases over a critical concentration, the fibers tend to get uneven dispersion and form clumps or balls, and even very flowable matrices might not pass through the congested fiber network properly. Therefore, the fresh matrix requires more vibration to lose its harsh static mode and form the mold [27, 101]. Some experiments showed that the critical value tends to decrease when the aspect ratio of fiber and filler volume is increased [126-129]. Furthermore, the high surface roughness and crimped or hook-end fibers result in a reduction in critical concentration and flowability [124, 130]. On the other hand, plastic viscosity, yield stress, and conditions of flow confinement of the fresh composite influence the fiber distribution and orientation, and accordingly the mechanical properties of the whole composite. In this line, for the same fiber content, the compressive strength would be reduced with the increasing yield stress of the fresh matrix. While, for the matrices with low yield stress, a well-ordered fiber alignment can be achieved, which directly helps improve the flexural property of the composite [128, 131].

Nevertheless, the reduction in workability due to the addition of fibers has been positively used to increase the thixotropy of the fresh matrix and enhance the shape stability and buildability of fiber reinforced geopolymer composites for extrusion and 3D concrete printing applications [113, 132, 133].

3.3 Drying shrinkage

Drying shrinkage of geopolymers is due to the high capillary pressure produced between wet and dry zones of the micropore network, which leads to specimen deformation and crack initiation [140]. To control the drying shrinkage, two approaches have been often followed: (1) the modification of the pore structure to minimize capillary porosity and to control water loss during curing [141], and (2) the inclusion of inert or reactive fillers and fibers [142].

Several studies have indicated that fiber content, fiber modulus, and fiber-binder interaction are the dominant factors in controlling the shrinkage of reinforced geopolymer composites [6]. Fig. 4 shows the influence of two fibers on controlling the shrinkage of fly ash-based geopolymer. The incorporation of PP and steel fibers even in small amount, 0.5 vol.%, reduced the drying shrinkage of the composite specimens significantly. Increasing the steel fiber content to 2 vol.% and above resulted in an almost no shrinkage [6, 101]. While, the similar reduction was not observed for the

same content of PP fiber, and even it showed an adverse effect when fiber content was increased to 4 vol.%. This can be ascribed to the poor compaction of the geopolymer composites at the presence of high volume of fiber [27]. Besides, the lower stiffness of the PP fibers integrated with weak fiber-binder interaction is other reasons for poor performance of the PP fiber compared to the steel fiber. Similar superior shrinkage performance was observed for PVA fiber reinforced geopolymers as compared with PP fibers due to the hydrophilic nature and higher stiffness of PVA fibers [143]. Besides, it was reported that using a longer fiber can (1) reduce [144], (2) increase [145], or not change [129] the shrinkage geopolymer composites. Furthermore, the shrinkage trend of fiber reinforced geopolymer composites is affected by the nature of the binder and curing conditions. For example, for the same type and amount of fiber, the shrinkage of slag-based geopolymer composite was reduced by variation of environmental humidity ranging from 50% to 95%, while fly ash-based geopolymer composite was less sensitive to environmental humidity [146].

Fig. 5a compares the yield strength in tension against the density of several fibers and geopolymer composites. Almost all the polymeric and carbon-based fibers have a lower density than geopolymer composites, while the inorganic and steel fibers have comparable or higher densities. The difference in density should be considered where the lightness of the composite is an important parameter. Fig. 5b shows the relative density of different fiber reinforced geopolymer composites compared to their plain specimens. The density of composite is directly influenced by fiber content and specific gravity of the fibers. When the specific gravity of the fiber is lower than the geopolymer matrix, the bulk density of the corresponding geopolymer composites is reduced [6]. However, this does not necessarily occur when fibers with a higher density than geopolymers are used. This means that when a high-density fiber is used the density of the composite can be (1) increased, (2) decreased, or (3) remained the same as the corresponding plain matrix. This is due to the fact that the difference in density is not the only governing rule and always extra porosity in the form of trapping air bubbles reduces the density of the composites, as seen in Fig. 3 [6]. Fig. 5c clearly shows that regardless of fiber types, the measured density of fiber reinforced geopolymer composites is lower than the calculated values using rule of mixtures [27]. Several parameters can influence the volume and structure of the porosity. For example, the pore volume fraction can be increased for fibers with a higher aspect ratio and the induced porosity is higher in cellulosic fibers which swell in the presence of water and shrink when the matrix becomes hardened [127, 147]. Therefore, debonding occurs at the fiber/matrix interaction in the form of porosity [93]. Compressive behavior 3.5

For the purpose of quality control, the compressive strength of concrete is a major parameter, and other mechanical properties, such as tensile strength and Young's modulus, are often estimated from this value using empirical equations. The compressive behavior of geopolymers highly depends on the brittleness, pore structure, micro-crack distribution, and boundary condition of the test, as seen in Fig. 6a and b. When a cementitious matrix is subjected to a compressive load, axial splitting micro-cracks are formed parallel to the direction of the compression. This is due to the concentration of transverse tensile stress in front of the splitting crack that causes them to grow in the direction of the compression load, as shown in Fig. 6c [6, 74, 155]. At the presence of fibers, the initiation and extension of cracks of mode I fracture (opening mode, i.e. tensile stress orthogonal to the local plane of the crack surface) and potential shear stress are reduced. This is because once a crack faces a fiber, it demands higher energy of fracture to pull the fiber out and then propagate.

Hence, the proportional limit and ultimate strength of the composites are increased [74]. This is strongly dependent on the fiber/matrix interaction and the stiffness and dispersion of the fibers [6]. If the interfacial bond is sufficient the trapped matrix between the fibers will be confined, and consequently a higher load-bearing capacity is achieved, as demonstrated in Fig. 6d [101, 156]. Besides, the stiffness of fiber itself is another important factor in the compressive behavior of the fiber reinforced composites. The fibers with low Young's modulus could be expected to behave similarly to the air-entrained concrete: the increase in air content will proportionally result in a higher degree of compressibility [143, 157]. This is associated with higher local fractures close to the fibers, which reduce the compressive strength of the whole composite [27, 158-160]. However, fibers with high Young's modulus not only sustain the internal compressive stress but also alleviate the internal concentrated stresses applied in different orientations by transferring them into a uniform distribution, therefore, they avoid stress concentration and local fractures, as shown in Fig. 6e [74].

Furthermore, it was observed that the fiber properties influence the strength development of the composite over time [6]. It was reported that the compressive strength of micro-steel fiber reinforced geopolymer composite improved at early ages at higher fiber fractions, however, it had a minor influence on the long-term compressive strength of the composite [101, 130, 161, 162]. In contrast, increasing the PP fiber content has shown a negligible effect on the early compressive strength of the composite while reduces the ultimate compressive strength (see Fig. 6f) [27, 115, 143]. The fiber-matrix interaction will be discussed in detail in the next section.

Fig. 6g shows the relative compressive strength of fiber reinforced geopolymers as compared with the plain samples. Noteworthy, as the data presented by relative values, where the compressive strength of the binder is extremely low, the influence of some fibers on the compressive strength of the composite is exaggerated. Regardless of the fiber types, the increase of compressive strength is more expectable when the fiber content is less than 2%, while above this value adverse effect of fiber is more possible. This can be attributed to the significant increase in porosity above the fiber's critical concentration that is often between 0.2% and 2%, as explained in Section 3.2 along with Fig. 6d [27, 101]. This effect is more severe in multifilament compared to the mono fibers [163]. Besides, the fiber length is another important factor, e.g. the compressive strength of carbon fiber content of different types of fibers on compressive strength of geopolymer composites. Interestingly, fibers with high Young's modulus such as steel and carbon fibers often increase the compressive strength of the composite even when a high fiber content is used. In contract, the fibers with lower Young's modulus than geopolymer matrix such as most of polymeric fibers reduce the compressive strength of the composites even when a small content is used.

3.6 Flexural behavior

the three basic modes of crack tip deformation, the opening (Mode I), the in-plane shear (Mode II), and the out-of-plane shear (Mode III)

Geopolymers usually fail at mode I (opening mode, i.e. tensile stress orthogonal to the local plane of the crack surface), the corresponding fracture stress of which is much smaller than those of modes II (sliding mode, i.e. shear stress parallel to the crack surface but orthogonal to the crack front) and III (tearing mode, i.e. shear stress parallel to the crack surface and to the crack front). This explains the weakness of geopolymers at bending in comparison with compression, as shown in Fig. 1 [74]. Reinforcing cementitious matrices is aimed to overcome such weakness by providing

a higher resistance to crack formation and propagation. Several mechanisms in relation to the flexural behavior of fiber reinforced geopolymer composites are explained in the following subsections.

3.6.1 Fiber-matrix interaction

When a fiber reinforced composite is subjected to a bending load, tensile stress induced by the bending moment is transformed into shear stress at the fiber-matrix interface and resisted through the adhesion and friction at their contact surfaces. This contact force not only affects the interface of both components but also acts at some distance far from the interface in the geopolymer matrix. Therefore, an annular region surrounding the fibers is formed by the dual action of fiber and matrix [6, 101, 172]. However, this force is maximum at the interface of both elements and dissipated by getting far from the surface to zero, as demonstrated in Fig. 7a [101]. This mechanism is similar to that of steel bar reinforced concrete that the fabricated ribs on the surface of the bar distribute the applied stress and consequently increase the load capacity of the section [173, 174]. All these mechanisms occur when there is a strong interfacial contact between fiber and matrix, e.g. when steel fiber is used. However, for hydrophobic fibers with small roughness, a weak interfacial contact is formed, and thus the stress transfer between fiber and matrix is reduced and each of them acts individually, as shown in Fig. 7b [27].

Several studies have shown the potential of surface treatment on enhancing the adhesion of fibers with hydrophobic nature, such as PP and PET fibers, with cementitious binders [175, 176]. For this purpose, several approaches such as mechanical modification (e.g. fibrillation and micro-indentation) [177], surface modification by chemical treatment (e.g. alkaline and silane treatment) [178-180], and plasma modification [176] have been employed. The main principles in all these methods are to increase the surface roughness and activation of polar groups of the fibers. However, sometimes they have adverse effects on fibers by decreasing the cross-section of the fibers which affects the mechanical properties of the composite [175, 176]. Moreover, for some applications such as when the strain hardening behavior of geopolymer composites is of interest, the surface of the hydrophilic fibers needs to be treated with oil to reduce the fiber-binder interaction by minimizing the adhesion [84, 87, 181]. Notably, the performance of chemically treated fibers may vary in different binders [84, 87, 181].

3.6.2 Development of fiber-matrix interaction over time

The development of fiber-matrix interaction is a time-dependent mechanism [6]. Due to the shrinkage, there is an absolute volume change through the cementitious matrix. Therefore, it occupies less physical volume leading to an increase in density and consequently mechanical properties [6, 172]. This mechanism occurs in fiber reinforced composites, and the strength of the matrix and its interfacial bond with fibers is increased over time, especially at early ages [162]. This fiber-matrix bond strength development is continued until it becomes strong enough to limit the subsequent shrinkage [182, 183]. This mechanism is also dependent on the type and surface roughness of the fiber. The fibers with hydrophilic characteristics and rough furrows at the surface such as steel fibers result in firm contact at the fresh state, which is strengthened by binder development [101]. Similarly, the presence of hydroxyl groups in PVA results in a strong hydrogen intermolecular bond, and thus exhibits a high bond strength in cementitious binders [86, 124, 184]. In contrast, hydrophobic fibers repel water and produce a weak interface contact between fiber and fresh matrix through trapping air bubbles among the corrugations of fiber surface. This weak contact later causes a debonding of fiber, and enlarging the gap between the two phases and,

therefore, reduces the stress transfer between fiber and matrix. This nullifies the effects of shrinkage on interfacial strength development over time [6]. A similar adverse effect was observed for some cellulosic fibers, which swell in the presence of water and shrink when the matrix becomes dried, and consequently a gap between fiber and matrix is formed [93]. This discussion shows the importance of shrinkage, which is often not considered in the models of fibrous cementitious materials since it coincides with the significant changes in elastic and viscoelastic of the matrix materials, but it plays a significant role in the mechanical development of fiber reinforced cementitious and geopolymer composites.

3.6.3 Effect of fiber content

In addition to the chemical and physical properties of a single fiber, the integral effects of the whole network of fibers, their specific surface, and their orientation within the matrix are other important factors in controlling the overall performance of the composite. In general, increasing the fiber content results in formation of multiple microcracks rather than few macrocracks, and therefore, the ductility of the matrix is increased, as shown in Fig. 7c. This can be determined by the actual cross-sectional area of fiber that cuts across any plane of the composite with a random distribution of fibers. The cross-sectional area is almost uniform through the continuous fiber reinforced composites, but it is randomly oriented at short fiber reinforced composites. Thus, many fibers will not penetrate into a random single plane and the reinforcement area is affected by the length of individual fibers [35]. The effect of orientation on the effective cross-sectional area of fibers in a single plane is recommended as ~54% for cementitious composites [185]. This means that ~54% of effectiveness can be expected on a cross-sectional area of a randomly distributed individual fiber in short fiber reinforced composite as compared with the perfect alignment. The total cross-sectional area of randomly oriented fiber at a planar intersection, *A*, can be expressed as:

$$A = 0.54 \times V_f \times A_c \tag{4}$$

where V_f is the volume fraction of fibers in the composite, and A_c is the cross-section area of the composite.

Fig. 7d-i shows the relative flexural strength of fiber reinforced geopolymer composites compared to the corresponding plain specimens. As the fiber content increases to less than ~8 vol.% the flexural strength of the composite is increased regardless of material type; however, above this value, the flexural strength is reduced, as shown in Fig. 7d. This value is much greater than that observed for compressive strength as discussed in Section 3.5, which can be explained by the fact that a homogenous matrix can be produced when a low fiber content is used and thus the considerably higher tensile strength of fibers enhances the flexural strength of the composite. Besides, the poor compaction of high fiber content composites during the fresh state results in an extremely porous structure and heterogeneous fiber-matrix interaction, as explained in Sections 3.2 and 3.4. Therefore, the flexural strength is reduced when the fiber content is higher than 8 vol.%. While, when the fiber content is in the range of 4-8 vol.%, the composite is still porous and a heterogeneous structure is expected, but the fiber-binder interaction is strong enough to overcome the weakness because of the porous structure. Thus, there exists an optimum fiber content for each fiber reinforced composite to obtain the highest mechanical strength. Fig. 7e-i compares the effects of fiber content for different types of fibers on the flexural strength of geopolymer composites.

Fiber content also influences the trend of strength development of the composites. At an early age, the flexural strength of the matrix is still developing and is much lower than that of the fibers.

Thus, increasing the fiber content and consequently enhancing the bridging effect is the dominant factor in the flexural behavior of the composites. In this way, increasing the fiber content results in formation of many microcracks instead of a few large macrocracks (see Fig. 7c) [27]. Here, the cracks are initiating locally where the applied stress is higher than the tensile strength of the binder and opened continuously. Therefore, the bridging fibers sustain and transfer stresses without rupturing. This continuous process results in formation of multiple microcracks and pseudo strain hardening if the material microstructure and associated microparameters controlling macroscopic behavior are carefully optimized according to the micromechanics-based material design theory [87, 89, 186, 187]. The geopolymer strength and fiber-binder interaction are developed over time, leading to an increase of the load-bearing capacity of the composite. Here, when the material is subjected to a flexural loading, the sudden release of concentrated stress leads to the formation of few macrocracks rather than many microcracks. This principle is important in designing ultra-high ductile composites such as strain hardening geopolymer composites, to keep a large difference between the ultimate strength of binder and the fiber while keeping the bonding in a level to avoid concentrated stress released [188]. For example, an oil treatment was adopted to tailor the interface PVA fibers and control the bonding and slip hardening behavior of the cementitious and geopolymer composites [84, 181].

3.7 Energy absorption and toughening mechanisms

Independent of how fiber influences the flexural strength, it always increases the energy absorption of the composite. In general, fiber reinforcements change the failure behavior of a geopolymer from a brittle toward a ductile mode. This can be explained by the fiber specific surface, which is directly related to the amount of energy that is absorbed in encounters between crack and fiber. In this way, energy absorption of weak brittle matrices can be increased through the post-cracking toughness, mainly through the bridging mechanism. Here, the physical properties of individual fibers, fiber fraction, fiber geometry and fiber length become more important. The same is true for strong brittle matrices, but in that case, the fibers have to achieve even greater efficiency through strength, bond, stiffness, orientation, and numbers in order to encounter the higher stored elastic strain energy that is released to form cracks [35]. These can be discussed at two levels, i.e. micro and macro.

3.7.1 Toughening mechanisms at the microlevel

The increased energy absorption observed in fiber reinforced composites is related to the toughening mechanisms, which is due to the integral adhesion and mechanical interactions between fiber and matrix, as illustrated in Fig. 8a. When a crack reaches to fiber, some energy is required for debonding and passing through it. If the interfacial contact zone is not sufficient in length or strong enough, the fiber debonds, and the crack obstructs and deflects in-plane or branches depending on the interaction of propagating cracks and position of the other fibers, as shown in Fig. 8b and c. In addition, depending on the effective length and strength of the interfacial zone, the fiber may be dragged under crack bridging or pulled out (see Fig. 8d). The bridging mechanism often occurs when the crack is opened continuously, and the bridging fibers sustain and transfer stresses without rupturing. This can be apparently observed where the stress transfer between fiber and matrix is low, e.g. at polymeric fiber reinforced geopolymers [27]. When a fiber with high stiffness is used, other mechanisms such as crack deflection and crack branching prevent the tendency of crack localization along a certain path, and thus increase the effectual crack path to release the stress and enhance the flexural toughness [74, 101]. These mechanisms can be frequently observed in steel fiber reinforced

geopolymers, as shown in Fig. 8e [101]. Besides, if the fiber-matrix interaction is strong, the accumulated stress may overcome the strength of the reinforcement and deform, rupture, or break it [74, 134, 197]. This mechanism is not favorable when brittle fibers are used: it was found that apart from a higher mechanical strength of basalt fiber compared to PVA fiber, due to the brittle nature basalt fiber cannot improve the failure behavior of the composite [124]. However, fiber rupture mechanism is the key parameter in ultra-ductile composite, where the significant ductility and energy absorption are achieved by the deformation of the fibers itself during crack bridging [27, 198]. The role of fiber-binder interaction in toughening mechanisms is shown in Fig. 8f.

Besides the role of fiber strength and interfacial fiber-matrix interaction, other factors including fiber fraction, uniform dispersion, fiber aspect ratio, and specific surface contact significantly influence in the energy absorption of a composite. For instance, it was observed that the weak contact between the overlapped graphene nanoplatelet with the geopolymer nullifies the high pull-out capacity of the material [74]. A similar observation was reported when multifilament fibers were used [163]. Next to this, the pull-out energy is increased by increasing the surface contact of the fibers. For example, the energy needed to pull out a graphene sheet with double surface contact is expected to be much higher than that of a nanofiber [199].

3.7.2 Toughening mechanisms at the macrolevel

In general, the toughening mechanisms that occur in microscale can be quantified in different ways at the macrolevel. Typically, for ductile materials, the energy absorption is measured by the area under the load-displacement curve at a specific displacement. This is because the entire experiment often lasts for a long time and should be truncated at a predefined point to make a comparison between different samples. To this end, several procedures have been suggested. For example, the energy absorption of micro-steel fiber reinforced geopolymer composites is measured using the area under flexural strength-deflection at the deflection value of 3δ and 5.5δ , where δ is the displacement of the first crack as suggested in ASTM C1018-97 (see Fig. 8g and h) [27, 101, 196]. Similarly, the flexural toughness is determined by obtaining the area under the load-deflection curve at the deflection value of l/150 following JSCE-SF4, where l is the length of the specimen [143]. However, in the case of geopolymer composites with a negligible post-cracking behavior, e.g. graphene nanoplatelet geopolymer composite, the energy absorption can be defined by the whole area under the load-displacement curve [74]. Likewise, the work of fracture was determined for silicon carbide geopolymer composites as the area under the load-displacement curve [151, 171, 190].

3.8 Impact toughness

Fiber reinforcement improves not only the static energy absorption but also the dynamic properties under impact and blast loadings. It is worth mentioning that there are very few studies available in the current literature to evaluate the dynamic properties of fiber reinforced geopolymers, and different experimental methods were used in each of them. Hence, a direct comparison between the results is not feasible. Thus, we provide a brief explanation of the results without going through the details below.

An experiment on basalt fiber reinforced geopolymer concrete using a 100 mm diameter split Hopkinson pressure bar (SHPB) system indicated that the impact properties of the geopolymer composites are highly dependent on the loading strain rate and mechanical properties of the binder [201]. It was found that the strain rate sensitivity is reduced in composites with higher strength. Furthermore, the energy absorption of the composites with higher strength binder is increased, while the deformation capacity is reduced. This reduction in deformation capacity is improved by incorporation of the fiber without having an influence on the dynamic compressive strength [201]. Similarly, testing of PVA fiber reinforced geopolymer composite using ITR-200, RADMANA impact test based on high-pressure gas punching showed that the incorporation of fiber changes the brittle impact failure mode of geopolymers to a ductile one [202]. Using another testing approach, a steel fiber reinforced geopolymer was evaluated through the ultimate failure of specimens (400 mm in diameter and 40 mm thickness) based on the number of 4.75 kg drops at the center. The inclusion of 1 % steel fiber improved the impact toughness of the geopolymer composite from 233 to 4124 N·m [203]. Next to these, another experiment was conducted to measure the effect of fiber content on the impact resistance of geopolymer composites using Zwick Charpy impact machine with a pendulum hammer of 1.0 J on unnotched rectangular cotton fiber reinforced geopolymer bars with dimensions $80 \times 20 \times 10$ mm. The results showed that the inclusion of 0.5 wt.% fiber into geopolymer matrix increased the impact strength twice. However, further increase in fiber content negatively affected the impact strength [204]. This adverse effect can be attributed to poor dispersion of the fiber into the matrix, as discussed in Section 3.2.

3.9 Elastic modulus and Poisson's ratio

The capacity of materials to sustain induced stress for every unit strain at an elastic state is determined as modulus of elasticity, which is considered as an important material index for structural designs. Fig. 9a shows the elastic modulus of the plain and fiber reinforced geopolymer composites. The elastic modulus of geopolymers with/without fibers is increased with the increase of compressive strength. When fiber is induced, the elastic modulus can be affected mainly based on the fiber stiffness and porosity of the composite. For example, when a small quantity of steel fiber was used, up to 1 vol.%, the elastic modulus was slightly increased, which is correlated to the considerably high stiffness of steel and its strong fiber-binder interaction [114, 167]. However, using up to 2 vol.% spiral steel and PP fibers, it was shown that the elastic modulus of steel fiber reinforced geopolymer concrete can be reduced or increased by a range of -18% to +16% of the plain sample. While the addition of up to 0.2 vol.% high strength PP fiber decreased the elastic modulus of the composite due to the induced porosity of the composite because of the geometrical characteristics of both fibers [136]. Likewise, for the nanofiber/particle reinforced geopolymers, the homogenous distribution influences the elastic modulus of the materials, i.e., increasing the content of well-dispersed graphene nanoplatelet into fly ash-based geopolymer up to 1 wt.% increased both elastic modulus and compressive strength of the composites [74]. However, such increment was observed only when less than 0.2 wt.% carbon nanotube was added into the geopolymer and further increase in fiber content exhibited a reverse effect, which can be ascribed to the imperfect distribution and homogenization [197]. Although several equations have been proposed for estimation of elastic modulus using compressive or flexural strengths, more investigations are required to confirm their applicability for different geopolymer composites [10, 74, 136, 138, 197].

Fig. 9b shows the Poisson's ratios of plain and steel fiber reinforced geopolymers, which are found to be between 0.08 to 0.22. An experiment showed that the Poisson's ratio of geopolymer concrete measured following ASTM C469-14 is ~0.22, which is reduced to about 0.15-0.21 by incorporating steel fibers [136]. However, the experimental data of Poisson's ratio have been rarely reported and only estimated using some equations available for cementitious composites. Therefore, more research is required to estimate Poisson's ratios for fiber reinforced geopolymers.

3.10 Thermal and fire resistance

The incombustibility of geopolymer is extremely superior to engineering thermoplastics. This paves the way for the development of several high-tech composites, which never reach flashover, ignition, or smoke generation even at flux exposure. Furthermore, geopolymer concrete shows much higher thermal resistance compared to OPC concrete [210, 211]. When fibers are included, the high-temperature performance of reinforced geopolymer composites is not only related to the individual properties of geopolymer or fiber but also dependent on the thermal compatibility between fiber and matrix. The following subsections provide more details about the properties of different fiber reinforced geopolymers.

3.10.1 Carbon fiber reinforced geopolymers

Lyon et al. [212] showed a carbon fiber geopolymer composite with a tensile strength of about 245 MPa, which sustained about 60% of its strength after exposure to fire of 800 °C. An almost similar result was observed for micro-carbon fiber reinforced geopolymers by retaining over 50% of compressive strength at 800 °C [213]. This is due to the sufficient interaction between carbon fiber and binder at elevated temperatures, which hinders the crack formation and matrix deformation [214-216]. Besides, it was reported that Sol-SiO₂ impregnation resulted in about 35% increase in the mechanical performance of the carbon fiber reinforced geopolymer at elevated temperature up to 900 °C and extended the carbon fiber oxidation [217]. Despite the high mechanical strength, thermal resistance, and energy absorption obtained for carbon fiber reinforced geopolymers, the high cost and partial oxidation of carbon at high temperatures limit the practical applications of them [214, 218].

3.10.2 Inorganic fiber reinforced geopolymers

In general, inorganic fibers are cost-effective alternatives for carbon fibers in high-temperature resistance. It was found that the mechanical strength of basalt fiber reinforced geopolymer increased when exposed to high temperatures up to 1000 °C, which was attributed to the improved bonding of basalt fiber with the matrix after sintering [124]. Similarly, a promoted retention on mechanical strength together with higher energy absorption was observed in MK-based geopolymers reinforced with high alumina fibers and recycled refractory particles at 600-1000 °C. This is due to the controlling of the volumetric contraction of the composite by the thermally stable fibers [219]. Likewise, high thermal stability was reported at temperatures of up to 1000 °C when other inorganic fiber such as silicon-carbide or AR-glass used in geopolymers [220, 221]. However, some studies reported defects in different inorganic fiber composites at high temperatures. For example, a basalt fiber reinforced geopolymer exhibited a flexural strength of about 194 MPa up to 600 °C without significant degradation, while it crystallized and melted at higher temperatures [222]. This can be compounded by oxygen transition through the porous matrix [214].

3.10.3 Steel fiber reinforced geopolymers

It was observed that fiber reinforced geopolymer concrete containing 0.5 vol.% steel fiber can have strength retention up to 600 °C [223]. In addition, another study concluded that the stainless steel reinforced geopolymer composite can retain about 59% and 44% of its flexural strength when it subjected to 800 and 1050 °C, respectively, and alumina chopped fiber can be used to strengthen the geopolymer for a higher yield strength at these temperatures [224].

3.10.4 Polymeric fibers reinforced geopolymers

The inclusion of volatilizable and low-temperature decomposable fibers in geopolymers is not recommended for high thermal applications as their decomposition at elevated temperature leads to a significant shrinkage and porosity formation in the composites [124, 159, 225, 226].

3.11 Durability

3.11.1 General

The durability of infrastructures is defined as the length of time it takes to necessarily repair or rehabilitate them as well as the frequency and intensity of maintenance required during their service life [227, 228]. The concerns on the durability of cementitious materials mainly correlate with the chemical instability at the presence of a chemical agent and material degradation under environmental loads such as freeze-thaw cycles and thermal cracking. Two main approaches can be employed to improve the durability of geopolymers, including (1) modification of the chemical composition, pore solution and pore structure of the geopolymer to sustain the chemical attacks [229-231], and (2) incorporation of the fibers/fillers to reduce shrinkage and thermal cracks, and thus minimize the chemical penetration to the system. However, the induced porosity due to the incorporation of fibers is an unfavorable parameter which can increase the penetration rate of chemical agents, as mentioned in Section 2.

3.11.2 Steel reinforced geopolymers

As discussed in Section 2.1.1, the main problem of steel reinforcement in cementitious materials is corrosion. In the absence of aggressive media, geopolymers are highly alkaline with a weak oxidative environment, which keeps the mild steel reinforcement in a passive state [232]. This is mainly due to the high alkaline pore solution of geopolymers (above pH 13.5) [233]. Also, the soluble silicates in the pore solution of the geopolymers act as an inhibitor [234]. This environment helps mitigate the corrosion of steel in geopolymers compared to OPC system [232, 234, 235]. Therefore, the best way to enhance durability is to minimize the penetration of the corrosive agent inside the matrix. As an example, it was indicated that a fly ash-based geopolymer with denser structure ensures higher protection to steel reinforcement against chlorides as compared with a porous metakaolin-based geopolymer [236]. Furthermore, the risk of steel corrosion is reduced in low-Ca fly ash compared to those containing higher levels of Ca, when the steel reinforced geopolymer composites are exposed to an environment with 5% CO₂. This is because of the formation of a large capillary pore network inside the geopolymers with high Ca content in comparison with the lower one [230, 237, 238]. In addition, increasing the content up to 1 vol.% steel fiber in fly ash-based geopolymer would help reduce the water absorption and sorptivity of the composite, and consequently, decreased the loss in compressive strength when exposed to chemical agents such as acid and sulfates [114]. This can be attributed to the reduction in shrinkage and formation of thermal cracks in fiber reinforced geopolymers compared to plane specimens, as discussed in Section 3.

When a penetrated agent reaches the steel reinforcement, an expansive corrosion product is formed that causes excessive internal pressure to widen the preliminary cracks and accelerate the deterioration of the composite [239, 240]. Here, different reactions occur between the binder and corrosive agent, which directly influence the mechanical properties of the composites. For example, Tennakoon et al. observed ten times lower chloride content at the rebar in geopolymer concrete than OPC concrete as well as significantly late corrosion onset in geopolymers, which was associated with lower chloride diffusion in the blended fly ash-slag based geopolymer [241]. Higher chloride

concentration in OPC can be ascribed to the formation of scarcely soluble calcium-containing chloride salts. While, the presence of soluble silicate ions in geopolymer pore electrolytes exerted a specific inhibition of rebar corrosion [234]. Moreover, the higher Na concentration resulted in a reduced ingress and distribution of chloride in geopolymer concrete [242].

Based on the rate and type of reactions, different effects on mechanical strength were observed. For example, steel fiber reinforced geopolymer showed an excellent sulfate attack resistant with less than 2% weight loss after six months of exposure to 3% H_2SO_4 solution as compared with ~27% weight loss of its OPC compartment. Interestingly, both geopolymer and OPC showed similar weight loss against sodium sulfate and chloride solutions, while in all cases, the compressive strength was considerably higher in geopolymer composites [114]. Likewise, steel fiber reinforced geopolymer composites did not show a noticeable reduction in impact and stiffness when exposed to sulfuric acid (pH = 1) for one month [202].

3.11.3 Inorganic, carbon, and polymeric fiber reinforced geopolymers

The concerns on the durability of geopolymer composites are not only limited to their resistivity against external chemical attack but also the internal interaction between fiber and geopolymer binder. This is more important for inorganic fiber reinforced geopolymers. For example, it was found that the alkali environment of geopolymers is severe for both glass and basalt fibers and reduces their tensile strength significantly. However, basalt fiber is less affected by acid attack compared to the glass fiber [56]. Moreover, a comparison between geopolymers reinforced with AR-glass, E-glass, basalt, and carbon fibers showed a significant reduction in flexural strength and mass loss of E-glass and basalt fiber reinforced geopolymers in the alkali environment over time, while the strength of AR-glass and carbon fiber reinforced geopolymers is even improved [243].

Next to this, the increased porosity induced by the poor compaction in fiber reinforced geopolymers is another important factor. For example, incorporation of 0.5 vol.% PP fiber into geopolymers increased the short- and long-term water absorption of the composites by about 22% and 43%, respectively, compared to the plane specimens, but it had a negative effect on the resistance to chloride penetration [244].

4 Application prospects

The application of the material covers a wide range of high-tech/high-cost to low-tech/low-cost mainly depending on the composition of the binder and fiber used to produce the composites, as demonstrated in Fig. 10. It is important to consider that having a proper conclusion for the efficiency of each composite should be outlined independently for different applications. Some examples of the application of fiber reinforced geopolymer composites are provided below.

Due to the availability and cost-effectiveness, steel fibers have been used widely in OPC concrete for structural applications. Similarly, steel fibers are used to reduce the shrinkage and increase the flexural strength, energy absorption, and post-cracking behavior of geopolymers [101]. The highly alkaline environment of geopolymers keeps the steel reinforcement in a passive state, and therefore, make it a durable composite for several infrastructural applications [232, 234].

Despite the high cost of PVA and PE fibers, due to their high mechanical strength, flexibility, and hydrophilic nature, some niche applications have been investigated for PVA and PE fiber reinforced geopolymers such as the development of strain hardening geopolymer composites, for which a concrete with ultra-high ductility and impact resistance is required [87, 245]. A similar application has been explored for PP fiber reinforced geopolymer to make the composite more eco-friendly and cost-effective [6, 27]. Furthermore, PVA and PP fiber reinforced geopolymers have

been potentially studied for extruding based 3D printing techniques to build up moldless structures with complex geometries and a minimum requirement of water curing [132, 133, 246].

The incombustible character of geopolymers together with superb high-temperature resistance of carbon and inorganic fibers can be used in the production of composites applicable where the thermal resistance is favorable [212, 247]. Also considering the high strength and lightness of carbon fibers, they can potentially be used in the manufacturing of lightweight, durable and strong large structures [248]. Besides, carbon-nanotube was used not only to increase the fracture energy of the geopolymer composite but also to provide electrical conductivity and piezo-resistivity response to monitor micro-crack formation [116, 249].

Inorganic fibers such as basalt and silicon carbide are cost-effective alternatives to carbon fibers in the manufacturing of high-temperature geopolymer composites, e.g. to develop a tensile test setup for high-temperature resistant composite at 1000 °C, or for fabrication metal molding tools [118, 124, 220].

Natural fibers are low-cost and usually flexible and can be used at high content as reinforcement in geopolymers. Several manufacturing processes have been proposed and applied to overcome the poor compaction of natural fiber reinforced geopolymers. For instance, at the presence of 8.3 wt.% short cotton fiber, roller compaction was used to force the geopolymer binder to penetrate among fiber network, and a composite with tensile strength of about 32 MPa was then produced [191].

5 Conclusions

In recent years, there has been a burgeoning interest in the development, characterization, and implementation of geopolymers for a wide range of applications such as sustainable construction and high-temperature resistance manufacturing. However, geopolymers are usually weak in tension and suffer from brittle failure. To overcome such weakness, numerous studies have been focusing on the incorporation of different types of fiber into geopolymers to obtain desirable mechanical and thermal properties for each specific application. Due to the variation of material and geometrical properties of fibers, the chemical composition of binder, casting procedure, and environmental condition different properties are obtained for different composites. This study provides a platform for efficient selection of the fiber and a better understanding of the underlying mechanisms for known parameters which influence the fresh and mechanical properties, thermal resistance and durability of the fiber reinforced geopolymer composites.

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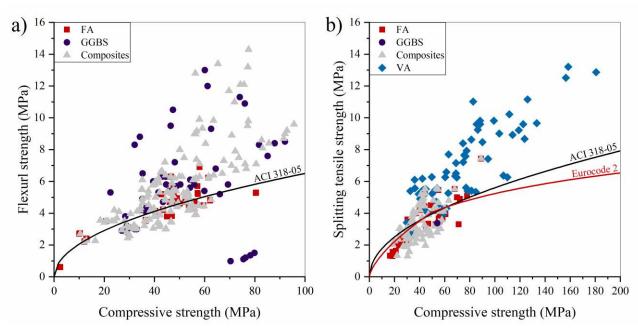


Fig. 1. a) Flexural strength and b) tensile strength against the compressive strength of different geopolymer composites. Adapted from Refs. [7-26].

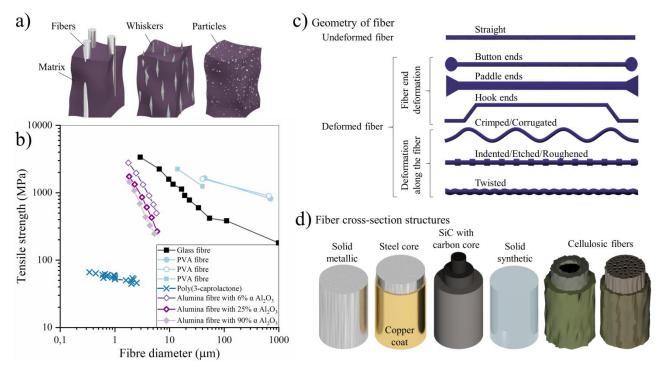


Fig. 2. a) Different types of fiber reinforced composite based on particle size; b) relation of tensile strength to fiber diameter; c) longitudinal geometry of fibers; d) cross-section structures of fibers. Adapted from Refs. [33, 83, 95, 97, 98, 106-109].

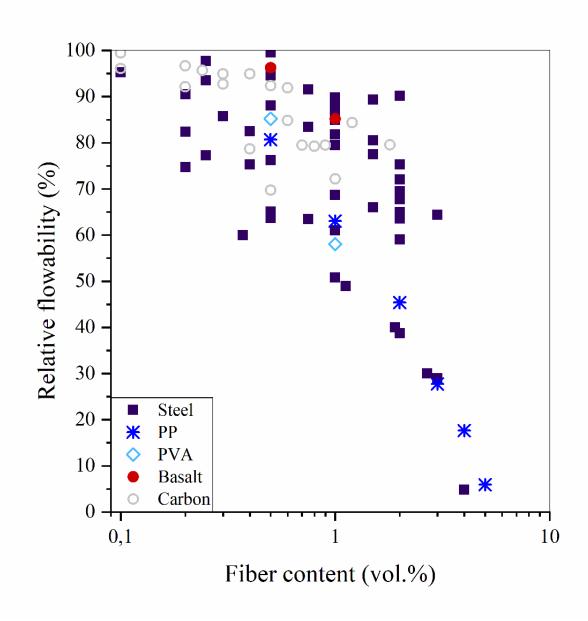


Fig. 3. Relative flowability of fiber reinforced geopolymer composites compared with plain matrices. Adapted from Refs. [6, 114, 124, 127, 129, 134-139].

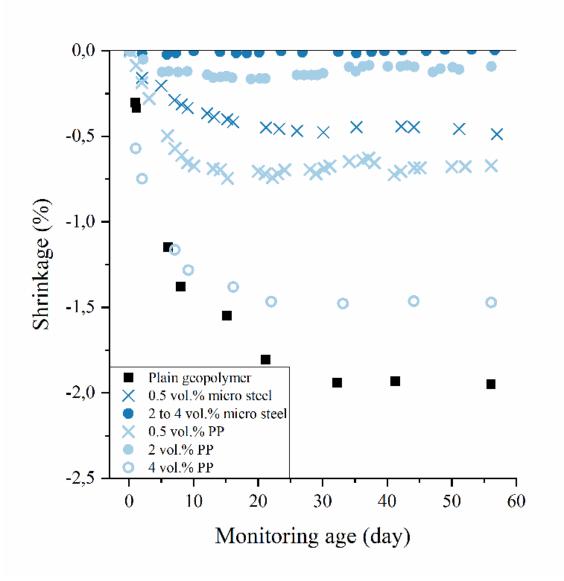


Fig. 4. Drying shrinkage of steel and polypropylene fiber reinforced geopolymer composites. Adapted from Refs. [<u>6</u>, <u>27</u>, <u>101</u>].

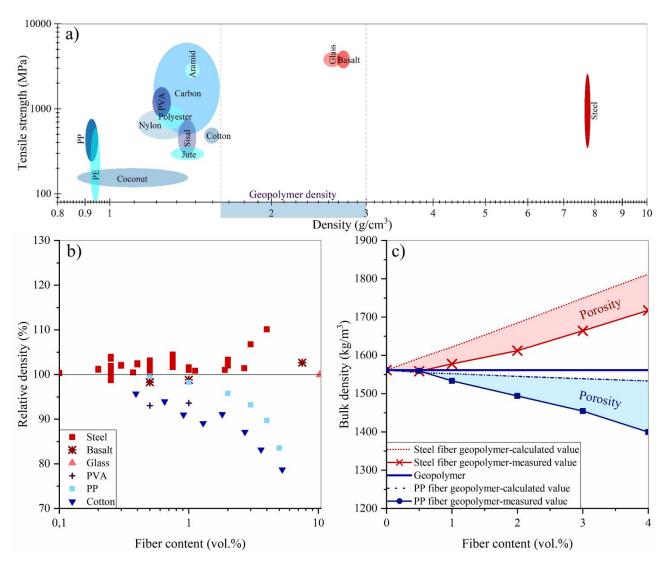


Fig. 5. a) Tensile strength against the density of different fibers; b) effects of fiber content on relative density; c) effects of fiber content on the bulk density of fiber reinforced geopolymer composites. Adapted from Refs. [6, 27, 101, 124, 137-139, 148-154].

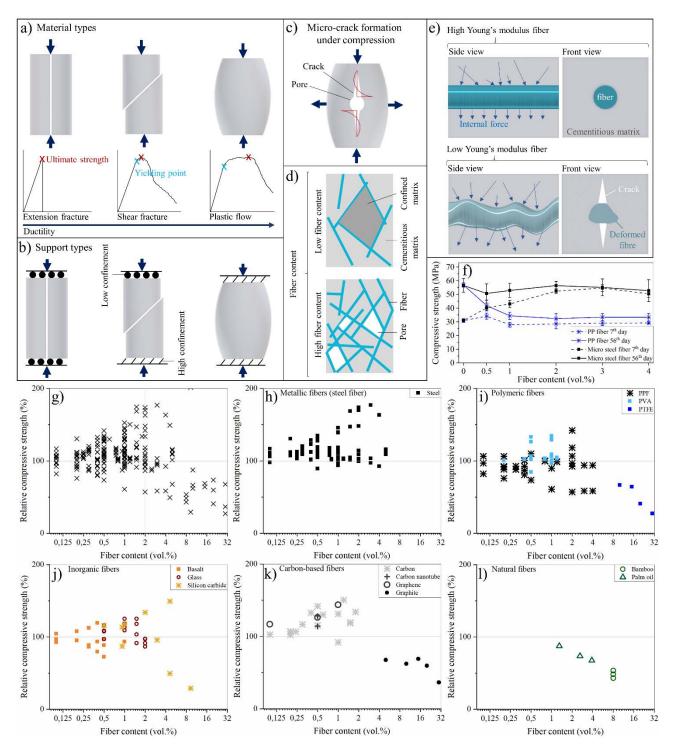


Fig. 6. Effects of a) material ductility and b) boundary condition on compression behavior; c) mechanism of crack formation close to the pores; d) influence of fiber content on structure of the composites; e) fiber performance under compression; f) development of compressive strength of fiber reinforced geopolymer composites over time; influence of fiber content g) all fiber types, h) steel fibers, i) synthetic polymeric fibers, j) inorganic fibers, k) carbon-based fibers, and l) natural polymeric fibers. Adapted from Refs. [74, 89, 114, 127, 129, 134-136, 138, 143, 163-171].

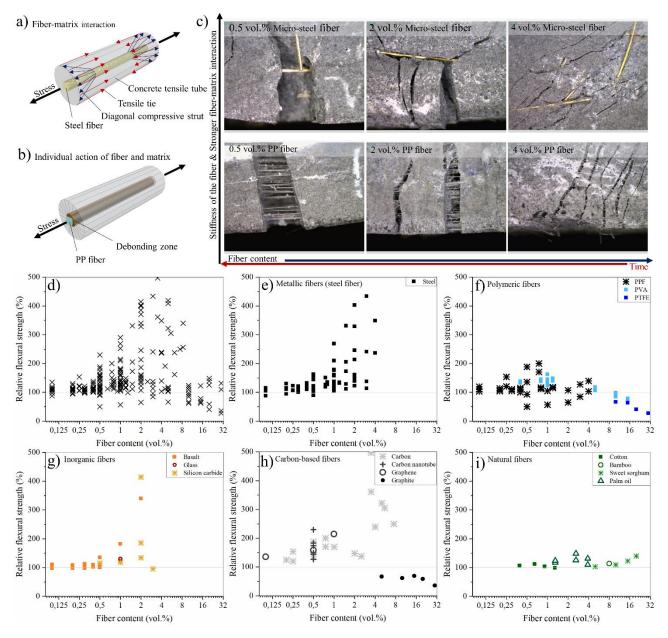


Fig. 7. a) Strong and b) weak fiber-matrix interactions; c) influences of volume fraction, type and stiffness of fiber on crack patterns of geopolymer composites; influences of d) all fiber types, e) steel fibers, f) synthetic polymeric fibers, g) inorganic fibers, h) carbon-based fibers, and i) natural polymeric fiber fraction on relative flexural strength of geopolymer composites. Adapted from Refs. [74, 114, 129, 136, 138, 143, 148, 151, 152, 165-167, 169, 171, 189-196].

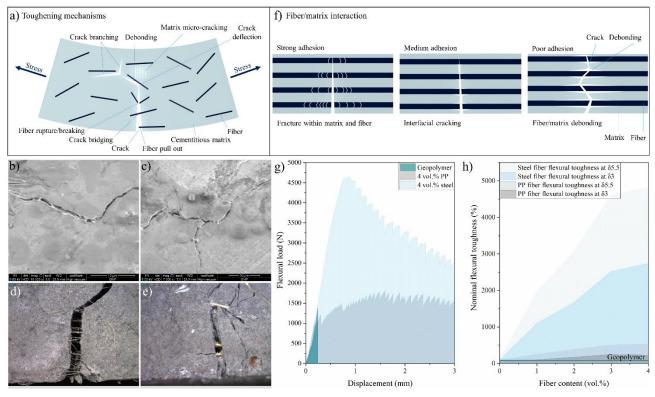


Fig. 8. a) Toughening mechanisms; b) and c) scanning electron microscopy images of toughening mechanism in graphene nanoplatelet reinforced geopolymer composites; optical microscopy of toughening mechanism in d) polypropylene and e) micro steel fiber reinforced geopolymer; f) fiber-matrix interaction; g) flexural stress against deflection and h) nominal flexural toughness of steel and PP fiber reinforced geopolymer composites. Adapted from Refs [6, 27, 35, 74, 101, 200].

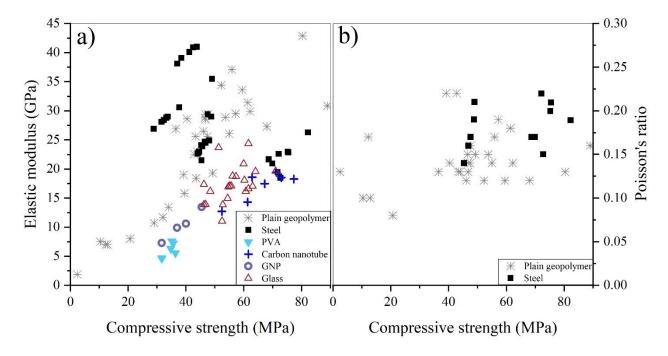


Fig. 9. a) Elastic modulus and b) Poisson's ratio to the compressive strength of geopolymer composites. Adapted from Refs. [74, 114, 130, 136, 138, 167, 197, 205-209].

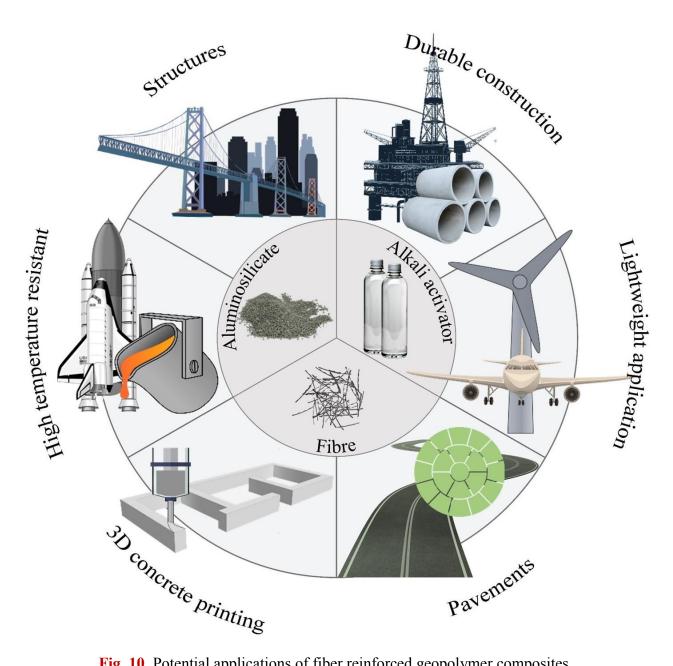


Fig. 10. Potential applications of fiber reinforced geopolymer composites.

Material category			Density (g/cm ³)	Tensile strength (MPa)	Elastic modulus (GPa)	Ultimate elongation (%)
Metallic		Steel	7.65-7.85	345-2850	200-210	0.5-3.5
Carbon-based		PAN	1.8-1.9	2500-7000	250-500	0.6–2.5
		Rayon	1.4-1.7	500-1500	35-60	2.5
		Mesophase pitch	1.6-2.2	1500-3500	200-900	0.3–0.9
		Graphene*		130000	1000	
		Carbon nanotube		11000-63000	1000-1800	
Polymers	Syntheti	c Polyvinyl alcohol	1.2-1.3	800-2500	29-42	5.7-7
		Polypropylene	0.9-0.95	240-760	1.5-10	15-80
		Polyethylene	0.92-0.97	80-3500	5-113	3-100
		Aramid	1.38-1.47	2300-3500	63-120	2-4.5
		Acrylic	1.16-1.18	270-1000	13.8-19.3	
		Polyethylene terephthalate	1.3-1.4	420-450	3.1-10	11.2
		Polyester	1.22-1.38	580-1100	15	35.0
		Nylon	1.13-1.41	440-1000	4.1-5.2	16-20
	Natural	Jute	1.3-1.5	250-350	26-32	1.5-1.9
		Sisal	1.34-1.45	280-750	13-26	3.0-5.0
		Coconut	0.87-1.4	120-200	19-26	10.0-25.0
		Bamboo	0.6-1.1	140-800	11-32	2.5-3.7
		Cotton	1.5-1.6	390-600	5.8-11	6.0-10.0
		Palm	1.3-1.46	21-60	0.6	
		Wool	1.3	160	3.5	
		Hemp	1.4-1.5	270-900	23.5-90	1-3.5
		kenaf	1.4	223-930	14.5-53	1.5-2.7
		Coir	1.15-1.46	95-230	2.8-6	15-51.4
		Banana	1.4	500	12.0	1.5-9
		Flax fabric	1.5	500-1500	50-70	
		Bagasse	1.3	222-290	17-27	1.1
		Abaca	1.5	400-980	6.2-20	1-10
Inorganic		– E-glass	2.5-2.62	3100-3800	72.4	4.8
		S-glass	2.46-2.49	4020-4650	86.9	5.4
		C-glass	2.6	3310	69	4.8
		AR-glass	2.7	3240	73	4.4
		Basalt	2.65-2.80	3000-4840	89-110	3.00-3.15
		Asbestos	2.55	620	160	
		Alumina	3.3-3.95	1700-2000	300-380	0.4
		Alumina-silica	3.4	1590-2550	200-248	0.8-1
		Silicon Nitride		2500-4800	195-300	
		Silicon carbide	2.5-2.7	2200-3450	221-250	
		Boron Nitride	7.65-7.85	2100	345	

 Table 1. Physical and mechanical properties of fibers. Adapted from Refs. [33-38].

*Graphene is not a fiber but widely used as reinforcement due to the high aspect ratio.