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Review

Geopolymer Antimicrobial and Hydrophobic Modifications: A Review

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Abstract: The article summarizes the state of the art in increasing antimicrobial activity and hydrophobic properties of geopolymer materials. Geopolymers are inorganic polymers formed by polycondensation of aluminosilicate precursors in an alkaline environment and are considered a viable alternative to ordinary Portland cement-based materials, due to their improved mechanical properties, resistance to chemicals, resistance to high temperature, and lower carbon footprint. Like concrete, they are susceptible to microbially induced deterioration (corrosion), especially in a humid environment, primarily due to surface colonization by sulphur-oxidizing bacteria. This paper reviews various methods for hydrophobic or antimicrobial protection by the method of critical analysis of the literature and the results are discussed, along with potential applications of geopolymers with improved antimicrobial properties. Metal nanoparticles, despite their risks, along with PDMS and epoxy coatings, are the most investigated and effective materials for geopolymer protection. Additionally, future prospects, risks, and challenges for geopolymer research and protection against degradation are presented and discussed.

Keywords: geopolymer; geopolymer composite; antimicrobial; hydrophobic; protection; deterioration

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1. Introduction

Geopolymers, as first named by Joseph Davidovits in late 1970s, are ceramic-like inorganic polymers formed by polycondensation of various precursor materials, primarily composed of at least partly amorphous silicon dioxide and aluminium oxide, in a strongly alkaline environment [1]. These precursors primarily include metakaolin (calcinated kaolinite) [2], fly ash (both class c and class f) [3], and granulated blast furnace slag [4]. Geopolymers are used as a binder for the manufacturing of geopolymeric concrete and other composites and are a viable alternative to materials based on ordinary Portland cement (OPC) [5]. In comparison to OPC-based materials, geopolymers exhibit higher compressive strength [6], higher resistance to extreme temperatures, lower thermal conductivity (especially in foamed form) [7,8], lower greenhouse gas emissions and lower energy requirements for manufacturing, which significantly reduces the carbon footprint of geopolymers in comparison to OPC-based concrete [9]. Like OPC, geopolymers are usually used in composite form (geopolymer concrete) with various types of additives, including silica sand, silica fumes [10], or various types of fibers (serving as a reinforcement to improve their tensile and flexural strength). Materials used in fiber form to reinforce geopolymers include carbon [11], basalt [12], polymers [13], or various waste or natural materials, such as glass, wool [14], ground wind-turbine blades [15], recycled steel fibers [16], hemp [17], or flax [18]. For more specialized applications, other types of additives may be used, such as glass microspheres [5], which significantly reduce geopolymer density without significantly compromising their mechanical properties, phase-change materials (which may reduce cracking by lowering temperature gradients within material) [19], or foaming agents (usually aluminium) [20].

Aside from application as a construction material, where they benefit from improved mechanical properties over OPC-based concrete, geopolymers may also be used as passive fire protection, as foamed geopolymers can withstand temperatures over 1000 °C and, due to its low thermal conductivity and heat resistance (as OPC-based concrete degrades in temperatures over 400 °C); this significantly increases the time needed for the temperature on the other side to increase enough for a fire to start, which gives additional time to put out the fire or evacuate the building [21]. It is also possible to either use prefabricated boards or spray the geopolymer mixture on other types of surface, including particleboards (wooden or from alternative material, such as rapeseed stalks) [22], polystyrene [23], or metals [24]. Geopolymer is also a viable material for 3D printing, as when compared to concrete, geopolymers have improved adhesion between layers and therefore a better ratio of mechanical properties when comparing 3D-printed geopolymers with cast geopolymers [25]. This also applies to geopolymer–Portland cement hybrid composites [26].

Geopolymers (as well as OPC-based concrete) are susceptible to microbially induced degradation (MIB) [27,28]. In dry environments, both types of material have antimicrobial properties, due to their alkaline nature (hydrated OPC is primarily composed of calcium hydroxide, while geopolymers have alkaline metal ions incorporated into their structure) [29]. However, in humid environments, geopolymer and concrete surfaces may be colonized by alkali-resistant bacteria, especially sulphur-oxidizing bacteria (which use sulphur oxidation as source of energy). The bacteria produce acidic compounds (such as sulphane or sulphuric acid) which both chemically degrade both types of material and lower the pH of their surface [29], which allows colonization by other microorganisms, including other species of bacteria [30], algae [31,32], fungi [33], lichens [34] etc., which further damage the surface, both chemically and mechanically. Geopolymers may also be more susceptible to microbial degradation due to their porous (zeolitic) structure [28].

Various methods of OPC-based concrete antimicrobial protection were developed and investigated, to both reduce the risk of microbially induced degradation and allow the use of concrete in aggressive environments, mainly in sewage systems [35]. The common protection methods include adding antimicrobial additives to concrete mixture (alternatively cement mortar, paste etc.) and surface protection by various coatings or mortars (which may have a similar composition to base material). Antimicrobial additives added into concrete mixture may be both inorganic and organic. Inorganic agents usually include metals (silver, nickel, copper etc.), their ions, or their compounds (copper oxide, zinc oxide etc.) [35]. Pure metals and their compounds may be used in the form of nanoparticles, which exhibit significant antimicrobial effect against a wide range of microorganisms [36,37]. Inorganic antimicrobial agents may, however, have side effects, such as toxicity and environmental risks. Organic antimicrobial agents include phthalocyanine compounds, quats, alkyl nitrobromide, various commercially available products (including ConShield and ConBlock MIC), and other compounds [35]. However, organic compounds have a shorter service life, due to their lower stability and temperature resistance [35]. Microorganisms may also quickly develop resistance to organic antimicrobial agents [38]. For surface protection of concrete, the best results were achieved by using various epoxy coatings (including modified epoxy coatings) and epoxy modified mortars, which prevented the formation of biofilm and concrete degradation in an extremely aggressive sewer environment. Specific types of protective cement mortars were also found to be effective [39–41].

High resistance to microbially induced degradation is necessary for applications of geopolymers (as well as other construction materials) in aggressive or humid environments, including sewers, sewage treatment plants, water (both freshwater and seawater), and other environments where such degradation may occur. It is also possible to use such enhanced geopolymers as protective mortar on building exteriors, which may be exposed to rainwater.

The article reviews the literature in the area of antimicrobial protection of geopolymers in its various methods, including surface protection, hydrophobic coatings, and antimicrobial additives. Potential applications, challenges, environmental risks, and future research prospects are also discussed. The review was carried out using multiple database articles or search engines. Primarily, ScienceDirect, Scopus, and ResearchGate were used. Various search terms were used, due to the review focusing on multiple types of geopolymer protection. The primary search term was "geopolymer" or "geopolymer composite" combined with "antimicrobial protection", "antimicrobial", "microbial degradation", "hydrophobic", and similar terms. Additional searches were performed based on information found (for example on the topic of geopolymers modified with epoxy resins). The variable search terms were necessary, as more methods of protection were investigated and for most search terms the results were few. For example, searching for "Antimicrobial AND geopolymer" at Scopus yielded 14 document results [42], while searching for "Antimicrobial AND concrete" at Scopus yielded 235 document results [43]. The review also preferred newer articles (published in the last 3 years).

2. Geopolymer Hydrophobic Properties and Modification

Modifying geopolymer or geopolymer surfaces with hydrophobic agents may protect them from humid environments or water exposure (such as during rain), which lowers the risk of the geopolymer being colonized by microorganisms due to its natural antimicrobial properties, based on its alkaline nature. The term "hydrophobic modification" may also refer to both surface protection by hydrophobic coatings and modification of bulk material. To make a distinction between hydrophobic modification and surface protection, this chapter only reviews hydrophobic modification of bulk material and hydrophobization coatings that do not form a barrier on the geopolymer surface and instead "penetrate" its surface layer, which gains hydrophobic properties without significant change in surface appearance. This approach to geopolymer protection may be useful, if it is not appropriate to change the geopolymer appearance, such as for decorative purposes.

Geopolymers are inherently less prone to water absorption than OPC-based materials, primarily due to their microporous structure (less porous than common concrete) and are therefore better for applications in humid or even underwater environments, including in seawater, for example, tests have shown that fly ash geopolymer had over two times lower water absorption when compared to OPC concrete after 28 days of submersion in artificial seawater [44]. Tests in demineralized water have likewise shown that geopolymer has over two times lower water absorption to OPC concrete, mainly due to lower capillary porosity. Increasing porosity and water absorption also leads to a decrease in compressive strength [45]. The geopolymer surface (which hardened either in contact with mold or on air) also absorbs water significantly slower to the surface of cut geopolymer, as the geopolymer surface may be seemingly hydrophobic, although it still absorbs water in a matter of minutes, while the cut surface absorbs water in a matter of seconds [46]. Geopolymer water resistance allows its use in underwater applications. It is possible, for example, to use the geopolymer as a base material for artificial reef as part of the effort to restore damaged marine ecosystems. For this purpose, the geopolymer may also be used as an "ink" in 3D printing [47]. The Australian company, "Earth Friendly Concrete", manufactures geopolymer material for artificial reef elements and other marine applications, including wharf and boat ramp construction [48].

One of the most investigated hydrophobization agents for geopolymers is polydimethylsiloxane, (PDMS, shown in Figure 1), one of the simplest silicone (siloxane) polymers. Low-molecular weight PDMS is commonly used in lubricants, antifoaming agents, and hydraulic fluids. At higher molecular weights, PDMS has rubber or resin properties and is used in caulks, sealants, or soft lithography [49].

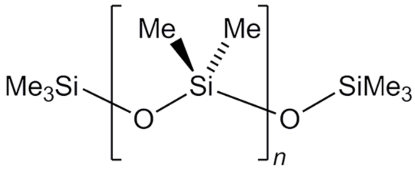

Figure 1. Polydimethylsiloxane molecule [49].

Multiple studies were performed to evaluate the effect of PDMS additives on geopolymer water absorption and other properties, including wettability (contact angle) or mechanical properties. One study investigated the effect of addition of PDMS into the fly ash/slag geopolymer on these properties. In particular, up to 3 wt.% of PDMS (with 0.5 wt.% increments) was used with no additional additives (such as aggregate or silica fumes). PDMS significantly increased the contact angle from 57.32° for pure geopolymer to 106.52° for geopolymer with 0.5 wt.% of PDMS and 127.64° for geopolymer with 3 wt.% of PDMS. Water absorption was also increased significantly with increasing PDMS content, from 6.96% (percentage of water weight absorbed into the corresponding amount of geopolymer, saturation test) for pure geopolymer, to 3.51% for geopolymer with 0.5 wt.% of PDMS, to 1.61% for geopolymer with 3 wt.% of PDMS. These results show that PDMS additive, even low content, significantly increase water absorption resistance and surface hydrophobicity. However, in this study, PDMS additive decreased the compressive strength of geopolymer by up to 28.3%, although the final value of compressive strength was still considered high enough for most applications (over 50 MPa) and the detrimental effect significantly lower for 0.5 wt.% PDMS content (69.5 MPa). The study also discovered a difference in pore structure, as the addition of PDMS changed the pore structure by causing the formation of larger pores, which caused the decrease in compressive strength [50].

In another study, PDMS was used as an additive to calcinated clay/slag geopolymer to geopolymer in addition to PVA fibers with a PDMS content of up to 5 wt.% and contact angle and water absorption were measured. In addition, compressive and tensile properties were investigated. The study used low-field nuclear magnetic resonance to determine water absorption by directly measuring the content of water within the geopolymer. The samples with 4 wt.% and 5 wt.% of PDMS reached the best results, including a significantly hydrophobic surface with a 120° contact angle (which did not decrease significantly in time) and water absorption up to 75% lower compared to the reference sample, with the hydrophobic properties being directly proportional to the amount of PDMS. Increasing content of PDMS also caused an increase in compressive strength (although it remained relatively low, at 26.5 MPa, due to the base material used) and a decrease in tensile strength. The study concluded that 4 wt.% of PDMS is an optimal content to ensure hydrophobic properties of the geopolymer, as too-large content may significantly increase the cost of the geopolymer [51].

A study on the metakaolin geopolymer has also confirmed the effect of PDMS on the hydrophobicity of geopolymers. In this case, PDMS was used with an unspecified silane coupling agent. The amount of PDMS used was up to 5 wt.% of the metakaolin base. For this PDMS content, the contact angle has increased from near zero (0.6°) to 127.5°. Total water sorptivity (absorption) decreased by up to 25%, with the sorptivity process being significantly slower with increasing PDMS content, due to PDMS layers on the pore walls. Another conclusion of this study was the proposition of a multistage sorptivity model, due to the limitations of the standard Hall's model and changes in the speed of water absorption into geopolymer in time [52].

Another study regarding PDMS additive investigated the effect of hydrophobic and hydrophilic fibers on a geopolymer hydrophobized by PDMS. The addition of hydrophobic fibers has improved the hydrophobic properties of resulting composite [53]. PDMS may also be used during the process of geopolymer foaming to create hydrophobic geopolymer foams [54]. The effect of PDMS and additional additives on geopolymer hydrophobicity and other properties is summarized in Table 1.

Table 1. Effect of PDMS on geopolymer properties.

Type of Geopolymer	PDMS Content	Water Absorption Compared to Sample without PDMS	Contact Angle	Other Effects	Reference
Fly ash/slag	0.5 wt.%	−49.5%	106.52° (+86%)	Lower compressive Strength (−5.4%)	[50]
Fly ash/slag	3 wt.%	−76.9%	127.64° (+123%)	Lower compressive Strength (−28.3%)	[50]
Calcined clay/slag (+ PVA fibers)	5 wt.%	−75%	120° (+586%)	Higher compressive Strength (+35%) and Lower tensile strength (−17%)	[51]
Metakaolin + Silane coupling agent	5 wt.%	−25%	127.5° (from near zero)	Absorption significantly slowed down for higher PDMS content	[52]
Metakaolin + Quartz powder	3.3 wt.%	−70.6%	127.5° (from near zero)	Absorption further Slowed down by hydrophobic Fiber additives	[53]

Aside from PDMS, various other compounds or materials were tested as a way to effectively achieve hydrophobic properties in the geopolymer. These include calcium stearate, which may be partly used to replace the geopolymer base and provide Ca^{2+} ions to the reaction, which leads to formation of calcium silicate hydrate. Using 5 wt.% of calcium stearate has achieved the best results in the cited study [55]. Other studies have reached hydrophobicity by using fatty acids with a catalyst (such as aluminium trichloride) [56,57], graphene nanoplatelets [58], graphene oxide modified by 3-aminopropyltriethoxysilane (APTES) [59] (graphene oxide also improves geopolymer mechanical properties [60]), butyl stearate [61], or hydrophobically modified silica fumes [62]. Certain materials of natural origin were also successfully investigated, including rice husk ash (as a way to recycle agricultural waste), which improves the hydrophobicity of both fly ash geopolymers and metakaolin geopolymers [63,64]. Rice husk ash may also be used to waterproof OPC-based concrete [65].

Commercially available primer/hydrophobization concrete (or, more generally, mineral material) coatings may also be used to make geopolymers hydrophobic. One study has tested various commercially available hydrophobization coatings and their ability to hydrophobize geopolymers, primarily based on siloxanes (such as PDMS) and styrene-acrylate, with the best results being achieved by multiple siloxane-based coatings (based on siloxanes and water or organic solvents). This again confirms the effect of siloxane-based geopolymer hydrophobization solutions [66].

3. Geopolymer Antimicrobial Additives

Manufacturing geopolymers with an antimicrobial additive may prevent their surface from being colonized by microorganisms and therefore prevent their microbial degradation. Various types of additives were tested for other types of concrete (especially OPC-based concrete), including both inorganic and organic agents. Inorganic agents are based on heavy metals, such as silver, copper, zinc, or other metals, with silver having the highest antimicrobial activity. They may be used in the form of ions, pure metals, metal oxides or other metal compounds. They may also be used in the form of nanoparticles. Organic agents include various types of compounds, including copper phthalocyanine or calcium formate. However, inorganic agents are considered better for applications as antimicrobial additive, due to their higher stability and lower risk of microorganisms developing resistance to them. However, inorganic agents may have side effects, such as toxicity or environmental risks (especially for nanoparticles) [67].

3.1. Inorganic Agents

3.1.1. Metal Ions

Some research was performed in the field of using certain types of metal ions, which were tested as an additive to geopolymers as a way to improve their antimicrobial activity. In one study, a metakaolin-based geopolymer was immersed in copper chloride solution for 24 h, until its color changed to green due to ion exchange of copper ions. This modified geopolymer suppressed the growth of oyster mushroom in sawdust at 300 ppm copper ion concentration in the geopolymer. However, this type of modification is unstable due to a lack of strong chemical bonds, as copper ions may be released by immersing geopolymers to water [68]. Another study investigated modifying geopolymers with silver and copper ions (as well as nanoparticles) as a method for enhancing geopolymers' water filtration ability, for the purpose of water treatment (disinfecting filters, slurry dewatering etc.). Using 3D printing to form geopolymer filter scaffolds also minimized the leaching of silver from the structure (both in the form of ions and nanoparticles) [69]. Silver ions with modified nanostructured synthetic zeolites (geopolymers) were also successfully tested as a method of protection against MRSA (Methicillin-resistant *Staphylococcus aureus*) [70]. Nanostructured zeolites modified with zinc, copper, and iron ions were also proven effective against MRSA [71].

3.1.2. Metal Nanoparticles

Metal or metal-oxide nanoparticles are widely used and investigated as an antimicrobial reagent for various applications, including medicine (against antibiotic resistant bacteria) and construction material protection [67]. Their small size and high specific surface allow them to destroy microorganisms by both disrupting their cell membranes and catalyzing reactions producing ROS (reactive oxygen species), such as peroxides, radicals, or superoxides, which cause cell death and DNA damage at high concentration, with titanium dioxide nanoparticles being photocatalytic (catalyzing ROS-producing reactions under UV radiation exposure) [72]. This makes nanoparticles a highly effective antimicrobial agent. However, nanoparticles may also be highly toxic and damaging to the environment, due to the ROS-producing and membrane-disrupting effect, as well as due to ion release and biomagnification in the food chain. Silver and copper (as well as copper oxide) nanoparticles are among the most toxic nanoparticles, while gold and titanium dioxide nanoparticles' toxicity is low. Toxicity also decreases with increasing particle size, primarily due to a lower rate of ion release [73,74].

Silver nanoparticles were investigated as an antimicrobial additive to geopolymers. In one study, geopolymer-bentonite composite with nanoparticle additive was tested as a possible method to disinfect water. The composite foam was prepared with 0.05 wt.% of silver nanoparticles and foamed with hydrogen peroxide and tested as a water filter for *Escherichia coli* bacteria, intestinal enterococci bacteria, and somatic coliphage viruses (bacteriophages infecting *E. coli*). While the efficiency of this type of filter against coliphages was low, its efficiency against *E. coli* and enterococci bacteria was significant, although it diminished over three weeks of continuous use, due to silver nanoparticles leaching out (the nanoparticle content was also lower than expected immediately after foaming, as nanoparticles were also leached out during the geopolymerization process) [69,75]. In another study, silver nanoparticles were adsorbed on the surface of silica (amorphous SiO_2 commonly used as an additive to geopolymers and OPC-based concrete) nanoparticles and used as an additive to the fly ash geopolymer with a 6 wt.% nanoparticle content. The composite exhibited a strong antimicrobial effect against both gram negative *Escherichia coli* and gram positive *Staphylococcus aureus*, reaching over 99% reduction of the bacteria population after 8 and 6 h, respectively. Reference cement mortar and geopolymers with just silica nanoparticles as an additive had no antimicrobial effect. However, silica nanoparticles improved the mechanical properties of the composite [76]. Additionally, carbon fibers were tested as a possible carrier for silver nanoparticles. In a study, silver nanoparticles were synthetized on the surface of an antibacterial-activated carbon fiber (material used in water treatment) and tested on *E. coli* bacteria cultures, reaching up to 91.1% reduction of bacterial population and a low silver release rate. Although this type of nanoparticle-enhanced carbon fiber was not yet tested as a reinforcement for geopolymers, it presents a potentially viable way to ensure nanoparticle dispersion in a geopolymer matrix and a low silver release rate, while simultaneously improving its tensile and flexural strength, as well as other properties, for which carbon fibers are commonly used [77,78].

Another type of investigated antimicrobial nanoparticles are ZnO (zinc oxide) nanoparticles, thanks to their photocatalytic properties. A study investigated ZnO-functionalized fly ash zeolite (geopolymer) and its ability to degrade Ciprofloxacin antibiotic and destroy *S. aureus* and *E. coli* bacteria, as a potential method to use this material as a protective coating. The zeolite was prepared by alkaline hydrothermal synthesis (at 550 °C), while ZnO nanoparticles were synthetized within the mixture during the process from $ZnCl_2$. The content of Zinc was also very high at 19.24 wt.% (content of ZnO was not specified). Modified zeolite achieved very high antimicrobial activity under UV-irradiation, completely inhibiting the growth of S. Aureus bacteria and reducing the formation of *E. coli* colonies by approximately four orders of magnitude, even under low 365 nm UVA (lowest-energy UV light) irradiation (1 and 2 kW-h m^{-2}—kilowatt-hour per square meter) and completely degrading Ciprofloxacin at 5.1 w L^{-1} (watt per liter). Directly synthetizing ZnO within the composite also prevents problems with nanoparticle aggregation [79]. Another study used a ZnO-SiO_2 nanohybrid consisting of SiO_2 nanoparticles (silica fumes) attached to ZnO nanorods. Incorporating this nanohybrid to fly ash geopolymer with a 6 wt.% (of fly ash used) content improved its mechanical strength, while simultaneously achieving significant antimicrobial activity against *E. coli* and *S. aureus* bacteria, with MBC (minimum bactericidal concentration) of the composite being 0.15 mg mL^{-1}, resp. 0.2 mg mL^{-1}. The composite also exhibited fungicidal properties against *Aspergillus niger* fungi, with 0.25 mg mL^{-1} minimum fungicidal concentration [80].

Titanium dioxide (TiO_2) is also a possible antimicrobial and self-cleaning additive to geopolymers, thanks to its low toxicity and photocatalytic effect, especially for outside applications, where the material is exposed to sunlight. A study tested a fly ash geopolymer with 5 wt.% of TiO_2 nanoparticles and its resistance against algae and fungi formation. The geopolymer composite reduced green algae formation by 54% and fungi formation by 24%, primarily by the oxidizing effect of TiO_2 irradiated by UV light [81]. Another study used a metakaolin geopolymer with 10 wt.% of TiO_2 or 5 wt.% of CuO nanoparticles and tested their effect on the inhibition of bacterial growth under UV irradiation by the means of the growth inhibition zone method (disc diffusion test), with disc-shaped geopolymer samples being used to inhibit bacterial growth in a petri dish, and by inoculating the sample, and by exposing the solution with bacteria, diluted to various degrees, to geopolymer samples for a specific amount of time and attempting to cultivate the bacteria after. While geopolymers with CuO nanoparticles did not inhibit the bacterial growth, as no inhibition zone formed around the sample in first phase of testing (due to too-low content, as presumed by authors), geopolymers with TiO_2 nanoparticles were considered "satisfactory" in inhibiting the growth of *E. coli*, *P. aeruginosa* (*Pseudomonas aeruginosa*), and *S. aureus* bacteria. The antimicrobial effect was also enhanced by using glass waste as an aggregate for the geopolymer [82].

Table 2 shows the antimicrobial effect of various geopolymers with a nanoparticle additive.

Table 2. Effect of nanoparticles on geopolymer antimicrobial properties.

Type of Geopolymer	Nanoparticles Type and Content	Effect	Reference
Metakaolin geopolymer/ Bentonite composite Foamed with H_2O_2	Silver, 0.05 wt.%	High inactivation efficiency Against *E. coli* and enterococci bacteria when used as water filter. Effect diminishes over time.	[69,75]
Fly ash/sand geopolymer	Silver nanoparticles attached on silica nanoparticles, 6 wt.% in total	99% reduction of *E. coli* and *S. aureus* populations in 8, resp. 6 h	[76]

Table 2. *Cont.*

Type of Geopolymer	Nanoparticles Type and Content	Effect	Reference
Fly ash hydrothermally synthetized zeolite	ZnO synthetized during composite preparation, 19.24 wt.% of Zinc	Complete inhibition of *S. aureus*, decrease of *E. coli* growth by 4 orders of magnitude and complete degradation of Ciprofloxacin under UVA irradiation	[79]
Fly ash	ZnO nanorods with attached SiO_2 nanoparticles, 6 wt.% in total	Strong antibacterial properties against *E. coli* and *S. aureus* and fungicidal properties against *A. niger*. Improved mechanical properties.	[80]
Fly ash	TiO_2, 5 wt.%	54% lower algae formation, 24% lower fungi formation.	[81]
Metakaolin + glass waste as aggregate	TiO_2, 10 wt.%	High inhibition capacity for *P. aeruginosa*, *E. coli* and *S. aureus* bacteria	[82]
Metakaolin + glass waste as aggregate	CuO, 5 wt.%	No inhibition zone formed for *P. aeruginosa*, *E. coli* and *S. aureus* bacteria	[82]

In addition to improving antimicrobial activity of geopolymers, nanoparticles may also improve other properties. For example, nanoparticles of SiO_2 (silica fumes) are commonly used to improve mechanical properties, chemical resistance, and water permeability of both OPC-based concrete and geopolymers. TiO_2 nanoparticles also improve compressive and flexural strength [83].

3.1.3. Metal Microparticles

Microparticles (particles with a size in the order of micrometers) may be a possible alternative to nanoparticles as a antimicrobial agent, due to their lower toxicity, lower risk for the environment, and lower price. However, they have not yet been sufficiently investigated as an antimicrobial additive to geopolymers. One study tested metakaolin geopolymers with the additive of 4 wt.% of silver, copper, and nickel microparticles by the disc diffusion test on gram-negative *E. coli* and gram-positive M.luteus (*Micrococcus luteus*), with antibiotic etalons (Cefazolin and Gentamicin) serving as control samples. Leachate from geopolymer composites was used. Copper and silver microparticles had a strong antimicrobial effect against *E. coli*, reaching 64.1% and 59.1% effectiveness, respectively, compared to antibiotic etalon, against *E. coli*. However, their effect was weaker against *M. luteus*, only reaching 10.3% and 12.8%, respectively, when compared to antibiotics. Nickel microparticles only reached 37.9% compared to antibiotics against *E. coli* and their effect was negligible against *M. luteus*. Silver and copper microparticles were, however, confirmed effective as an antimicrobial geopolymer additive, as even with a low inhibition zone diameter against some bacteria, microparticles may still prevent colonization of the geopolymer surface, and therefore microbial degradation. Copper microparticles may also be favorable over silver due to their lower price [84].

3.2. Organic Agents

Despite their worse suitability for application as an antimicrobial additive in geopolymers, due to their lower stability and risk of microbial resistance when compared to inorganic agents, some organic compounds were investigated for use in geopolymer composites. One study investigated fly ash geopolymer spheres (4–5 mm in diameter) coated with the antibiotic Amoxicillin or silver nanoparticles. These microspheres were tested by the disc diffusion test on *E. coli* bacteria. Both samples with amoxicillin and nanoparticles were effective, making geopolymer microspheres a potential carrier medium for both types of antimicrobial agent. [85] However, using antibiotic as an antimicrobial additive to geopolymers may lead to their release into the environment, especially for applications in humid or underwater environments, furthering the problems with antibiotic resistance and environmental damage [86]. Another investigated organic antimicrobial agent is triclosan (triclocarban). When used as an antimicrobial additive to geopolymers, triclosan may significantly increase geopolymers' antimicrobial activity, even with a low content (0.5 wt.%) and against both Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria [87]. However, triclosan is a known pollutant, toxic to organisms and aquatic ecosystems [88], and bacteria may develop resistance to it, similarly to other organic antimicrobial agents, making its use as an antimicrobial additive to geopolymers inadvisable [89].

4. Geopolymer Surface Protection

The area of protecting geopolymer surface by various antimicrobial or at least bacteria-resistant coatings is not sufficiently investigated currently, as there are few studies about the topic. However, as geopolymers are mineral-based materials, similarly to OPC-based concrete, and also due to their applications as concrete, including applications in very aggressive environments, such as sewers, research about similar protection of other mineral-based materials may serve as a starting point for geopolymer surface protection. For example, a study investigated potential ways to protect geopolymers against sulphur and iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*), which cause microbially induced deterioration, in cooling tower basins of geothermal power plants. This study used commercially available epoxy resin coatings (Amercoat 351 and 358, Sikagard 62), epoxy-modified cement mortar (Sikagard 75 with EpoCem), latex-modified cement mortar, and SewperCoat, a calcium aluminate cement mortar. The coatings were tested by exposure to A. ferrooxidans in special test cells simulating the environment of expected application (40 °C, 2.59 pH). After 60 days, epoxy-based coatings and SewperCoat had shown no signs of biofilm, although some films were blistered, while other types of coatings and uncoated concrete had developed a bacterial biofilm. This indicates a significant resistance of epoxy-based coatings and special protective OPC-based mortars against sulphur-oxidizing bacteria [40]. If epoxy-based coatings may be bonded to geopolymers with significant adhesion/surface layer penetration, they may also be used for their protection.

Some studies have investigated the potential use of epoxy-based coatings on geopolymers. One study tested epoxy resins and commercially available epoxy-based coatings (Izolak, Gorepox G, and Sinepox), along with pure epoxy resin and acrylic paint Ecolor BKH, as a potential method of geopolymer surface protection. Although epoxy-based coatings did not provide significant hydrophobic surface properties, they did improve the tribological properties of geopolymer, by lowering the coefficient of friction and improving wear resistance. Similar results were achieved with pure epoxy resins and acrylic paint. This study therefore shows that epoxy-based coatings may be used on geopolymers [66]. Another study tested acrylic coating Revacryl UF 4210, which may be applied as a coating on various types of geopolymers [49]. Additionally, at least one study tested epoxy-based and acrylic coatings and their ability to protect geopolymer mortar from aggressive environments. The study used epoxy coating Sikagard-63 and two-component acrylic waterproofing coating SikaTop Seal 107. Coated geopolymer samples were exposed to various chemical environments by immersion in 10% solutions of ammonium nitrate, sodium chloride, and sulphuric acid. After 60 days of exposure, the uncoated reference samples were significantly deteriorated (worst deterioration was caused by sulphuric acid) while both epoxy-based coating and acrylic coating improved geopolymer resistance against chemically aggressive environments, with acrylic coating achieving better results [90].

However, although few studies investigated modifying geopolymers with protective coatings, many studies investigate using geopolymers as protective coatings, for multiple types of material, including steel, other geopolymers, or even OPC-based materials. Similar to OPC-based materials, geopolymers may be used as a mortar on other types of concrete, with various types of modifications, including epoxy resins or nanoparticles. When used as a mortar to coat other geopolymer or OPC-based materials, this approach allows easy repairs to the coating (as it is possible to simply reapply newly prepared mortar) and lowers the total price, as using mortar modified with potentially expensive additives is more viable than using them as an additive to the whole bulk of material. Geopolymer coatings also have a strong adhesion to geopolymer substrate and OPC-based concrete, although their adhesion to metals, such as steel, is poor [91,92].

Various types of geopolymer, additives etc., were investigated as a methods to apply geopolymer-based materials as coatings. One study investigated geopolymer coating on steel as protection against high temperatures (thermal barrier) and the influence of geopolymer properties on adhesion between geopolymers and steel. In particular, the effect of the Si:Al ratio in geopolymers (which was modified by either adding sodium aluminate, sodium silicate, or cabosil to the geopolymer mixture) on the adhesion was observed. The strongest adhesion was achieved with Si:Al = 2.5 (the highest), with the adhesion strength reaching over 3.5 MPa. However, increasing the Si:Al ratio also increased thermal expansion of the geopolymer [93]. Another study used geopolymers as a potential anti-corrosive coating for steel structures. Metakaolin geopolymer with up to 1 wt.% of reduced graphene oxide was used, along with other additives, including lubricant, dispersant, anti-foaming agent, and calcium hydroxide. The geopolymer itself significantly improved the steel corrosion resistance, however, the best results were achieved with 0.1 wt.% of graphene oxide, increasing steel corrosion resistance by two orders of magnitude when compared to bare steel [94].

In addition to being used as coating for geopolymers (as well as other construction materials, including OPC-based concrete), epoxy resins may also be used as geopolymer additive, with the resulting composite being used as protective coating. One study investigated epoxy-modified geopolymer coatings on steel as another corrosion protection method. Fly ash-bauxite residue-based geopolymer (alternatively called red mud) with 10 wt.% epoxy resin (with hardener) was used as anti-corrosive coating. The geopolymer had shown excellent corrosion protection properties, while the addition of bauxite residue improved its adhesion to steel (with best results being achieved at 25% bauxite residue content) [95]. Another study, while likewise investigating the anti-corrosion protection of metakaolin geopolymer-epoxy resin coated steel, used 2 wt.% silica fumes additive and up to 15 wt.% of mechanochemically grounded TiO_2 powder, along with 10 wt.% of epoxy resin (with hardener). This composite was confirmed to be stable in water, as well as in salt-rich environments (confirmed by an accelerated salt fog test) and showed bactericidal properties (against *E. coli* and *S. aureus*). Additionally, 10 wt.% of TiO_2 also improved adhesion between the geopolymer and steel substrate. The study declared this type of composite suitable for coating buried steel pipelines and other steel structures [96]. The application potential for using geopolymer-epoxy coatings as protection of undersea structures was also investigated. A study used a metakaolin geopolymer with up to 30 wt.% epoxy resin content and the anticorrosive properties were determined by measuring the compressive strength of the composite after submersion in seawater. Epoxy resin-geopolymer composites degraded slower due to exposure to seawater compared to pure geopolymers, with the samples with 30 wt.% of epoxy resin even hardening under seawater (especially for samples with shorter curing time in range of 1 or 7 days) [97].

Additionally, studies were also investigating the influence of epoxy resin additive on geopolymer mechanical properties [98–100], with epoxy–geopolymer composites having significantly improved mechanical properties, including compressive or flexural strength when compared to geopolymers. The effects are summarized in Table 3. Geopolymer-epoxy composites have improved compressive and flexural strength when compared to geopolymers, although the reinforcing effect of epoxy resin is lower for geopolymers, which have high compressive and flexural strength by themselves (such as slag geopolymers, which have improved mechanical properties over metakaolin and fly ash geopolymers [101]). Some contents of epoxy resin in specific types of geopolymer (especially geopolymers based on furnace slag) may also lead to worse mechanical properties, at least with a short curing time, although the mechanical properties may level out [102].

Table 3. Effect of epoxy resin on geopolymer mechanical properties.

Type of Geopolymer	Epoxy Resin Type/Content and Other Additives	Effect on Mechanical Properties	Reference
Metakaolin	DGEBA resin + DICY hardener, 20 wt.%	Compressive strength—50.6 MPa (+150%) Flexural strength—5.4 MPa (+108%)	[98]
Fly ash/slag	Waterborne epoxy emulsion + waterborne hardener, 4 wt.%	Compressive strength—65.1 MPA (+8%) Flexural strength—7.7 MPa (+8%)	[99]
Fly ash	Epojet® epoxy resin, 20 wt.%	Compressive strength—49 MPa (+63%)	[100]
Metakaolin	Epojet® epoxy resin, 20 wt.%	Compressive strength—51 MPa (+21%)	[100]
Metakaolin/slag	12.5 wt.% (only 1 day curing time)	Compressive strength—16 MPa (−23%)	[102]

As mentioned above, one of the possible applications of protective geopolymer coating (modified by epoxy resins, antimicrobial nanoparticles, or microparticles etc.) is the protection of OPC-based concrete, most widely used in construction material, including the repair of older concrete structures, thanks to superior geopolymer mechanical properties and chemical resistance. This also applies for aggressive environments, such as seawater. A study investigated fly ash and metakaolin geopolymers as a concrete protection method against chloride-induced corrosion (such as in seawater, as both concrete and rebar may corrode and degrade quickly there), while chloride ion penetration was measured. The study used the wetting/drying cycles method, 15 days immersion in 3.5% aqueous solution of NaCl, followed by 15 days drying at ambient temperature. Both types of geopolymer exhibited good adhesion to concrete substrate and significantly increased its resistance against chloride permeability and corrosion, lasting up to 4 wetting/drying cycles before significant chloride ion penetration occurs [103]. Another study likewise investigated this type of geopolymer application in marine environments, using the metakaolin geopolymer with up to 30 wt.% of epoxy resin as protective coating. The addition of epoxy resin significantly reduced or even nearly prevented (at 20 wt.% content) the deterioration of geopolymers in simulated marine environments after up to 56 days of exposure (as compressive and flexural strength of geopolymer coating was not diminished after this time with epoxy additive) [104].

5. Potential Nanoparticle Leaching from Antimicrobial Geopolymers

One of the biggest risks of antimicrobial geopolymers is the potential release of antimicrobial nanoparticles into the environment, due to their destructive effects on water ecosystems and the risk of release into the atmosphere as dust biomagnification in organisms [73,74,105]. Aside from investigating alternatives for nanoparticles, such as metal microparticles, it is necessary to assess whether nanoparticles are leached from particular geopolymer composites and potentially the rate of leaching and total amount of nanoparticles that can be leached. Some studies did investigate the rate of nanoparticle leaching. For example, a study that used 0.05 wt.% of silver nanoparticles as a water disinfection method discovered that leaching of silver nanoparticles decreased sharply after 4 h of testing and remained very low after that (<1 μg/L of deionized water used to flush the geopolymer and further lowered to <0.2 μg/L during the 3-week experiment), in total, only 4.6% of silver were leached out after 4 h. The study also proposed ways to mitigate the leaching further, such as using different silver impregnation methods or creating geopolymers with lower porosity [75]. In another previously mentioned study, a low release rate was achieved by adsorbing silver nanoparticles on activated carbon fibers (although without using them as geopolymer additive) [77].

Geopolymers may also be used to stabilize/immobilize various pollutants [106], including heavy metals and their ions [107], or filter them from water [108], due to their adsorption properties, which also speaks in their favor regarding their ability to stabilize nanoparticles used to enhance their antimicrobial properties. Other types of nanoparticles, including iron oxide nanoparticles, are even used to enhance their pollutant immobilization properties [109]. However, the issue of the potential risk of geopolymers releasing nanoparticles into the environment is not yet sufficiently investigated [105] and careful tests and/or LCA (life-cycle assessment) of geopolymer composites with nanoparticles (or other antimicrobial additives) should be performed before the application of any particular geopolymer composites, to minimize risks for public health and the environment.

6. Conclusions

The review shows the importance and various methods of hydrophobic and antimicrobial protection of geopolymers. Alternatively, it also shows the possibility of using geopolymers (including those with hydrophobic or antimicrobial modifications) as surface protection of other materials, including steel and OPC-based materials. Siloxanes, such as PDMS, appear to be one of the best types of additive to achieve hydrophobicity, while antimicrobial metals (especially silver, copper, or titanium dioxide), in the form of ions, nanoparticles, and microparticles, may serve as effective antimicrobial or photocatalytic additives. Geopolymers may also be modified with epoxy resins, to improve their mechanical properties, durability, and adhesion to other types of surface, such as steel or OPC-based concrete. This makes modified geopolymers an ideal surface protection method in aggressive environment, including marine applications.

Microbially induced degradation of construction materials presents a lasting problem for durability of OPC-based concrete, metal structures etc., which also leads to higher CO_2 emissions from OPC/metal manufacturing and additional needs and expenses for repairs and replacement of structures, leading to possible problems with infrastructure and building deterioration. Geopolymers, including hydrophobically and antimicrobially modified geopolymers, may be used to both improve the durability of new structures, while also being usable to preserve the existing ones, although the risks of the potential release of dangerous materials, such as nanoparticles, should be considered with every particular composite and tests of their release into the environment should be considered before application.

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