Properties and Durability Performance of Lightweight Fly Ash Based Geopolymer Composites Incorporating Expanded Polystyrene and Expanded Perlite

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Abstract: In this study, the use of expanded polystyrene and expanded perlite as lightweight aggregates for the preparation of lightweight geopolymers is tested. The geopolymers’ performance was evaluated through physical, mechanical and thermal testing. Polypropylene fibers were used as reinforcement agents, while the long-term durability was assessed through repeated wet–dry and freeze–thaw cycles and sorptivity tests. The results showed that the introduction of lightweight aggregates in the geopolymer mixes decreased the compressive and flexural strength of the specimens by 77% and 35%, respectively. However, the density and thermal conductivity were substantially improved because of the addition of low-density aggregates. The fiber reinforcement of lightweight samples led to a drastic increase in flexural strength by 65%, leaving unaffected the compressive strength and density of the specimens. The freeze–thaw and sorptivity tests were also improved after the introduction of both aggregates and fibers. Lightweight geopolymer composites exhibiting density in the range of 1.0–1.6 g/cm$^3$, compressive strength of 10–33 MPa, flexural strength of 1.8–6.3 MPa, thermal conductivity of 0.29–0.42 W/mK, and sorptivity of 0.031–0.056 mm/min$^{0.5}$ were prepared.

Keywords: lightweight geopolymer; expanded polystyrene; expanded perlite; mechanical properties; thermal conductivity; microstructure; durability

1. Introduction

Lightweight building materials, offering superior thermal and acoustic performance, have seen a substantial increase in demand in recent years. Indeed, these materials efficiently minimize construction dead load, construction time, and labor expenses involved in handling or transportation and are responsible for significant energy savings within buildings [1–4].

Today, several cement-based, lightweight products including load-bearing (bricks, cladding panels, slabs, reinforced concrete beams, etc.) or non-loading-bearing elements (building partitions, road foundations, energy absorption systems, etc.) have found widespread use in many construction applications [5]. In most cases, the main constituent of such products is ordinary Portland cement (OPC), a well-established material in the building sector whose production is rising by 9% annually around the globe [6,7]. However, its production accounts for large amounts of carbon dioxide (CO$_2$) emissions corresponding to an average of 6% of global emissions. At the same time, non-renewable natural resources are consumed during the calcination process, such as limestone and clay [6,8]. Therefore, the unsustainable nature of OPC combined with the ever-increasing demand makes the research and development of alternative building materials more crucial than ever.

A subgroup of alkali-activated materials, named geopolymers [9–12], is a promising cement replacement in view of sustainable building materials’ production, cutting down on natural resources and energy use [13,14], as well as valorizing several waste
The synthesis of these materials is based on the alkali activation of a solid aluminosilicate precursor, often an industrial waste or by-product (fly ash, slag, CDWs, etc.), at mild curing conditions. The products have exceptional properties such as excellent early-age performance, high mechanical properties, good long-term service, and durability performance [18–20].

A field of geopolymers’ applications is related with the development of lightweight components [5,21,22]. The development of lightweight geopolymers follows that of the OPC counterparts, including two basic methods: (a) foaming [23,24] and (b) porous material filling [25,26]. Among them, the second offers simplicity since it involves the mixing of hollow or porous particles (expanded perlite [27], expanded polystyrene [28], expanded clay [29], expanded glass granules [26], exfoliated vermiculite [30], pumice [27], etc.) into the geopolymer slurry to create lightweight geopolymer materials. The nature of such particles can reduce the density of the final products, limit the heat and sound transmission, and adjust the amount of water that will be adsorbed by the material [5]. Additionally, many hollow or porous particles may be produced on an industrial scale or developed from waste materials, making them readily available and reasonably priced.

Expanded polystyrene (EPS) is a thermoplastic that is incredibly light, durable, and inexpensive, exhibiting low thermal conductivity. The main applications of EPS involve lightweight packaging and a variety of thermal insulation products [31]. However, after the end of its life cycle, EPS can cause serious environmental issues since it is often either landfilled or burned [32]. Several recycling techniques have been proposed [33], although they sometimes include the use of dangerous solvents [34]. A reliable method to recycle EPS in the building sector is by incorporating EPS particles in lightweight building materials [35,36]. Another material that is widely used in building material production is expanded perlite (ExP). ExP originates from natural volcanic rocks and obtains a porous structure after the appropriate processing. It is commonly used as a filler or cement replacement and as an insulator in cases of acoustic, thermal, and fire applications [37–39].

Lately, several research studies are reported concerning the utilization of EPS [4,28,40–49] and ExP [27,50–52] in the geopolymer technology as lightweight aggregates. In these studies, emphasis has been placed on understanding the correlation between the composition, structure, and properties of the produced materials. Specifically, the effect of the aggregate’s introduction on the physical properties, mechanical strength, and thermal characteristics of the produced geopolymers has been widely studied [27,28,40,43,51]. Moreover, the interfacial transition zone between matrix and aggregate, a key factor for the microstructure of these composite materials, has also been investigated [4,41,42,47,48]. However, a crucial aspect of the service life of such building materials is their long-term behavior under various conditions and environments that has been scantly reported [49].

In this study, EPS and ExP are utilized as lightweight aggregates in the preparation of geopolymer composites. The performance of the lightweight aggregates is investigated by measuring physical, mechanical, and thermal properties. Then, the geopolymers are reinforced with short plastic fibers to improve their flexural strength and the behavior after the first crack is examined. The microstructure of the lightweight geopolymer composites is investigated through an electronic microscope to explore the bonding between the matrix and aggregates/fibers. Finally, the durability performance of the composites is evaluated by means of wet–dry and freeze–thaw cycles and sorptivity tests.

2. Materials and Methods

Fly ash (FA) from the power station of Megalopolis in Greece (Type F, according to ASTM C618) was used as raw material and it was pulverized to obtain the typical fineness of the ones used in the industrial formulation of cementitious materials (d50 = 20 µm). Its particle size distribution (Laser Particle Analyser MALVERN Mastersizer 2000) is shown in Figure 1, while the chemical composition, determined by XRF (PaNalytical Epsilon 1), and the mineralogical composition, determined by XRD (Bruker D8 ADVANCE/Diffrac.Eva v3.1 software), are presented in Table 1 and Figure 2, respectively. Figure 1 and Table 1 also
show the particle size distribution and chemical composition of the ExP used as one of the lightweight aggregates in this study.

Figure 1. Particle size distributions of FA (a) and ExP (b).

Table 1. Chemical composition of FA and ExP (% wt.).

| Composition | FA      | ExP    |
|------------|---------|--------|
| SiO₂       | 44.15   | 72.51  |
| Al₂O₃      | 16.99   | 13.73  |
| Fe₂O₃      | 9.39    | 1.28   |
| CaO        | 15.15   | 1.39   |
| MgO        | 2.89    | 0.37   |
| K₂O        | 2.00    | 3.67   |
| Na₂O       | 0.57    | 3.98   |
| SO₃        | 4.60    | -      |
| TiO₂       | 0.75    | 0.15   |
| P₂O₅       | 0.25    | -      |
| LOI *      | 2.76    | 2.92   |

* Loss on ignition.

Figure 2. Mineralogical composition of FA.
The geopolymer synthesis involved the preparation of the activation solution and the mixing with the raw materials and aggregates/additives. Specifically, NaOH (>99%, CAS: 1310-73-2) anhydrous pellets were dissolved in distilled water. Then, soluble Si in the form of alkali silicates (Na$_2$SiO$_3$ with SiO$_2$ = 27.56–28.39% wt. and Na$_2$O = 8.53–8.79% wt., Multiplass SA, Athens, Greece) was added and the solution was stirred for 1 h and left for 24 h to naturally cool down before use. Afterward, FA, activation solution, and aggregates/additives were mechanically mixed (standard mortar mixer: Controls 65-L0005) to form a homogenous slurry, which was casted, mildly vibrated, left at room temperature for 2 h, and cured at 70 °C for 48 h.

ExP (developed by NTUA [53]) and EPS (purchased by Fragoulakis supply company, Greece) were added in the geopolymer slurries as lightweight aggregates and their incorporation degree was set in the range of 3.0–15.0 and 0.5–3.0% wt., based on FA content, respectively. It must be noted that the range of incorporation was determined through preliminary testing. Crucial properties of ExP and EPS are presented in Figure 1, Tables 1 and 2. Polypropylene fibers (SikaFiber® P/P, 12 mm) were also used as a reinforcement in the geopolymer composites. The polypropylene (PP) fibers were introduced into the geopolymer mixes on a range of 0.25–1.0% v/v according to previous literature [54,55]. ExP or EPS were dry mixed with FA prior the addition of the activation solution, while PP fibers were added after the preparation of the geopolymer slurries.

From previous work [56], it was concluded that the optimum synthesis conditions of the FA matrix were the ones with $Si/Al^1 = 3.14$, $Na/Al^2 = 1.25$, $s/l^3 = 3.2$ ($^1$ Si/Al is the silicon to aluminum molar ratio and associates the total silicon quantity with aluminum content of the fly ash; $^2$ Na/Al is the alkali-to-aluminum-molar ratio and associates the sodium quantity in the activation solution with the aluminum content of the fly ash precursor; $^3$ s/l is the solids to liquids mass ratio; “S” refers to the sum of fly ash, NaOH (from NaOH reagent and waterglass) and SiO$_2$ (from waterglass) masses while “P” refers to the water added), $T = 70$ °C, and $t = 48$ h. This synthesis had density of 1.7 g/cm$^3$, 7 days’ flexural (FS), and compressive (UCS) strength of 3.4 MPa and 53.7 MPa, respectively. By the incorporation of EPS, ExP, and/or PP fibers, adjustments in the water content (solids/liquids) were applied to achieve workable slurries. Figure 3 presents the synthesis procedure of the lightweight geopolymer composites, while Table 3 shows the prepared samples along with their coding.

The lightweight geopolymers were characterized based on the density (according to mass to dimensions equation) and the mechanical and thermal properties. In particular, UCS and FS strength measurements were performed to prismatic specimens ($4 \times 4 \times 16$ cm) according to EN 196-1 after 7 days of aging. The modulus of elasticity was also measured following ASTM C 469. For these measurements, cylindrical specimens ($20 \times 10$ cm) were prepared and tested after 7 days of aging. For the measurements, strain gauges supplied by KYOWA CO., LTD were applied to the specimens. The post-cracking behavior of the fiber-reinforced products was assessed by loading 28-day prismatic ($4 \times 4 \times 16$ cm) specimens. Load and deflection values were exported by the application of a servo-controlled hydraulic machine and a linear variable-displacement transducer (length = $10.000 \pm 0.001$ mm) at a loading rate of $20 \mu$m/s. The flexural toughness, first crack, and residual strengths were calculated according to ASTM C 1018. The thermal conductivity was measured by means of the heat flow meter method, on a NETZSCH HFM 446 Lambda Heat Flow Meter, based on EN12667 and ASTM C518. The mean temperature and temperature difference between the plates were both set at 10 °C.

| Aggregate | Density (g/cm$^3$) | Water Absorption (%) | UCS (MPa) | $\lambda$ (W/mK) | Particles with d < 2 mm (%) | d > 2 mm (%) |
|-----------|-------------------|----------------------|------------|------------------|-----------------------------|--------------|
| EPS       | 0.038             | 1.0                  | 0.46       | 0.035            | 2.3                         | 97.7         |
| ExP       | 0.090             | 4.5                  | 0.30       | 0.039            | 85.1                        | 14.9         |
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Figure 3. Synthesis procedure followed in this study.

Table 3. Geopolymeric samples prepared in this study.

| Samples       | FA (% wt.) | Waterglass (% wt.) | NaOH (% wt.) | H₂O (% wt.) | EPS * (% wt.) | ExP * (% wt.) | PP Fibers (% v/v) |
|---------------|------------|--------------------|--------------|------------|-------------|-------------|------------------|
| GEO_REF       | 56.1       | 37.5               | 5.2          | 1.2        | -           | -           | -                |
| GEO_0.5EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 0.5         | -           | -                |
| GEO_1.0EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 1.0         | -           | -                |
| GEO_1.5EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 1.5         | -           | -                |
| GEO_2.0EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 2.0         | -           | -                |
| GEO_2.5EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 2.5         | -           | -                |
| GEO_3.0EPS    | 56.1       | 37.5               | 5.2          | 1.2        | 3.0         | -           | -                |
| GEO_3.0ExP    | 56.1       | 37.5               | 5.2          | 1.2        | -           | 3.0         | -                |
| GEO_6.0ExP    | 56.1       | 37.5               | 5.2          | 1.2        | -           | 6.0         | -                |
| GEO_9.0ExP    | 56.1       | 37.5               | 5.2          | 1.2        | -           | 9.0         | -                |
| GEO_12.0ExP   | 56.1       | 37.5               | 5.2          | 1.2        | -           | 12.0        | -                |
| GEO_15.0ExP   | 56.1       | 37.5               | 5.2          | 1.2        | -           | 15.0        | -                |
| GEO_3.0EPS_0.25PP | 56.1 | 37.5       | 5.2          | 1.2        | 3.0         | -           | 0.25             |
| GEO_3.0EPS_0.50PP | 56.1 | 37.5       | 5.2          | 1.2        | 3.0         | -           | 0.50             |
| GEO_3.0EPS_0.75PP | 56.1 | 37.5       | 5.2          | 1.2        | 3.0         | -           | 0.75             |
| GEO_3.0EPS_1.00PP | 56.1 | 37.5       | 5.2          | 1.2        | 3.0         | -           | 1.00             |

* Fly ash based.

The durability performance was assessed based on three tests: (i) sorptivity tests (determination of absorption rate by capillary suction during initial contact in water—ASTM C1585), (ii) wet–dry cycles (repeated wetting and drying of hardened specimens, record of material losses, water content changes, volume changes—ASTM D 559M, tested after 28 days of aging), and (iii) freeze–thaw cycles (repeated rapid freezing and thawing in water, record of specimens’ changes—ASTM C 666, tested after 28 days of aging). In each test, three specimens per synthesis were tested to check repeatability.

The microstructure of the lightweight geopolymer composites was investigated through scanning electron microscopy (SEM) on a JEOL JSM-S600 microscope. Fragments of composite samples were coated with gold prior the conduction of the measurements. The aggregates distribution inside the geopolymer matrix was also examined by stereomi-
crosscopy using a Zeiss Stemi 2000C stereo-microscope equipped with an Axio Cam ErC5 digital camera.

3. Results and Discussion
3.1. Lightweight Geopolymers

The introduction of EPS beads has a great effect on the density reduction in the produced geopolymeric composites but at the same time negatively affects their mechanical behavior (Figure 4). Indicatively, specimens containing 3% wt. EPS led to a reduction in density by 40% with proportional reduction in FS (37%) and higher reduction in UCS (77%) after 7 days of curing. This fact is attributed to the high dilution of the binding matrix by the presence of EPS beads causing a severe decrease in the mechanical strength. Similar behavior is also observed by other authors [4,43].

Figure 4. Mechanical properties and density of geopolymers containing EPS (a) and ExP (b) particles.

Contrary to the EPS effect, the introduction of ExP particles inside the geopolymer matrix did not yield the same positive effect on the density of the final products (Figure 4). Even after the introduction of 15% wt. ExP into the geopolymer mix, the density was reduced by only 27% (at 7 days). Similar results are reported by Top et al. [27]. This phenomenon is attributed to the higher particle size of EPS beads, as well as the fragility of ExP particles. Concerning fragility, the larger ExP particles are destroyed during the mechanical mixing of the geopolymer slurries resulting in lower volume fractions inside the matrix in relation to the EPS beads.

The aforementioned observations are confirmed by stereoscopic analysis of the samples. Figure 5 presents images showing the distribution of EPS and ExP particles inside the geopolymer matrix of samples containing 3% wt. EPS and 15% wt. ExP. The ExP led to worse distribution and therefore to higher density values in relation to EPS.

The analysis of the results showed that the lightweight geopolymer composite containing 3.0% wt. EPS and 0.5% v/v PP fibers holds the best combination of properties with a density of 1.0 g/cm³, and a UCS and FS of 12.7 MPa and 5.7 MPa, respectively. Figure 7 shows a fiber-reinforced specimen when subjected to flexural strength testing.
Nevertheless, this study can be used as the basis for the development of lightweight building materials that can serve in structural or nonstructural applications by controlling the EPS addition [57]:

- **Products for structural applications (UCS > 17 MPa, d > 1.35 g/cm$^3$) when the EPS addition is lower than 2% wt.**
- **Products for nonstructural applications (UCS < 17 MPa, d < 1.35 g/cm$^3$) when the EPS addition is higher than 2% wt.**

3.2. Matrix Fiber Reinforcement

The sample prepared by 3% wt. EPS was selected for fiber reinforcement experiments since it exhibits the lowest density combined with affordable mechanical strength (UCS of 12.4 MPa, FS of 2.2 MPa). The effect of PP fiber incorporation on the UCS and FS (at 7 days) of the lightweight geopolymer composites containing 3% wt. EPS is presented in Figure 6. There is a substantial boost on the FS of the specimens with the gradual incorporation of PP fibers in the geopolymer matrix. Indeed, the introduction of 1.0% $v/v$ fibers achieves almost three times higher FS values in comparison with the unreinforced sample. However, mixes containing PP fibers higher than 0.5% $v/v$ led to reduced workability, making the casting and compaction of the geopolymer slurries difficult without significant improvement of the FS (~9.5%). The UCS and density of the composites remained almost unaffected for the whole fiber incorporation range.

**Figure 4.** Mechanical properties and density of geopolymers containing EPS (a) and ExP (b) particles.

**Figure 5.** Stereoscopic images for geopolymer samples containing: (a) containing 3% wt. EPS and (b) 15% wt. ExP.

From the aforementioned results, EPS particles showed that they are the most effective agents for reducing the density of the geopolymer, keeping at the same time sufficient mechanical strengths. Apart from that, the utilization of EPS waste enhances the sustainability of the produced composites. In the case of ExP, an optimization of the mixing process must be developed to avoid the destruction of the ExP particles.

Nevertheless, this study can be used as the basis for the development of lightweight building materials that can serve in structural or nonstructural applications by controlling the EPS addition [57]:

- Products for structural applications (UCS > 17 MPa, d > 1.35 g/cm$^3$) when the EPS addition is lower than 2% wt.
- Products for nonstructural applications (UCS < 17 MPa, d < 1.35 g/cm$^3$) when the EPS addition is higher than 2% wt.
The analysis of the results showed that the lightweight geopolymer composite containing 3.0% wt. EPS and 0.5% PP fibers transformed the deflection-softening behavior of the reference geopolymer to deflection-hardening behavior. This is clearly visible by the enhancement of the area under the nonlinear portion of the load deflection curves in the case of the reinforced product. Therefore, the reinforced composite’s curve clearly indicates the transition from brittle to ductile behavior when PP fibers are added [58,59].

Figure 6. UCS and FS of geopolymers reinforced with PP fibers.

Figure 7. Fiber-reinforced specimen under flexural strength testing.

To assess the post-cracking behavior of the selected reinforced matrix (3.0% w/w EPS and 0.5% v/v PP), measurements according to ASTM C 1018 were performed. Indeed, a research study on flexural behavior of FA-based geopolymer composites is underway. Figure 8 presents the load–deflection curves of the reference (GEO_REF) and reinforced (GEO_3EPS_0.5PP) samples. The incorporation of the PP fibers inside the geopolymer matrix greatly improved the behavior of the material after the first crack. In particular, the incorporation of 0.5% v/v PP fibers transformed the deflection-softening behavior of the reference geopolymer to deflection-hardening behavior. This is clearly visible by the enhancement of the area under the nonlinear portion of the load deflection curves in the case of the reinforced product. Therefore, the reinforced composite’s curve clearly indicates the transition from brittle to ductile behavior when PP fibers are added [58,59].
The post-cracking behavior of the reinforced product has also been quantified according to ASTM C 1018 (Table 4). Table 4 includes the average response quantities for flexural behavior of the examined samples. The ductile behavior of the reinforced geopolymer composite is confirmed by the values of the toughness indices; $I_{10} > 10$ and $I_{20} > 20$ [60]. Furthermore, the toughness of the reinforced geopolymer is notably increased after the first crack.

Table 4. Average response quantities for flexural behavior.

| Quantities   | Unit | GEO_REF | GEO_3EPS_0.5PP |
|--------------|------|---------|----------------|
| First crack  |      |         |                |
| Load         | N    | 0.808   | 0.684          |
| deflection   | mm   | 0.027   | 0.028          |
| Toughness    | Nm   | 0.020   | 0.020          |
|              |      |         |                |
| $d_{5}$      | Load | -       | 0.960          |
| deflection   | mm   | -       | 0.085          |
| Toughness    | Nm   | -       | 0.080          |
| $I_{5}$      | -    | -       | 4.8            |
| $R_{5,10}$   | -    | -       | 115.8          |
|              |      |         |                |
| $d_{10}$     | Load | -       | 1.091          |
| deflection   | mm   | -       | 0.156          |
| Toughness    | Nm   | -       | 0.170          |
| $I_{10}$     | -    | -       | 10.6           |
| $R_{10,20}$  | -    | -       | 129.3          |
|              |      |         |                |
| $d_{20}$     | Load | -       | 1.160          |
| deflection   | mm   | -       | 0.297          |
| Toughness    | Nm   | -       | 0.34           |
| $I_{20}$     | -    | -       | 23.5           |
| Ultimate crack | Load | -       | 1.197          |
| deflection   | mm   | -       | 325.3          |
| Toughness    | Nm   | -       | 0.390          |

Table 4 also presents the elastic modulus values of the reference geopolymer and the reinforced composite. The incorporation of EPS and PP fibers in the geopolymer matrix had as an effect the reduction in the elasticity modulus. Both EPS ($\approx 0.5$ GPa) and PP fibers ($\approx 4.0$ GPa) possess low modulus values and the dilution of the geopolymeric matrix with such materials leads to products with improved ductile behavior.
3.3. Microstructure Analysis

Figure 9 presents SEM micrographs of the matrix containing 3% wt. EPS and 0.5% v/v PP, showing the good dispersion of fibers in the geopolymer matrix. In particular, the PP fibers seem to surround the EPS beads, enhancing the strength of the matrix (Figure 9a) [61]. The EPS beads exhibit a good cohesion with the matrix. Furthermore, the incorporation of PP fibers leads to a moderate degree of bonding with the geopolymer matrix, as shown by Figure 9b. This fact is confirmed by the weak interfacial transition zone and the almost smooth surface of the PP fibers, showing that little quantity of the geopolymer matrix covers the PP fibers surface. The moderate bonding degree of PP fibers has also been referenced by other authors [58,62].

![SEM images of fiber-reinforced matrix (3% wt. EPS and 0.5% wt. PP fibers) received at low (a) and high (b) magnification.](image)

Figure 9. SEM images of fiber-reinforced matrix (3% wt. EPS and 0.5% wt. PP fibers) received at low (a) and high (b) magnification.

3.4. Thermal Performance

The thermal performance of the produced geopolymers was determined by thermal conductivity measurements, presented in Table 5.

Table 5. Thermal conductivity values of selected geopolymer samples.

| Sample         | Density (g/cm³) | Measured Temperatures (°C, K) | Thermal Conductivity (W/(m·K)) |
|----------------|-----------------|-------------------------------|-------------------------------|
| GEO_REF        | 1.72            | 9.0, 5.1                      | 0.538                         |
| GEO_1.5EPS     | 1.28            | 8.9, 5.6                      | 0.418                         |
| GEO_3EPS       | 1.03            | 9.5, 6.8                      | 0.321                         |
| GEO_6ExP       | 1.51            | 9.9, 6.3                      | 0.481                         |
| GEO_15ExP      | 1.20            | 9.7, 6.4                      | 0.441                         |
| GEO_3EPS_0.5PP | 0.98            | 10.2, 7.9                     | 0.291                         |

The incorporation of lightweight aggregates leads to the reduction in the samples’ density, which is also reflected in their thermal conductivity values. A comparison between the different lightweight aggregates showed that the EPS was more effective in reducing the density and therefore the thermal conductivity of the produced geopolymers. The product containing 3% wt. EPS exhibit a thermal conductivity of 0.32 W/mK. Furthermore, the reinforcement of the geopolymers with PP fibers resulted in a slightly lower value of thermal conductivity (0.29 W/mK). The overall reduction in the thermal conductivity value by the incorporation of both EPS beads and PP fibers exceeds 45%.
3.5. Durability Performance

3.5.1. Sorptivity Tests

In Figure 10, the water absorption plots of the reference sample (GEO_REF) and the reinforced composite (GEO_3EPS_0.5PP) are presented. Both samples exhibit a similar water absorption rate through capillary suction. The GEO_3EPS_0.5PP sample initially absorbs a higher amount of water. However, after 40 min of testing, a reversal of this phenomenon was observed and the water absorption rate of the GEO_REF sample became higher. It is worth mentioning that the geopolymer paste has the ability to absorb water like OPC cement paste, while EPS and PP fibers behave as water barriers. However, the pronounced capillary pores of the geopolymer composite leads to an initial higher absorption rate in relation to the reference one. Then, the insulating nature of both EPS and PP fibers takes place, lowering the final water absorption of composite. Therefore, the EPS and PP fibers occupy a high fraction of the specimens' volume (~80%), resulting in a slight reduction in the water absorption values. Figure 11 presents the specimens submitted to sorptivity tests.

![Figure 10. Water absorption (%) vs. time (min) for the reference and reinforced samples.](image)

![Figure 11. Photo of the tested specimens.](image)

To export the sorptivity values of the samples, diagrams of the water absorption per unit area (i) vs. square root of time \( (t^{0.5}) \) were plotted. The slope of the curves indicates the sorptivity value. Indicative sorptivity curves are shown in Figure 12 for the GEO_REF and GEO_3EPS_0.5PP samples.
In Table 6, the sorptivity values of both specimens are listed, as they resulted from linear regression. In addition, the same table presents $R^2$ factors that reveal the goodness of the data fitting. The fitting of the sorptivity values is near excellent for all the tested specimens. The sorptivity of the reference geopolymer was calculated at 0.0555 mm/min$^{0.5}$, while that of the reinforced counterpart was found to be lower (0.0314 mm/min$^{0.5}$). These are satisfactory values since they lie within the acceptable range set for the sorptivity of cementitious materials [63].

**Table 6.** Sorptivity and $R^2$ values of tested geopolymers.

| Samples            | Sorptivity (mm/min$^{0.5}$) | $R^2$ (%) | Average S (mm/min$^{0.5}$) |
|--------------------|------------------------------|-----------|----------------------------|
| GEO_REF            | 0.0586                       | 99.8      | 0.0555                     |
|                    | 0.0551                       | 99.3      |                            |
|                    | 0.0527                       | 98.9      |                            |
| GEO_3EPS_0.5PP     | 0.0311                       | 99.6      | 0.0314                     |
|                    | 0.0319                       | 99.0      |                            |
|                    | 0.0312                       | 98.0      |                            |

3.5.2. Wet–Dry and Freeze–Thaw Performance

The performance of the GEO_REF and GEO_3EPS_0.5PP samples after 50 cycles of wetting/drying and freezing/thawing is shown in Figure 13. No significant weight loss (<1%) and corrosion of the specimens were recorded during the wetting/drying of both reference and reinforced geopolymers. In particular, the specimens’ appearances were examined through visual inspection and no surface deterioration or peeling effect was observed.

Concerning the freeze–thaw performance, a considerable reduction in the reference specimens’ mass was recorded (~7%) that was also supported by the visual inspection (Figure 14). Indeed, the reference specimens displayed extended corrosion with collapsed corners. However, with the reinforcement of the specimens with PP fibers, as well as the introduction of EPS beads that act as lightweight aggregates, the matrix reversed the performance of FA geopolymers through accelerating freeze–thaw testing. In particular, that the reinforced sample exhibits significant mass stability (<1.2%) after 50 cycles was also validated by the visual inspection.
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• Figure 14. Reference (left) and reinforced (right) specimen after the end of freeze–thaw cycles.

4. Conclusions

The conclusions of these study can be drawn as follows:

• EPS and ExP can efficiently be introduced to a geopolymer matrix and reduce the
total weight of the geopolymer products. Among the two lightweight aggregates,
EPS achieves a better combination of physical, mechanical, and thermal properties,
mainly because of its stability and better distribution inside the geopolymer matrix.
The incorporation of 3% wt. EPS led to the enhancement of the thermal performance of
the samples (40% reduction in thermal conductivity) but at the same time deteriorated
their mechanical performance (77 and 37% reduction in UCS and FS, respectively).

• The aggregate incorporation rate controls the final product’s properties and subse-
sequently its applications in the building sector. Indeed, EPS content lower than
2% wt. gives lightweight building materials for structural applications (USC > 17 MPa,
d > 1.35 g/cm$^3$), while EPS content higher than 2% wt. gives lightweight building
materials for nonstructural applications (USC < 17 MPa, d < 1.35 g/cm$^3$).

• The moderate flexural behavior of the EPS-based composites is substantially improved
by the addition of 0.5% v/v PP fibers (61%). The incorporation of EPS and fibers
transformed the post-cracking behavior from fragile to ductile, considerably increasing
the materials’ toughness.

• A comparison between the reference and reinforced composite samples showed that
the incorporation of both lightweight aggregates and plastic fibers led to a beneficiary
effect on the long-term performance. The capillary water absorption was reduced
while the behavior after repeated freezing and thawing was greatly improved.
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References
1. Castañeda, D.; Silva, G.; Salirrosas, J.; Kim, S.; Bertolotti, B.; Nakamatsu, J.; Aguilar, R. Production of a Lightweight Masonry Block Using Alkaline Activated Natural Pozzolana and Natural Fibers. Constr. Build. Mater. 2020, 253, 119143. [CrossRef]
2. Yang, Y.; Zhou, Q.; Deng, Y.; Lin, J. Reinforcement Effects of Multi-Scale Hybrid Fiber on Flexural and Fracture Behaviors of Ultra-Low-Weight Foamed Cement-Based Composites. Cem. Conc. Compos. 2020, 108, 103509. [CrossRef]
3. Gallego-Schmid, A.; Chen, H.-M.; Sharmina, M.; Mendoza, J.M.F. Links between Circular Economy and Climate Change Mitigation in the Built Environment. J. Clean. Prod. 2020, 260, 121115. [CrossRef]
4. Colangelo, F.; Rovilli, G.; Ricciotti, L.; Ferrándiz-Mas, V.; Messina, F.; Ferone, C.; Tarallo, O.; Cioffi, R.; Cheeseman, C.R. Mechanical and Thermal Properties of Lightweight Geopolymer Composites. Cem. Conc. Compos. 2018, 86, 266–272. [CrossRef]
5. Tale Masoule, M.S.; Bahrami, N.; Karimzadeh, M.; Mohasanati, B.; Shoaei, P.; Ameri, F.; Ozbakkaloglu, T. Lightweight Geopolymer Concrete: A Critical Review on the Feasibility, Design, Durability Properties, and Microstructure. Ceram. Int. 2022, 48, 10347–10371. [CrossRef]
6. Amran, Y.H.M.; Alyousef, R.; Alabdujabbar, H.; El-Zeadani, M. Clean Production and Properties of Geopolymer Concrete: A Review. J. Clean. Prod. 2020, 251, 119679. [CrossRef]
7. Gartner, E. Industrially Interesting Approaches to “Low-CO2” Cements. Cem. Conc. Res. 2004, 34, 1489–1498. [CrossRef]
8. Andrew, R.M. Global CO2 Emissions from Cement Production, 1928–2018. Earth Syst. Sci. Data 2019, 11, 1675–1710. [CrossRef]
9. Singh, B.; Ishwarya, G.; Gupta, M.; Bhattacharyya, S.K. Geopolymer Concrete: A Review of Some Recent Developments. Constr. Build. Mater. 2015, 85, 78–90. [CrossRef]
10. Luukkonen, T.; Abdollahnejad, Z.; Yliniemi, J.; Kinnunen, P.; Illikainen, M. One-Part Alkali-Activated Materials: A Review. Cem. Conc. Res. 2018, 103, 21–34. [CrossRef]
11. Panitsa, O.A.; Kioupis, D.; Kakali, G. Thermal and Microwave Synthesis of Silica Fume-Based Solid Activator for the One-Part Geopolymerization of Fly Ash. Environ. Sci. Pollut. Res. 2022, 29, 59513–59523. [CrossRef]
12. Tee, K.F.; Mostofizadeh, S. An Experimental Study of the Effects of Low-Calcium Fly Ash on Type II Concrete. Ceramics 2021, 4, 600–617. [CrossRef]
13. Turner, L.K.; Collins, F.G. Carbon Dioxide Equivalent (CO2-e) Emissions: A Comparison between Geopolymer and OPC Cement Concrete. Constr. Build. Mater. 2013, 43, 125–130. [CrossRef]
14. McLellan, B.C.; Williams, R.P.; Lay, J.; van Riessen, A.; Corder, G.D. Costs and Carbon Emissions for Geopolymer Pastes in Comparison to Ordinary Portland Cement. J. Clean. Prod. 2011, 19, 1080–1090. [CrossRef]
15. Kioupis, D.; Skaropoulou, A.; Tsivilis, S.; Kakali, G. Alkali Leaching Control of Construction and Demolition Waste Based. MATEC Web Conf. 2018, 149, 01064. [CrossRef]
16. Peng, Y.; Unluer, C. Analyzing the Mechanical Performance of Fly Ash-Based Geopolymer Concrete with Different Machine Learning Techniques. Constr. Build. Mater. 2022, 316, 125785. [CrossRef]
17. Li, Y.; Min, X.; Ke, Y.; Liu, D.; Tang, C. Preparation of Red Mud-Based Geopolymer Materials from MSWI Fly Ash and Red Mud by Mechanical Activation. Waste Manag. 2019, 83, 202–208. [CrossRef]
18. Provis, J.L. Geopolymers and Other Alkali Activated Materials: Why, How, and What? Mater. Struct. 2014, 47, 11–25. [CrossRef]
19. Rasaki, S.A.; Bingxue, Z.; Guarecuco, R.; Thomas, T.; Minghui, Y. Geopolymer for Use in Heavy Metals Adsorption, and Advanced Oxidative Processes: A Critical Review. J. Clean. Prod. 2019, 213, 42–58. [CrossRef]
20. Chindaprasirt, P.; Lao-un, J.; Zaetang, Y.; Wongkvanklom, A.; Phoo-ngernkham, T.; Sata, V. Thermal Insulating and Fire Resistance Performances of Geopolymer Mortar Containing Auto Glass Waste as Fine Aggregate. J. Build. Eng. 2022, 60, 105178. [CrossRef]
21. Bai, C.; Colombo, P. Processing, Properties and Applications of Highly Porous Geopolymers: A Review. Ceram. Int. 2018, 44, 16103–16118. [CrossRef]
22. Zhang, X.; Bai, C.; Qiao, Y.; Wang, X.; Jia, D.; Li, H.; Colombo, P. Porous Geopolymer Composites: A Review. Composites Part A Appl. Sci. Manuf. 2021, 150, 106629. [CrossRef]
23. Kioupis, D.; Zisimopoulou, A.; Tsivilis, S.; Kakali, G. Development of Porous Geopolymers Foamed by Aluminum and Zinc Powders. Ceram. Int. 2021, 47, 26280–26292. [CrossRef]
24. Novais, R.M.; Pullar, R.C.; Labrincha, J.A. Geopolymer Foams: An Overview of Recent Advancements. Prog. Mater. Sci. 2020, 109, 100621. [CrossRef]
25. Liu, M.Y.J.; Alengaram, U.J.; Jumaat, M.Z.; Mo, K.H. Evaluation of Thermal Conductivity, Mechanical and Transport Properties of Lightweight Aggregate Foamed Geopolymer Concrete. Energy Build. 2014, 72, 238–245. [CrossRef]
26. Humur, G.; Çevik, A. Mechanical Characterization of Lightweight Engineered Geopolymer Composites Exposed to Elevated Temperatures. *Ceram. Int.* **2022**, *48*, 13634–13650. [CrossRef]

27. Top, S.; Vapur, H.; Alltner, M.; Kaya, D.; Ekicibil, A. Properties of Fly Ash-Based Lightweight Geopolymer Concrete Prepared Using Pumice and Expanded Perlite as Aggregates. *J. Mol. Struct.* **2020**, *1202*, 127236. [CrossRef]

28. Li, Z.; Chen, W.; Hao, H.; Khan, M.Z.N.; Pham, T.M. Dynamic Compressive Properties of Novel Lightweight Ambient-Cured EPS Geopolymer Composite. *Constr. Build. Mater.* **2021**, *273*, 122044. [CrossRef]

29. Ouda, A.S.; Rashad, A.M. An Investigation on the Performance of Lightweight Mortar-Based Geopolymer Containing High-Volume LECA Aggregate against High Temperatures. *Environ. Sci. Pollut. Res.* **2022**, *29*, 26631–26647. [CrossRef] [PubMed]

30. Medri, V.; Papa, E.; Mazzocchi, M.; Laghi, L.; Morganti, M.; Francisconi, J.; Landi, E. Production and Characterization of Lightweight Vermiculite/Geopolymer-Based Panels. *Mater. Des.* **2015**, *85*, 266–274. [CrossRef]

31. Doroudiani, S.; Omidian, H. Environmental, Health and Safety Concerns of Decorative Mouldings Made of Expanded Polystyrene in Buildings. *Build. Environ.* **2010**, *45*, 647–654. [CrossRef]

32. Poletto, M.; Dettenborn, J.; Zeni, M.; Zattera, A.J. Characterization of Composites Based on Expanded Polystyrene Wastes and Wood Flour. *Waste Manag.* **2011**, *31*, 779–784. [CrossRef]

33. Shin, C. Filtration Application from Recycled Expanded Polystyrene. *J. Colloid Interface Sci.* **2006**, *302*, 267–271. [CrossRef]

34. Amianti, M.; Botaro, V.R. Recycling of EPS: A New Methodology for Production of Concrete Impregnated with Polystyrene (CIP). *Cem. Concr. Compos.* **2008**, *30*, 23–28. [CrossRef]

35. Sayadi, A.A.; Tapia, J.V.; Neitzert, T.R.; Clifton, G.C. Effects of Expanded Polystyrene (EPS) Particles on Fire Resistance, Thermal Conductivity and Compressive Strength of Foamed Concrete. *Constr. Build. Mater.* **2016**, *112*, 716–724. [CrossRef]

36. Babu, K.G.; Babu, D.S. Behaviour of Lightweight Expanded Polystyrene Concrete Containing Silica Fume. *Cem. Concr. Res.* **2003**, *33*, 755–762. [CrossRef]

37. Vaou, V.; Panias, D. Thermal Insulating Foamy Geopolymers from Perlite. *Miner. Eng.* **2010**, *23*, 1146–1151. [CrossRef]

38. Kotwica, Ł.; Pichów, W.; Kapeluszna, E.; Różycka, A. Utilization of Waste Expanded Perlite as New Effective Supplementary Cementitious Material. *J. Clean. Prod.* **2017**, *140*, 1344–1352. [CrossRef]

39. Yilmazer Polat, B. Self Healing of Alkali Active Mortars with Expanded Perlite Aggregate. *Case Stud. Constr. Mater.* **2022**, *17*, e01225. [CrossRef]

40. Posi, P.; Ridtitirud, C.; Ekvong, C.; Chammanee, D.; Janthowong, K.; Chindaprasirt, P. Properties of Lightweight High Calcium Fly Ash Geopolymer Concretes Containing Recycled Packaging Foam. *Constr. Build. Mater.* **2015**, *94*, 408–413. [CrossRef]

41. Shi, J.; Liu, B.; Liu, Y.; Wang, E.; He, Z.; Xu, H.; Ren, X. Preparation and Characterization of Lightweight Aggregate Foamed Geopolymer Concretes Aerated Using Hydrogen Peroxide. *Constr. Build. Mater.* **2020**, *256*, 119442. [CrossRef]

42. Dueramae, S.; Sanboonsiri, S.; Suntadyon, T.; Aoudta, B.; Tangcharapat, W.; Jongpradist, P.; Pulngern, T.; Jitsangiam, P.; Jaturapatakkul, C. Properties of Lightweight Alkali Activated Controlled Low- Strength Material Using Calcium Carbide Residue— Fly Ash Mixture and Containing EPS Beads. *Constr. Build. Mater.* **2021**, *297*, 123769. [CrossRef]

43. Souza, T.B.; Lima, V.M.E.; Araujo, F.W.C.; Miranda, L.F.R.; Melo Neto, A.A. Alkali-Activated Slag Cellular Concrete with Expanded Polystyrene (EPS)—Physical, Mechanical, and Mineralogical Properties. *J. Build. Eng.* **2021**, *44*, 103387. [CrossRef]

44. Farhad, A.; Ayoub, D.; Zohaib, A. Development of Lightweight Rubberized Geopolymer Concrete by Using Polystyrene and Recycled Crumb-Rubber Aggregates. *J. Mater. Civ. Eng.* **2020**, *32*, 04019345. [CrossRef]

45. Qadir, G.; Rashid, Y.; Hassan, A.; Vall, E.; Saleh, S.; Salim, K. Development and Mechanical Testing of Porous-Lightweight Geopolymer Mortar. *Building 2021*, *11*, 1. [CrossRef]

46. Rashid, Y.; Alnaimat, F.; Mathew, B. Energy Performance Assessment of Waste Materials for Buildings in Extreme Cold and Hot Conditions. *Energies 2018*, *11*, 3131. [CrossRef]

47. Long, W.-J.; Lin, C.; Tan, X.-W.; Tao, J.-L.; Ye, T.-H.; Luo, Q.-L. Structural Applications of Thermal Insulation Alkali Activated Materials with Reduced Graphene Oxide. *Materials 2020*, *13*, 1052. [CrossRef]

48. Traven, K.; Wisniewski, W.; Češnovar, M.; Ducman, V. Microstructural Characterization of Alkali-Activated Composites of Lightweight Aggregates (LWAs) Embedded in Alkali-Activated Foam (AAF) Matrices. *Polymers 2022*, *14*, 1729. [CrossRef] [PubMed]

49. Kakali, G.; Kioupis, D.; Skaropoulou, A.; Tsivilis, S. Lightweight Geopolymer Composites as Structural Elements with Improved Insulation Capacity. *MATEC Web Conf.* **2018**, *149*, 01042. [CrossRef]

50. Szabó, R.; Dolgos, F.; Debreczeni, Á.; Musci, G. Characterization of Mechanically Activated Fly Ash-Based Lightweight Geopolymer Composite Prepared with Ultrahigh Expanded Perlite Content. *Ceram. Int.* **2022**, *48*, 4261–4269. [CrossRef]

51. Zhong, W.L.; Fan, L.F.; Zhang, Y.H. Experimental Properties of Lightweight Slag Based Geopolymer. *Ceram. Int.* **2022**, *48*, 20426–20437. [CrossRef]

52. Wang, Z.; Su, H.; Zhao, S.; Zhao, N. Influence of Phase Change Material on Mechanical and Thermal Properties of Clay Geopolymer Mortar. *Constr. Build. Mater.* **2016**, *120*, 329–334. [CrossRef]

53. Angelopoulos, P.M.; Maliachova, C.; Papakonstantinou, K.; Taxiarhou, M.; Diplas, S. Structural and Physical Characteristics of Fine Perlite Expanded with a Novel Perlite in a Vertical Electric Furnace. *Miner. Process. Extr. Metall.* **2016**, *125*, 71–80. [CrossRef]

54. Tayeh, B.A.; Akeed, M.H.; Qaidi, S.; Bakar, B.H.A. Influence of Microsilica and Polypropylene Fibers on the Fresh and Mechanical Properties of Ultra-High Performance Geopolymer Concrete (UHP-GPC). *Case Stud. Constr. Mater.* **2022**, *17*, e01367. [CrossRef]
55. Al-mashhadani, M.M.; Canpolat, O.; Aygörmez, Y.; Uysal, M.; Erdem, S. Mechanical and Microstructural Characterization of Fiber Reinforced Fly Ash Based Geopolymer Composites. Constr. Build. Mater. 2018, 167, 505-513. [CrossRef]

56. Panagiotopoulou, C.; Tsivilis, S.; Kakali, G. Application of the Taguchi Approach for the Composition Optimization of Alkali Activated Fly Ash Binders. Constr. Build. Mater. 2015, 91, 17-22. [CrossRef]

57. Neville, A.M. Properties of Concrete, 5th ed.; Pearson Education Limited: Essex, UK, 2011.

58. Shaikh, F.U.A. Deflection Hardening Behaviour of Short Fibre Reinforced Fly Ash Based Geopolymer Composites. Mater. Des. 2013, 50, 674–682. [CrossRef]

59. Kim, D.J.; Naaman, A.E.; El-Tawil, S. Comparative Flexural Behavior of Four Fiber Reinforced Cementitious Composites. Cem. Concr. Compos. 2008, 30, 917–928. [CrossRef]

60. Barr, B.I.G.; Liu, K.; Dowers, R.C. A Toughness Index to Measure the Energy Absorption of Fibre Reinforced Concrete. Int. J. Cem. Compos. Lightweight Concr. 1982, 4, 221–227. [CrossRef]

61. Alberti, M.G.; Enfedaque, A.; Gálvez, J.C.; Picazo, A. Recent Advances in Structural Fibre-Reinforced Concrete Focused on Polyolefin-Based Macro-Synthetic Fibres. Mater. Construcción 2020, 70, e206. [CrossRef]

62. Ranjbar, N.; Talebian, S.; Mehrali, M.; Kuenzel, C.; Cornelis Metselaar, H.S.; Jumaat, M.Z. Mechanisms of Interfacial Bond in Steel and Polypropylene Fiber Reinforced Geopolymer Composites. Compos. Sci. Technol. 2016, 122, 73–81. [CrossRef]

63. Hall, C. Water Sorptivity of Mortars and Concretes: A Review. Mag. Concr. Res. 2015, 41, 51–61. [CrossRef]