



Influence of wood pretreatment and fly ash particle size on the performance of geopolymer wood composite

Bright Asante^{1,2} · Goran Schmidt³ · Ronaldo Teixeira² · Andreas Krause^{1,3} · Holmer Savastano Junior²

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Abstract

In search for greener building materials, geopolymer wood composites (GWC) were produced through alkali activation of fly ash, using pine and eucalypt wood particles. The study examined the influence of grinding fly ash, wood species and hot water treatment of wood particles on the physical properties and specific compressive strength of GWC before and after 200 cycles of soaking and drying. Ash-grinding affected particle size distribution, as the hot water pretreatment of the wood affected its extractives. The particle size analysis showed that grinding decreased the mean particle size of raw ash by 55% and played a major role in the composite's properties, as lower densities and specific strength with high water absorption were recorded for GWC from raw ash than from ground ash. The ash-grinding step doubled the specific strength of the composites before the aging test. A decrease in specific strength (15–32%) was observed for all composites after the soaking and drying cycles. Hot water washing of the wood resulted in a 47% and 67% reduction in the extractive content of the pine and eucalypt particles, respectively. An improvement of 27% and 3% was noted in specific strength values respectively for GWC with treated pine and eucalypt particles. In general, lower specific strength was recorded for pine-based composites than eucalypt ones, due to the fast impregnation and high water absorption from the mixture by pine particles. It was revealed that hot water treatment of wood improves GWC properties less compared to wood species or fly ash particle size.

1 Introduction

Current research aims at finding solutions to the ever-increasing population and its demand for infrastructure and accommodation, coupled with high waste accumulation. The cascade use of secondary resources, such as postconsumer thermoplastic waste or combustion byproducts, helps avoid solid wastes, keeps carbon in the material cycle and upcycles low value resources by substituting imported virgin building products. The production of Ordinary Portland Cement (OPC) contributes to a significant amount of CO₂ in the

environment. These emissions from OPC production and the environmental awareness of climate change have compelled society to seek for second generation materials with less environmental impact, with geopolymer being one of the prominent alternatives. Geopolymer (an alkali-activated cement) is estimated to produce about 55–75% less CO₂ compared to OPC (Yang et al. 2013). Since the discovery of geopolymer by Davidovits in 1970s, research has been ongoing to ascertain how best to utilize this cementitious building material.

Geopolymers are made-up of mineral compositions containing high amounts of aluminium (Al) and silicon (Si) and they are amorphous. In general, they can be produced of any material source that is rich in Si and Al. Currently, major research efforts for this binder focus on utilizing industrial wastes such as slag and fly ash as an alternative to natural raw material minerals such as kaolinite (Kumar et al. 2010; Kielé et al. 2020). Geopolymer is produced by alkaline activation of any aluminosilicate source material (Bakharev 2005). The reaction process results in the dissolution of the reactive aluminosilicate. The dissolved slurry undergoes polycondensation to produce a material with desired mechanical properties (Sofi et al. 2007). During the reaction

✉ Bright Asante
bright.asante@uni-hamburg.de

¹ Institute of Wood Sciences, University of Hamburg,
Leuschnerstrasse 91c, 21031 Hamburg, Germany

² Department of Biosystems Engineering, University
of São Paulo, Av. Duque de Caxias Norte 225, Jd. Elite,
Pirassununga, SP 13635-900, Brazil

³ Johann Heinrich Von Thünen Institute, Federal Research
Institute for Rural Areas, Forestry and Fisheries, Institute
of Wood Research, Leuschnerstrasse 91, 21031 Hamburg,
Germany

process, there is a gradual release of water. The geopolymer forms an amorphous three-dimensional network of aluminate and silicate units with charge balancing cation. Curing happens at ambient temperature and accelerates at elevated temperature (Sarmin et al. 2014).

Since geopolymer may be produced from many different raw material resources, specific characterization, pretreatment and processing procedures need to be considered. Each source of raw material differs in composition (e.g. alkali metal content and ratio), particle size and morphology. The geopolymerization varies with its raw materials and hence results in different microstructure, chemical and mechanical properties (Vickers et al. 2015).

The annual production of fly ash in the world from coal combustion is estimated to be around 700 Mt (million tons) (Ferreira et al. 2003; Argiz et al. 2015). Fly ash has mainly been used as a replacement for OPC because of its beneficial properties, especially with respect to its high compressive strength compared to cement (Abdullah et al. 2011). The replacement of OPC with fly ash up to 60% by mass is a notable development (Kumar et al. 2007). At present, multiple researches are focused on fly ash utilization as a precursor material for geopolymer, with large interest in cleaner production and minimizing waste.

In Brazil, about 4 Mt of fly ash are generated per year with the annual utilization for incorporation into cement and concrete accounting for about 30% of total fly ash production (Izidoro et al. 2012) and serves as a major industrial application for this inorganic residue in the country (Rohde et al. 2006). The low utilization potential and the operation of new coal-based thermal power plants are likely to increase the quantity of fly ash (Izidoro et al. 2012). Fly ash mainly consists of Fe_2O_3 , SiO_2 , Al_2O_3 with some potential toxic substances such as heavy metals from the coal and polyaromatic hydrocarbons that condense from the flue gas (Misengue et al. 2016). The large-scale storage and improper disposal of this waste act as a major source of air, water and land pollution (Ahmaruzzaman 2010). This present study is intended to not only mitigate and minimize the accumulation of fly ash but also to address the utilization of this waste in the synthesis of a high value added product.

The physical properties of fly ash—such as particle sizes and surface area—affect its reactivity, as well as the chemical and mechanical behavior of the geopolymer product formed (Erdoğan and Türker 1998; Van Jaarsveld et al. 2003). This indicates that particle size of the material is an important factor when it comes to the material selection, as it influences the reaction rate. According to Rosas-Casarez et al. (2018), it influences the rate of dissolution of aluminosilicate in the precursor material as the smaller particle size requires less time, hence a faster polymerization reaction.

For this reason, Rosas-Casarez et al. (2018) proposed that the activation and reactivity of fly ash could be improved by

adequate grinding. Mechanical grinding affects the microstructure of ash, causing a weakening in the vitreous chemical bonds of Si–O or Al–O. Beside the fact that it accelerates the dissolution of these bonds, it shortens the equilibrium time, gelation time, and the structuring of the new crystalline phases and the different reaction products, specifically the hydrated sodium aluminosilicate gel, which is known as the reaction product that gives the mechanical properties to the geopolymer (Rosas-Casarez et al. 2018).

Another way of steering geopolymer composite properties is the addition of lignocellulosic raw materials. Wood particles have been used as fillers in geopolymer wood composites (GWC) to reduce the density of the product (Sarmin 2016; Kielé et al. 2020). Halas et al. (2011) reported both positive and negative effects of the fly ash geopolymer with sawdust as filler. Halas et al. (2011) showed that a higher amount of sawdust had a negative effect on the compressive strength of the specimens. Duan et al. (2016) stated that lignocellulosic waste had a positive effect on the main properties of fly ash geopolymer and showed that the addition of sawdust (without any special pretreatment) improved the cracking resistance while drying. Wood as a lignocellulosic material mainly consists of lignin, cellulose, hemicellulose and extractives. Ye et al. (2018) studied the effect of lignin, cellulose and hemicellulose on geopolymer composites. The authors concluded that the degree of geopolymerization was clearly lowered by the alkaline degradation of hemicellulose, and higher concentrations of lignin and hemicellulose had a negative effect on the flexural and compressive strength of the geopolymer composites.

Although fly ash geopolymers have shown their applicability to wood, the variation in wood species and the complexity of wood offer drawbacks such as compatibility and long-term durability issues for these composites. The wood component, upon contact with the high alkali environment in the fly ash geopolymer, will lead to the leaching of non-structural polysaccharides and extractives from the wood. This might affect the interfacial reactions between geopolymer and wood, and the GWC properties. However, the intensity and the components (non-structural polysaccharides and extractives) that may leach out from the wood may differ among wood species. To avoid this negative impact from the non-structural polysaccharides and extractives, Ferraz et al. (2011) suggested removing these inhibitors by hot water (100 °C) pretreatment; this remains one of the cheapest extraction methods for wood. The easy accessibility and availability of water (as a solvent) make this pretreatment method more sustainable compared to other pretreatment methods. Hot water alters the chemical composition and the surface morphology of the biomass (Therasme et al. 2018) by removing some of the components—mainly extracts. To date, no report has been found neither in relation to the effect of pretreating the raw materials nor a comparison of these effects (i.e. wood species, hot water treatment of

wood together with fly ash particle size) on the performance of GWC.

This research investigates the influence of preparation of raw material on the physical properties, specific compressive strength and durability of geopolymer wood composites (GWC). The study of raw material focused on fly ash particle size (pre and post grinding) and hot water treatment of wood. In addition, the effect of two wood species on the GWC properties was assessed.

2 Materials and methods

2.1 Materials

Sodium silicate (Na_2SiO_3) pellets (SiO_2 63%, Na_2O 18%) and sodium hydroxide pellets (NaOH , 98%) were supplied by Dinâmica (Brazil), debarked sawn wood (*Eucalyptus grandis* W.Hill and *Pinus taeda* L.) was supplied by the Wood and Wood Structures Laboratory, São Carlos Engineering School (LAMEM/EESC) of the University of São Paulo (USP). Class F fly ash was supplied by Pozo Fly (Brazil).

2.1.1 Fly ash composition

The fly ash was divided into two groups. One group was ground further using an Astecma (model mb 20) ball mill for 1 h, whereas the other group remained in its raw state. The composition of the chemical oxides of the starting material (raw fly ash) was detected by X-ray fluorescence (XRF), using a PANalytical Axios Advanced. The results are shown in Table 1.

2.1.2 Characterization of wood particles and fly ashes

The morphology of the wood particles pre and post treatment was assessed using the field emission scanning electron microscope (FESEM) Quanta FEG Type 250, FEI Electron Optics (SN: D9122), Netherlands. The wood samples were gold-coated before imaging. Particle size distribution (PSD) and X-ray diffraction (XRD) studies were carried out on the raw and ground fly ashes. The PSD and XRD studies were done in a Partica Laser Scattering Particle Size Distribution Analyzer LA-950V2 and Rigaku Miniflex600 diffractometer, respectively. The XRD was carried out using a $\text{Cu-K}\alpha$ wavelength, 40 kV and 20 mA, in a 2θ range of 5° – 70° . Scanning electron microscopy (SEM) was conducted on both sets of ashes. SEM was carried out using the LEO 1525 GEMINI test machine. The fly ash samples were carbon-coated before imaging.

Table 1 Chemical composition (% by mass) of fly ash from XRF test

Component	Al_2O_3	SiO_2	SO_3	K_2O	Na_2O	CaO	TiO_2	Fe_2O_3
Share (%)	22.47	64.29	0.81	2.97	0.51	1.74	1.36	6.31

2.1.3 Lignocellulose materials processing and hot water pretreatment

Sawn wood pine and eucalypt boards with densities of 0.39 g/cm^3 and 0.56 g/cm^3 respectively, were cut to dimensions of $25 \text{ mm} \times 30 \text{ mm} \times 50 \text{ mm}$. These pieces of wood were milled and later sieved with a Manupen sieve vibrator for 1 h to separate the wood into different particle size fractions. Wood particles that could pass through the 1 mm sieve but which were retained in the 0.6 mm sieve were used for both pine and eucalypt. Hot water pretreatment was carried out on both sets of sieved particles according to the method described by Cabral et al. (2017). Water was heated up to 100°C in a 3.5 L container and 31.25 g of wood particles were introduced per 1 L water for 30 min. Finally, the recovered particles were washed with 1 L of tap water and placed in an oven at 60°C , until a moisture content of around 10% was reached.

2.1.4 Chemical composition of lignocellulose materials

The extract content of the wood samples was analyzed using the Accelerated Solvent Extraction (ASE 350) from Thermo Fisher Scientific (Dionex). Extraction was done using 2 g of wood under the conditions stated in Table 2. Wood particles that could pass through the 1 mm sieve but which were retained in 0.6 mm sieve were used for both pine and eucalypt in the extraction process. Extraction was first done using petrolether, followed by acetone/ water and lastly with water alone. The total extract was the summation of the extract content in these processes. The extractive-free wood was hydrolyzed for sugars using the method described by Lorenz et al. (2016). The extractive-free samples were then finely ground (vibrating mill, Duke).

Pre-hydrolysis Approximately 200 mg was weighed into a reaction vessel. The sample was mixed with 2 mL of 72% cold H_2SO_4 after which it was hydrolyzed in a thermostat for 1 h at 30°C . After one hour, the reaction of the

Table 2 Extraction conditions for extractive content

Solvent	Petrolether	Acetone/ H_2O (9:1)	H_2O
Static [min]	10	10	10
Cycles	2	2	2
Pressure [bar]	100	100	100
Temperature [$^\circ\text{C}$]	70	70	90

pre-hydrolysis was stopped by the addition of 6 mL of distilled water. Next, the suspension was transferred together with 50 mL of water into a volumetric flask and the samples were post-hydrolyzed by autoclave at 120 °C under 1.2 bar pressure (40 min for pine and 30 min for eucalyptus). After cooling the volumetric flasks, the condensed lignin was filtered off as a hydrolysis residue by means of a G4 glass filter crucible. From the filtrate, about 1 ml was taken for the sugar analysis. The hydrolysis residue was washed thoroughly with distilled water, dried at 105 °C and determined gravimetrically.

2.2 Composite preparation

The alkaline solution for activation was prepared using molar solutions of 3 M Na₂SiO₃ and 12 M NaOH in a weight ratio of 2.5:1. The solution was allowed to cool to ambient conditions prior to use. Fly ash was first dry-mixed with 20 wt% wood particles for 2 min. Water was then added to the solid mixture of fly ash and wood for an additional 2 min. The ratio of water to solid material was kept constant at 0.16 for all mixtures. Finally, the mixture was activated for 2 min at an alkaline solution to fly ash ratio of 0.47 for all mixtures. The activated mixture was cast in a 50 mm × 100 mm cylinder mold and allowed to stand at 25 ± 2 °C for 2 h before oven curing for 4 h at 103 ± 2 °C. To avoid cracks forming due to rapid moisture loss, samples were kept in plastic before oven curing. The oven-cured samples were kept in the climate chamber (20 °C, 65% RH) for 7 days before all physical and compressive strength tests were carried out.

2.3 Composite testing

2.3.1 Water absorption, density and apparent porosity

In determining water absorption, dry bulk density and apparent porosity, the recommendations based on Testing Methods for Fiber Reinforced Cement-based Composites (RILEM 1984) were used. 7-day old 50 mm × 100 mm specimens were removed from the climate chamber (20 °C and 65% RH) and cut to ~50 mm × 25 mm (diameter × height). The specimens were submerged in water for 24 h at room temperature. The specimen was then suspended in water and the immersed mass (*M_i*) was measured. The wet mass (*M_u*) was measured by withdrawing the sample from the water and lightly wiping its surface to remove excess water using a clean, dry cloth. After drying the specimen (to a constant mass) in an oven with air circulation (105 ± 5 °C), the dry mass (*M_s*) was obtained. The following equations were used to obtain the water absorption, apparent density and apparent porosity of the specimens.

$$\text{Water absorption}(\%) = \frac{M_u - M_s}{M_s}, \quad (1)$$

$$\text{Dry bulk density}(\text{g/cm}^3) = \frac{M_s}{M_u - M_i} \times d, \quad (2)$$

$$\text{Apparent porosity}(\%) = \frac{M_u - M_s}{M_u - M_i}. \quad (3)$$

2.3.2 Specific compressive strength

The compressive strength of 7-day old cylindrical samples (50 × 100 mm) was measured using an Emic DL30000N. The samples were compressed using a 300 kN load cell and a constant loading rate of 1 mm/min. The specific compressive strength (specific strength) was calculated by dividing the compressive strength by the sample density (mass per volume). An average of six samples was reported for each group.

2.3.3 Accelerated aging testing

The accelerated aging test involved a comparative analysis of the mechanical performance of the composites, before and after 200 soak/dry cycles. Specimens were successively immersed in water at 20 ± 5 °C over the course of 170 min, followed by a resting phase of 10 min, after which they were exposed to a temperature of 70 ± 5 °C for 170 min in a ventilated oven; the final resting phase being 10 min. This procedure was based on the recommendations of the EN 494 (1994) standards. Each soak/dry set represents one cycle and was performed for 200 cycles (Teixeira et al. 2012).

2.4 Statistics and data presentation

Statistical analysis was performed with JMP 14.2 software from the SAS Institute. All values presented in this study are mean values. Error bars are represented with the standard deviations. Statistical analysis (ANOVA) was applied to identify differences in density, water absorption, porosity and specific compressive strength between pine-based and eucalypt-based GWC, hot water treated and untreated GWC and for GWC from ground and raw fly ash. Comparisons of means were performed using the Tukey test at 5% significance level.

3 Results and discussion

3.1 Characterization of raw materials

3.1.1 Characterization of wood particles before and after treatment

The morphology and appearance of the pine and eucalypt wood particles before and after hot water treatment are presented in Fig. 1. From Fig. 1 it can be seen the major difference arose from the color change of wood particles. With hot water treatment of the particles, the wood color changed from light yellowish to dark yellowish for the pine and from light brown to dark brown for eucalypt particles. This color change might be a result of the removal of some extracts and drying of particles after treatment. FESEM images (Fig. 2) show that the pine particles appeared to be shorter in length while the eucalypt particles were slender and longer. The properties (density, fiber length, shear

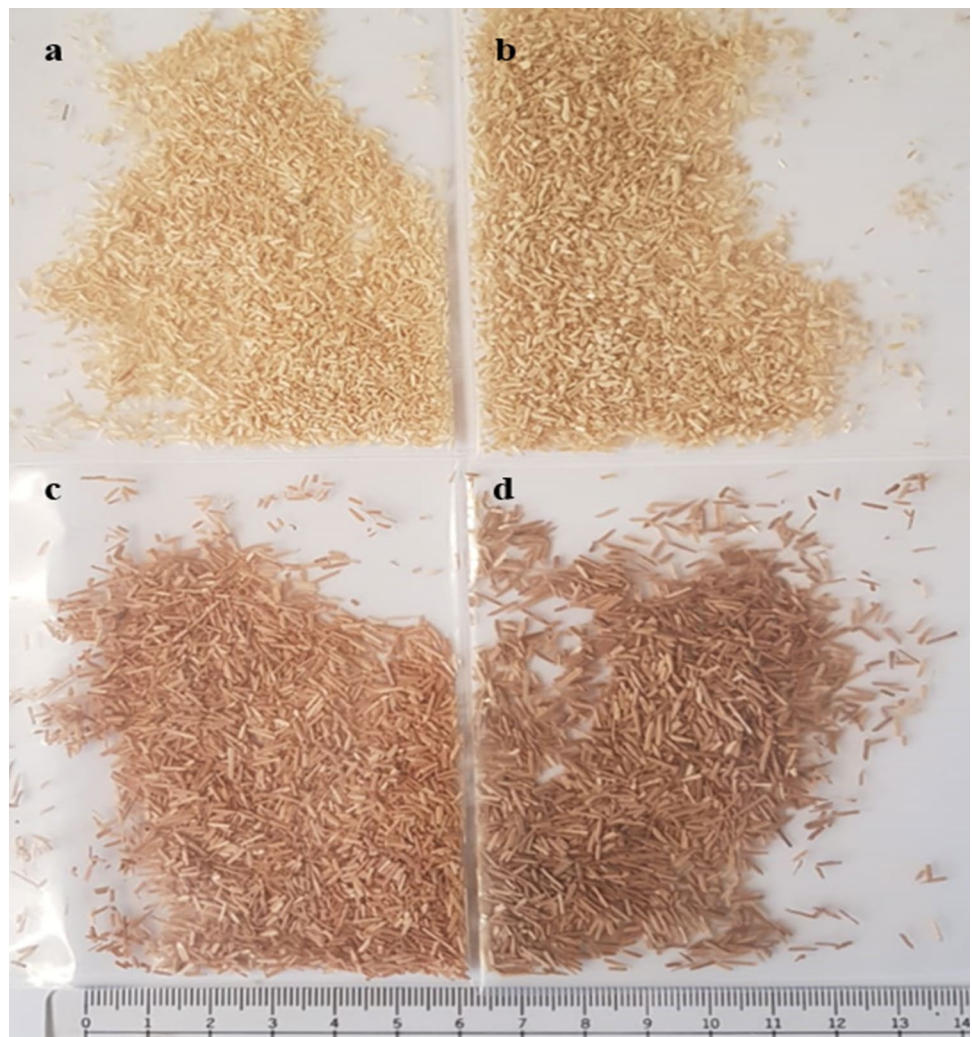
strength) of the wood itself might have influenced the shape of the particles obtained with the same milling system. No observable changes were seen on the surfaces of the wood particles, indicating that morphology effects due to mechanical interlocking do not affect strength changes.

3.1.2 Characterization of raw and ground fly ashes

Figure 3 shows the particle size distribution and SEM of raw (a, b) and ground (c, d) fly ash. In this work, the particle size distribution was determined by the mean diameter as well as the cumulative percentage below a certain grain diameter (CPFT). The CPFT was classified for the diameter below 10% (D10), 50% (D50) and 90% (D90). The mean size of raw fly ash was 28.54 μm and 12.95 μm for ground fly ash. Through grinding, there was a 54.6% decrease in the mean particle size.

The fine ash particle fraction in D10 shifted from 2.95 to 1.78 μm . The major reason for the decreased mean particle size is found in the D90 class. Figure 3a shows a peak at

Fig. 1 Wood particles before and after hot water treatment: **a** untreated pine; **b** treated pine; **c** untreated eucalypt; **d** treated eucalypt



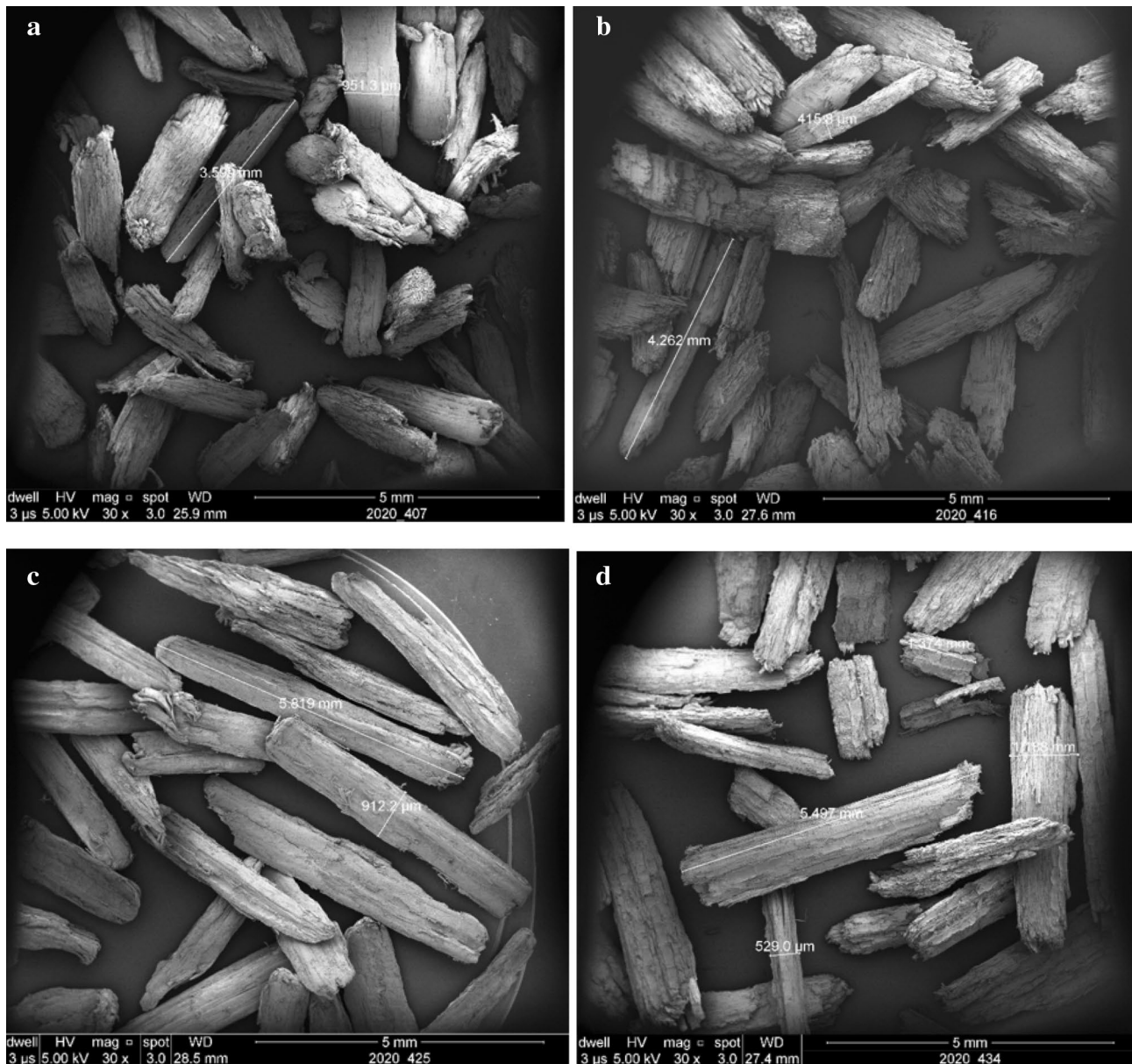


Fig. 2 FESEM images of wood particles before and after hot water treatment: **a** untreated pine; **b** treated pine; **c** untreated eucalypt; **d** treated eucalypt

roughly 100 μm , whereas this peak practically disappears after being ground (Fig. 3c). The grinding process might not only reduce the particle size of the fly ash but homogenize the grain structure, which may facilitate the alkaline activator to access the aluminosilicate. The surface and particles were studied using a SEM test. At the same magnification, the ground fly ash showed a smaller shape and more uniform particles than the raw fly ash (Fig. 3b and d). XRD was used to identify the crystallinity of the ash materials (Fig. 4). The identification phases obtained (with Match Phase Identification 3.8.0.137) showed that the main compounds in both the raw and ground ashes are mullite (M) and quartz (Q). There

was no apparent change in the mineralogy of ground material; Rosas-Casarez et al. (2018) made similar observations.

3.2 Characterization of geopolymer wood composite

3.2.1 Effect of species and pretreatment on physical properties

Table 3 shows the resulting water absorption, bulk density and apparent porosity of the GWC based on untreated and treated pine and eucalypt. The GWC based on pine gave a

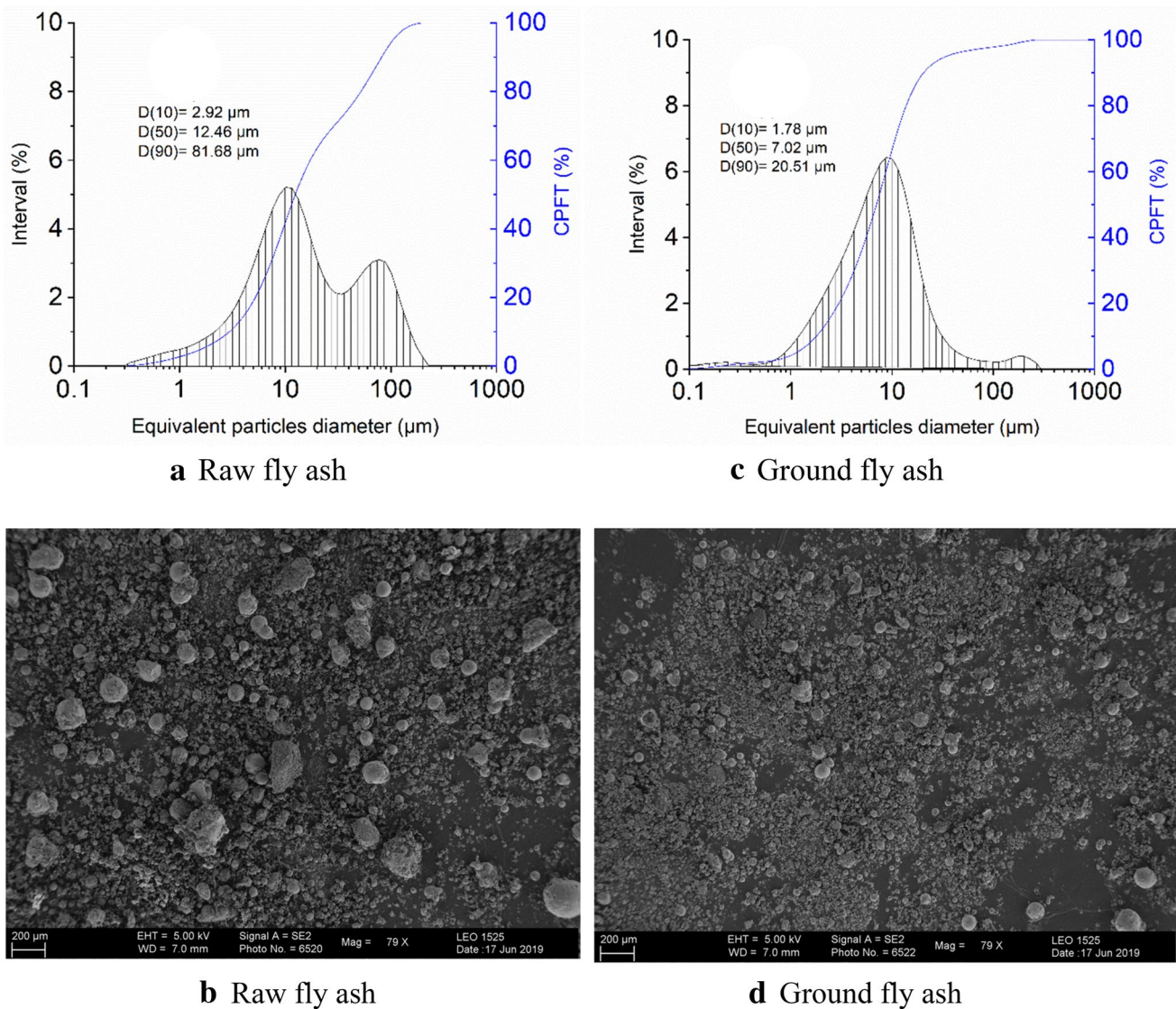


Fig. 3 Particle size distribution and SEM for raw (a, b) and ground (c, d) fly ash

lower dry bulk density compared to those from eucalypt. The results indicate a significant difference in density between pine-based and eucalypt-based composites. Eucalypt had a higher apparent density (0.56 g/cm^3) than pine (0.39 g/cm^3), which might have contributed to the final bulk density of the GWC. Similar densities were obtained for hot water treated and untreated samples for both wood species. There was no significant difference between composites formed from hot treated and untreated wood species.

Comparable porosity was recorded for all samples, with no significant difference between species and treatments. This porosity measurement with water might work for pure concrete or mortar but is no good for mortar containing a high amount of wood, as in this case. This is because in pure geopolymer mortar, the water might easily fill up the voids

after 24 h immersion. In a GWC, the wood might hold some amount of water, which adds up to the water in the void. This might have accounted for the higher porosity values in all samples. After 24 h water immersion, pine-based GWC had the greatest water absorption rates (about 53%), while eucalypt recorded the lowest water absorption rates (about 46%). This difference in water absorption between the pine-based and eucalypt-based composites seems to arise from the different densities of the GWC. This clearly shows an inverse relation between water adsorption and density, that is, an increase in the density of the composite made from eucalypt led to a reduction in its water absorption. Sarmin (2016) reported similar observations: that denser GWC from wood flour had a lower water absorption rate compared with a less dense GWC from wood particles.

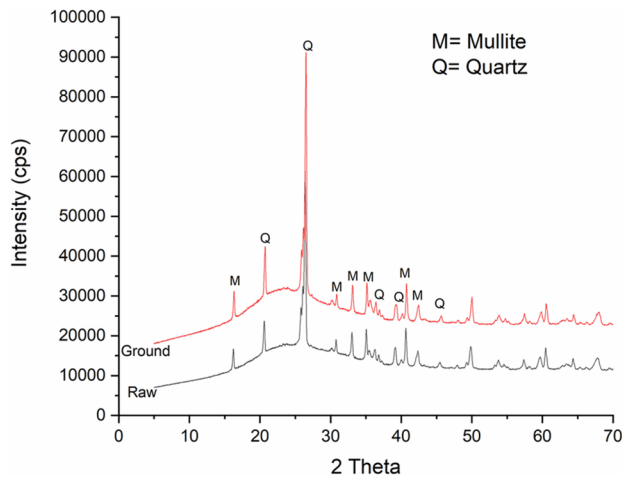


Fig. 4 X-ray (powder) diffraction analysis of raw and ground fly ashes

Another possible reason for the differences in water absorption could be a property of the wood itself, as it is well known that lower density coniferous wood takes up more water than higher density broadleaved wood species. Hence, the lower apparent density of pine than eucalypt might have led to a higher water uptake in the pine-based composite than in the eucalypt. Moslemi et al. (1995) ascertained that wood cement incompatibility leads to a large amount of free internal spaces within the wood cement matrix and could be a possible cause for great moisture adsorption of composites. Mahzabin et al. (2013) further reported that, without proper encasing of wood particles by cement particles, the hygroscopic nature of wood complicates the water absorption outcome among poorly compacted composites. Therefore, the low water absorption of the eucalypt-based composite could be due to the greater compatibility of this species with the geopolymer matrix. However, there was no significant difference between hot water treated and untreated GWC within the same wood species.

3.2.2 Effect of species and pretreatment on specific compressive strength

Pine-based composites recorded a compressive strength of 1.15–1.50 N/mm² while eucalypt-based composites had 2.49–2.59 N/mm², untreated – treated GWC respectively.

Table 3 Mean comparison (standard deviation) of physical properties of geopolymer wood composites (GWC) from ground fly ash

GWC	Wood treatment	Bulk density (g/cm ³)	Water absorption (%)	Porosity (%)
Pine	Untreated	0.88 ^a (0.03)	53.53 ^a (5.04)	47.21 (2.80)
Pine	Treated	0.88 ^a (0.01)	51.99 ^a (2.80)	45.76 (1.96)
Eucalypt	Untreated	1.03 ^b (0.02)	46.01 ^b (2.48)	47.13 (1.45)
Eucalypt	Treated	1.02 ^b (0.03)	45.93 ^b (2.29)	46.79 (1.09)

Means in the same column with same letters are not significantly different ($p > 0.05$)

The eucalypt composite density is 16% higher than that of pine, which may have risen from the different wood species' densities. The density difference affects the composite strength. Hence, density effects shall be eliminated for better comparability of the species and pretreatment effect on strength. Figure 5 shows the resulting specific compressive strength of the GWC based on untreated and treated pine and eucalypt particles. In this study, the selection of wood species was found to have a significant influence on the strength of composites formed. Eucalypt-based composites recorded significantly higher specific compressive strength compared to pine-based composites. The hot water pretreatment increased specific strength by 27.4% for pine-based and 3.1% for eucalypt-based GWC. However, a significant difference was only observed between hot water treated and untreated pine-based GWC. This shows that the pretreatment was relatively effective for pine compared to eucalypt. GWC with treated wood had a higher specific strength, which could be due to the wood particle's improved compatibility with the geopolymer, which resulted in effective bonding and increased maximum load transfer capacity.

The chemical composition of the treated and untreated wood particles is summarized in Table 4. It is a fact that hot

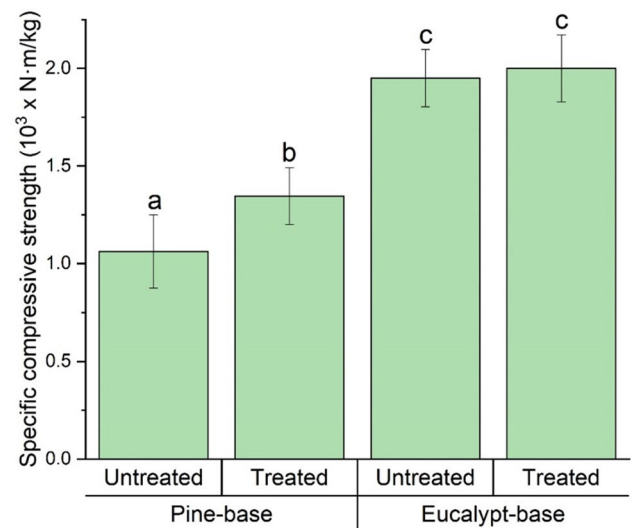


Fig. 5 Specific compressive strength of geopolymer wood composites from ground fly ash

Table 4 Chemical composition of treated and untreated wood particles (%)

Component (%)	Species			
	Pine untreated	Pine treated	Eucalypt untreated	Eucalypt treated
Hydrolysis residue	29.20	29.20	28.10	29.20
Xylose	7.18	7.29	11.12	11.53
Glucose	42.42	42.61	47.89	50.05
Mannose	9.36	9.57	1.02	1.03
Galactose	2.00	2.07	0.79	0.90
Arabinose	1.22	1.27	0.20	0.22
Rhamnose	0.15	0.14	0.20	0.22
Acid soluble lignin	0.45	0.46	2.41	2.60
Other extracts	2.79	1.47	4.08	1.33

water extraction alters the chemical composition of wood by fractionating accessible sugars and hemicelluloses (Pelaéz-Samaniego et al. 2013, 2014). Due to the solvent polarity, it was expected that the hot water treatment would remove water-soluble extracts, such as non-structural carbohydrates, their saccharic acids, inorganic components and degradation products (alcohols, ketones) (Sluiter et al. 2008, 2010; Davison et al. 2013). The xylose, glucose, mannose, galactose, arabinose and rhamnose however, remained unaffected. The main portion of those sugars form part of the structural macromolecules and the apparent perceptual increase after treatment is an effect of the removal of other extracts. The hot water treatment removed 1.32 and 2.75% for pine and eucalypt, respectively. The analytical extraction agents, water, acetone–water and petrol ether reflect the range of polar to non-polar solvents. Aprotic polar solvents such as acetone cover a wider range of reactions due to their intermediate polarity. The extracted substances might comprise tannins, gums, sugars, starches and color producing chemicals (TAPPI 2007). Although a difference in strength was observed for pine, the extract yield was twice as high in eucalypt. This indicates, that one of the above-mentioned pine specific extracts causes the lower incompatibility of this species with the geopolymer matrix. Further investigations must focus on identifying the exact substance interacting with the geopolymerization.

Hot water treatment of wood particles by boiling is a similar process to cooking of wood chips in pulping, which

is largely influenced by wood density. Zañão et al. (2019) stated that the density differences between eucalypt and pine significantly affect the impregnation of these two woods. Low-density woods are impregnated faster than high-density woods when boiling in water. A similar phenomenon might have occurred in this study, as the fast impregnation and high water absorption by the pine particles might have decreased the amount of water available for ionic transport within the mixture and led to the lower specific strength. By this same principle, it was expected that pine-based GWC show higher water absorption (Table 3), with more advantages regarding specific strength increase with the hot water treatment than eucalypt-based GWC. Wilson and White (1986) reported that hardwoods are usually strong in compression, tension and shear, while softwoods are strong in tension but weak in shear. This might have contributed to the difference between the two composites. Since no observable changes were seen on the surfaces of the wood particles (Fig. 1) after treatment, it can be concluded that the morphology effects caused by mechanical interlocking did not affect changes in strength; rather, the wood species, shape of the wood particles and the removal of extracts did.

3.2.3 Effect of fly ash particle size on physical properties

For this test, the eucalypt-based GWC were used since they performed better than the pine-based GWC. Table 5 shows that composites made from ground fly ash recorded

Table 5 Effect of fly ash particle size on the mean (standard deviation) of the physical properties of the geopolymer wood composites (GWC) made with eucalypt

Type of fly ash	Eucalypt treatment	Bulk density (g/cm ³)	Water absorption (%)	Porosity (%)
Raw	Untreated	0.91 ^a (0.02)	53.13 ^a (1.60)	48.11 (0.62)
Raw	Treated	0.92 ^a (0.02)	50.96 ^a (2.17)	47.18 (1.11)
Ground	Untreated	1.03 ^b (0.03)	46.01 ^b (2.66)	47.13 (1.57)
Ground	Treated	1.02 ^b (0.03)	45.93 ^b (2.42)	46.79 (1.16)

Means in the same column with same letters are not significantly different ($p > 0.05$)

greater densities than those from raw ash. After 24 h water immersion, composites from raw fly ash had the greatest water absorption rates while ground fly ash recorded the lowest water absorption rates. Significant differences were observed in densities and water absorption of composites from ground and raw fly ashes. The differences in water absorption may be attributed to the different densities of the GWC, owing to the smaller particles of the ground ash getting closely packed to fill up spaces within the composite thereby increasing the density with a reduction in water absorption. Another possibility might be the reduction of particle size through grinding, which resulted in an increased polymerization reaction and forming of a dense structure, with decreased water absorption. However, within the same fly ash group no significant differences were found between hot water treated and untreated composites. The apparent porosity ranged from 46.79 to 47.13% for ground fly ash and 47.18–48.11% for the samples from raw fly ash (Table 5), with no significant differences between the composites.

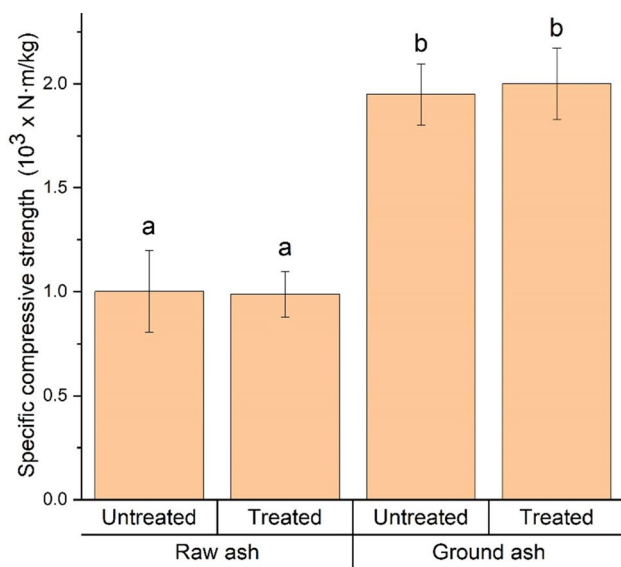


Fig. 6 Effect of fly ash particle size on specific compressive strength of GWC made from eucalypt

Table 6 Mean comparison (standard deviation) of eucalypt-based geopolymer wood composite before and after 200 cycles of soak/dry conditions

Species	Type of fly ash	Wood treatment	Specific compressive strength (10³× N m/kg)		% decrease
			Before aging test	After aging test	
Eucalypt	Raw	Untreated	1.00 ^a (0.20)	0.83 ^a (0.22)	17.00
Eucalypt	Raw	Treated	0.99 ^a (0.11)	0.84 ^{ab} (0.16)	15.15
Eucalypt	Ground	Untreated	1.95 ^b (0.15)	1.32 ^{bc} (0.14)	32.31
Eucalypt	Ground	Treated	2.00 ^b (0.17)	1.67 ^c (0.10)	16.50

Means in the same column with same letters are not significantly different ($p > 0.05$)

3.2.4 Effect of fly ash particle size on specific compressive strength

Compressive strength is 1.10–1.19 N/mm² (composites from raw ash) and 2.49–2.59 N/mm² (composites from ground ash), untreated—treated GWC, respectively. Hence, density effects shall be eliminated for better comparability of the grinding on the strength results. The ash-grinding step doubled the specific compressive strength (Fig. 6). Using raw fly ash resulted in about 1×10^3 N m/kg whereas ground fly ash yielded about 2×10^3 N m/kg. With the same ash group, no significant difference was observed for hot water treated and untreated GWC. However, significant differences were observed between the GWC from ground and raw fly ash. The 54.63% decrease in the mean particle size by grinding led to a 94.9% (untreated) and 102.4% (treated) increase in the specific strength.

Grinding results in a larger surface area, which allows for a greater dissolution of alumina and silica in alkaline activation of the fly ash. In addition, smaller particle size requires less time to produce crystalline structures and gels that provide stability to the geopolymer, as well as more homogeneity in the matrix and more rigid bonds (Rosas-Casarez et al. 2018). Kim and Lee (2017) who made a similar observation, discovered that geopolymer from finer ground bottom ash had the highest compressive strength compared to medium and coarse ground bottom ashes. The lower strength from the raw fly ash may be compensated by prolonging the reaction-mixing time to promote dissolution (Ziegler et al. 2016) and adding more soluble silica to dissolve the large particles (Kim and Lee 2017). Additionally, the particle fraction with diameters beyond 100 µm could be sieved out prior to processing.

3.3 Effect of accelerated aging on specific compressive strength of GWC

The specific compressive strengths of eucalypt-based geopolymer composites after 200 cycles of soak/dry accelerated aging test are shown in Table 6. A significant difference was observed between the strength of composites from ground and raw ash. A similar pattern to the specific

strength (Fig. 6) was observed after the aging test, as GWC from ground ash yielded higher strength before and after the 200 cycles than those from raw ash. This difference may be attributed to the difference in water absorption of the GWC samples. Water absorption by composites containing wood particles has several effects on their properties and affect the long-term performance. According to Lin et al. (2002), moisture penetration may degrade the mechanical properties of composites by three different mechanisms. The first involves the diffusion of water molecules inside the micro gaps between the polymer chain, while the second involves capillary transport into gaps and flaws at fiber and matrix interface. Lastly, it may induce swelling of wood particles, which propagates microcracks in the matrix.

Water absorption is related to specific compressive strength as GWC from raw fly ash recorded the highest water absorption and lower specific strength values before and after the accelerated aging test. By increasing reactive surface through grinding, a denser composite material was formed with reduced water absorption and increased compressive strength. Thokchom et al. (2009), who studied the effect of water absorption on the durability of fly ash based geopolymer mortar, made similar observations. The authors found that samples with higher water absorption had the lowest compressive strength. A decrease in this specific strength could be observed for all composites after the cyclic test. However, the highest percentage decrease in strength was recorded for the GWC from ground and untreated wood. The specific strength after aging for ground fly-ash and water treatment decreased notably. In contrast to the previous results on specific strength, these results indicate that there are eucalypt-specific factors that affect the geopolymerization. Nevertheless, this effect is negligible compared to pine. Apart from this, no significant differences were observed between hot water treated and untreated composites.

4 Conclusion

This study analyzed the influence of grinding fly ash, wood species and hot water wood pretreatment on geopolymer wood composite (GWC) properties. It revealed that hot water treated wood improves GWC properties less compared to wood species or ash grinding.

Grinding decreased the mean particle size of raw fly ash by more than 50% and homogenized the particle size distribution. There was an increase in the specific surface area of the fly ashes with grinding, which contributed to their reactivity. Consequently, specific compressive strength doubled for all GWC made from ground ash.

The wood species significantly influenced the GWC's specific compressive strength, as eucalypt-based composites yielded strength nearly double as high as pine ones.

Furthermore, the wood species affected the composite's densities and played a vital role in the water absorption of the GWC. The eucalypt composite density was 16% higher than the pine counterpart, which rose from the different wood species densities. The lower apparent density of pine led to a higher water uptake in the pine-based composite than in the eucalypt-based composite.

The hot-water pre-treatment markedly increased (27%) the specific compressive strength of pine-based GWC, but not those of the eucalypt-based GWC. Washing out the pine-specific extracts led to a better compatibility between geopolymer and wood. Further investigations must focus on identifying the extract substance interacting with the geopolymerization. Alternative wood and non-wood (such as bamboo and bagasse) species shall be screened for their suitability.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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