Composites & nanocomposites

Influence of wood pretreatment, hardwood and softwood extractives on the compressive strength of fly ash-based geopolymer composite

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ABSTRACT

This paper investigated the specific compressive strength (specific strength) of fly ash-based geopolymer composites with four hardwood extractives and two softwood extractives, as well as specific wood extractives. Additionally, the effect of the portion of pine wood (i.e., sapwood and heartwood) and wood pretreatment with NaOH were considered. Geopolymer paste (with extractives) and geopolymer wood composites (GWCs) were cured at 60 °C for 24 h. The samples were stored in a climate chamber (20 °C, 65% RH) for 7 days before finally testing under compression. From the results, the specific strengths of geopolymers with hardwood extractives were not significantly affected. However, geopolymers containing pine extractives showed the most significant reduction in specific strength. There were no significant differences in the specific strengths of geopolymers containing polyphenols and resin acid. Generally, geopolymers containing fatty acids recorded the lowest specific strengths. There was no difference between the GWCs with untreated sapwood and heartwood. However, the wood pretreatment led to a 21% and 10% increase in the specific strengths of GWCs with sapwood and heartwood, respectively. The findings of this study form the basis for improved GWCs production and a wide range of applications for green composite materials.

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Introduction

Inorganic bonded wood composites (IBWC) are one of the major building and construction components. Examples of IBWC include ceramic-bonded, gypsum-bonded, magnesia-bonded and Portland cement-bonded wood composites. Common applications of IBWC include flooring, tiling, prefabricated housing, façade, ceiling, and exterior and partition walls. Wood plays a very important role in IBWC, acting either as an aggregate or reinforcing element serving as to reduce the densities of the products [1], while also improving tensile strength, flexural strength, toughness and energy absorption capacities through bridging cracks [2]; the inorganic matrix binds the wood particles, providing mechanical strength, low permeability, good chemical resistance, and excellent fire resistance behavior [3–5]. Among the IBWC, Portland cement-bonded wood composites dominate the market share. Ordinary Portland cement (OPC) remains the main binding agent in these composites. It is an undisputed fact that the production of OPC continues to be one of the major contributors of CO_2 emissions. With the keen search to finding suitable replacements for this binder, recent researches have shown that geopolymer, an alkali activated cement, serves as a possible alternative [6–8].

Wood is a natural composite comprising mainly of cellulose, lignin and hemicellulose as structural components and non-structural polysaccharides and other extractives. Wood shows different characteristics, which differ in a wide range among species, and even between the same species. Wood is broadly categorized into softwood and hardwood. In general, softwoods have a simpler basic structure with relatively less variation in structure compared with those of hardwoods.

Among the structural components of wood, Ye et al. [9] found that a lower content of cellulose, hemicellulose, and lignin (i.e., 5 wt%) increases the flexural and compressive strengths of pure meta-kaolin-based geopolymer composites. Furthermore, above this content, the authors observed that both hemicellulose and lignin reduced the composites' compressive and flexural strengths. Alkaline degradation of hemicellulose lowered the degree of geopolymerization [9]. This drawback asks for different pretreatments and surface modification of wood before utilizing it in high alkaline inorganic matrices. Different pretreatment and modification methods based on alkaline hydrolysis, extraction and retention of sugars and hemicelluloses have been applied to minimize inhibition problems [10–12]. Alkaline hydrolysis degrades hemicelluloses and sugars into non-inhibitory substances, while aqueous extraction removes inhibitory water-soluble substances [13]. Retention treatment seals the inhibitory substances in the wood by forming a thin coating layer around the wood preventing the release of the inhibitory substances [14].

Despite the fact that wood reduces the density and improves on the strength properties of IBWC, their utilization in high alkaline environments causes leaching out of non-structural polysaccharides/low molecular weight carbohydrates, extractives and some structural components like hemicellulose. The kind and amount of these extractives differ by species and the portion of the tree (i.e., sapwood or heartwood), so they may have different inhibitory effects on setting, strength and geopolymerization process. Jorge et al. [15] established that the properties of IBWC are influenced by the addition of wood as well as the binder type. In the study of the influence of hot water wood pretreatment and fly ash particle size on the performance of geopolymer wood composites (GWC), Asante et al. [16] determined that forming a GWC with *Eucalypt grandis* wood produced better mechanical and physical properties than those made with *Pinus taeda*. The authors recorded a 3 and 27% increase in specific strengths of the Eucalypt-based and pine-based GWCs, respectively, after hot water washing of the wood. This clearly indicates there were some wood extractives hindering the geopolymerization or causing the incompatibility between the wood and the geopolymer. The same authors concluded that the lower specific strength and physical properties of the GWC from pine wood were as a result of the poor incompatibility between the pine and the geopolymer matrix. However, the research was limited to one softwood and one hardwood and as to what group or type of extractives might be causing this incompatibility. Regardless, there is little or no established research about the influence of these inhibitory extractive substances on the properties of geopolymer composites.

The understanding of how extractives from various hardwood and softwood species affect the properties of GWC will serve as the basis for better preparation for these composites as well as a diverse application

of environmentally friendly building materials. Using a fly ash-based geopolymer, extractives from four hardwood species and two softwood species were tested in order to understand how wood extractives affect the specific compressive strength (specific strength) of a geopolymer. Additionally, the effects of sapwood and heartwood extractives as well as specific extractives on the specific strength of fly ash geopolymer were studied. Lastly, the influence of the pretreating of sapwood and heartwood with NaOH on specific strength was also considered.

Materials and methods

Materials

Class F fly ash (i.e., mass contents of $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$) was obtained from the GK Kiel GmbH power plant in Kiel, Germany. The chemical oxide compositions of the fly ash as detected by X–ray fluorescence (XRF) are shown in Table 1. Betol 50 T (Na_2SiO_3) was purchased from Woellner, Germany, and NaOH (analytical grade) was purchased from VWR, Germany. Betol 50 T and NaOH were used as received to produce the activator solution. Pycnogenol, tannic acid, linoleic acid, oleic acid and abietic acid (Sigma-Aldrich, Germany) and condensed tannin (from Natural Resource Institute Finland) were used. For the study, four hardwood species (*Eucalypt grandis*, *Eucalypt camaldulensis*, Port Jackson [*Acacia saligna*], and Black wattle [*Acacia mearnsii*]) and two softwood species (spruce [*Picea abies*] and pine [*Pinus sylvestris*]) were used. Figure 1 shows the morphology and size of wood particle used for extraction.

Extractives preparation

To study the influence of hardwood and softwood extractives on the strength properties of a geopolymer, wood particles (4 hardwood and 2 softwood species) were mixed with 1% NaOH solution (Table 2). After 20 min of mixing in the 1% NaOH solution, the wood particle was filtrated to separate the liquid and solid phases. It has been reported that wood extractives are relatively stable at temperatures between 60 and 100 °C [17]. For this reason, the mass concentration of extractives (i.e., liquid) was measured for each extractive by drying in the oven at

60 °C for 36 h. The extractive was then used to study its effect on specific compressive strength of a pure fly ash-based geopolymer.

Yield of extractives

The yield of all extractives is presented in Table 3. The yield ranges from 1.54 to 1.96%. Overall, B. wattle (more details of sample code are given in Table 3) had the highest mass concentration of extractives with *E. grandis* recording the lowest. The percentage yield of extracts (i.e., dry matter content) of the pine sapwood was slightly lower than that from the heartwood. This comes as no surprise as the sapwood plays the role of sap conduction, storage of photosynthate and synthesis of extractives, the heartwood's functions being long-term storage of the extractives in living trees [18]. In addition, heartwood is more soluble than sapwood, which suggests that a greater amount of substance can be leached out during the extraction process [19].

Sample preparation

Geopolymer with softwood and hardwood extractives

The alkaline activator solution for geopolymer activation was prepared according to the method described by Asante et al. [20] using Betol 50 T (i.e., Na_2SiO_3) and 10 M NaOH in a weight ratio of 2.5:1. The solution was allowed to cool to ambient conditions prior to use. Figure 2 shows the manufacturing process for the geopolymers contain extractives. Fly ash was mixed with the activator solution in a mass ratio of 2:1 for 5 min. Finally, 3% of the extractive solution (i.e., based on fly ash weight) was added to the mixture for 5 min (Table 4). The mixture was cast in a cylindrical mold: 50×100 mm^2 and cured at 60 °C for 24 h. To avoid rapid moisture loss leading to cracks, samples were kept in low density polyethylene plastic before oven curing. The oven-cured samples were kept in the climate chamber (20 °C, 65% RH) for 7 days before compressive strength tests were carried out.

Geopolymer wood composites

To study the influence of the portion of pine wood pretreatment on the properties of a fly ash geopolymer, sapwood and heartwood particles were treated

Table 1 Chemical composition of fly ash in weight percentage share (%) by XRF analysis

Component	Al_2O_3	SiO_2	SO_3	K_2O	Na_2O	CaO	TiO_2	MgO	Fe_2O_3	P_2O_5	LOI[*]
Share (%)	20.53	54.18	0.01	1.51	0.51	3.36	0.84	1.50	6.31	0.66	4.18

Loss on ignition (LOI[*]) at 1000 °C

Figure 1 The morphology of wood particle used for extraction of wood extractives.
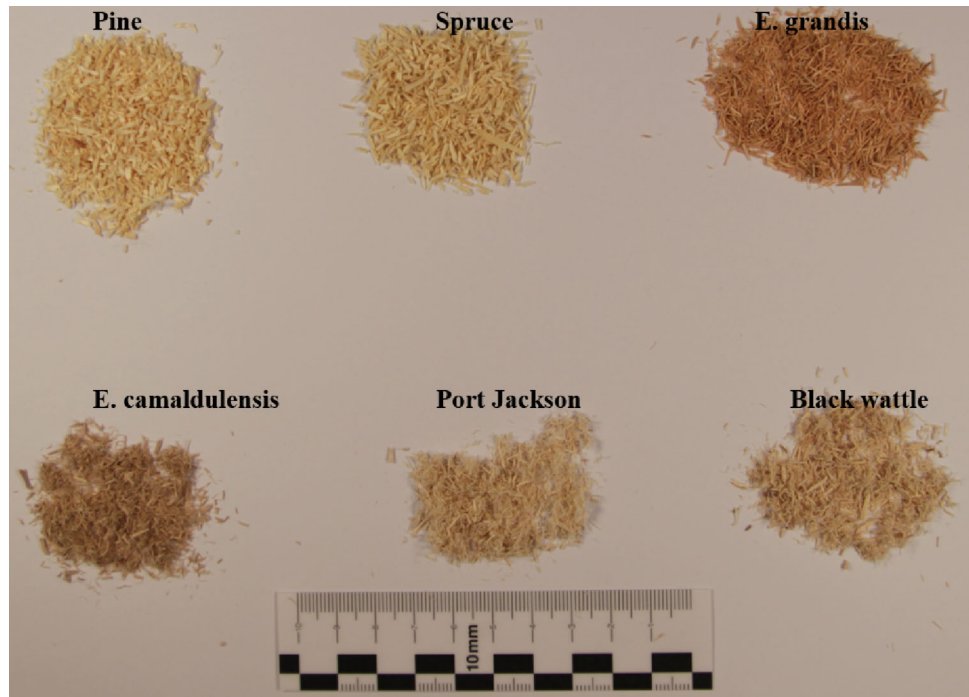
Table 2 Extraction method

Mass conc. of NaOH (%)	Vol. NaOH (ml)	Mass wood (g)	Contact time (mins)
1	1000	100	20

as shown in Table 2. After 20 min of mixing in the 1% NaOH solution, the wood particle was filtrated to separate liquid and solid phases. The sapwood and heartwood extractives, collected separately, were used in geopolymer preparation according to Table 4. The solid particles were dispersed in 2250 mL distilled water (i.e., water: wood particles), before finally washing with 1000 mL distilled water. Finally, wood particles were dried in an oven at 60 °C for 36 h and later kept in the climate chamber (20 °C, 65% RH) until the moisture content was, after 7 days, at 10–12%.

The geopolymer wood composite was prepared in accordance with Table 5 (see Fig. 3). Fly ash was first

Table 3 Dry matter content (%) of extractives

Wood species	Code	Yield (%)
Eucalypt grandis	E. grandis	1.54
Eucalypt camaldulensis	E. camal	1.58
Acacia saligna	P. jack	1.80
Acacia mearnsii	B. wattle	1.96
Picea abies	Spruce	1.73
Pinus sylvestris	Pine	1.81
Pine Sapwood	Sap	1.61
Pine Heartwood	Heart	1.82

mixed with wood (dry mass) for 3 min; water was

Figure 2 Manufacturing process of hardened geopolymer paste (i.e., geopolymer with wood extracts).

Fly ash — Activator solution — Wood extract solution — 60 °C curing 24 h → Hardened geopolymer paste
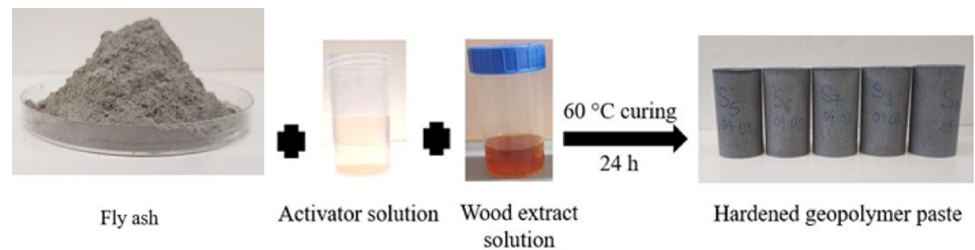
Table 4 The mix design of fly ash geopolymer with wood extractives

	Fly ash: Activator	Na$_2$SiO$_3$: NaOH (Activator)	% Extract
Control	2:1	2.5:1	0
Samples with extract	2:1	2.5:1	3

*For the control sample, 3% by mass of fly ash of the NaOH solution used for the extraction was added

Table 5 Preparation of geopolymer wood composite

Proportion	Fly Ash: activator	Fly ash: wood (dry mass)	Fly ash: additional water
Mass ratio	2:1	4:1	5.3:1

added and then mixed for 3 min and finally, the alkaline solution was added and mixed for 4 min. The activated mixture was cast in 50 mm^3 molds and cured at 60 °C for 24 h. To avoid rapid moisture loss leading to cracks, samples were sealed in plastic before oven-curing. The oven-cured samples were kept in the climate chamber (20 °C, 65% RH) for 7 days, compressive strength tests being carried out on the 7th day.

Geopolymer with softwood specific extractives

Pycnogenol and condensed tannin were dissolved in water to form a concentration of 0.12%. More details about the condensed tannins can be found in the previous study [21]. Then, 5 g of abietic and oleic acids were dissolved separately in 20 ml of ethanol, after which 20 ml of 1% NaOH solution was added prior to adding to the geopolymer mortar during sample preparation. 5 g of liquid linoleic acid was used as received, 35 ml of 1% NaOH solution being added hereafter. Next, 5 g of tannic acid was dissolved in 40 ml of 1% NaOH solution. (NB: To make easy comparisons to control samples, 1% NaOH solution was used for dissolving extract or added to the geopolymer paste after extract addition to keep sodium (Na) ions as close to that of the control

samples as possible). The geopolymer paste samples were all prepared according to Table 4. It should be noted that the purified chemicals bought and the extracted compounds may not be 100% the same due to the purification of the former. However, we assume they are the same. In addition, in an extraction process such as that used in the current study, most of the compounds leach out together instead of individually. However, as a way to simplify and understand their effect on strength, specific extracts bought were used separately.

Test conducted

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the untreated and treated pine wood (i.e., sapwood and heartwood) samples were recorded by a Vertex 70 powder FTIR spectrometer equipped with a diamond ATR from (Bruker Optics, Germany) in the range of 4000–500 cm^{-1}.

Analysis of pine sapwood and heartwood extracts

Aliquots (50 ml ea.) of the alkaline extractives of pine sap- and heartwood were acidified with o-phosphoric acid (VWR, purity 85%) to a pH-value of 7 and extracted with dichloromethane (DCM, Th. Geyer) in a separation funnel by shaking out. The extraction of acidified aliquot was carried out at least three times, and the organic phase was combined afterward. A subsequential extraction stage starts with an additional acidifying step to a pH-value of 2 and extraction as described. After combining the sub-fractions
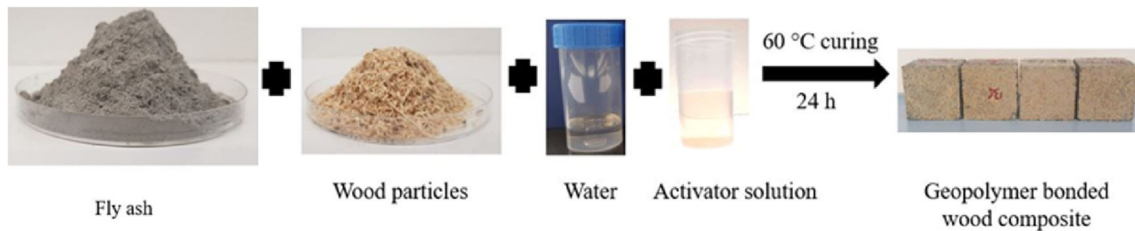
Figure 3 Manufacturing process of geopolymer wood composites.

of each extraction step, DCM was removed with a rotary evaporator (IKA RV 10 basic) at atmospheric pressure and a water bath temperature of 45 °C. The extractives were removed to a weight flask and weighed out after removal of the residual DCM-phase. Two fractions called "pH 7" and "pH 2" were produced by liquid–liquid-extraction.

During the DCM-extraction, some of the extractive parts sediments due the acidic conditions of the solution. Therefore, a further aliquot (40 ml) of each alkaline extractive sample was precipitated in cold water (1:10, V:V) dropwise and filtered with a cellulose filter. Before weighing out, the residues were dried to mass constancy in a desiccator over silica gel and phosphorus pentoxide subsequently.

The dried extractives were prepared for GC–MS/FID analysis by dissolution in an acetone solution with the internal standard fluoranthene (β = 200.06 μg/ml). The solutions with a concentration of 10 mg/ml DCM-extracts were filtered with a syringe filter (cellulose, 0.45 μm) subsequently. GC/MS-FID analyses (Agilent 6890; Column: VF-1701 (60 m, 0,25 mm ID, 0,25 μm Film); 2.0 ml/min He; 45 °C, 4 min, 3 K/min, 280 °C, 20 min; Split 15:1; FID 280 °C, 40 ml/min H_2, 450 ml/min synth. Air; Recording: 20 Hz; MSD: Agilent 5975B, MSD-Transfer: 280 °C, mass range 19–550 m/z) were conducted for characterization of the pine wood extractives. Besides the standard characterization of the composition, additional measurements were done for more detailed insights into higher molecular structures which are not detectable by the described characterization. For this purpose, an online derivatization with tetramethylammonium hydroxide (TMAH) on DCM extracts (pH-value of 2) was carried out on a Py-GC/MS-FID system. 10 μl of DCM extracts was weighed into a small pyrolysis cup, and 20 μl TMAH

solution (10 wt%) was added. The GC/MS-FID measurements of derivatized samples were conducted under the following parameters: Agilent 6890; Column: VF-5 ms (60 m, 0,25 mm ID, 0,25 μm Film); 1.9 ml/min He; 45 °C, 4 min, 3 K/min, 325 °C, 20 min; Split 15:1; FID 350 °C, 40 ml/min H_2, 450 ml/min synth. Air; Recording: 20 Hz; MSD: Agilent 5975B, MSD-Transfer: 350 °C, mass range 20–550 m/z). Quantification of the GC/MS-FID results was carried out using the relative area of the compounds relating the area of the internal standard for standard measurements. The derivatized samples were evaluated by using the ratio of substance area to total area.

Specific compressive strength testing

The compressive strength of 7 day aged cylindrical samples (50 × 100 mm^2) was measured using a hydraulic universal testing machine (UTM) by MTS Systems Corporation (Eden Prairie, Minnesota, US). The MTS UTM was equipped with a Zwick model 1485 control panel (ZwickRoell GmbH & Co. KG, Ulm, Germany). The samples were compressed with a load cell capacity of 250 kN and with a crosshead speed rate of 1 mm/min. The compressive strength was calculated by dividing the maximum force (N) by the cross-sectional area (mm^2) of the sample. The specific strength was calculated by dividing the compressive strength by the density of the geopolymer composite. The average value of five samples was reported for each group.

Statistical analysis

The statistical analysis was performed using Origin Pro software. An analysis of variance (ANOVA) was

conducted to identify differences between the samples' specific compressive strength. Comparisons of means were performed using the Fisher LSD at 5% significance level. The values presented in this study are all means, and the error bars represent standard deviations. Means with same letters are not significantly different; $p > 0.05$.

Results and discussion

Characterization of pine sapwood and heartwood particles before and after NaOH pretreatment

Morphology

The morphology and appearance of the pine wood particles before and after 1% NaOH treatment are presented in Fig. 4. Here, it can be seen that the major difference arose from the color change of the wood particles, which changed from pale yellowish to light brown for the sapwood and from yellowish to dark brown for the heartwood. Wood color is primarily determined by the amount and chemical nature of the prevalent extractives [22]. Molecules having chromophore bonds that are responsible for light absorption at specific wavelengths are lignin and phenolic extractives, and their derivatives [23, 24]. Wood discolorations may result from drying as the moisture in wood changes [25]. Baar et al. [22] stated that for any porous materials like wood in contact with water, the phenomenon of surface darkening arises from a change in the refractive index, as water enters air-filled pores. Drying the wet treated particles after the NaOH pretreatment led to the color change. As the NaOH solution evaporated, some chemicals soluble in the NaOH solution in the wood may have been transported to the evaporating surface. This may have left these chemicals behind and caused discoloration. The color change might be as a result of the movement of extracts and the drying of particles after treatment as a similar observation which was made by Asante et al. [16].

Fourier transform infrared spectroscopy (FTIR)

The structural differences in pine sapwood and heartwood before and after NaOH treatment can be evaluated by Fourier transform infrared spectroscopy
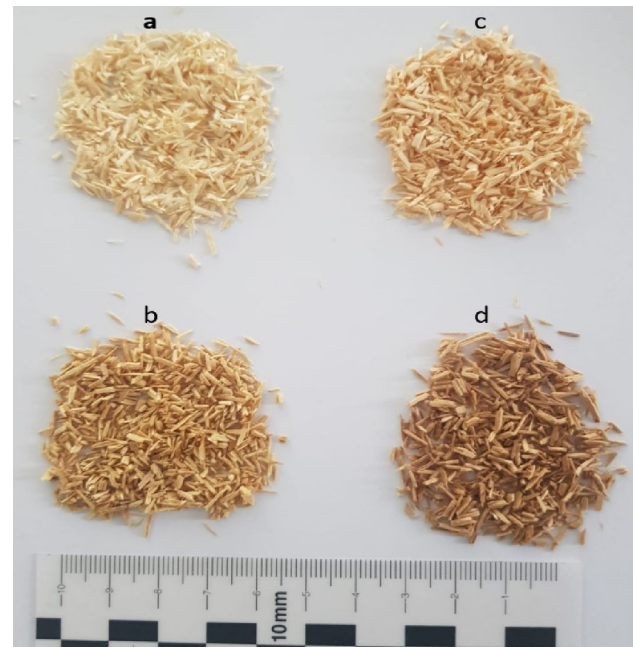
Figure 4 Morphology of pine wood particles before and after NaOH treatment: **a** untreated sapwood; **b** treated sapwood; **c** untreated heartwood; **d** treated heartwood.
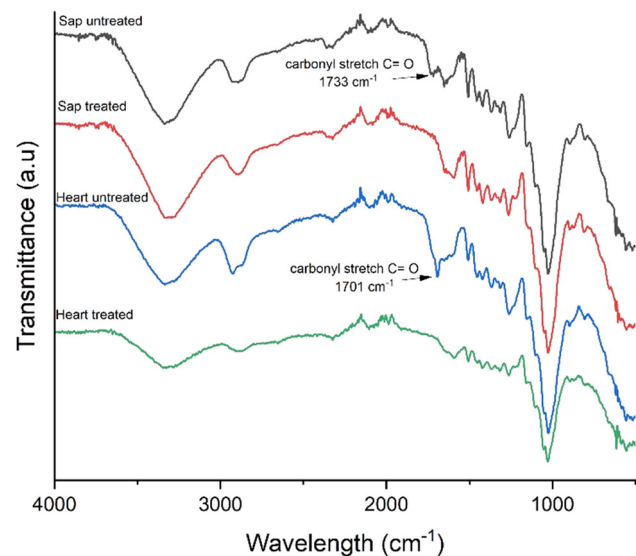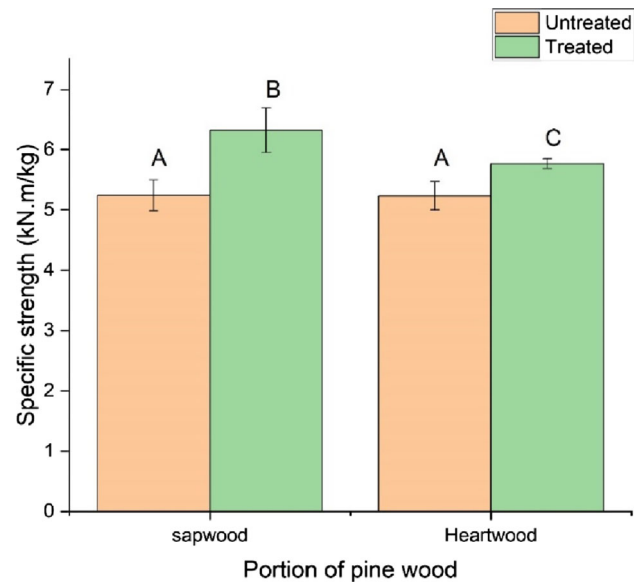

Figure 5 FTIR of untreated and NaOH treated pine sapwood and heartwood.

[26]. Figure 5 shows the FTIR spectrum for explicating the chemical changes which occur after treating the pine wood samples with NaOH. In the spectra, the transmittance around 2910–2928 and 1369–1371 cm^{-1} is attributed to the C–H stretching and bending vibration in cellulose [27]. The transmittance band of the C–O stretch vibrations in

cellulose and hemicelluloses is around 1029–1033 cm^{-1}, which is the highest intensity band [28]. Furthermore, the vibrations around 1701 and 1733 cm^{-1} in both untreated sapwood and heartwood, respectively, are attributed to the C=O stretching of methyl ester and carboxylic acid [27, 28]. The absence of this spectrum in both the treated sapwood and heartwood represents the major difference in Fig. 5. Similar observations were made by Zhong et al. [27, 28] after treating Fir and pine wood, respectively, with NaOH solution. According to Zhong et al. [27], this indicated the removal of pectin, waxy and natural oils covering the external surface of the cell wall by the alkali treatment.

Effects of pretreatment and portion of pine wood used in geopolymer wood composite

Since pinewood was mostly affected negatively (section "GC/MS-FID analysis of pine sapwood and heartwood extractives extracted with NaOH"), the sapwood and heartwood were used for further analysis. The effect of the portion of pine wood (i.e., sapwood and heartwood) used in GWC production is shown in Fig. 6. Due to the higher solubility of heartwood vs. sapwood suggesting that a greater amount of substance could be leached out [19] to disturb the geopolymerization, it was expected that the specific strength of these two composites would be different. This being said, the results in Fig. 6 show that the specific strength of fly ash-based GWCs in both untreated pine sapwood and heartwood was not significantly different. Based on this observation, there is reason to believe that similar components but in small amount might be leaching out when both untreated sapwood and heartwood were used in the GWC formulation. However, with the 1% NaOH pretreatment, a significant difference was observed between the GWCs from the sapwood and heartwood. The pretreatment of the sapwood and heartwood led to an increase in the specific strengths of both GWCs. Due to their ability to remove extractives and inhibitory contaminants from wood, NaOH increases surface roughness and increases surface wettability [29]. As a result of the NaOH treatment, the wood surface area may have been increased for bonding with the geopolymer, due to the roughness being increased [29] and therefore the specific strength increasing. Be that as it may, the treatment led to a 21% and 10% increase in the specific strength

Figure 6 Specific compressive strength of fly ash geopolymer wood composite with treated and untreated pine sapwood and heartwood.

of GWCs with sapwood and heartwood, respectively. This indicates the NaOH treatment was more pronounced in the pine sapwood than the heartwood. In comparing the surface roughness of sapwood and heartwood in *Acacia mangium* after NaOH treatment, Redzuan et al. [29] observed that the surface roughness of sapwood increased more than that of heartwood (as the cells of sapwood are more permeable to liquid than the heartwood). The authors concluded that the NaOH treatment was more effective for the sapwood than the heartwood. This might have led to the significant difference between the specific strength of the GWCs with sapwood and the heartwood in this present work. The difference in specific strength between the GWC with treated and untreated wood particles could be the small amount of compounds that might have leached out into the geopolymer matrix when the latter was used directly in the GWC formulation. That is to say, the amount of extracts leaching out of the wood (sapwood and heartwood) could be small due to lack of enough water for the movement of compounds from the wood to the geopolymer matrix and/or the shorter time taken for the geopolymer containing wood to consolidate. However, when the wood particles were treated in NaOH solution before using in GWC formulation, most of these strength-reduction compounds were extracted out. Thus, more compounds and materials leached into the NaOH solution during

pretreatment of the wood than when the wood was used directly (without treatment) to produce GWC.

In contrast to these results, Sarmin et al. [30] demonstrated with a NaOH-treated *Picea abies* veneer that the debonding strength between the veneer embedded in a blend of fly ash/metakaolin geopolymer was reduced compared to the untreated one. It is possible that the strength of sapwood and heartwood treated samples may increase not only due to the removal of extracts, but also due to the removal of hemicelluloses, as Ye et al. [9] found that hemicelluloses act as one of the major components of wood that hinders geopolymerization. The increase in strength suggests that washing wood with NaOH solution is one possible way of removing inhibitory substances in wood before use in a GWC. However, this should be further confirmed in the future work.

Influence of pine sapwood and heartwood extractives on the specific strength

The effect of pine sapwood and hardwood extractives on the pure fly ash-based geopolymer is shown in Fig. 7. The specific strength of the control sample was significantly different from the geopolymers with pine extractives. This indicates that there are pine specific extractives which hinder the geopolymerization process thereby reducing the strength. However, among the geopolymers with extracts, no significant difference was observed between the specific strengths of the ones containing sapwood and heartwood extractives. According to Cabangon et al. [19], heartwood has higher solubility than sapwood suggesting larger amounts of substance that could be leached out during the extraction process. Despite the fact that the diversity of compounds is higher in sapwood extracts than in hardwood extracts, some similar compounds were extracted from both the sapwood and the heartwood (section "Effect of softwood specific extracts on the specific compressive strength of pure fly ash geopolymer"), although the amount (i.e., the yield) of the extracts was different (see Table 3). The similar nature of the compounds extracted might have resulted in the strength behaviors of the geopolymer with sapwood extract and the heartwood extract. It is likely that one or a combination of these extracts might have caused the reduction in the specific strength of the geopolymer.
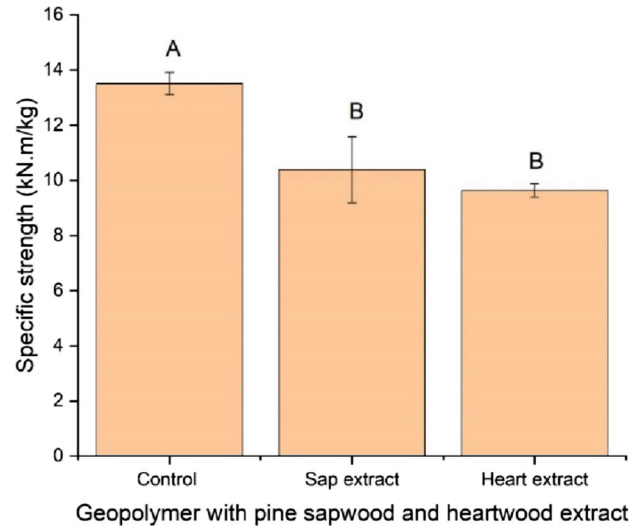

Figure 7 Specific compressive strength of pure fly ash geopolymer with pine sapwood and heartwood extracts.
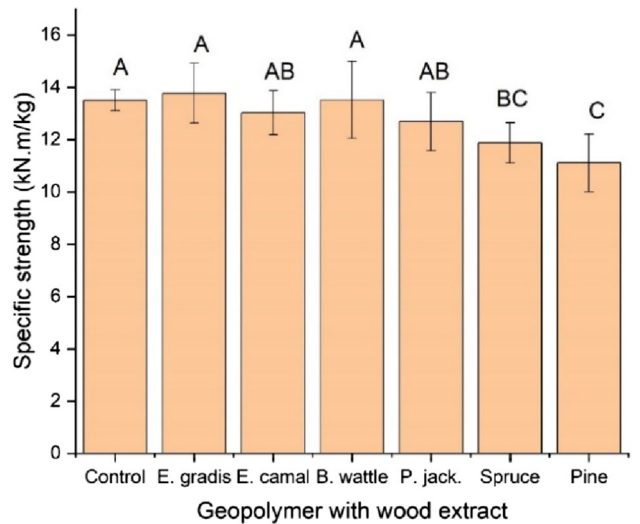

Figure 8 Specific compressive strength of pure fly ash geopolymer with hardwood and softwood extractives (Means with same letters are not significantly different; $p > 0.05$).

Effects of softwood and hardwood extract on the specific strength of fly ash geopolymer

Figure 8 shows the specific strength of a geopolymer with different hardwood and softwood extractives. Specific strength values of 11.11 kN m/kg and 11.87 kN m/kg were recorded for geopolymers with pine and spruce softwood, respectively, while a range of 12.69–13.77 kN m/kg was recorded for geopolymers with hardwood extractives. In comparison with the control (13.51 kN m/kg), it can be seen

that the specific strength of the geopolymers with hardwood extracts was not significantly affected. However, the specific strength of geopolymers with softwood extractives was significantly affected; with geopolymers containing pine extractive recording the least strength. The differences in specific strength between the geopolymers with hardwood extracts and the softwood extracts could be as a result of the differences in compounds being leached out from these wood into the geopolymer matrix. There are considerable differences between extractives in softwoods and hardwoods. For example, resin acids are found only in softwoods, but not in hardwoods while fatty acids are present in both hardwood and softwood in different composition and quantity [31, 32]. In the present work, when fatty acids and resin acid were tested in geopolymer, there was a reduction in the specific strength (see section "Effect of softwood specific extracts on the specific compressive strength of pure fly ash geopolymer"). The authors believe that the fatty acids tested were not present in the hardwood extracts since the specific strengths of geopolymers with hardwood extracts were not affected (Fig. 8). On the basis of this assumption, the authors postulate that resin acids, which are only present in softwoods as well as being abundant in pine wood, might be one of the contributing extracts that caused the differences in specific strengths. That is to say the different compounds in softwoods and hardwoods may have reacted differently in the geopolymers, resulting in different specific strengths. Similarly, Asante et al. [16] found that a GWC made of eucalypt wood would have a higher specific compression strength than one made of pine wood. The same authors concluded that there might be pine specific extractives hindering the geopolymerization process and therefore, causing a reduction in strength.

GC/MS-FID analysis of pine sapwood and heartwood extractives extracted with NaOH

From the aliquots (50 ml) of alkaline extractive solutions, a portion of DCM-soluble compounds could be extracted in various amounts depending on the pH-value during liquid–liquid extraction. The heartwood sample shows a higher amount of DCM-soluble with approx. 0.6 g considering the aliquot volume. Thereof, 47% of the DCM-extract from the heartwood

sample is attributable to the first extraction step at pH-value 7, while 52% is accounted to pH-value 2. In the case of sapwood, the amounts of each pH-value step were allocated in reverse order (pH-value 7: 57%; pH-value 2: 43%). Besides the DCM-soluble fractions, solid non-DCM-soluble fractions were found due precipitation from the liquid phase. From these aliquots, only small amounts of probably lignin-derived compounds were found (heartwood: 0.1 g, sapwood: 0.005 g). This comes as no surprise as NaOH pretreatment is known to partially solubilize lignin [33, 34]. Nevertheless, the percentage solubility of lignin-derived compounds was slightly higher in the heartwood than in the sapwood. This may be due to the high amount of lignin in pine heartwood when compared to pine sapwood, as reported by Bertaud and Holmbom [35].

Table 6 shows the composition of the DCM-soluble extracts from the alkaline extractives corresponding to their pH-value. It can be seen that the alkaline extractives consist of terpenoic compounds like pinene, carene as monomeric terpenes, terpineol and borneol as representatives of alcohols of monocyclic and bicyclic terpenes, respectively. Overall, higher amount of terpenes were found in the heartwood than in the sapwood. Similar observations were reported for radiata pine by Uprichard and Lloyd [36] and Ingram et al. [37]. Asides from this, non-specific low molecular weight substances like alcohols, ketones and acids (only in pH = 2 samples) also occur in each sample. Furthermore, typical compounds for pine wood extractives like salts and esters of abietic acid and stilbenes also occur predominantly in the heartwood samples, whereas high amounts of vanillin, p-Cymen-8-ol and pimarol were found at the acidic fraction of sapwood extractives.

Table 7 shows the distribution of higher molecular compounds, which are detectable due derivatization of the alkaline pine wood extractives. For this method, mainly aliphatic carboxylic acids can be detected by forming the corresponding methyl esters. Thereby a typical distribution between the composition of the heartwood and the sapwood extractives can be seen. The pine extractives mostly feature resin acids, lower terpenes, and fatty acids [38]. The GC-detectable compounds of sapwood extractives consist of up to 39 wt% of saturated and unsaturated fatty acids while terpenoids and resin acids account for an amount of 26 wt%; in the extractives from heartwood, terpenoids and resin acids occur

Table 6 Semi-quantification of DCM-extractable compounds of alkaline extractives from pine sap- and heartwood at pH-value 7 and 2 in relation to internal standard (IS) area

| Order of retention	Compound	Relative Area			
		Heartwood		Sapwood	
		pH 2	pH 7	pH 2	pH 7
1	Butanol, 2-methyl-2-	0.032	0.032	0.008	0.014
2	Butanone, 3-methyl-2-	0.034	0.015		
3	1,3-Dioxolane, 2,2,4-trimethyl-		0.005		0.005
4	Acetic acid	0.041		0.023	
5	Isobutyl methyl ketone	0.011	0.011	0.013	0.011
6	Pentanol, 1-				0.015
7	α-Pinene	0.023	0.021		
8	2-Heptanone				0.040
9	3-Carene	0.024	0.023		
10	Hexanoic acid			0.532	
11	Fenchol		0.030		
12	Pinocarveol				0.029
13	cis-Verbenol				0.099
14	Unknown Terpene		0.026		
15	(-)-4-Terpineol	0.015	0.082		0.029
16	Endo-Borneol	0.015	0.094		0.029
17	Similar to α-Terpineol		0.024		
18	α-Terpineol	0.047	0.304		0.027
19	p-Cymen-8-ol		0.054		0.182
20	similar to p-Cymen-8-ol		0.054		0.182
21	cis-Carveol				0.043
22	Guaiacol, 4-vinyl-	0.042			
23	α-Muurolene	0.018	0.012		
24	β-Cadinene	0.010			
25	α-Calacorene	0.006			
26	Vanillin	0.015	0.158		0.705
27	α-Campholenaldehyde				0.055
28	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)				0.027
29	Pimara-8(14),15-diene	0.010			
30	Isobutyl phthalate (softener)	0.010			0.018
31	13-Epi-Manoyl oxide	0.005			
32	Fluoranthene (IS)	1.000	1.000	1.000	1.000
33	Pimaral	0.123	0.095		0.034
34	Naphthalene, 1-phenyl- (impurity IS)	0.013	0.013	0.012	0.014
35	Isopimara-7,15-dienal	0.053	0.040		0.017
36	Pimarol (spectrum not confirmed)	0.074	0.055		0.125
37	Dehydroabietal	0.016	0.012		0.012
38	trans-3,5-Dimethoxystilbene	0.027	0.022		
39	Dehydroabietic acid methyl ester	0.037	0.028		
	Methyl dehydroabietate				0.014
40	Abietal (spectrum not confirmed)	0.019	0.013		
41	Methyl abietate	0.012			
42	Dehydro-4-epiabietol				0.017
43	4′-Methoxy-2-hydroxystilbene	0.684	1.309		

Table 7 Semi-quantification of DCM extractable compounds of alkaline extractives from pine sapwood and heartwood at pH-value 2 after derivatization with TMAH

No	Compound	Relative area (%)	
		Sapwood	Heartwood
1	Methyl dehydroabietate	26.0	33.6
2	Methyl sandaracopimarate	4.5	19.7
3	Methyl abietate		15.7
4	trans-3,5-Dimethoxystilbene		9.0
5	Nonanedioic acid dimethyl ester	10.3	
6	7-Oxodehydroabietic acid methyl ester	7.7	2.9
7	x-Octadecenoic acid, methyl ester	6.7	
8	Cyclotrisiloxane, hexamethyl-	4.2	0.2
9	Cyclotetrasiloxane, octamethyl-	3.9	0.3
10	Methyl 7-methoxyabieta-6,9(11),8(14),12-tetraen-18-oate	3.7	3.7
11	Nonanoic acid, methyl ester	3.7	0.3
12	Hexanoic acid, methyl ester	3.6	0.7
13	Hexadecanoic acid, methyl ester	3.4	2.8
14	Octanoic acid, methyl ester	2.3	0.2
15	Cyclopentasiloxane, decamethyl-	1.9	0.4
16	Methyl abieta-8,13(15)-dien-18-oate		1.8
17	Hexadecanoic acid, 14-methyl-, methyl ester	1.8	0.4
18	Stigmasta-3,5-dien-7-one	1.7	
19	similar to Methyl sandaracopimarate		1.7
20	Benzaldehyde, 3,4-dimethoxy-	1.7	0.4
21	Hexanal	1.3	
22	Octanedioic acid, dimethyl ester	1.1	
23	Decanedioic acid, dimethyl ester	1.0	
24	Octadecanoic acid, methyl ester	1.0	0.7
25	Cyclohexasiloxane, dodecamethyl-	1.0	0.6
26	Heptanoic acid, methyl ester	0.9	
27	Benzoic acid, 3,4-dimethoxy-, methyl ester	0.9	0.2
28	Undecanedioic acid, dimethyl ester	0.8	
29	Cycloheptasiloxane, tetradecamethyl-	0.7	0.2
30	Cyclooctasiloxane, hexadecamethyl-	0.6	
31	Decanoic acid, 9-oxo-, methyl ester	0.5	
32	Decanoic acid, methyl ester	0.5	0.2
33	Tetradecanoic acid, methyl ester	0.5	0.2
34	Cyclononasiloxane, octadecamethyl-	0.4	
35	Benzoic acid, methyl ester		0.4
36	Siloxane compound	0.3	
37	Heptadecanoic acid, methyl ester	0.3	
38	Cyclodecasiloxane, eicosamethyl-	0.3	
39	Alpha-Terpineol		0.3
40	x,y-Octadecadienoic acid methyl ester	0.3	
41	Acetophenone, 3,4-dimethoxy-	0.2	
42	Tetradecanoic acid, x-methyl-, methyl ester	0.2	

predominantly, with an amount of up to 51 wt% of the GC-detectable substances. Meanwhile aliphatic carboxylic acids represent only a small amount (up to 5 wt%) of the extractives. Most of the fatty acids are present as glycerides, the predominant acids being oleic and linoleic in pine wood [36]. The authors further stated that the relative amounts of these two acids changed on transition from sapwood to heartwood. Although resin acids that exist both in sapwood and heartwood higher concentrations are present in the heartwood. Uprichard and Lloyd [36] found that resin acids predominate and constitute between 70 and 80% of the pine heartwood's total extractives. The total amount of extract is higher in heartwood (see Table 3); however, the diversity of compounds is higher in sapwood samples than in hardwood samples (Table 7). The five compounds with the highest amounts represent, in the case of heartwood up to 78 wt% of the GC-detectable compounds, these compounds representing only 41 wt% in the sapwood samples. Martinex-Inigo [39] and Turtola [40] reported that the total resin acid concentration in Scots pine heartwood is much higher than in sapwood, but the composition of resin acids was similar. In a study by Arshadi et al. [41], Scots pine heartwood contained up to five times more extractives than sapwood. Furthermore, the authors reported that resin acids were mainly associated with heartwood, but fatty acids were found more in sapwood.

Effect of softwood specific extracts on the specific compressive strength of pure fly ash geopolymer

It is a well-established fact that in high alkaline environments, non-structural wood compounds such as polyphenolics (tannins), dyes, simple sugars, resin and fatty acids are dissolved from wood [42, 43]. One of the major differences in extract composition between the sapwood and heartwood of pine is their proportion of fatty and resin acids (section "Effect of softwood specific extracts on the specific compressive strength of pure fly ash geopolymer"). The sapwood contains more fatty acids while the heartwood contains more resin acids as was also reported by Uprichard and Lloyd [36] and Back and Allen [44]. For these reasons, in order to understand the influence of specific extractives on the strength of a fly ash-based geopolymer, the authors of the present work
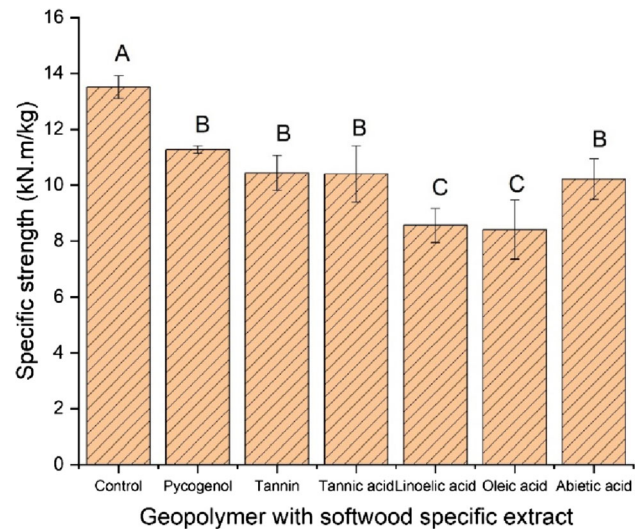
Figure 9 Specific compressive strength of pure fly ash geopolymer with softwood specific extracts.

considered two fatty acids (linoleic and oleic acids), one resin acid (i.e., abietic acid) and three polyphenols (i.e., condensed tannins, pycnogenol and tannic acids).

A lower specific strength was recorded for all the tested specific extractives when compared to the control group (Fig. 9). There was no significant difference between geopolymer composites containing polyphenols (i.e., pycnogenol, tannin and tannic acid) and resin acids (abietic acid). Generally, geopolymers containing linoleic and oleic acids (fatty acids) recorded the lowest specific strengths. Although Portland cement differs from a geopolymer in some ways, similar observations were made by Tugrul Albayrak et al. [45], who found out oleic acid and sunflower oil (containing oleic and linoleic acids) decrease the compressive strength of concrete.

In a process called saponification, Shill et al. [46] and Shill et al. [47] found that esters of fatty acids reacted at high temperatures with free sodium hydroxide in a fly ash geopolymer to produce sodium carboxylate, which is a salt. Furthermore, Shill et al. [46] determined that soap and salt compounds, such as sodium carboxylate and sodium phosphates, were present in the fly ash geopolymer mortar after saponification had occurred. The authors defined this process of the formation of soap compounds on a geopolymer as saponification of a geopolymer. It is believed that the formation of soap compounds in geopolymer took place when the fatty acids (i.e., linoleic and oleic acids) were exposed to

the geopolymer at 60 °C, resulting in the saponification of the geopolymer. This caused the geopolymer to weaken and lose its compressive strength, as was also observed by Shill et al. [46].

It was discovered that geopolymers containing fatty acids and resin acid/polyphenols differed significantly in specific strength. Since all extractive compounds investigated in this study reduced the specific strength of the geopolymer, the combined effect of these specific extractives could even be greater. However, this might depend on other factors, such as the amount and nature of wood extractives present in the mixture as observed in cement [48–51].

Conclusions

In this study, fly ash-based geopolymer composites were produced to investigate the influence of four (4) hardwoods and two (2) softwoods extractives on the specific compressive strength. The authors focused more on the influence of pine wood's difference in heartwood and sapwood, and their extractives on fly ash-based geopolymer as the greatest reduction in specific strength was observed for the geopolymer containing pine extracts. The following conclusions were made from the study:

- The specific strengths of geopolymers with hardwood (i.e., *E. grandis*, *E. camaldulensis*, P. jackson and B. wattle) extracts were not affected, while those with the softwood (i.e., spruce and pine) were reduced.
- The highest specific strength reduction was observed in geopolymer with pine extract.
- The total amount of extract (the yield) is higher in heartwood than in sapwood of pine. However, the diversity of compounds is higher in sapwood extract than in heartwood extract.
- All the tested specific extracts (i.e., pycnogenol, tannin, tannic acid, abietic acid, linoleic and oleic acids) recorded lower specific strengths when compared to the control, suggesting that the combined effect of these specific extractives could even be greater on the GWC strength and geopolymer-wood compatibility.
- Among the single pure compounds investigated in this present study, the fatty acids (i.e., linoleic and oleic acids) led to the greatest reduction in specific strength in the geopolymer.

- There was no difference between the GWCs with untreated sapwood and heartwood. However, with NaOH pretreatment of the wood there was a 21% and 10% increase in the specific strength of GWCs with sapwood and heartwood, respectively.

Declarations

Conflict of interest The authors declare no conflict of interest that could have appeared to influence the work reported in this paper.

Ethical approval All authors certify that no human experiments were used.

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