



Development of bentonite-based organo-geopolymer hybrid wood binder

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Abstract

The study addresses concerns associated with formaldehyde-based adhesives in wood panel board production by proposing geopolymer-based wood binders as promising, formaldehyde-free alternatives. Using bentonite, the research delves into the development and performance properties of this geopolymer wood binder. The BET method was employed for the surface characterization of precursor raw materials for binder preparation. Si and Al elements identified through XRF analysis were correlated with characteristic bands in the FTIR spectrum. Alkaline activation solutions, employing sodium silicate and sodium hydroxide with a molar ratio range of 0.5 to 2.5 ($\text{SiO}_2:\text{Na}_2\text{O}$), revealed that binders with a molar ratio of 2.5 exhibited lower pH and higher adhesion strength. Different geopolymer formulations at solution to powder ratios (s/p) of 1.33, 3, and 3.5 determined s/p 3.5 as optimal for bentonite-based organo-geopolymer binders. Viscosity, gel time, pH, and solids content were examined, showing the effectiveness of substituting 10% silica fume to enhance the geopolymerization process and improve adhesion. Modifications using citric acid, sucrose, paraffin, pMDI, triacetin, and resorcinol demonstrated wet bonding strength comparable to urea formaldehyde adhesive. Analytical techniques, including FTIR spectroscopy, XRD analysis, and SEM EDX analysis, provided insights into functional groups, crystallographic properties, and microstructural characteristics. The concentration of Si and Al compounds on the bonding line, coupled with Na element diffusion, was observed through these analyses. Light microscopy of lap shear samples revealed a thinner bonding line, affirming effective binder penetration into wood cell lumens in bentonite-based organo-geopolymer binder formulations.

1 Introduction

Geopolymerization is a process in which three-dimensional aluminosilicate polymeric materials are formed in alkaline media by utilizing solid aluminosilicates and alkali hydroxides or alkali metal silicate solutions. This process, referred to as the geopolymerization process (Hajimohammadi et al. 2008), generates polymers consisting of a repeating silicate unit ($-\text{Si}-\text{O}-\text{Al}-\text{O}-$). In geopolymerization technology, pozzolanic substances with high aluminosilicate content, such

as kaolin, metakaolin, feldspar, industrial waste fly ashes, metallurgical slag, and mining waste, serve as primary or secondary binders (Singh et al. 2015). The reactivity of these aluminosilicate sources depends on their chemical structure, mineral composition, particle size, and glassy phase content. Geopolymer production avoids using resources with crystalline silicon and aluminum due to their low reactivity towards alkaline solutions (Rees 2007). Aluminosilicates with small particle size and high surface area ($30\text{m}^2/\text{g}$) are preferred for the reaction (Rees 2007; Provis et al. 2009). It has been reported that any substance in amorphous form containing silicon (Si) and aluminum (Al) can serve as a source for geopolymer production (Davidovits 2008).

Secondary binder materials in geopolymer production are typically silicon-rich substances such as silica fume, altering the Si/Al ratio in the formulation. The key criterion for

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selecting these materials is that they dissolve faster than the primary material, releasing silicon into the environment and acting as silicate-activating solutions (Rees 2007). Alkaline activators like sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3), and potassium silicate (K_2SiO_3) are commonly used in geopolymer production.

In the geopolymerization process, the silicate concentration in the environment and the presence of aluminum in the reaction medium are crucial parameters affecting various properties of the geopolymer (Singh et al. 2015; Duxson and Provis 2008). The molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in geopolymer pastes intended for the construction industry is reported to be between 3.0 and 3.8 (Singh et al. 2015). Nevertheless, this ratio alone cannot fulfill the strength, performance, and durability expectations of the relevant materials. The formulation of the geopolymer, mixing procedure, as well as the additives and fillers used, along with the curing method and temperature, are crucial parameters.

The geopolymer's hardening time increases with a higher Si/Al ratio in the initial mixture. Introducing compounds like sucrose and citric acid to the geopolymer mixture can serve as accelerators or retardants. Sucrose is absorbed by Ca, Al, and Fe ions. Subsequently, it acts as a retarder by influencing the Si/Al ratio through the formation of insoluble metal complexes. (Singh et al. 2015). The hardening temperature of geopolymer binders, prepared with different chemical compositions, ranges between 20 °C and 85 °C, with increased durability as the hardening time extends.

Recently developed geopolymeric materials are notable for their high resistance to elevated temperatures, fire effects, and their tolerance to acidic and salty environments. Moreover, employing geopolymers in applications like roads, railways, sustainable building materials, pollutant encapsulation, and radioactive blocking offers the benefit of minimizing CO_2 emissions during production (Rees 2007; Ye et al. 2018; Provis et al. 2009).

Wood board production technology has seen substantial advancements, particularly in the last half century. Despite notable changes in adhesive and resin types, along with their chemical compositions, the primary objectives in wood board production remain focused on achieving lower costs, superior moisture resistance, and enhanced mechanical performance properties. Numerous studies on wood adhesive development utilize natural phenolic compounds, tannins, technical lignin, cellulose, plant-derived starch, and other renewable resources, often derived from bio sources. These are employed either in the formulation of formaldehyde containing adhesives used in wood board products or as substitutes for adhesives (Pizzi 2016; Gönültaş 2018). Additionally, it has been noted that incorporating pozzolanic materials into binder formulations for wood-based

panels, traditionally produced with formaldehyde containing adhesives, reduces formaldehyde emissions due to the rough, irregular, and porous structures of these materials (Kim 2009). Triacetin (glycerintriacetate) serves as an accelerator compound capable of reacting with cellulose in formaldehyde-free bio-based adhesive formulations (Xi and Pizzi 2020). pMDI (polymeric 4,4'-diphenylmethane diisocyanate) and resorcinol are recognized for enhancing wet strength properties through improved cross-linking in wood adhesives (Pizzi and Mittal 2017). Additionally, paraffin emulsion finds utility in both wood-based panel production (Xi et al. 2019) and enhancing water repellent properties in geopolymer formulations (Reeb et al. 2021).

In recent years, there has been a growing interest in developing geopolymer composites that incorporate lignocellulosic fibers and waste wood sawdust (Berzins et al. 2017; Pan et al. 2020; Ye et al. 2018). Concurrently, the emergence of geopolymer polymer binders has introduced a new eco-friendly class for the production of wood-based panels (Bahrami et al. 2019; Shalbafan et al. 2016, 2020). Binders for wood-based panels were formulated using various precursors such as kaolin, metakaolin, silica fume, and fly ash. These geopolymer binders underwent thorough characterization tests. The adoption of geopolymers as binders in wood-based panels has shown improvements in board durability, hardness, and resistance to flame, acid, fungi, and mold (Allahverdipoorazar et al. 2021; Bahrami et al. 2019; Pan et al. 2020). Enhanced durability and adhesion performance properties can be achieved by physically or chemically modifying geopolymer wood-based panel binders using organic-inorganic hybrid modification technologies. Incorporating organic and inorganic fibers and water-resistant polyurethanes can contribute to this enhancement (Pan et al. 2020).

Bentonites, containing smectite group minerals, find application in various industries, including ceramics, iron ore pellets, foundry sand, drilling mud, nuclear waste barriers, cat litter, insecticides, medicine, paint, food, rubber, cosmetics, and plastics. These minerals, such as calcium montmorillonite and sodium montmorillonite, are common in bentonites, along with smaller amounts of illite and non-clay minerals like zeolite, quartz, silica polymorphs, and opal (Önal and Sarıkaya 2007; Grim and Güven 1978; Gong et al. 2016).

In this study, these enduring goals are addressed by exploring new methods, especially through the development of a bentonite-based geopolymer that eliminates carcinogenic formaldehyde. The study involves the formulation of a binder using bentonite sourced from mining areas in the Marmara region of Turkey at solution/powder (s/p) ratios of 1.33, 3, and 3.5 (Shalbafan et al. 2016). The bentonite-based geopolymer as a binder for wood-based panel is

developed at various alkaline activator concentrations, with a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio ranging between 0.5 and 3.5, and characterized using different methods.

2 Materials and methods

2.1 Raw materials

Bentonite (Akerkim, İstanbul, Türkiye), kaolin (Akerkim, İstanbul, Türkiye), and silica fume (Akerkim, İstanbul, Türkiye) served as aluminosilicate sources (precursors) in geopolymer wood panel binder formulations. For the alkali activator preparation, sodium hydroxide (Analytical grade, Merck) and sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio: 3.48, pH 11.36, density 1.35 g/cm^3 , Merck, Darmstadt, Germany) were utilized. Other additives (citric acid, sucrose, pMDI, resorcinol, and triacetin) are of analytical grade. Urea formaldehyde adhesive (65% solids, 1.17 formaldehyde: urea molar ratio, pH 8.55) and paraffin solution (60% solids, density 0.95 g/cm^3) were supplied by KEAS (Gebze, Türkiye) company. The properties of the prepared wood panel binder were compared with those of commercial urea formaldehyde adhesive and kaolin-based geopolymer.

2.2 Binder preparation

The properties of geopolymer are known to vary depending on the Si: Al molar ratio during the preparation process. The precursors, acting as binding materials, require activation in an alkaline environment. In this study, an activating solution for the binder material was prepared using 8 M NaOH and Na_2SiO_3 (sodium silicate). Five different alkali activator solutions with $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratios (silicate modulus) of 0.5, 1, 1.5, 2, and 2.5 were prepared using 8 M NaOH. These solutions were then used in geopolymer formations.

For the geopolymer binder preparation, formulations (Table 1) with kaolin, and bentonite as well as alkali activator mass ratios (solution to powder ratio - s/p) of 1:1, 1:1.33, 3, and 3.5 were created. Additionally, formulations with ratios of 1.66 for kaolin (which does not exhibit binder properties due to high viscosity and immiscibility), and 1, 2, and 2.5 for bentonite were also tested.

Alkaline activation solutions were prepared 24 h prior to use for cooling and to ensure homogeneity. During the preparation of geopolymer binder formulations, kaolin and bentonite were mechanically mixed with the alkaline activation solution (1500 rpm) for 30 min at laboratory temperature. In various formulations, the aluminosilicate mass was adjusted by the mass of the corresponding additive. Following the

Table 1 Variable compositions of the precursor powder in geopolymer binder

Group	Mass content in geopolymer binder (%)				Total mass of precursor and additives to alkali activation solution (% w/w)	Solution to powder ratio (s/p)
	Bentonite	Kaolin	Silica fume	Other additives		
K1		100			75	1.33
K2		100			75	1.33
K3		100			75	1.33
K4		100			75	1.33
K5		100			75	1.33
K6		100			28.5	3.5
B1	100				33.3	3
B2	100				33.3	3
B3	100				33.3	3
B4	100				33.3	3
B5	100				33.3	3
B6	100				28.5	3.5
B7	90		10		28.5	3.5
B8	98			2 citric acid	28.5	3.5
B9	98			2 sucrose	28.5	3.5
B10	90			10 parafine	28.5	3.5
B11	80			20 parafine	28.5	3.5
B12	80			20 pMDI	28.5	3.5
B13	95			5 resorcinol	28.5	3.5
B14	80			20 triacetin	28.5	3.5
B15	85		10	5 resorcinol*	28.5	3.5

*10% glyoxal by weight of resorcinol

initial mixing, additives were introduced to the formulations, and homogeneity was achieved through an additional 20 min of mechanical mixing. Citric acid and sucrose were added to the formulations in powder form, while paraffin, pMDI, resorcinol, and triacetin were added as liquids.

2.3 Testing methods

Surface area values of the precursor raw materials were determined in the samples through nitrogen (N_2) gas adsorption in a liquid nitrogen environment at 77 K, utilizing the BET (Brunauer-Emmett-Teller) technique on the Micromeritics Tristar II device (Micromeritics Instrument Company, Norcross, USA). Analyses were conducted after subjecting approximately 1 g of the sample to a degassing process in a vacuum oven at 150 °C for 6 h. To determine the chemical composition of the raw materials serving as aluminosilicate sources in geopolymer production, a X-ray fluorescence spectrometer (XRF) (Rigaku Supermini200 model, SQX software program, Rigaku, Tokyo, Japan) was employed.

The curing (gel time) and viscosity values of the prepared geopolymer wood binder were assessed using the standard method applied for urea formaldehyde adhesive (Bahrami et al. 2019). Viscosity was determined at 20 °C at 10 rpm using a Brookfield DV-II+ Pro viscometer RVHV-4 and 5 spindles (Brookfield, Middleboro, USA). For gel time determination, approximately 10 g of the sample was placed in a 100 °C water bath on a magnetic stirrer in a 25 ml beaker. The gel time was identified when the sample gelled and became unmixable. Three repetitions were conducted for each sample.

The adhesion performance of the geopolymer binder, prepared using precursor minerals and activators, was evaluated through a lap shear test. It was compared with lap shear samples prepared using commercial urea formaldehyde adhesive as a control sample. The UF adhesive was cured by the addition of a 20% ammonium chloride solution, constituting 2% based on the solid adhesive. Flawless beech (*Fagus orientalis*) veneers of 3 mm thickness, 25 mm width, and 115 mm length were employed for this purpose.

The veneers were conditioned by maintaining them at 20 °C and 65% relative humidity for two weeks before usage. The lap shear test specimen is illustrated in Fig. 1. A binder of 210 g/m² was applied to an area of 25 mm x 25 mm on one side of the veneers and combined with the unglued veneer. The resulting two-layer test sample was pressed using a laboratory-type Carver (3969 Bench Top, Carver Inc., Wabash, USA) hot press at 140 °C for 5 min with 4.5 mm thick metal thickness control rods (Bahrami et al. 2019). Following the process, the samples were conditioned at 20 °C and 65% relative humidity for two weeks. Bond strength values in the samples were determined on a universal testing machine (Shimadzu AG-IC, Shimadzu Corporation, Kyoto, Japan) at a speed of 3 mm/min. Before the wet bonding tests, the samples were immersed in 20 °C water for 24 h, and after the process, the surfaces were dried with paper towels and tested. Ten tests were performed for each sample.

Before FTIR analysis, cured geopolymer binder samples, which were cured at 100 °C for 12 h, underwent an additional drying process in an oven at 50 °C for another 12 h. Subsequently, FTIR spectra were obtained using the Bruker Tensor 37 device (Bruker Optik GmbH, Ettlingen, Germany) ATR module to examine the functional groups in the structure of the samples, which were ground into powder in a mortar. Measurements were conducted in the wavelength range of 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹, totaling 32 measurements. The spectra were evaluated using Bruker OPUS software.

The adhesion performance of the geopolymer binder is significantly influenced by the amorphous nature of the polymer. Therefore, information was gathered about the crystallographic properties of the cured geopolymer binder using the X-ray diffraction (XRD) analysis method. The geopolymer binder, cured by being kept in an oven at 100 °C, was ground and sieved through a 200-mesh sieve before analysis. XRD analysis was carried out on a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) instrument at ambient temperature, utilizing a nickel-filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). It was examined under the conditions of a

Fig. 1 Lap shear specimen

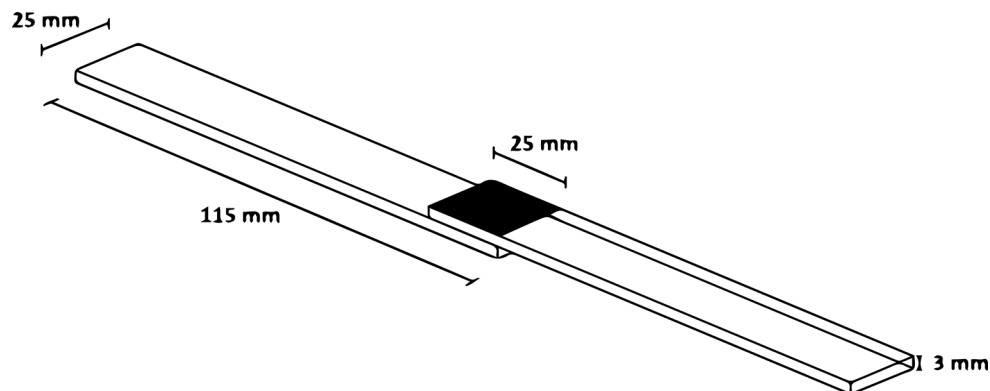


Table 2 Chemical composition of the raw materials based on XRF

Element (mass, %)	Kaolin	Silica Fume	Bentonite
MgO	6.05	4.14	2.71
Al ₂ O ₃	15.30	0.17	14.30
SiO ₂	62.10	87.6	75.90
P ₂ O ₅	0.11	-	-
SO ₃	3.22	1.14	-
CaO	10.6	0.20	1.38
TiO ₂	0.49	-	0.07
Fe ₂ O ₃	0.56	0.54	0.84
K ₂ O	-	1.97	-
Na ₂ O	-	1.63	-
ZnO	-	-	3.70

0.5°/min, scanning rate, a 2 Θ 5°-80° diffraction angle, and 0.02°/s step intervals.

The surface interface interaction between wood and geopolymer was examined using a stereo optical microscope (Carl Zeiss, Stemi 305, Germany) on samples approximately 1 cm³ in size. Images were exported using ImageView software. Microstructural characterizations of the adhesion area on lap shear samples, prepared with geopolymer binder, were conducted using a scanning electron microscope (SEM) (Carl Zeiss/Gemini 300, Carl Zeiss AG, Oberkochen, Germany). The samples, cut into cubes of approximately 1 cm³, were dried under vacuum in a vacuum oven at 60 °C for 24 h. Subsequently, the surfaces of the samples were coated with gold and palladium using a Leica/ACE600 at an intensity of 20 mA for 30 s. An energy-dispersive X-ray spectroscopy (EDX) analysis was performed using a QUANTAX analysis system (Bruker, XFlash 6-100, Germany) to detect the distribution and diffusion patterns of silicon, aluminum, and sodium elements in the bonding line of the samples by mapping.

3 Results and discussion

3.1 Characterization of the raw materials

Surface area measurements (BET analysis) were conducted for the purpose of surface characterization in precursor samples. The surface areas of kaolin and silica fume were determined to be 15.16 m²/g and 21.58 m²/g, respectively, while the bentonite sample exhibited a surface area of 65.59 m²/g. It has been reported that higher surface area values can lead to increased viscosity and improved solubility properties in the alkaline activator (Bahrami et al. 2019). Additionally, it is suggested that a lower surface area in the geopolymer binder generally results in lower strength values (Singh et al. 2015).

Table 3 pH and viscosity values of activation solution with different silicate modulus (SM)

Activator Solution	pH	Viscosity (cP)
Sodium silicate	11.76	39
SM 0.5	13.48	14
SM 1	12.85	16
SM 1.5	12.33	20
SM 2	12.15	22
SM 2.5	11.95	26

The chemical components of precursor raw materials were identified through XRF analysis. Upon examination of the results in Table 2, it is evident that SiO₂, Al₂O₃, MgO, and CaO are the primary components. Notably, the bentonite sample demonstrates a high percentage of the components essential for geopolymer production, with the sum of SiO₂ and Al₂O₃ reaching 90.20%. This composition suggests the material's potential use in geopolymer applications (Yahya et al. 2013). The Si/Al ratio for kaolin and bentonite samples was determined as 4.05 and 5.30, respectively. The Si/Al ratio plays a crucial role in influencing the geopolymer's microstructure, mechanical properties, compressive strength, and application suitability (Davidovits 1991). Specifically, a Si/Al ratio > 4 enhances mechanical properties (He et al. 2016; Duxson et al. 2007).

3.2 Characterization of geopolymer binder

The alkaline activation solutions utilized in formulating the geopolymer as a binder for wood-based panel were prepared using sodium silicate, with a SiO₂:Na₂O molar ratio (silicate modulus -SM) ranging from 0.5 to 2.5. The pH and viscosity properties of these solutions were determined and are presented in Table 3. Notably, it was observed that especially originating from polyose and partial lignin tended to darken on the wood material's surface due to the strong alkaline effect (pH 13.48) in the activation solution with a molar ratio of 0.5 (Ye et al. 2018). The high alkalinity is recognized to have a degrading impact on wood components (Pizzi 2014).

Geopolymer binder formulations were produced employing kaolin, silica fume, and bentonite (Table 4). These formulations underwent characterization, with parameters such as viscosity, gel time, pH, and solids content being determined.

In addition to the formulations listed in the table, kaolin was used with an alkaline s/p ratio of 1, while formulations with bentonite ratios of 1, 1.33, 1.5, and 2 were attempted. However, it was discovered that these formulations couldn't be utilized as a wood binder due to their high solids content and viscosity, preventing effective mixing even in a mechanical stirrer. Based on the viscosity and solid content results, it was determined that the most suitable s/p ratio for

Table 4 Properties of geopolymer binders

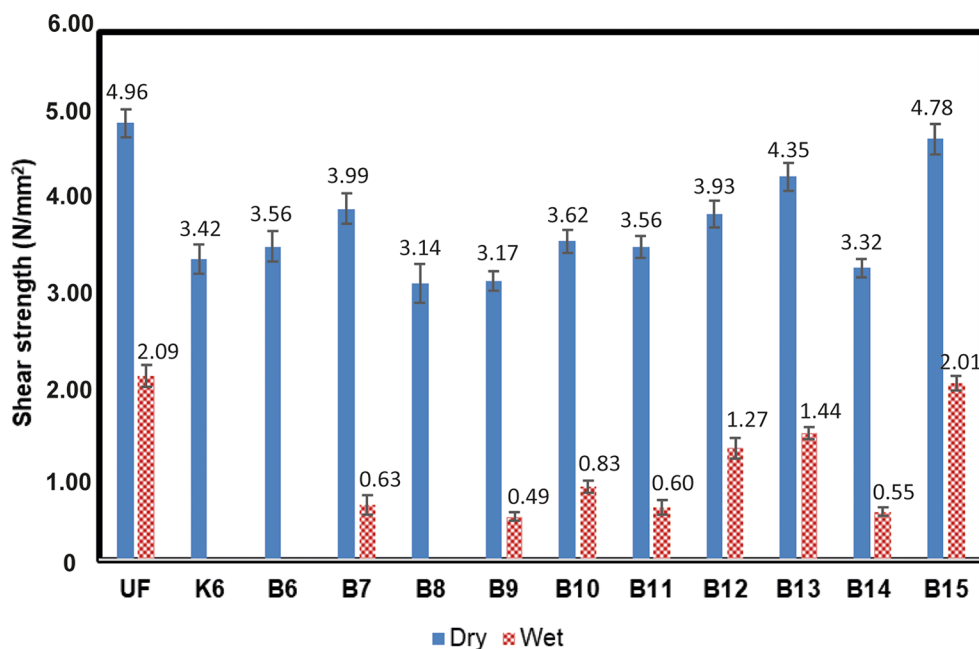
Group	Alkaline activator molar ratio (SiO ₂ :Na ₂ O)	Binder type	Solution to powder ratio (s/p)	Viscosity (cP)	Gel time (s)	pH	Solid content (%)
K1	0.5	Kaolin	1.33	316	252	12.86	64.15
K2	1	Kaolin	1.33	312	175	12.65	65.10
K3	1.5	Kaolin	1.33	278	114	11.94	66.68
K4	2	Kaolin	1.33	407	103	11.77	66.07
K5	2.5	Kaolin	1.33	608	134	11.79	65.77
K6	2.5	Kaolin	3.5	172	335	12.21	52.48
B1	0.5	Bentonite	3	1690	127	13.56	51.10
B2	1	Bentonite	3	1820	86	12.69	51.61
B3	1.5	Bentonite	3	1865	160	12.26	52.33
B4	2	Bentonite	3	2320	107	12.18	52.94
B5	2.5	Bentonite	3	3290	83	12.02	52.45
B6	2.5	Bentonite	3.5	2610	92	12.20	51.92
B7	2.5	Bentonite + 10% Silica fume	3.5	2570	94	12.25	52.68
B8	2.5	Bentonite + 2% Citric acid	3.5	3525	81	12.18	51.39
B9	2.5	Bentonite + 2% Sucrose	3.5	2980	125	12.21	51.84
B10	2.5	Bentonite + 10% Paraffine	3.5	2970	118	12.20	51.06
B11	2.5	Bentonite + 20% Paraffine	3.5	3060	103	12.17	51.11
B12	2.5	Bentonite + 20% pMDI	3.5	3180	76	12.17	52.25
B13	2.5	Bentonite + 5% Resorcinol	3.5	3010	70	12.09	51.69
B14	2.5	Bentonite + 20% Triacetin	3.5	2975	77	12.14	52.37
B15	2.5	Bentonite + 10% Silica fume + 5% Resorcinol+(10% glyoxal ^a)	3.5	2930	68	12.08	51.83

bentonite-based geopolymer is 3, whereas this ratio should be 3.5 for bentonite-based organo-geopolymer hybrid wood binder. Viscosity values of 3180 cP were observed for the B12 sample with an s/p ratio of 3.5, and even at this viscosity, the binder could be easily applied to the beech wood test samples. The viscosity and gel time values (K5) determined in geopolymer formulations prepared with kaolin, as reported by Bahrami et al. (2019), were found to be similar to the values obtained in this study. The addition of silica fume to the geopolymer formulation was demonstrated to reduce viscosity and extend gel time, aligning with similar results reported in the literature (Shalbafan and Thoemen 2020). The utilization of silica fume is noted to enhance the geopolymerization process by forming a dense matrix, improving geopolymer solidification, early-stage strength development, and reducing porosity. Consequently, this leads to mechanical and microstructural improvements as well as increased resistance to acids (Khater 2013; Lee et al. 2016; Okoye et al. 2016). Formulations prepared with bentonite (B1-B15) exhibited a lower solids ratio than those prepared with kaolin due to the higher s/p ratio (3 and 3.5). This enhancement improves the spreadability of the geopolymer binder on the wood surface (Shalbafan et al. 2016, 2020). It is noted that a higher water glass content in the geopolymer binder formulation also enhances the solubility of aluminosilicates (Heah et al. 2012). In geopolymer binders

prepared with both kaolin and bentonite, pH values were similar in samples with comparable alkaline activator molar ratios. Additionally, it was observed that geopolymer binder pH values decrease as this molar ratio increases. Therefore, starting from the B7 sample, formulations with an alkaline activator molar ratio of 2.5, which is more suitable for wood materials, were prepared. When comparing group B7 and group B15, it is observed that the presence of resorcinol in the formulation leads to an increase in viscosity, accompanied by a decrease in solid contents, gel time, and pH value. This rise in viscosity can be attributed to reactions occurring between resorcinol and glyoxal in the formulation.

3.3 Shear strength of lap-shear sample

Lap shear test samples were prepared with the formulations to measure the adhesion performance of the geopolymer binder, and both wet and dry bonding strength values were examined (Fig. 2). After immersing lap shear samples prepared with K1-K6 and B1-B6 binders in water at 20 °C for 24 h, it was observed that the samples separated and lacked wet bonding strength. In terms of dry bonding strength, the best results (K4-K5 and B4-B5) were obtained in the samples prepared with the activation solutions with a molar ratio of 2 and 2.5 SiO₂:Na₂O. Consequently, in the subsequent stage of the study, geopolymer binder formulations

Fig. 2 Bond strength of lap shear specimens

were prepared using only the activation solution with a molar ratio of 2.5. The lower pH values of these formulations, compared to other examples, make them preferable for binders used in wood materials.

The inclusion of 10% silica fume (B7) in the bentonite-based geopolymer formulation not only enhanced the dry bonding strength of the binder but also improved its wet bonding strength properties. Interestingly, the addition of citric acid as an additive did not show improvement in either dry or wet bonding properties, while the incorporation of sucrose not only improved wet strength but also increased the gel time (Singh et al. 2015). Samples B10 and B11 were modified with 10% and 20% paraffin, respectively. It has been demonstrated that using up to 10% paraffin in geopolymer binder formulations positively affects both dry and wet adhesion performance. Samples B12 and B13 contained 20% pMDI and 5% resorcinol, respectively, resulting in significantly higher dry and wet bonding strength values compared to the B6 sample. Although the B14 sample, which contained 20% triacetin, exhibited wet bonding strength, there was no improvement in the dry bonding strength value. In the case of the B15 sample, a bentonite-based organo-geopolymer hybrid wood binder containing 5% resorcinol, 10% glyoxal (based on resorcinol, w/w), and 10% silica fume, the dry strength value was very close to the UF control sample, and the highest wet strength value (2.01 N/mm²) within the geopolymer binder formulations studied was determined.

3.4 ATR-FTIR spectroscopy

The presence of amorphous silica (Si-O symmetric vibration) is indicated by a strong band in the 1003–1056 cm⁻¹ region in powdered precursor samples (Fig. 3), as reported in studies (Bahrami et al. 2019; Pan et al. 2020). The peak in the 795 cm⁻¹ region is identified as the Al-Mg-OH tension peak in three samples (Kumar and Lingfa 2020). In kaolin and bentonite samples, the peak at 913 cm⁻¹ is associated with the Al-Al-OH tension (Ravindra Reddy et al. 2017; Kumar and Lingfa 2020; Eren and Afsin 2008; Zhirong et al. 2011), while this peak is unclear in the silica fume sample. The regions identified for the bentonite sample represent SiO₄ tetrahedron vibration peaks. The peak at 1003 cm⁻¹ is reported to be characteristic of the layered silicate montmorillonite mineral and is related to the triple degenerate Si-O tension. Additionally, the bands at 515 cm⁻¹ and 452 cm⁻¹ are associated with Al-O-Si and Si-O-Si stretching vibrations, respectively (Eren and Afsin 2008; Zhirong et al. 2011).

Due to the similar masses of aluminum and silicon atoms, the broad band in the range of 1200–1000 cm⁻¹ in the FTIR spectrum generally corresponds to the mixed overlap of Si-O-Si, Al-O-Si, and Al-O-Al bonds (Chen et al. 2016). The peak at approximately 1640 cm⁻¹ in geopolymer binder samples represents the stretching and bending vibrations of water-borne hydroxyl groups in the samples (Bahrami et al. 2019; Pan et al. 2020; Shalbafan and Thoemen 2020; Ye et al. 2018). The Si-O chain structures in aluminosilicate powder samples change with the formation of Al-O-Si bonds after the geopolymerization process. This change causes the 1050 cm⁻¹ Si-O bond peak in powder samples to

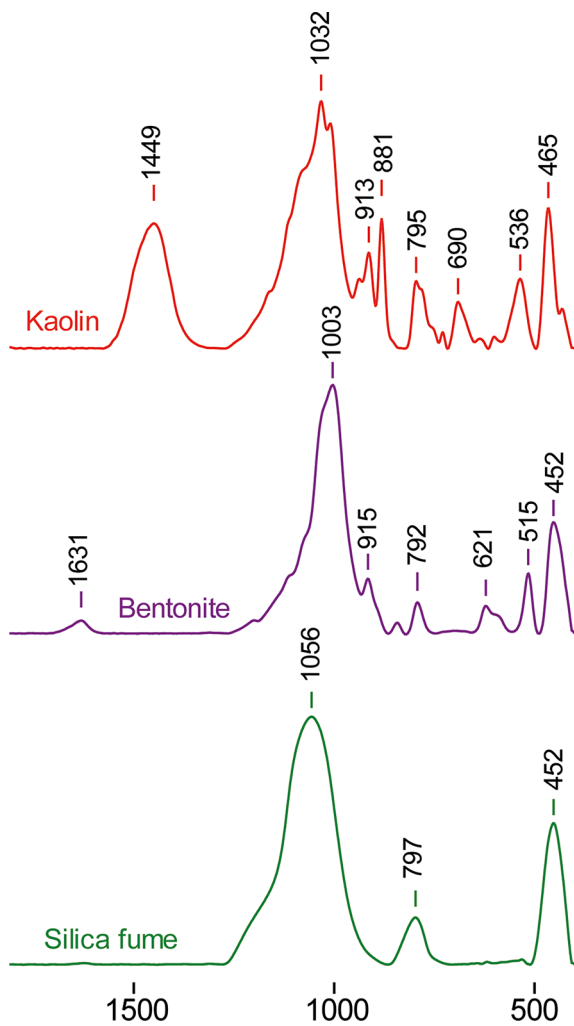
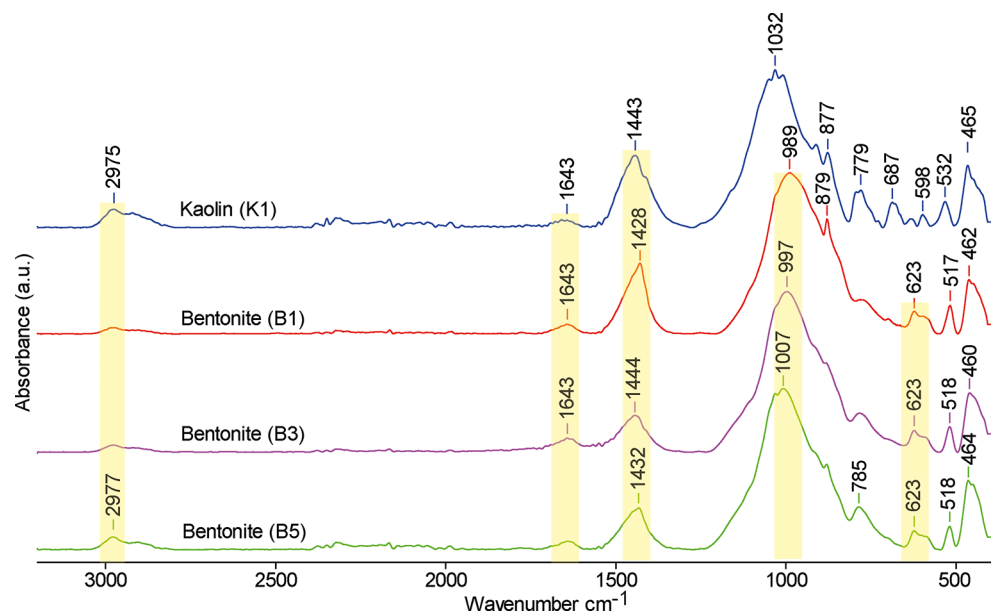


Fig. 3 Stacked FTIR spectra for precursors

Fig. 4 Stacked FTIR spectra for geopolymer binders (K1, B1, B3, and B5)



shift to the 900–1000 cm^{-1} asymmetric vibration region in geopolymers (Bahrami et al. 2019). The shift of the peak in the relevant region up to 950 cm^{-1} in geopolymer samples is claimed to indicate a better geopolymerization process (Shalbafan and Thoemen 2020). In bentonite-based geopolymer samples, this peak was determined at lower wavelengths. The peak observed in the 1440 cm^{-1} region in all samples is reported to be the O-C-C band tension vibration caused by atmospheric carbonation (Shalbafan et al. 2020). In the polymerization process of kaolin-based geopolymer samples (K1), the 690 cm^{-1} region is identified as the Al-O-Si cyclic structure symmetric tension vibration region (Bahrami et al. 2019) (see Fig. 4).

Si-O-Si and Al-O-Si tensions, indicating alkali aluminosilicate network formation in geopolymer samples, were identified in the 687 cm^{-1} region in kaolin-based binder formulations (Shalbafan and Thoemen 2020; Chen et al. 2016). The same peak for bentonite-based geopolymers was determined in the 623 cm^{-1} region. The peaks observed in the 464 cm^{-1} region were associated with Si-O-Al bending vibration (Chen et al. 2015; Moolenaar et al. 1970). The peak seen in the 783–787 cm^{-1} region in bentonite-based geopolymer formulations (Fig. 5) is linked to the asymmetric stress in the Al-O-Si bond (Allahverdiipoorazar et al. 2021).

3.5 XRD analysis

XRD patterns of precursor powder samples and geopolymer binders are depicted in Figs. 6 and 7. The XRD pattern of the kaolin sample comprises quartz, kaolinite, and illite as the main crystal phases, whereas bentonite comprises zincite, acmite, christobalite, faujasite, and calcium silicate phases.

Fig. 5 Stacked FTIR spectra for geopolymer binders with an s/p ratio of 3.5

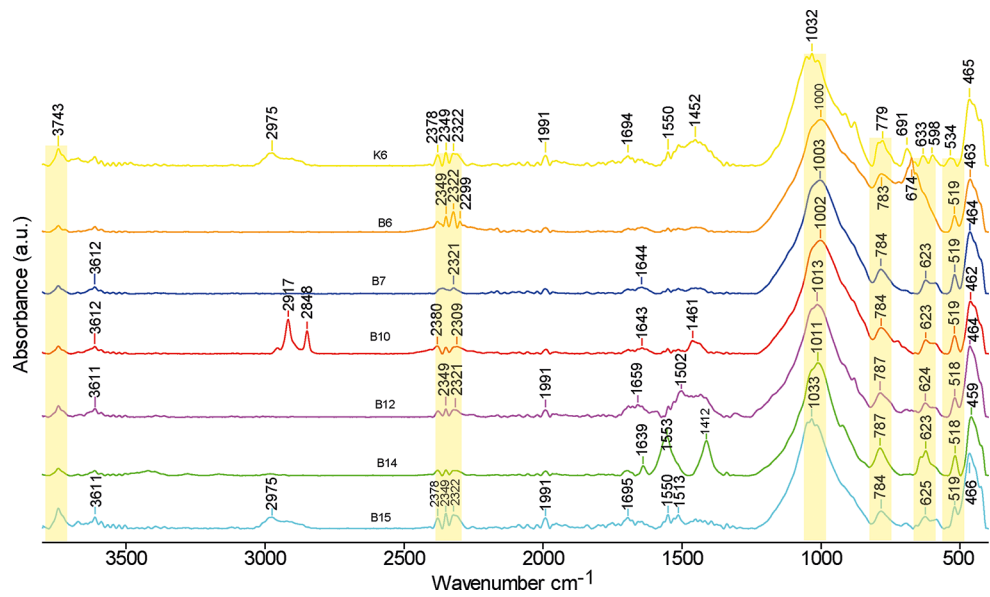
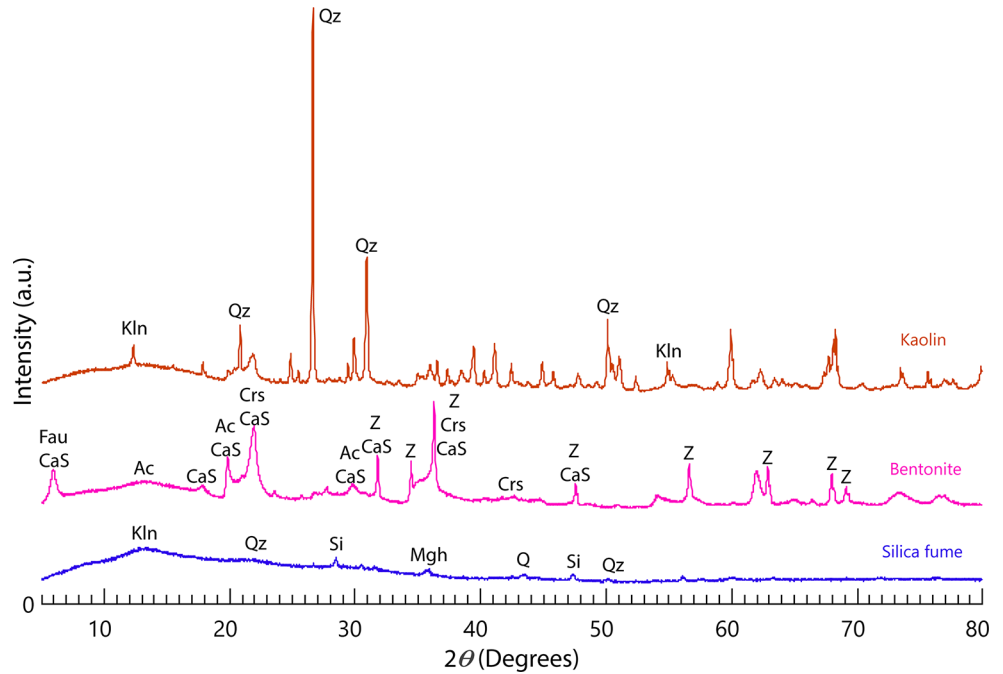


Fig. 6 XRD patterns of the precursors (Quartz: Qz, Kaolinite: Kln, Muscovite: Ms, Aemite: Ac, Cristobalite: Crs, Calcium silicate: CaS, Faujasite: Fau, Silicate: Si, Maghemite: Mgh)



The presence of an amorphous phase in silica fume is evident from the halo band between 14° and 28° (Hekimoğlu et al. 2021; Yavuz et al. 2022).

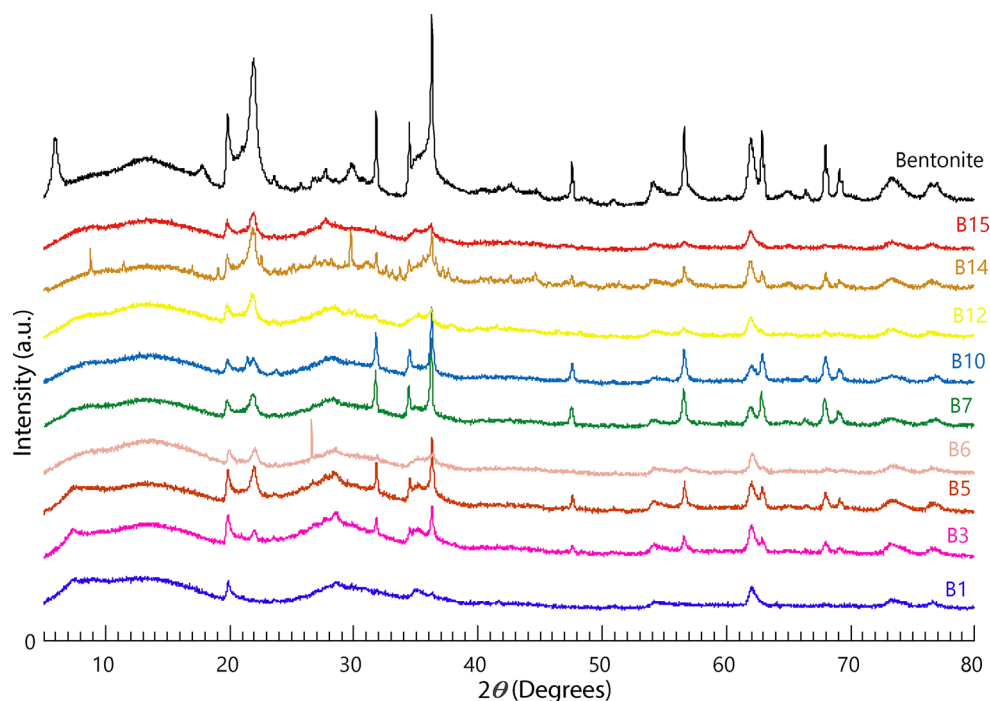
According to the phase analysis results of the B15 geopolymer sample, augite, monalbite, enstatite, and magnesium ferrous oxide were formed in the geopolymerization process as a result of the reaction between bentonite, silica fume, and alkaline activation solution. The peak intensity of calcium silicate and faujasite, determined at 5.85° in bentonite, disappears in geopolymer samples.

When XRD patterns are examined, broad and less intense peaks are observed in samples with lower crystallinity, while samples with higher crystallinity exhibit sharp peaks

(Eren and Afşin 2008). The short amorphous halo positions in the 6°-18° and 22°-40° 2θ regions in the geopolymer samples reveal the typical amorphous geopolymer structure (Bahrami et al. 2019; Allahverdiipoorazar et al. 2021; Heah et al. 2012). The first distribution peak is associated with the amorphous aluminosilicate gel, and the second is linked to the glassy phase of the geopolymer components (Chen et al. 2016; Bahrami et al. 2019). These peak regions play a crucial role in characterizing geopolymer binders, and changes in the peaks have been reported to affect performance properties (Davidovits 2008; Bahrami et al. 2019).

It is stated that as the Si: Al molar ratio decreases in geopolymer samples, the crystallinity index decreases (Chen et

Fig. 7 XRD patterns of the geopolymer binders



al. 2016). The Al_2O_3 phase is defined by the 21.67° peak. While this peak is determined when the s/p ratio of the geopolymer is 2 and below, it cannot be detected at ratios of 3 and 4 (Chen et al. 2016). In the typical XRD pattern of geopolymer samples, amorphous phase peaks are typically determined between 5° - 10° , 27° - 40° , 15° , and 40° 2θ . This region is reported to play a fundamental role in characterizing the adhesion properties of geopolymer samples (Pan et al. 2020; Bahrami et al. 2019).

3.6 Microstructural characterization and elemental distribution

The bonding interface of the lap shear test samples was examined using a light microscope (Fig. 8). It has been reported that when bonding wood with a geopolymer binder, a thinner bond line is achieved if the geopolymer effectively penetrates the wood cell lumens (Allahverdipoorazar et al. 2021). Thinner bond line formation is observed in samples B7, B13, and B15, which exhibit higher adhesion strength compared to other formulations. The addition of silica fume to the binder formulation is known to enhance the penetration of the binder into the wood (Bahrami et al. 2019), improving the mechanical and technological properties of the boards by penetrating the geopolymer binder into the wood cell lamellae. The particle size of the aluminosilicate used in the geopolymer penetration into the wood material is also reported to be crucial. Effective penetration of the geopolymer into wood cells requires the diffusion of binder molecules into the wood cells (Prud'Homme et al. 2010).

SEM images of the bonding lines and EDX analysis spectra of wood samples bonded with kaolin (K6) and bentonite-based geopolymer binders are presented in Fig. 9. The micromorphological properties, as well as the distribution of Si, Al, and Na elements, were examined in images taken on the cross sections of the bonding lines of the lap shear samples bonded with geopolymer binders. According to the EDX mapping results, Si and Al compounds are concentrated at the bonding lines of the samples and are distributed uniformly, with a particularly better distribution observed in bentonite-based geopolymer samples. Homogeneous distribution is reported to be crucial for achieving good mechanical properties, especially in wood samples bonded with binders (Chen et al. 2016).

Moreover, the Na element from the alkaline activator solution in the geopolymer formulation is observed to be distributed by diffusion in the cross-section of the bonding line, especially towards the parts close to the bonding line. This diffusion is believed to be concentrated in areas near the adhesion line, likely facilitated by the moisture in the geopolymer. The presence of an alkaline wood layer, resulting from alkali accumulation on the adhesion line, was revealed by FTIR analysis. It is reported that wood components in this layer undergo degradation due to the alkaline effect, making them less durable than other wood parts in tensile tests (Pan et al. 2020; Ye et al. 2018). Therefore, achieving a well-distributed alkaline effect is desirable. A narrow alkali-wood interface layer is more likely to result in adhesion failure.

Fig. 8 Light microscope image of the bonding lines of the lap shear samples

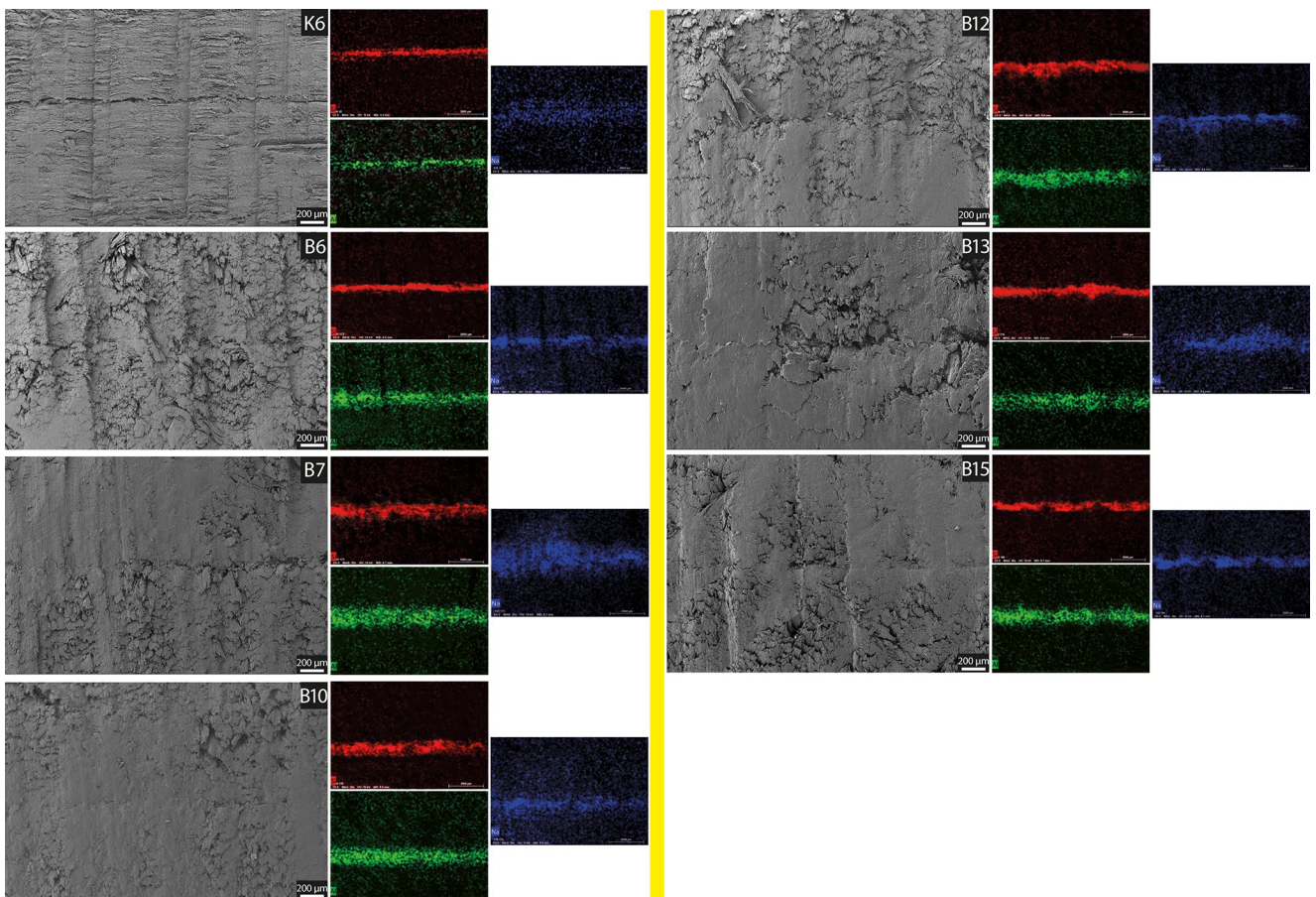
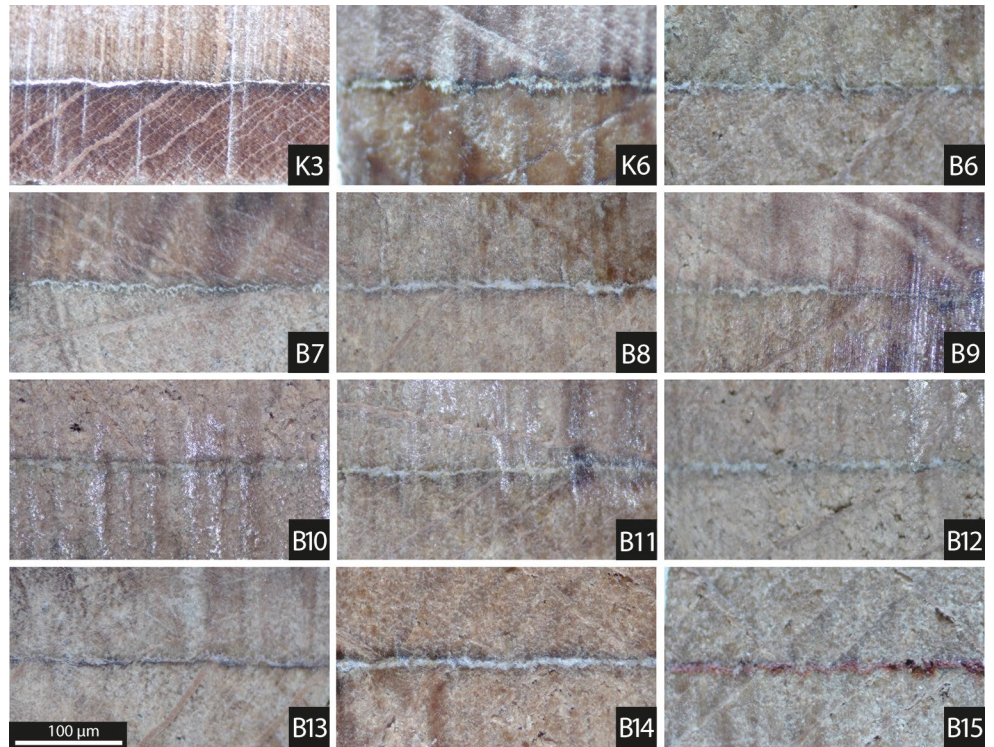


Fig. 9 SEM/EDX images of bonding interface of the lap shear sample (red: Si, green: Al, blue: Na)

Geopolymer binders and additives are recognized for their effective coating properties on wood fiber surfaces. Circular and plate-like structures on the surface, as reported by Chen et al. (2016), were also observed in samples bonded with geopolymer binders (see supplementary file).

4 Conclusion

This study demonstrates the potential of bentonite-based geopolymer as an alternative to petroleum-based urea formaldehyde adhesives commonly used in the wood-based panels industry, offering a formaldehyde-free solution for wood-based panel adhesives. Various parameters, including precursor type, alkaline activation solution molar ratio, and solution to powder (s/p) ratio, were found to exert a substantial influence on the adhesion properties. Additionally, the incorporation of paraffin, pMDI, and resorcinol in bentonite-based organo-geopolymer hybrid wood binders showed promise in enhancing wet strength properties. Incorporating paraffin into the geopolymer binder formulation imparts waterproof properties, while organic additives, such as pMDI and resorcinol commonly used in formaldehyde-containing adhesive formulations, enhance the geopolymer binder's bonding to the wood cell wall. BET analysis indicated a substantial surface area of 65.59 m²/g for bentonite samples, generally contributing to the favorable bonding properties of aluminosilicate samples in geopolymer production. Bentonite emerged as a cost-effective alternative to traditional materials like kaolin and metakaolin. XRF analysis indicated that the bentonite sample had a high SiO₂ and Al₂O₃ composition (90.20%), making it well-suited for the geopolymerization reaction. In the geopolymerization process, the activation solution, composed of sodium silicate and sodium hydroxide, demonstrated optimal binder pH values and bonding strength in formulations with SM 2 and SM 2.5 molar ratios. The study explored different solution to powder ratios (s/p), a critical factor affecting geopolymer binder adhesion performance, revealing that the most effective ratios for bentonite-based geopolymers as a binder for wood-based panel were s/p 3 and 3.5. The introduction of 10% silica fume in the geopolymer binder formulation not only enhanced the geopolymerization process but also exhibited positive effects on rheological properties and performance characteristics, particularly in wet bonding strength. Based on the lap shear adhesion test outcomes, the introduction of organic amendments, such as citric acid (B8), sucrose (B9), and triacetin (B14), in bentonite-based geopolymer binder formulations exhibited either ineffective or limited effects on adhesion properties. In contrast, formulations incorporating 10% paraffin (B10), 20% pMDI (B12), and 5% resorcinol (B13) demonstrated improvements in

both dry and wet bonding strength values. Notably, the B15 sample (10% silica fume + 5% resorcinol + glyoxal, accounting for 10% of resorcinol) exhibited dry and wet bonding strength comparable to UF adhesive. The characteristic bands identified in the FTIR spectra of precursor raw materials align with the XRF analysis results. Geopolymer binders presented peaks in the FTIR spectra associated with Si-O-Si and Al-O-Si bonds, supporting the formation of aluminosilicate networks during the geopolymerization process. XRD patterns of geopolymer binders revealed peaks linked to the glassy phase of the amorphous aluminosilicate gel and geopolymer components. Microscopic analysis of the bonding line in lap shear test samples prepared with bentonite-based geopolymer indicated a thinner bond line resulting from effective geopolymer binder penetration into wood cell lumens. SEM analysis and EDX mapping of the bonding line highlighted concentrated compounds at the bonding line, with Na elements from the activation solution dispersing through diffusion towards the inner regions of the bonding line.

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Data availability "Data will be made available on request."

Declarations

Competing interests The authors declare no competing interests.

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References

- Allahverdipoorazar F, Shalbfan A, Berthold D (2021) Geopolymer as a multifunctional mineral binder to produce laminated veneer lumber: effect of various aluminosilicate powder types on panels and geopolymer binder features. *Eur J Wood Prod* 79:349–362
- Bahrami M, Shalbfan A, Welling J (2019) Development of plywood using geopolymer as binder: effect of silica fume on the plywood and binder characteristics. *Eur J Wood Prod* 77(6):981–994
- Berzins A, Morozovs A, Gross U, Iejavs J (2017) Mechanical properties of wood-geopolymer composite. *Engineering for Rural Development* 16:1167–1173. <https://www.tf.lbtu.lv/conference/proceedings2017/Papers>
- Chen T, Niu M, Xie Y, Wu Z, Liu X, Cai L, Zhuang B (2015) Modification of ultra-low density fiberboards by an inorganic film formed by Si-Al deposition and their mechanical properties. *BioResources* 10(1):538–547
- Chen T, Wu Z, Niu M, Xie Y, Wang X (2016) Effect of Si–Al molar ratio on microstructure and mechanical properties of ultra-low density fiberboard. *Eur J Wood Prod* 74:151–160
- Davidovits J (1991) Geopolymers: inorganic polymeric new materials. *J Therm Anal Calorim* 37(8):1633–1656
- Davidovits J (2008) *Geopolymer Chemistry and Applications*, 2nd ed. Geopolymer Institute, ISBN 4th ed. 9782951482098
- Duxson P, Provis JL (2008) Designing precursors for geopolymer cements. *J Am Ceram Soc* 91(12):3864–3869
- Duxson PSWM, Mallicoat SW, Lukey GC, Kriven WM, Van Deventer JS (2007) The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers. *Colloids Surf a* 292(1):8–20
- Eren E, Afsin B (2008) An investigation of Cu (II) adsorption by raw and acid-activated bentonite: a combined potentiometric, thermodynamic, XRD, IR, DTA study. *J Hazard Mater* 151(2–3):682–691
- Gong Z, Liao L, Lv G, Wang X (2016) A simple method for physical purification of bentonite. *Appl Clay Sci* 119:294–300
- Gönültaş O (2018) Properties of pine bark tannin-based adhesive produced with various hardeners. *BioResources*
- Grim RE, Güven N (1978) *Bentonites, Geology, Mineralogy, Properties and uses*. Development in Sedimentology, vol 24. Elsevier, Amsterdam
- Hajimohammadi A, Provis JL, Van Deventer JS (2008) One-part geopolymer mixes from geothermal silica and sodium aluminate. *Ind Eng Chem Res* 47(23):9396–9405
- He P, Wang M, Fu S, Jia D, Yan S, Yuan J, Zhou Y (2016) Effects of Si/Al ratio on the structure and properties of metakaolin based geopolymer. *Ceram Int* 42(13):14416–14422
- Heah CY, Kamarudin H, Al Bakri AM, Bnhussain M, Luqman M, Nizar IK, Liew YM (2012) Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers. *Constr Build Mater* 35:912–922
- Hekimoğlu G, Nas M, Ouikhalfan M, Sarı A, Tyagi VV, Sharma RK, Saleh TA (2021) Silica fume/capric acid-stearic acid PCM included-cementitious composite for thermal controlling of buildings: thermal energy storage and mechanical properties. *Energy* 219:119588
- Khater HM (2013) Effect of silica fume on the characterization of the geopolymer materials. *Int J Adv Struct Eng* 5:1–10
- Kim S (2009) The reduction of indoor air pollutant from wood-based composite by adding pozzolan for building materials. *Constr Build Mater* 23(6):2319–2323
- Kumar A, Lingfa P (2020) Sodium bentonite and kaolin clays: Comparative study on their FT-IR, XRF, and XRD. *Materials Today: Proceedings*, 22, 737–742
- Lee NK, An GH, Koh KT, Ryu GS (2016) Improved reactivity of fly ash-slag geopolymer by the addition of silica fume. *Advances in Materials Science and Engineering*, 2016
- Moolenaar RJ, Evans JC, McKeever LD (1970) Structure of the aluminate ion in solutions at high pH. *J Phys Chem* 74(20):3629–3636
- Okoye FN, Durgaprasad J, Singh NB (2016) Effect of silica fume on the mechanical properties of fly ash based-geopolymer concrete. *Ceram Int* 42(2):3000–3006
- Önal M, Sarıkaya Y (2007) Thermal behavior of a bentonite. *J Therm Anal Calorim* 90(1):167–172
- Pan D, Ye H, Wang X, Zhang Y (2020) Modified geopolymer-based Wood Adhesive using Waterborne polyurethane. *BioResources* 15(4):7573–7585
- Pizzi A (2014) Synthetic adhesives for wood panels. *Reviews Adhes Adhes* 42:85–126
- Pizzi A (2016) Wood products and green chemistry. *Ann for Sci* 73(1):185–203
- Pizzi A, Mittal KL (eds) (2017) *Handbook of adhesive technology*. CRC
- Provis JL, Hajimohammadi A, Rees CA, Van Deventer JSJ (2009) Analysing and manipulating the nanostructure of geopolymers. In *Nanotechnology in Construction 3: Proceedings of the NICOM3* (pp. 113–118). Springer Berlin Heidelberg
- Prud'Homme E, Michaud P, Peyratout C, Smith A, Rossignol S, Joussein E, Sauvat N (2010) Geomaterial foam to reinforce wood. *Strategic Mater Comput Design: Ceramic Eng Sci Proc* 31:3–10
- Ravindra Reddy T, Kaneko S, Endo T, Reddy L, S (2017) Spectroscopic characterization of bentonite. *J Lasers Opt Photonics*, 4(3)
- Reeb C, Pierlot C, Davy C, Lambertin D (2021) Incorporation of organic liquids into geopolymer materials-A review of processing, properties and applications. *Ceram Int* 47(6):7369–7385
- Rees CA (2007) *Mechanisms and kinetics of gel formation in geopolymers*. Doctoral dissertation, The University of Melbourne
- Shalbfan A, Thoemen H (2020) Geopolymer-bonded laminated veneer lumber as environmentally friendly and formaldehyde-free product: Effect of various additives on geopolymer binder features. *Appl Sci* 10(2):593
- Shalbfan A, Welling J, Hasch J (2016) Geopolymers as potential new binder class for the wood based composite industry. *Holzforshung* 70(8):755–761
- Shalbfan A, Nadali A, Thoemen H (2020) A multifunctional mineral binder for plywood production: the effect of manufacturing parameters on bonding quality. *Materials* 13(10):2360
- Singh B, Ishwarya G, Gupta M, Bhattacharyya SK (2015) Geopolymer concrete: a review of some recent developments. *Constr Build Mater* 85:78–90
- Xi X, Pizzi A (2020) No-aldehydes glucose/sucrose-triacetin-diamine wood adhesives for particleboard. *J Renew Mater* 8(7):715
- Xi X, Wu Z, Pizzi A, Gerardin C, Lei H, Zhang B, Du G (2019) Non-isocyanate polyurethane adhesive from sucrose used for particleboard. *Wood Sci Technol* 53:393–405
- Yahya Z, Abdullah MMAB, Hussin K, Ismail KN, Sandu AV, Vizureanu P, Razak RA (2013) Chemical and physical characterization of boiler ash from palm oil industry waste for geopolymer composite. *Rev Chim* 64(12):1408–1412
- Yavuz E, Gul NIK, Kockal NU (2022) Characterization of class C and F fly ashes based geopolymers incorporating silica fume. *Ceram Int* 48(21):32213–32225
- Ye H, Zhang Y, Yu Z, Mu J (2018) Effects of cellulose, hemicellulose, and lignin on the morphology and mechanical properties of metakaolin-based geopolymer. *Constr Build Mater* 173:10–16

Zhirong L, Uddin MA, Zhanxue S (2011) FT-IR and XRD analysis of natural Na-bentonite and cu (II)-loaded Na-bentonite. Spectrochim Acta Part A Mol Biomol Spectrosc 79(5):1013–1016

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