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Preparation and Characterization of Geopolymers Based on Metakaolin with the Addition of Organic Phase PVA

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Abstract: Geopolymers have excellent physical and mechanical properties, so they can be used as a substitute for ordinary polymers. Geopolymers are ceramic materials, which exhibit the property of brittleness, which can be a limitation in some structural applications. To overcome this shortcoming, a new group of materials (organic geopolymers) was developed. The aim of this work is the synthesis of organic (hybrid) geopolymers. A geopolymer based on metakaolin was synthesized as a reference sample, while polyvinyl alcohol was added as an organic phase for synthesizing a hybrid geopolymer. It was concluded that the systems follow the rule of behavior in liquid systems. The chemical composition of the samples was determined by X-ray fluorescence analysis (XRF). Structural and phase characterization of hybrid and reference materials were analyzed using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), which revealed new phases in the PVA-added samples. The results show that the content of added PVA in the reaction mixture affects the phase composition of the synthesized materials. To examine the possibility of adsorption of the samples, Ultraviolet-visible spectroscopy (UV/VIS) was used. The morphology was analyzed using a scanning electron microscope with energy dispersive spectroscopy (SEM/EDS), where efflorescence was observed and identified. After characterizing the geopolymer with the addition of PVA, we obtained a material that was far more porous than the basic sample, and we can conclude that we have synthesized a material that shows good mechanical properties.

Keywords: inorganic geopolymer; organic (hybrid) geopolymer; PVA; metakaolin



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1. Introduction

A study of geopolymers extracted from different types of waste materials indicates that geopolymers are a superior replacement for regular polymers, especially considering the environmental impacts of solid wastes and the sustainability issues related to the use of natural materials and energy. Geopolymers represent an innovative group of porous ceramic materials characterized by low energy consumption during production for construction purposes; they are cheap and environmentally friendly with low emissions of CO₂ [1,2]. The cement industry pollutes the atmosphere; in this, industry geopolymers are favored because of their unique purity. For these reasons, they are considered “green materials”. These materials show excellent mechanical properties, thermal stability, resistance to strong acids and open flames, long-term durability, and recyclability, which makes them applicable in many fields. On the other hand, geopolymers are ceramic materials; as such they are highly brittle, and have low conductivity, and poor toughness against fracture. The brittleness of geopolymers may be a limitation in some structural applications. To overcome this limitation, a new class of geopolymer composites with an organic matrix has recently been developed [3]. Mixing two different systems, organic and inorganic, has been

found to contribute to some improved properties, such as adjustment time, workability, reduced shrinkage, and enhanced mechanical properties and durability [4]. In addition to enhancing the brittleness of the inorganic phase, the production of organic–inorganic hybrids [5] aimed to improve organic polymer’s fire resistance and reduce the smoke produced by their combustion. The development of hybrid materials is a valuable research field which has yielded materials with new properties derived from the mutual interactions of two chemically incompatible phases [6]. By creating the chemical composition of the components, it is possible to obtain different materials with different properties, the application of which depends on the ratio of organic and inorganic phases [7].

Hybrid materials can be used for all applications in which the use of a pure geopolymer is limited by its brittleness, such as the production of thermal insulation or heat-resistant boards with improved durability. Moreover, these materials can show useful archeological properties in restoring and repairing damaged concrete and masonry [7].

Various organic compounds, such as ethylene glycol, marble waste, epoxy resin, and polyvinyl alcohol (PVA) [8], as well as many other organic liquids, are added to the alkali-activated material to improve its characteristics.

PVA is a synthetic hydrophilic linear polymer that is colorless, odorless, and soluble in water. Dissolved in water, it has excellent chemical, mechanical, and physical properties. PVA is a raw material for “vinyl”, the first synthetic fibers of high strength from which PVA hydro-gel is made [9]. In addition, PVA is used as a raw material for films and acetyl resins, as well as a textile processing agent, an adhesive agent, a polymerization stabilizer of polyvinyl chloride, and an inorganic binder [9]. PVA also presents an excellent barrier to oxygen and other external influences. Unlike most vinyl polymers, PVA is not prepared by polymerizing the appropriate monomer. PVA consists predominantly of 1,3-diol bonds $[-CH_2-CH(OH)-CH_2-CH(OH)-]$, as shown in the idealized formula, but also contains several percent 1,2-diol $[-CH_2-CH(OH)-CH(OH)-CH_2-]$, depending on the polymerization conditions of the vinyl ester precursor. The physical properties of the synthetic polymer PVA depend on the method of preparation, molecular weight, tacticities (isotactic, syndiotactic, or atactic PVA), the degree of polymerization, and the degree of hydrolysis. By increasing the molecular weight and degree of hydrolysis, various properties such as viscosity, dissolution resistance, adhesion strength, tensile strength, and film formation are improved [10].

For the broad application of geopolymer, the major issue is the transition from the research stage to commercialization, for which the main requirements are geopolymer standardization and public education. Further research is needed to study the long-term durability of geopolymer and the environmental and economic benefits of utilizing waste materials to produce geopolymer. One factor that affects the environment is the presence of heavy metals in the soil, water, and air. The most common heavy metals found in the environment, as water pollutants, are cadmium, zinc, lead, copper, and chromium [11]. In earlier research, materials that proved to be effective for zinc and lead immobilization did not show the same effectiveness for cadmium adsorption. Maingi et al. [12] investigated the adsorption of cadmium (Cd) on geopolymers made from ordinary clay and rice husk, while others [13] investigated the adsorption of cadmium ions on fly ash-based geopolymer particles. Mladenovic et al. [14] studied the adsorption of Cd from aqueous solutions by alkaline activated materials: geopolymers, based on metakaolin as a precursor, proved to be effective in the process of adsorption of Cd ions from water.

Other scientists [15] have investigated the use of metakaolin-based geopolymers as cationic dye adsorbents in the treatment of water systems. In the above-mentioned work, scientists monitored the adsorption of methylene blue (MB), while in our research, we monitored whether this material can absorb by incorporating PVA. The synthesis of metakaolin-based geopolymer with PVA is unique. Geopolymers based on metakaolin would find application for purification.

Previous research has shown that PVA as an organic phase is most often used in the form of fibers [8]. In the literature, hybrid materials were synthesized starting from different

molar concentrations of bases, 8M, 12M, and 16M [8]. Samples with a higher content of NaOH in the alkaline activator give better physicochemical and mechanical characteristics, and for this reason, an alkaline activator with a concentration of 12M NaOH was used for the hybrid synthesis. A strong exothermic reaction occurs when applying the alkaline activator concentration of 16M NaOH exothermic reaction occurs. Unlike in the literature, PVA was used in powder form and not in fiber form. The chemical composition of the samples was determined using X-ray fluorescence analysis (XRF). The structural analysis of the hybrid materials was determined by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), while the morphology was determined using a scanning electron microscope with energy dispersive spectroscopy (SEM/EDS).

2. Materials and Methods

2.1. Materials

As a solid precursor for synthesizing geopolymers and hybrid materials, metakaolin (MK) was used. MK is obtained by thermal activation–calcination of kaolin clay which was first dried, ground, and sieved. Thermal activation is based on heating kaolin clay to dehydroxylate kaolinite and remove organic impurities. Thermal activation was performed in a laboratory furnace with programmed heating in an air atmosphere in the temperature range from 30 to 750 °C, a heating rate of 10°/min, and a retention time of 750 °C for three hours. Cooling was spontaneous to room temperature. An alkaline activator mix of aqua solution of a concentration of 12 mol/dm³ of NaOH and Na₂SiO₃ was used.

PVA, manufactured by MERCK-ALKALOID, Skopje, was used as the organic phase for synthesizing hybrid materials. In this paper, a sample of referent geopolymer (S₀) and samples with an addition of 1% PVA (S₁) and 2% PVA (S₂) were synthesized.

The reference geopolymer (S₀) was formed from MK and an alkaline activator, which were stirred for 10 min, then poured into molds of certain dimensions, and then left at room temperature for 24 h. After that, obtained samples were dried in an oven for 48 h at a temperature of 60 °C. MK was used for the synthesis of the hybrid geopolymer and for the synthesis of the inorganic part with the addition of the organic phase of PVA. The mass of added PVA was 1% and 2% of the MK mass. PVA was homogenized with MK and added to the appropriate volume of alkaline activator. The mixture was homogenized and then poured into molds of certain dimensions, which were left at room temperature for 24 h. After that, obtained samples were dried in an oven for 48 h at a temperature of 60 °C.

2.2. Methods and Characterization

In this paper, the influence of temperature on the thermodynamic parameters of the alkaline activator was monitored. Changes in density, sound velocity, and refractive index were monitored. Ivanović et al. [16] present a more detailed description of the methods used in the paper.

Determination of surface groups of synthesized samples was done based on Boehm titration [17] and was calculated by Equation (1):

$$Q\left(\frac{\text{mmol}}{\text{g}}\right) = \frac{(C_2 - C_1)}{m} \quad (1)$$

where C₁ represents NaOH or HCl solution concentration before titration, C₂ is NaOH or HCl solution concentration after titration, and m is the mass of the geopolymer sample.

2.2.1. X-ray Fluorescence Analysis (XRF)

XRF analysis was used to determine the chemical composition of all samples. It is a method that enables qualitative and quantitative analysis of almost all elements from Na to U present in an unknown sample. The analysis is non-destructive, with high precision and accuracy, and it is possible to determine several elements at the same time. The principle of operation of the XRF device is based on the measurement of the wavelength (WD XRF) or energy (ED XRF) of photons and the intensity of the characteristic radiation emitted from

the sample. XRF analysis was performed by the existing preparation via the fundamental method on the NEX ED-XRF apparatus without any calibration.

2.2.2. X-ray Diffraction (XRD)

For XRD analysis, a generator voltage of 40.0 kV and a current of 40.0 mA were used. Angular recording ranges from 5° to 80° (2θ) were used for all tested powders in the continuous scanning mode with a step length of 0.02° at a speed of $5^\circ/\text{min}$. The PDXL2 software package (version 2.8.3.0) [18], equipped with the ICDD reference database [19], was used to identify the phases. The selected PDF card was used for phase identification: nepheline ($\text{NaAlSi}_3\text{O}_8$, PDF: 01-083-1618), albite ($\text{NaAlSi}_3\text{O}_8$, PDF: 00-019-1176), quartz (SiO_2 , PDF: 01-083-2466), and muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, PDF: 01-079-2363).

2.2.3. Fourier-Transform Infrared Spectroscopy (FTIR)

Functional groups of samples were studied by FTIR spectroscopy. Samples were dusted and evenly dispersed in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). Spectra were obtained at room temperature using a Bomem (Hartmann & Braun) MB-100 spectrometer. Spectral data of the samples were collected in the region from 4000 to 400 cm^{-1} .

2.2.4. Ultraviolet-Visible Spectroscopy (UV/VIS) Analysis

To examine the possibility of adsorption of the samples, UV/VIS spectroscopic analysis was used. The samples were dusted and mounted on a UV-2600 carrier by Shimadzu Corporation.

2.2.5. Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM/EDS)

Analysis of the microstructure of the obtained geopolymer samples was performed on Au-coated samples, using a JEOL JSM 6390 LV electron microscope. The analysis of microstructural properties of selected samples using a scanning electron microscope allowed examination of the fine details of material structure, morphological appearance, and grain shape of synthesized samples as well as semi-quantitative determination of chemical composition (EDS analysis).

3. Results and Discussion

3.1. Influence of Temperature on Thermodynamic Parameters of Alkaline Activator

Alkali activators play a vital role in geopolymerization. An alkaline activator of 12M NaOH concentration was chosen to synthesize the hybrid geopolymer material. The reason for selecting this molarity is that numerous studies have shown that the best characteristics of geopolymers are achieved with higher concentrations of NaOH solution, but still not too high due to the exothermic reaction when dissolving NaOH in water. The higher concentration of NaOH as a component of alkali activator (10M NaOH and higher) led to the highest dissolution rate of Si^{4+} and Al^{3+} ions in aluminosilicate materials compared with the lower NaOH concentration, which led to a higher degree of geopolymerization [20].

Figure 1 shows the effect of temperature (ranging from 15 – 60°C) on thermodynamic parameters (density, refractive index, and sound velocity) of the alkaline activator. The geopolymerization process takes place at 60°C , which is also the maximum temperature for testing the thermodynamic parameters of the alkaline activator. The influence of the concentration of the alkaline activator on the geopolymerization process [21] and the influence of the thermodynamic parameters of the alkaline activators was investigated during earlier research [16]. The obtained results show that the values of all measured parameters increase with increasing molarity of the solution. The influence of molarity is most pronounced in viscosity testing. Alkali activator with 8M NaOH solution shows more than four times higher viscosity than systems with a lower molar concentration of NaOH solution. For all thermodynamic parameters for the tested systems, the rule observed in liquid systems has been confirmed, i.e., that they decrease with increasing temperature due to the thermal expansion of the liquid [22].

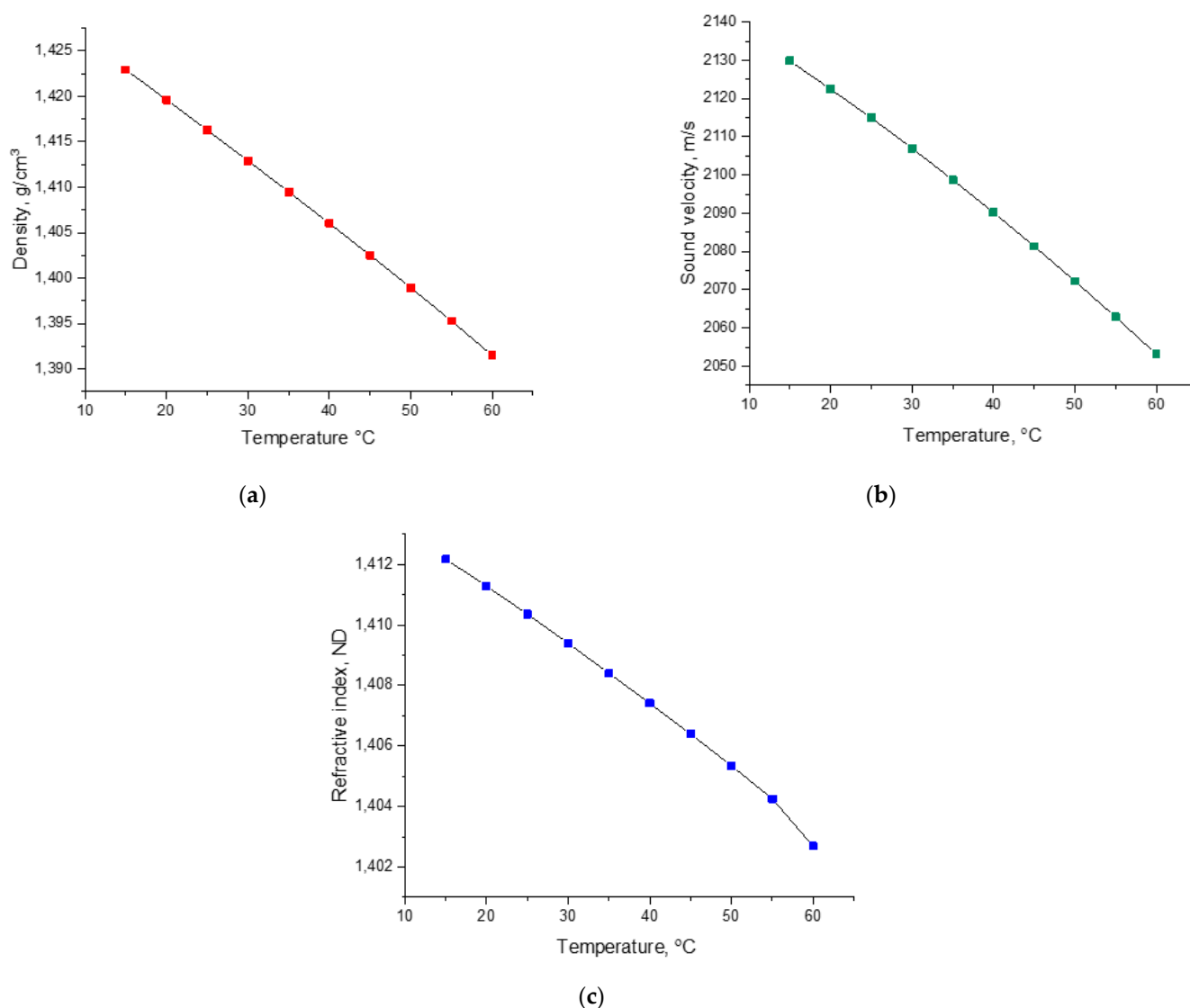


Figure 1. Effect of temperature on thermodynamic parameters of alkaline activator: (a) density; (b) velocity of sound; (c) refractive index.

Based on Figure 1, it is concluded that the analyzed system also confirms the behavior of technical systems, that there is a decrease in the value of parameters with increasing temperature due to the thermal expansion of the liquid, but the values become more linear. These characteristics of the alkaline activator enable the solid phase to be relatively easily homogenized within this system. Homogenization is very important to achieve a better dissolution of the solid phase. A new aluminosilicate phase (reference geopolymer), i.e., a hybrid material (aluminosilicate phase and organic polymer), appears.

3.2. Surface Groups and Chemical Composition of Geopolymer and Hybrid Materials

Total acidic and basic surface groups were determined by Boehm titration [17]. The obtained results show that the most acidic surface groups are found in sample S₁, and the least in S₂, while the most basic surface groups are found in sample S₀ and the least in S₂. The determination of surface groups such as phenolic, lactone, and carboxyl groups did not give adequate results because their content in this type of material is below the detection limits. The amounts of acidic and basic groups of synthesized samples are shown in Table 1.

Table 1. Total acidic and basic surface groups of synthesized samples.

Geopolymer Material	Acidic Groups (mmol g ⁻¹)	Basic Groups (mmol g ⁻¹)
S ₀	4.50	6.83
S ₁	5.68	6.62
S ₂	4.42	6.43

The obtained results of the chemical composition of MK and hybrids materials are presented in Table 2. MK, as an amorphous product of kaolin dehydration, is characterized by high pozzolanic activity. The reactivity of pozzolan is higher if the total content of the three main oxides (SiO₂ + Al₂O₃ + Fe₂O₃) is higher. When pozzolans are used for the production of cement, mortar, and concrete, it is desirable that the content of the three main oxides in the pozzolanic material is greater than 70% and that it contains as much of the amorphous phase as possible [23].

Table 2. Chemical composition of geopolymer and hybrid materials.

Oxides (mas %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	TiO ₂	CaO	K ₂ O	SO ₃	L.O.I. *
MK	55.03	35.44	3.89	0.89	0.62	1.38	2.07	0.68	0.44
S ₀	62.23	23.83	3.15	5.90	0.90	0.91	1.35	0.80	0.93
S ₁	64.23	19.39	3.05	5.69	0.99	0.94	3.01	0.94	1.76
S ₂	65.03	18.26	3.09	5.75	1.01	0.93	2.96	0.96	2.01

* loss of ignition.

The chemical composition of the examined MK (Table 2) was 55.03% SiO₂ and 35.44% Al₂O₃, and 3.89% Fe₂O₃ made up over 90% of the total composition of MK. Based on these values, it is clear that this MK has high pozzolanic activity. By comparison with data from the literature [24] for MK, with a chemical composition of 55.22% SiO₂, 33.07% Al₂O₃, and 5.23% Fe₂O₃, which was said to meet the standard of pozzolanic activity, we can conclude that the examined MK also has a very good pozzolanic activity and in that sense, there is a good potential for the production of building materials.

In the case of the S₁ and S₂ samples, the percentage composition of SiO₂ is higher than the percentage composition of the S₀ sample, while the proportion of Na decreases with the addition of PVA. Samples with an added organic phase also exhibit good pozzolanic activities because the share of three main oxides is greater than 70%. For S₁, this share is 86.67%, and for S₂ it is 86.38%.

The values of other oxides are approximate for all samples.

3.3. Characterization of Geopolymer and Hybrid Materials

3.3.1. XRD Analysis of Hybrid Geopolymers

Based on the analysis of the results on the powder diffractograms shown in Figure 2, it is noticeable that in the angular range between 18~36°, there is a slightly elevated background which is characteristic of geopolymers synthesized by alkaline activation using metakaolin [22]. Clearly defined peaks indicating a phase of high crystallinity belong to quartz, which is found in the starting material and represents a non-reactive phase during the process [25]. The results clearly show that the content of added PVA in the reaction mixture affects the phase composition of the synthesized materials.

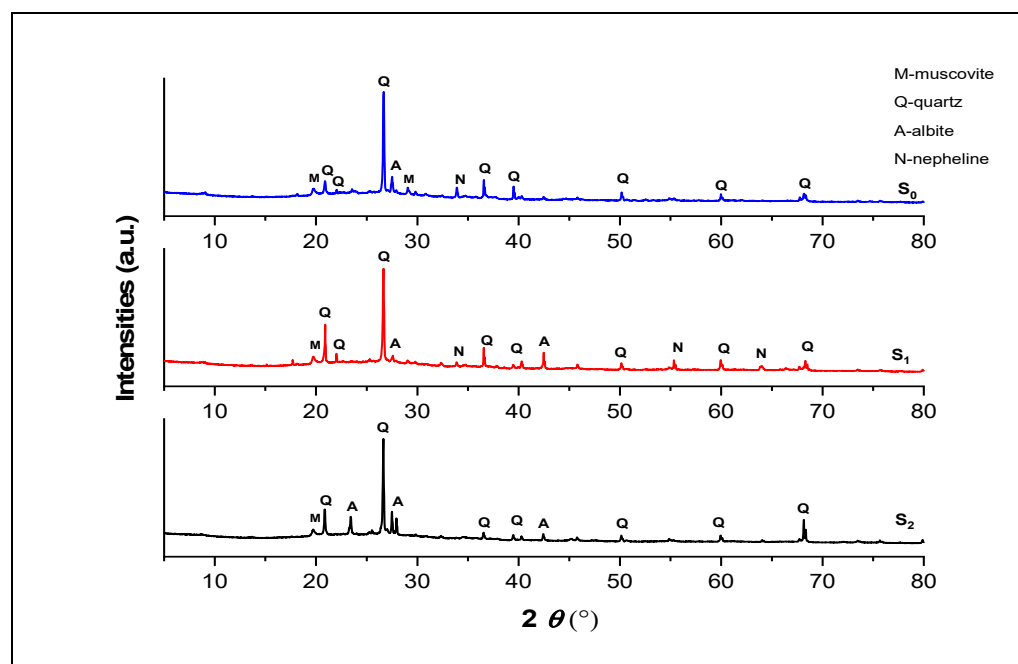


Figure 2. XRD results of investigated samples: S_0 , S_1 , and S_2 .

The powder diffractogram clearly shows that the S_1 geopolymer, in addition to quartz, also contains peaks of sodium aluminosilicate phases corresponding to nepheline and albite. The appearance of nepheline was observed in S_0 and S_1 samples while it is not identified in the S_2 sample; that can be explained by the fact that nepheline is a secondary mineral that can be found in clay deposits and represents a part of a kaolinite mixture. With the addition of 1% of PVA in the reaction system, the decreasing peak intensities of the nepheline phase in the S_1 sample are evidenced due to XRD measurements. This phenomenon indicates that PVA addition likely leads to particular disintegration of nepheline during the geopolymerization process. Since nepheline is not detected in S_2 samples it is most likely that disintegration is complete and contributes to the formation of the amorphous part. Through the process of geopolymer networking and activation with PVA in the system, it is obvious that a higher amount of PVA leads to an increase of the amorphous phase. The increase of the amorphous phase is another indicator that the tested material shows good pozzolanic activities. The addition of PVA most likely contributes to Al-Si weakening bonds in aluminosilicates where Al and Si can form a lattice in the amorphous matrix, while some secondary mineral phases stay unreacted with and forms semi-crystalline in geopolymer material [26]. It is observed from the diffraction results that these materials are semi-crystalline. Kljajević et al. [27] observed the appearance of nepheline in the research by analyzing thermally treated metakaolin-based geopolymers without the addition of organic matter. One part of PVA most likely acts with reactive silicon from the mixture and can be defined as filler that strengthens the geopolymer matrix [28]. The addition of PVA to the basic reaction mixture during the synthesis of geopolymers most likely affects the migration of Na, Al, and Si in the silicate matrix where their precipitation and reorganization from dissolved phases occurs [25]. On the powder diffractogram of the S_2 geopolymer, a higher presence of albite peaks was observed, and it can be said that this material primarily consists of quartz and sodium trialumosilicate or albite. In addition to these phases, residual muscovite peaks were identified, which most likely stay unreacted in the geopolymer matrix from primary metakaolin. The results indicate that the crystalline phases are not involved in the geopolymerization reaction but are present as inactive fillers in the geopolymer binder.

The obtained results follow from the previous research, where only amorphous phases in raw materials are reactive and involved in the geopolymerization process [9]. From the

presented results, it is clear that PVA added in powder form has a different effect on the phase composition of the final geopolymer material compared to those in which there is no change in phase composition when adding PVA fibers during the synthesis process [29].

3.3.2. FTIR Analysis of Hybrid Geopolymers

The results of the FTIR analysis are presented in Figure 3. The FTIR spectrum of synthesized samples and pure PVA were compared. Based on the obtained results, it can be concluded that the wider peak at 3400 cm^{-1} , which occurs in all samples, is a consequence of the tension vibration -OH (hydrogen bond) [28,30]. The maximum at the wave number 1452 cm^{-1} for S_1 and 1398 cm^{-1} for the S_2 sample refers to the bending vibration -CH_2 .

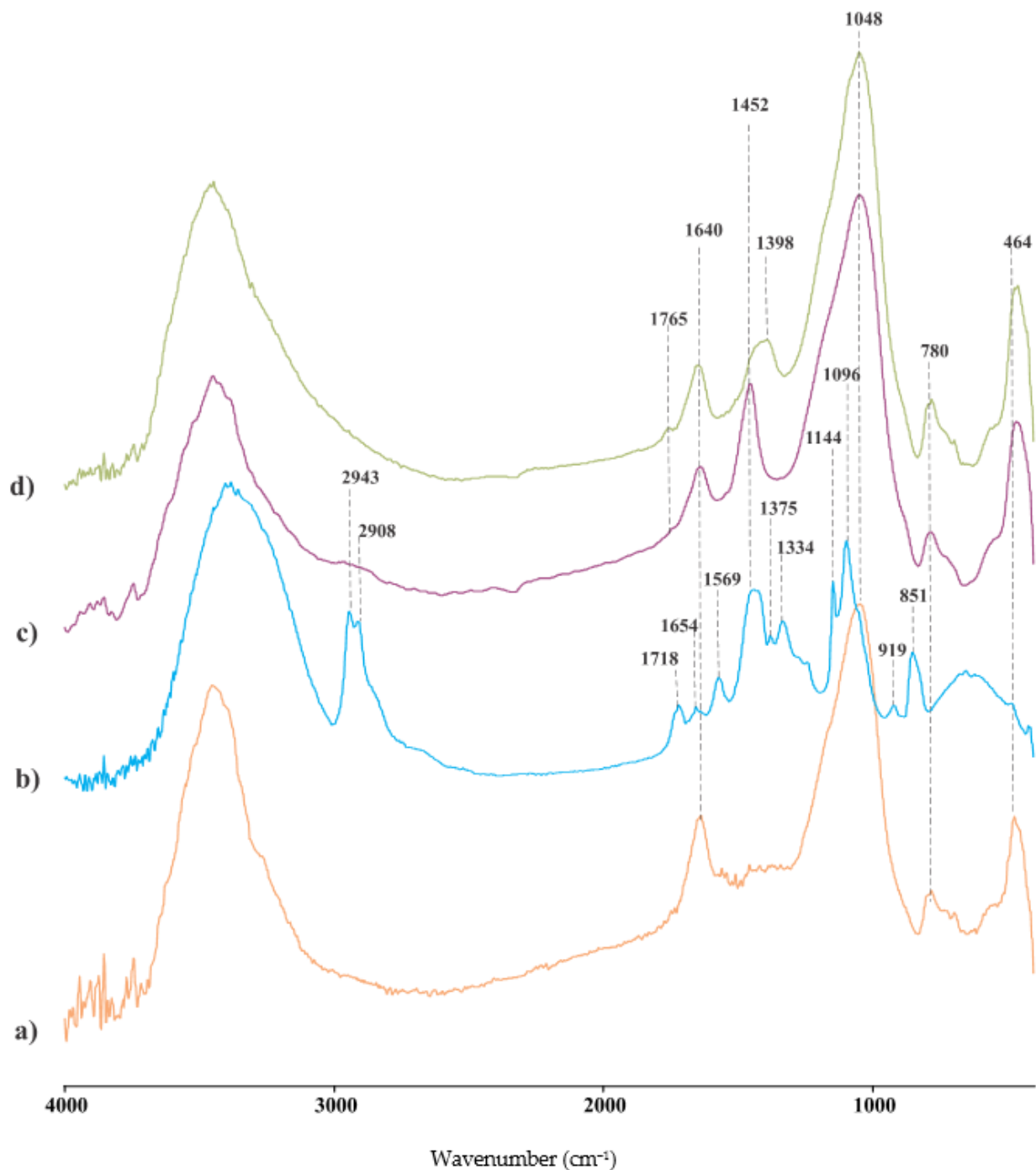


Figure 3. FTIR spectrum of the sample, (a) S_0 , (b) PVA, (c) S_1 , (d) S_2 .

The peaks at 2943 cm^{-1} and 2908 cm^{-1} , which occur in pure PVA, are connected by symmetrical and antisymmetric vibrations of stretching C–H from alkyl groups, while the peak at 1718 cm^{-1} is attributed to tensile vibrations C=O and C–O from acetate group residues after polyolysis (vinyl acetate) [28,30,31]. Mild peaks, which occur in the S_1 geopolymer at 1765 cm^{-1} , can be associated with the ester group of PVA based on its chemical structure. Vibration bands at 1640 cm^{-1} are attributed to the vibration of stretching of physically adsorbed water molecules on the surface of the samples. These bands occur at the same wavelength for S_0 , S_1 , and S_2 geopolymer samples. The vibration band at 1050 cm^{-1} corresponds to Si–O stretching of tetrahedra in which silicon is surrounded by three bridging oxygen and one non-bridging oxygen (Si–, “Non-Bonding”) [32].

The vibration bands that occur in PVA are at: 1654 cm^{-1} , tensile vibrations=C–H [33]; 1569 cm^{-1} , bending vibration –OH [34]; 1375 cm^{-1} , bending vibrations–OH, –C–O–H in-plane bending vibrations, –CH₃ out-of-plane bending vibrations, –CH₂– rocking and twisting vibrations [33]; 1138 cm^{-1} , elongation C–O [30,31]; 1083 cm^{-1} , C–O–C; stretching C=O and bending OH (amorphous PVA sequence) [30,31]; 919 cm^{-1} , CH₂ asymmetric plane oscillation [31]; 822 cm^{-1} , elongation C–C [34].

The peak at 780 cm^{-1} can be explained by the presence of quartz, as shown by XRD analysis.

3.3.3. UV/VIS Spectroscopy Analysis

Using UV-2600 by Shimadzu Corporation, the absorbance of the synthesized samples was determined at a wavelength from 250 to 1000 nm. Barium-sulfate was used as a reference sample. The results of investigated samples are given in Figure 4.

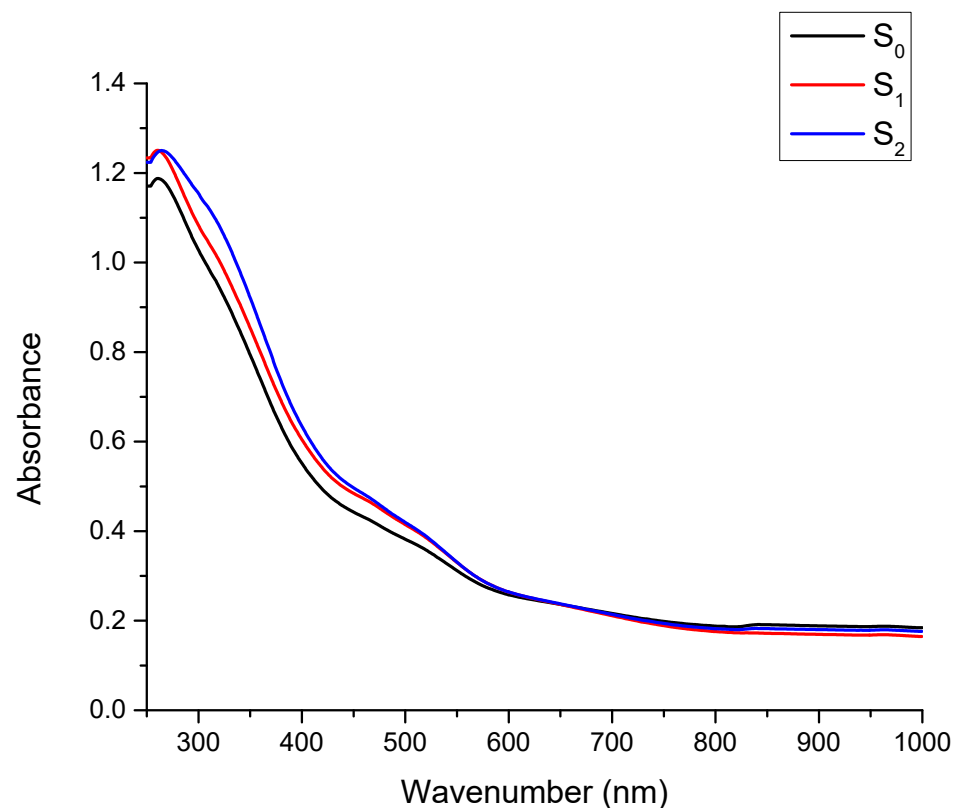


Figure 4. UV/VIS spectra of all samples.

By analyzing the spectrum, it can be concluded that materials with PVA absorb at a wavelength of 265 nm. In the graphic, we can see that the sample marked with S_0 , has the lowest absorbance, and absorbs at a wavelength of 260 nm with an absorbance of 1.17. Such a low absorbance can be attributed to the presence of an amorphous phase in the

sample, which can be seen on XRD. Slightly higher absorbances can be seen for S_1 and S_2 , 1.22 and 1.23, respectively. Increased absorbance occurs due to the presence of a carbonyl group as a chromophore, which absorbs at a wavelength of around 265 nm.

3.3.4. SEM/EDS Analysis of Organic–Inorganic Hybrid Geopolymers

SEM and EDS analyses of the synthesized samples are presented in Figure 5. Micrographs obtained by scanning electron microscopy can be used to study the pores within the matrix, as well as the matrix itself. Based on SEM micrographs of S_0 and synthesized hybrids, it can be seen that there was a change in the composition, which the XRD and FTIR methods confirmed. The structure and distribution of the pores were changed by adding PVA to the structure of the geopolymer. PVA coats the sample particles and prevents their contact with water [35]. Based on the results of the EDS analysis, shown in Table 3, the content of Si is significantly higher than Al, which was expected, and it was confirmed by XRF analysis.

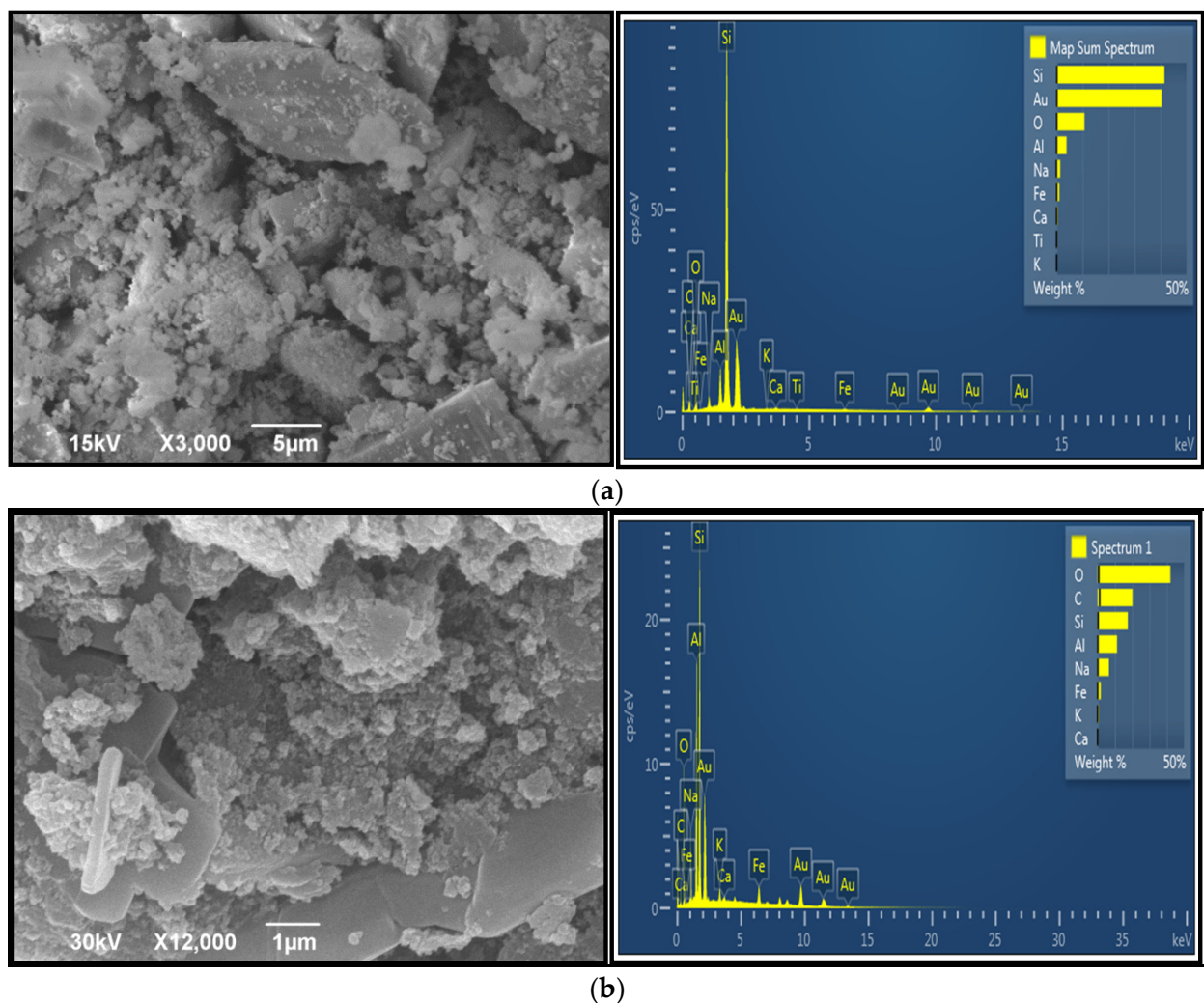


Figure 5. Cont.

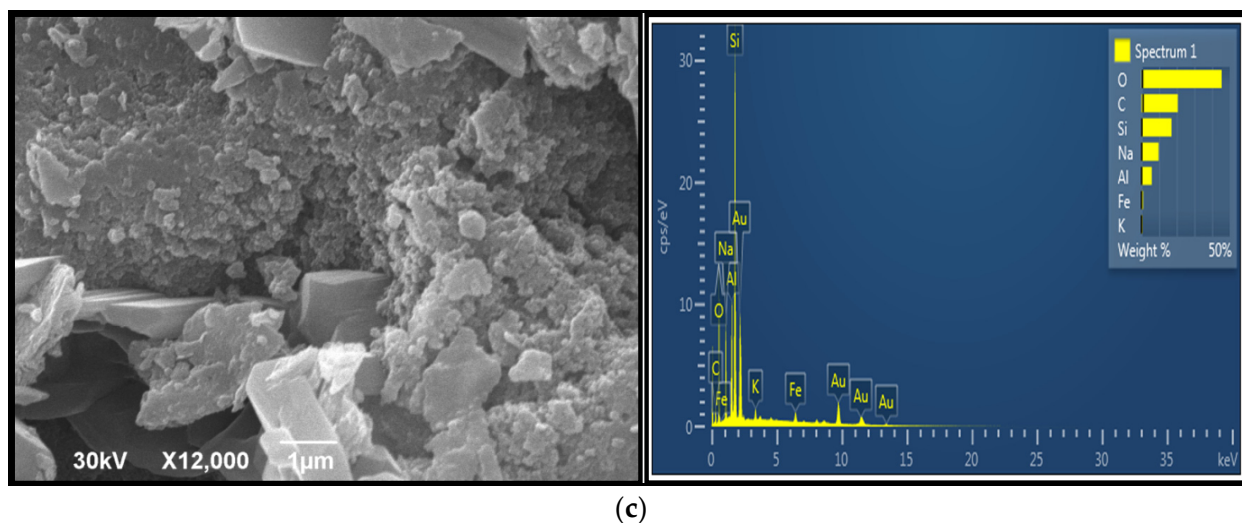


Figure 5. SEM micrographs and EDS analysis of geopolymer samples: (a) S_0 , (b) S_1 , (c) S_2 .

Table 3. EDS results of samples S_0 , S_1 , and S_2 .

S_0			S_1			S_2		
Element	Wt%	Standard Label	Element	Wt%	Standard Label	Element	Wt%	Standard Label
C	/		C	20.12	C Vit	C	20.57	C Vit
O	10.78	SiO ₂	O	42.09	SiO ₂	O	45.39	SiO ₂
Na	1.43	Albite	Na	6.53	Albite	Na	9.73	Albite
Al	3.88	Al ₂ O ₃	Al	11.23	Al ₂ O ₃	Al	5.83	Al ₂ O ₃
Si	41.50	SiO ₂	Si	17.42	SiO ₂	Si	17.00	SiO ₂
K	0.17	KBr	K	0.65	KBr	K	0.53	KBr
Ca	0.44	Wollastonite	Ca	0.21	Wollastonite	Ca	/	
Ti	0.23	Ti	Ti	/		Ti	/	
Fe	1.11	Fe	Fe	1.74	Fe	Fe	0.95	Fe
Au	40.46	Au	Au	/		Au	/	
Total:	100.00	Total:	Total:	100.00		Total:	100.00	

The results of the EDS analysis were determined based on the entire surface of the samples. Sodium hydroxide had a significant effect during geopolymerization even in the presence of polyvinyl alcohol. It appears that the OH[−] ion gets involved in the C–C bond scission of polyvinyl alcohol molecules, the CO₂-capture reaction, and favors salt precipitation [36]. Salt evaluation on the surface of geopolymer has been noticed and identified as efflorescence. The key components of efflorescence are Na₂CO₃, NaHCO₃, and different sodium silicate components. High concentrations of alkali activators cause significant efflorescence. With the alumina's enriched content, the efflorescence's extent decreased with alkali dosage. With the enhancement of silica content, the frequency of the efflorescence of geopolymer decreases. The surface of the hybrid geopolymer changed from hydrophilic to hydrophobic, which remarkably inhibited the capillary absorption and diffusion of water and condensed the leaching of solvable alkali ions. PVA was used as an additive to modify MK-based geopolymer and probably moderated efflorescence by consuming Na⁺ ions to design an amorphous gel phase [37].

On micrographs showing the surface of hybrid samples, S_1 and S_2 magnified 12,000 times, 1 μm crystal particles can be observed. Since PVA dissolves in water, it is easily incorporated

into the structure of geopolymers. As the geopolymerization reaction progresses, the polymer precipitates at the same time, forming a polymer film. On the other hand, the effect of the alkali activator with sodium hydroxide as its component was to bring about an enhancement in the viscosity of PVA, most probably due to gel formation. The gel formation was favored at higher sodium hydroxide concentrations and a longer duration of treatment [38]. Polymer films can fill the space between the pores and form bridges in the geopolymer structure; if the geopolymer material is loaded with a certain force, the polymer film that fills this space can absorb the energy generated by the external force, so that the mechanical properties are improved in this way [39]. By adding 1% PVA (Figure 5b), the polymer film combines with the geopolymerization product and forms a stable structure, which could improve the mechanical properties of the hybrid geopolymer material related to reference geopolymer samples. The addition of 2% PVA (Figure 5c) forms a similar structure which differs from the literature with the addition of the same percentage of PVA in cement mortar [35], where a material with lower compressive strength is formed compared to the material with the addition of 1% PVA. As far as efflorescence is concerned, Figure 5a shows this phenomenon on the surface of individual crystallites. With the addition of PVA, either 1% or 2%, no efflorescence is observed on the surface of the crystallites. As explained above, coatings with PVA film most likely prevent water evaporation, migration of Na^+ and OH^- ions, and reaction with CO_2 and H_2O from the air.

4. Conclusions

In this paper, the synthesis of hybrid geopolymer material (S_1 and S_2) was performed. Based on the obtained results and research, the following was confirmed:

The influence of temperature on the thermodynamic parameters of the alkaline activator confirmed the behavior of liquid systems; with increasing temperature, the values decrease due to thermal expansion, and with increasing molarity, the values become more linear. Total acid and base surface groups were determined by Boehm titration. The obtained results show that the most acidic surface groups are in S_1 , and the least in S_2 , while the most basic surface groups are in S_0 without the addition of PVA, and the least in S_2 . XRF analysis showed a significantly higher Si content leading to the appearance of crystalline phases. Synthesized hybrids changed the phase composition, which was confirmed by the XRD method. In addition to the quartz identified in all geopolymer samples, there are also peaks of sodium aluminosilicate phases corresponding to nepheline and albite. FTIR analysis shows the incorporation of PVA into the structure of geopolymers. As the most pronounced peak at 780 cm^{-1} , the share of quartz is prominent in this case as well, following the XRD analysis. XRD analysis also showed phase changes and the appearance of nepheline, which was confirmed by FTIR analysis with the appearance of peaks at 480 cm^{-1} . SEM/EDS analysis confirmed the change in phase composition as well as XRD analysis. The internal structure, pore distribution, and size composition of the modified sample changed with the inclusion of PVA. PVA has strong cohesiveness and water retention, so smaller amounts of PVA accelerate hydration while increased amounts negatively affect the rate of hydration. Effects of efflorescence on geopolymer materials were observed based on SEM analysis. EDS analysis confirmed XRF analysis that the S_1 content is significantly higher than Al. The presence of Na was also detected, which was observed in XRD analysis with the appearance of sodium aluminosilicate phases of nepheline and albite. Based on the UV/VIS analysis, it can be assumed that the synthesized samples can be used as potential adsorbents. Samples with added organic phase also exhibit good pozzolanic activities, based on which the material can be recommended for use in construction.

Compared to the literature data, the hybrid material is far more porous than the basic sample, which could have been expected. After the characterization of geopolymers with the addition of PVA, and based on data from the literature [39], we can conclude that we have synthesized a material that should show better mechanical properties.

Author Contributions: M.I. and S.N. conceptualized the research, designed and prepared the research plan, synthesized the samples, and wrote and revised the manuscript. L.K. and M.N. wrote part of the manuscript and analyzed obtained results. M.I. and I.R. analyzed thermodynamic parameters of the alkali activator system. M.M. contributed to analysis and discussion of the XRD results. M.I. together with S.K., completed DRIFT analysis. S.K. also examined surface groups. L.K. and M.I. contributed to the interpretation of the SEM results. All the authors contributed to the literature research, data analysis, and the preparation of the manuscript. All authors have read and agreed to the published version of the manuscript.

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References

1. Shi, C.; Fernández Jiménez, A.; Palomo, A. New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cem. Concr. Res.* **2011**, *41*, 750–763. [[CrossRef](#)]
2. Van Deventer, J.S.J.; Provis, J.L.; Duxson, P. Technical and commercial progress in the adoption of geopolymer cement. *Min. Eng.* **2012**, *29*, 89–104. [[CrossRef](#)]
3. Hussain, M.; Varley, R.J.; Cheng, Y.B.; Mathys, Z.; Simon, G.P. Synthesis and thermal behavior of inorganic–organic hybrid geopolymer composites. *J. Appl. Polym. Sci.* **2005**, *96*, 112–121. [[CrossRef](#)]
4. Sugama, T.; Brothers, L.E.; Van de Putte, T.R. Acid resistant cements for geothermal wells: Sodium silicate activated slag/fly ash blends. *Adv. Cem. Res.* **2005**, *17*, 65–75. [[CrossRef](#)]
5. McNaught, A.D.; Wilkinson, A. Compendium of chemical terminology. In *The Gold Book*, 2nd ed.; Blackwell Scientific Publications: Oxford, UK, 1997.
6. De Santis, R.; Catauro, M.; Di Lucy, S.; Manto, L.; Raucchi, M.G.; Ambrosio, L.; Nicolais, L. Effects of polymer amount and processing conditions on the in vitro behaviour of hybrid titanium dioxide/polycaprolactone composites. *Biomaterials* **2007**, *28*, 2801–2809. [[CrossRef](#)] [[PubMed](#)]
7. Kickelbick, G. Introduction to Hybrid Materials. In *Hybrid Materials: Synthesis, Characterization, and Applications*; Kickelbick, G., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007. [[CrossRef](#)]
8. Zahid, M.; Shafiq, N.; Nooriza, S.; Razak, A.; Tufail, R.F. Investigating the effects of NaOH molarity and the geometry of PVA fibers on the post-cracking and the fracture behavior of engineered geopolymer composite. *Constr. Build. Mater.* **2020**, *265*, 120295. [[CrossRef](#)]
9. Mohamed, I.M.A.; Yasin, A.S.; Barakat, N.A.M.; Song, S.A.; Lee, H.E.; Kim, S.S. Electrocatalytic behavior of a nanocomposite of Ni/Pd supported by carbonized PVA nanofibers towards formic acid, ethanol and urea oxidation: A physicochemical and electro-analysis study. *Appl. Surf. Sci.* **2018**, *435*, 122–129. [[CrossRef](#)]
10. Finch, C.A. *Polyvinyl Alcohol—Developments*; John Wiley & Sons Ltd.: London, UK, 1992.
11. Markert, B.; Friese, K. *Trace Elements—Their Distribution and Effects in the Environment*; Elsevier Science: Amsterdam, The Netherlands, 2000; Volume 4, pp. 187–213.
12. Maingi, F.M.; Mbuvi, H.M.; Ng'ang'a, M.M.; Mwangi, H. Adsorption of Cadmium Ions on Geopolymers Derived from Ordinary Clay and Rice Husk Ash. *Int. J. Mater. Chem.* **2018**, *8*, 1–9. [[CrossRef](#)]
13. Onutai, S.; Kobayashi, T.; Thavorniti, P.; Jiemsirilars, S. The adsorption of Cadmium Ions on Fly Ash Based Geopolymer Particles. *Key Eng. Mater.* **2018**, *766*, 65–70. [[CrossRef](#)]
14. Mladenović, N.; Kljajević, L.; Nenadović, S.; Ivanović, M.; Čalija, B.; Gulicovski, J.; Trivunac, K. The Applications of New Inorganic Polymer for Adsorption Cadmium from Waste Water. *J. Inorg. Organomet. Polym. Mater.* **2020**, *30*, 554–563. [[CrossRef](#)]
15. Marouane, E.A.; Saliha, A.; Mohammed, E.A.; M'hamed, T. Preparation, Characterization, and Application of Metakaolin-Based Geopolymer for Removal of Methylene Blue from Aqueous Solution. *J. Chem.* **2019**, *2019*, 4212901. [[CrossRef](#)]
16. Ivanović, M.; Nenadović, S.; Pavlović, V.P.; Radović, I.; Kijevčanin, M.; Pavlović, V.B.; Kljajević, L. The influence of thermodynamic parameters on alkaline activators of geopolymers and the structure of geopolymers. *Maced. J. Chem. Chem. Eng.* **2021**, *40*, 107–117. [[CrossRef](#)]
17. Boehm, H.P. Chemical identification of surface groups. *Adv. Catal.* **1966**, *16*, 179–274.
18. *PDXL*, version 2.8.3.0, Integrated X-ray Powder Diffraction Software. Rigaku Corporation: Tokyo, Japan, 2011.

19. *Powder Diffraction File P-D, Announcement of New Data-Base Release 2012*; International Centre for Diffraction Data (ICDD): Newtown Square, PA, USA, 2012.
20. Cong, P.; Cheng, Y. Advances in geopolymer materials: A comprehensive review. *J. Traffic Transp. Eng. Engl. Ed.* **2021**, *8*, 283–314. [[CrossRef](#)]
21. Ivanović, M.; Kljajević, L.; Gulicovski, J.; Petkovic, M.; Jankovic-Castvan, I.; Bučevac, D.; Nenadović, S. The effect of the concentration of alkaline activator and aging time on the structure of metakaolin based geopolymer. *Sci. Sinter.* **2020**, *52*, 219–229. [[CrossRef](#)]
22. Guo, L.; Wu, Y.; Xu, F.; Song, X.; Ye, J.; Duan, P.; Zhang, Z. Sulfate resistance of hybrid fiber reinforced metakaolin geopolymer composites. *Compos. Part B Eng.* **2020**, *183*, 107689. [[CrossRef](#)]
23. Badogiannis, E.; Tsivilis, S.; Papadakis, V.; Chaniotakis, E. The effect of metakaolin on concrete properties. In Proceedings of the International Congress: Challenges of Concrete Construction, Scotland, UK, 9–11 September 2002; Dhir, R.K., Hewlett, P.C., Cetenyi, L.J., Eds.; Thomas Telford: Telford, UK, 2002; pp. 81–89.
24. Ilić, B.U. *ticaj termički i mehanohemijski aktivirane kaolinске глине na mehanička svojstva i strukturu cementnih kompozita*. Ph.D. Thesis, Fakultet Tehničkih Nauka, Univerzitet u Novom Sadu, Novi Sad, Serbia, 2016.
25. He, J.; Zhang, J.; Yu, Y.; Zhang, G. The strength and microstructure of two geopolymers derived from metakaolin and red mud-fly ash admixture: A comparative study. *Constr. Build. Mater.* **2012**, *30*, 80–91. [[CrossRef](#)]
26. Zhang, P.; Han, X.; Hu, S.; Wang, J.; Wang, T. High-temperature behavior of polyvinyl alcohol fiber-reinforced metakaolin/fly ash-based geopolymer mortar. *Compos. Part B Eng.* **2022**, *244*, 110171. [[CrossRef](#)]
27. Kljajević, L.; Nenadović, M.; Ivanović, M.; Bučevac, D.; Mirković, M.; Nikolić, N.M.; Nenadović, S. Heat Treatment of Geopolymer Samples Obtained by Varying Concentration of Sodium Hydroxide as Constituent of Alkali Activator. *Gels* **2022**, *8*, 333. [[CrossRef](#)]
28. Lee, S.V.; Halim, N.A.; Arof, A.K.; Abidin, Z.H.Z. Characterisation of poly(vinyl alcohol) coating mixed with anthocyanin dye extracted from roselle flower with different nitrate salt. *Pigment Resin Techn.* **2013**, *42*, 146–151. [[CrossRef](#)]
29. Zhang, S.; Gong, K.; Lu, J. Novel modification method for inorganic geopolymer by using water soluble organic. *Mater. Lett.* **2004**, *58*, 1292–1296. [[CrossRef](#)]
30. Mansur, H.S.; Sadahira, C.M.; Souza, A.N.; Mansur, A.A.P. FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogen with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Mater. Sci. Eng. C* **2020**, *28*, 539–548. [[CrossRef](#)]
31. Delanu, I.M.; Stoica, A.; Stroescu, M.; Dobre, L.M.; Dobre, T.; Jinga, S.; Tardei, C. Potassium sorbate release from poly(vinyl alcohol)-bacterial cellulose films. *Chem. Pap.* **2012**, *66*, 138–143. [[CrossRef](#)]
32. Karlsson, C.; Zanghellini, E.; Swenson, J.; Roling, B.; Bowron, D.T.; Börjesson, L. Structure of mixed alkali/alkaline-earth silicate glasses from neutron diffraction and vibrational spectroscopy. *Phys. Rev. B* **2005**, *72*, 064206. [[CrossRef](#)]
33. Electronic Supplementary Material (ESI) for RSC Advances. Available online: <http://www.rsc.org/suppdata/c5/ra/c5ra25983e/c5ra25983e1.pdf> (accessed on 15 August 2022).
34. Asran, A.S.; Henning, S.; Michler, G.H. Poly vinylalcohol-collagen-hydroxyapatite biocompositenanofibrous scaffold: Mimicking the key features of natural bone at the nanoscale level. *Polymer* **2010**, *51*, 868–876. [[CrossRef](#)]
35. Fan, J.; Li, G.; Deng, S.; Wang, Z. Mechanical Properties and Microstructure of Polyvinyl Alcohol (PVA) Modified Cement Mortar. *Appl. Sci.* **2019**, *9*, 2178. [[CrossRef](#)]
36. Zhang, J.; Wang, S.; Guo, Y.; Xu, D.; Gong, Y.; Tang, X. Supercritical water oxidation of polyvinyl alcohol and desizing wastewater: Influence of NaOH on the organic decomposition. *J. Environ. Sci.* **2013**, *25*, 1583–1591. [[CrossRef](#)]
37. Xiao, R.; Ma, Y.; Jiang, X.; Zhang, M.; Zhang, Y.; Wang, Y.; Huang, B.; He, Q. Strength, microstructure, efflorescence behavior and environmental impacts of wasteglass geopolymers cured at ambient temperature. *J. Clean. Prod.* **2020**, *252*, 119610. [[CrossRef](#)]
38. Hebeish, A.; Abdel-Gawad, I.I.; Basily, I.K.; El-Bazza, S. Degradation of poly(vinyl alcohol) in strongly alkaline solutions of hydrogen peroxide. *J. Appl. Polym. Sci.* **1995**, *30*, 2321–2327. [[CrossRef](#)]
39. Kim, J.H.; Robertson, R.E. Effects of Polyvinyl Alcohol on Aggregate-Paste Bond Strength and the Interfacial Transition Zone. *Adv. Cem. Based Mater.* **1998**, *8*, 66–76. [[CrossRef](#)]

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