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The Influence of Alumino-Silicate Matrix Composition on Surface Hydrophobic Properties

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Abstract:

The purpose of this investigation is to investigate the hydrophobicity of geopolymers, new alumino-silicate materials and the influence of Si/Al ratio on their surface properties. Contact angle measurement (CAM) as reliable indicator of hydrophobicity was determined for synthesized geopolymers using water and ethylene-glycol as reference liquids. Geopolymers were synthesized from various precursors: kaolin, bentonite and diatomite. Characterization of phase structure and microstructure was performed by XRD, FTIR, SEM/EDX methods. Contact angle measurements confirmed that the geopolymers synthesized from metakaolin are the most porous, which can be explained by the smallest Si/Al ratio. The maximum value of contact angle and free surface energy (110.2 mJ/m²) has been achieved for geopolymer synthesized by diatoms (GPMD). SEM micrograph of GPMD shows a homogeneous surface with some longitudinal cavities in the gel and is significantly different from the micrographs of other two geopolymer samples, GPMB and GPMK.

Keywords: Metakaolin; Metadiatomite; Metabentonit; Geopolymer; Contact angle.

1. Introduction

The group of inorganic polymers, which are macromolecules linked by covalent bonds and having -Si-O-M-O- backbone, where M denotes principally aluminum and secondarily other metals such as iron are known as geopolymers [1,2]. In the field of civil engineering, geopolymer-based materials are also referred to as “alkali-activated cements” or “chemically-bonded ceramics” which can be obtained from raw materials with low (or zero) CaO content, such as metakaolin [3, 4], clay [5, 6] and other natural silico-aluminates [7] as well as industrial process wastes such as coal fly ash [8], lignite bottom ash [9] and metallurgical slag [10]. Technology of geopolymer materials is progressively overcoming the challenges associated to its commercialization with the increase of several practical applications. The progress on standardization and the successful design of pathways with a

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good combination of safety, cost reduction, desired properties and the ease with which they can be used, are the key parameters that will influence the development of geopolymers in the field of cements and concretes, fire resistant, insulating and purification materials [11]. Protecting the surface of geopolymer is essential for improving its durability under certain exposure conditions [12]. Permeability or waterproof property is a very important parameter for geopolymers as it indicates the degree of reaction and long-term durability. When the surface of a geopolymer is dry and subjected to aggressive liquids, the geopolymer absorbs the majority of the liquid because of the capillary force. This absorption leads to a durability problem and reduces the service lifetime of the product. Therefore, the geopolymer must be protected from water penetration. The water contact angle is a significant factor because hydrophobicity will slow the water penetration through the material, improving the durability. Therefore, with an increasing contact angle, less wetting of the composite will occur. The knowledge of the hydrophobicity of the geopolymer samples obtained by determining static water contact angle makes to define a possible surface modifier in terms of the type of applications of geopolymers.

The aim of this paper is to investigate the water contact angle of several geopolymers and how the precursor types and their physicochemical characteristics affect geopolymer properties. Geopolymers were synthesized in order to obtain their optimal composition for achieving determined hydrophobic/hydrophilic properties.

2. Materials and Experimental Procedures

The kaolinite and diatomite used are high quality obtained from Rudovci, Lazarevac, Serbia. Physicochemical properties of kaolin were investigated in previous work by Nenadović *et al* [13] are suitable for thermal treatments planned in this research. Bentonite in powdered form was obtained from the Lieskovec deposit (near Zvolen, Central Slovakia). This deposit is currently mined by Envigeo Inc., Slovakia. The sample of bentonite was used without further purification.

Kaolinite, bentonite and diatomite were thermally treated by calcining at 750 °C for 1 hour. The reference geopolymers (GP) were formed from all three thermally treated samples and the alkaline activator solution (solid/liquid ratio was approximately one), which were mixed for 10-15 minutes and then left at room temperature for one day. Finally, the mixtures were kept in a sample drying oven for 48 hours at 60 °C. The alkaline solution was prepared from sodium silicate (volume ratio $\text{Na}_2\text{SiO}_3/\text{NaOH} = 1.5$) and 2 M NaOH (analytical grade). According to the “alkali activation theory” [14] alkali plays an important role in the chemical reaction [15]. After this reaction step, all samples were aged for 28 days, which is required time period to finish the polymerization process [16].

All samples of geopolymers were characterized by X-ray diffraction analysis (XRD) using Ultima IV Rigaku diffractometer, equipped with Cu $K\alpha_{1,2}$ radiation, with a generator voltage of 40.0 kV and a generator current of 40.0 mA. The 2θ range of 5°-80° was used for all powders in a continuous scan mode with a scanning step of 0.02° at scan rate of 5 °/min. Phase analysis was done by using the PDXL2 software (version 2.0.3.0 - Rigaku Corporation, Japan), with reference to the patterns of the International Centre for Diffraction Database (ICDD) PDF-2 Database, version 2012.

The functional groups of all samples were studied using FTIR spectroscopy. Samples were powdered finely and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). Spectra were taken at room temperature using a Bomem (Hartmann & Braun) MB-100 spectrometer set to give undeformed spectra. The spectral data of the samples were collected in the 4000-400 cm^{-1} region.

The microstructure analyses of the geopolymer materials were performed on Au-coated samples using JEOL JSM 6390 LV electron microscope at 25 kV.

Contact angles were measured by the direct optical sessile drop method, using home-made equipment (Laboratory of atomic physics, INS Vinča, Serbia). The liquid droplet of 2 μ L volume was deposited by a micro pipette pointed vertically down onto the sample, and the angle was captured by a high resolution camera (Konig electronic, Netherlands) and analyzed using imaging software (ImageJ 1.45s, Wayne Rasband, National Institutes of Health, USA) with a contact angle measurement plug-in (LB-ADSA, A.F. Stalder, LB-ADSA, Biomedical Imaging Group, EPFL, [ON LINE] visited 2005 [17]).

3. Results and Discussion

The results of chemical analysis of natural materials, bentonite, diatomite, and kaolin samples show different values of Si/Al ratio [13, 18, 19]. For bentonite this ratio is 3.0, diatomite, 8.0 and kaolinite, 2.3. In the process of geopolymerization of three different precursors (MK, MB and MD) in alkaline activator solution formation of geopolymers (GPMK, GPMB and GPMD) is done.

3.1. FTIR-analysis

Fig. 1 shows the results of FTIR analysis of natural materials (kaolinite, bentonite and diatomite), heat-treated to 750 °C and of the geopolymer synthesized samples. Phase evolution for kaolinite, metakaolin and geopolymer obtained by MK can be monitored by FTIR absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material, as shown in Fig. 1a. As a previous research has confirmed [20-22] kaolin shows pronounced peaks at 3969 cm^{-1} , 3620 cm^{-1} , 3567 cm^{-1} , 2924 cm^{-1} and 1637 cm^{-1} ; which can be explained by physical adsorption and deformation of O-H bonds. As for the metakaolin and thermally treated kaolin at 750 °C, one can observe fewer peaks as more stable material than kaolin is formed. Newly created peaks are confirmed at 3435 cm^{-1} , 2924 cm^{-1} and 1633 cm^{-1} . After polymerization and aging of 28 days, more stable structure (Fig. 1a) with defined peaks at 3450 cm^{-1} and 1655 cm^{-1} is obtained. Kaolin phase has defined peaks on 1033 cm^{-1} , 1104 cm^{-1} , 913 cm^{-1} , 792 cm^{-1} and 752 cm^{-1} change into metakaolin, and newly formed peaks appears at 1063 cm^{-1} and 806 cm^{-1} . In the final stage of polymerization pronounced peaks appears at some lower values on 1036 cm^{-1} and 786 cm^{-1} (Fig. 1a). As a result of the alkaline activation process of metakaolin, the Al-O asymmetric stretch band shifts towards lower frequencies at around 998 cm^{-1} (GP sample), indicating the formation of an alkaline aluminosilicate gel [23, 24]. According to the literature, in the 800-550 cm^{-1} region there are vibration bands attributed to Secondary Building Units (SBUs). SBUs are made of joined SiO_4 and AlO_4 tetrahedra forming variously membered rings [21, 22], which give rise to an over-tetrahedral form of middle-range order. Fig. 1b presents the results of FTIR analysis of bentonite, thermally treated bentonite at 750 °C (metabentonite) and geopolymers synthesized from metabentonite. For bentonite a polymerization similar situation occurs, where each degree of polymerization gives a more stable material. For natural bentonite revealed clearly defined peaks at 1037 cm^{-1} , 915 cm^{-1} and 799 cm^{-1} . Also bentonite peaks are defined at 526 cm^{-1} and 468 cm^{-1} . During the heat treatment and phase change on 750 °C, FTIR analysis revealed peaks at higher values: 1047 cm^{-1} and 791 cm^{-1} and confirmed the existence of peaks at 555 cm^{-1} and 478 cm^{-1} . Peak at 1047 cm^{-1} was unchanged even after the final stage of the polymerization, while the value of peak at 791 cm^{-1} increased to 795 cm^{-1} . Geopolymer synthesized from metabentonite and was aged for 28 days shows peaks at 3447 cm^{-1} and 1654 cm^{-1} . After the final stage of polymerization well defined peak appears at 476 cm^{-1} (Fig. 1b).

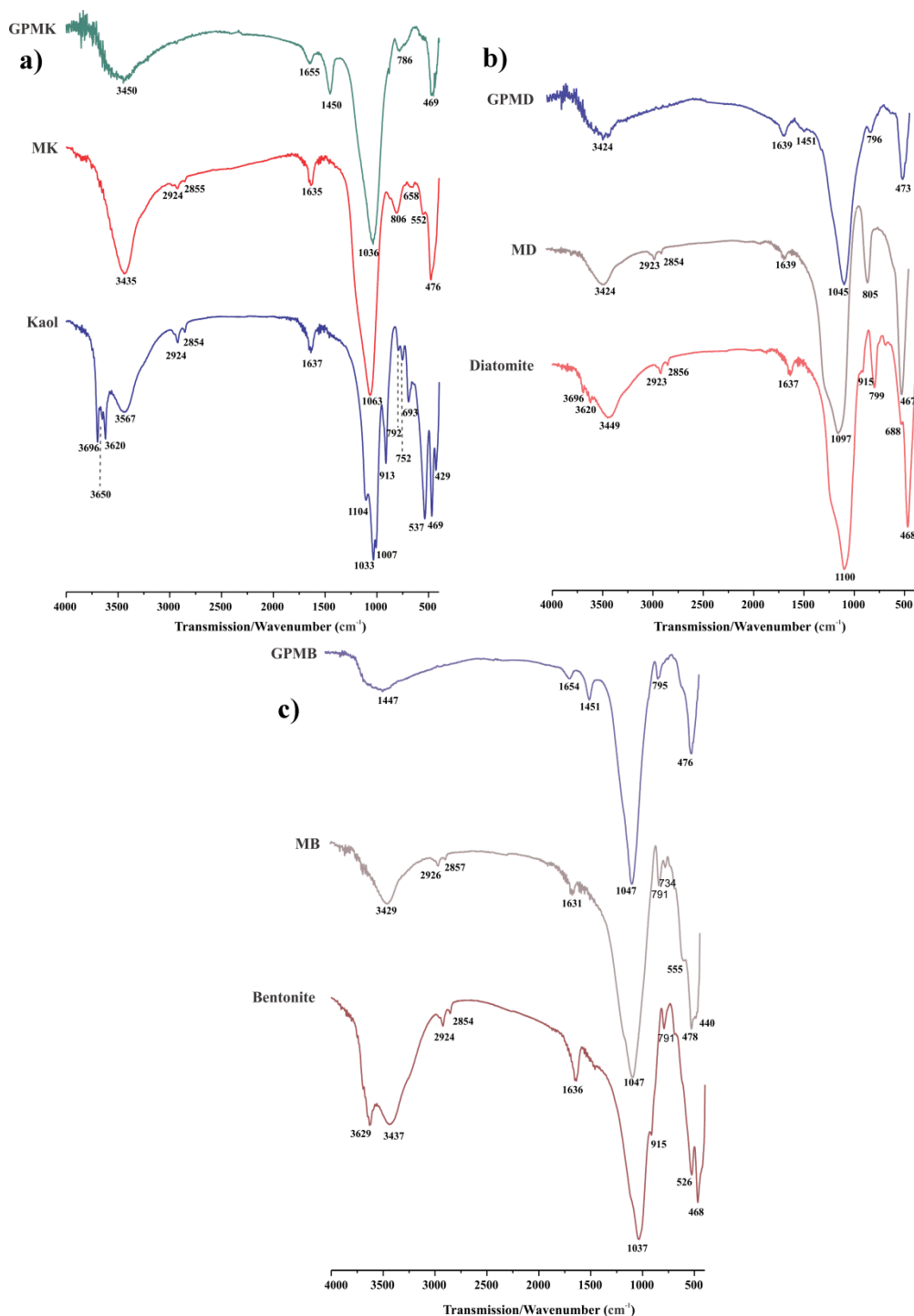


Fig. 1. FTIR spectra of a) Kaol, M Kaolinite and GPMK b) Bentonite, M Bentonite and GPMB and c) Diatomite, M Diatomite and GPMD.

Fig. 1c presents the results of FTIR analyzes of diatomite, thermally treated diatomite on 750 °C (metadiatomite) and geopolymers synthesized from metadiatomite. One can observe peak shift to lower values compared to the results of the previous two samples. Pronounced peaks at 3424 cm⁻¹ and 1639 cm⁻¹ are clearly defined after the final phase of polymerization. They are exactly defined in the range from 3450 cm⁻¹ to 1640 cm⁻¹. The sample synthesized by the

diatoms in the natural state has well defined peaks at 1100 cm^{-1} , 915 cm^{-1} and 799 cm^{-1} . Phase change of diatoms after thermal treatment on $750\text{ }^{\circ}\text{C}$ gives clearly defined peaks at lower values 1097 cm^{-1} and 805 cm^{-1} . After terminal stage of polymerization, peaks are even at lower values, 1045 cm^{-1} and 796 cm^{-1} . Natural diatoms (Fig. 1c) have clearly defined peak at 468 cm^{-1} . After thermal treatment this peak is shifted to 467 cm^{-1} , and after the final stage of polymerization the peak is located at 473 cm^{-1} .

In all FTIR spectrums which are explained in previous text the special area of geopolymers spectrum are related to Si–O stretching band is located in the range $1000\text{--}1200\text{ cm}^{-1}$, and the Si–O bending bands are found at 800 cm^{-1} and between 890 and 975 cm^{-1} . When the high full width at half maximum (FWHM) of some band is wider, it is known that phases of non-ordered structure increase the band width due to the existence of significant fluctuations of geometric parameters, i.e., bond lengths and angles [25]. The band at approximately 1100 cm^{-1} is assigned to the Si–O stretching of tetrahedrons in which silicon is bound to 4 bridging oxygen atoms. Another band at 1050 cm^{-1} is assigned to the Si–O stretching of tetrahedrons in which silicon is surrounded by 3 bridging oxygen units and one non-bridging oxygen (Si–NBO) [21, 22, 26]. The second structure (Si–NBO) of geopolymers is directly related to the hydrophobicity of the geopolymer molecules. Also, the position of the main Si–O–X stretching band (X = Si, Na, or H) gives an indication of the length and angle of the bonds in a silicate network [27]. A shift of the Si–O–X stretching band towards lower wave numbers indicates lengthening of the Si–O–X bond, reduction in the bond angle, and thus a decrease of the molecular vibrational force constant [28]. This shift can be also attributed to an increase of the fraction of silicon sites with non-bridging oxygen atoms (NBO) [23] i.e. the possibility of binding to the opposing charge molecules.

3.2. Structural and morphological characterization

3.2.1. XRPD characterizations

The inorganic polymer binders (geopolymers) are normally amorphous or semi-crystalline, as is clearly seen in Fig. 2. Metakaolin and metadiatomite based geopolymers are a prevailingly amorphous character; while metabentonite based geopolymer has semi-crystalline structure.

Bentonites are naturally occurring clay mineral mixtures that are mainly composed of smectite, i.e. montmorillonite clay (at least 70 wt.%) [29]. Among of generally composed of mineral of bentonite from Lieskovac [18] area the most common is montmorillonite. Except it's in metabentonite based geopolymer is identified pyrophyllite. In the ideal case, the structural formula is expressed by $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. The structural units of smectite can be derived from the structures of pyrophyllite. Unlike pyrophyllite, the 2:1 silicate layers of smectite have a slight negative charge owing to ionic substitutions in the octahedral and tetrahedral sheets. The structural formula of smectites of the dioctahedral aluminous species may be represented by $(\text{Al}^{2-}_y\text{Mg}^{2+}_y)(\text{Si}^{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2M^{+}/_{x+y} n\text{H}_2\text{O}$, where M^+ is the interlayer exchangeable cation expressed as a monovalent cation and where x and y are the amounts of tetrahedral and octahedral substitutions, respectively ($0 \leq x + y \leq 0.6$). The smectites with $y > x$ are called montmorillonite. All of those phases may exist in this type of geopolymer, because there is overlapping of peaks (Fig. 2a).

Fig. 2b and 2c show the XRD patterns of the metadiatomite and metakaolin based geopolymer samples. The both of geopolymer samples were amorphous phases as indicated by broad hump at the region of $25\text{--}35^{\circ} 2\theta$. The main crystal phases containing quartz (SiO_2) (ICCD No. 892 79) and muscovite (ICCD No. 170 49). The reason for this lies in the fact that the kaolin mainly consists of high-defected kaolinite with some impurities of feldspar and quartz. Metakaolinite, in contrast to kaolin [13], was composed of an amorphous phase and a semi crystalline structure. Quartz could be identified as a component of metakaolinite. Clearly the quartz in the metakaolinite is not solved in the geopolymerization reaction. After the

process of geopolymerization, the original broad peak of metakaolin is shifted to the higher values of 2θ angles ($30^\circ 2\theta$), indicating the dissolution of the metakaolin amorphous phase and the formation of a new amorphous phase in the geopolymer [30].

The broad amorphous background feature in the region $2\theta = 15\text{--}35^\circ$, present in GPMK and GPMK samples suggests that the main reaction product formed is “alkaline aluminosilicate gel” with low-ordered crystalline structure. In the geopolymer obtained from metadiatomate only quartz is identified as a crystalline phase (Fig. 2b)

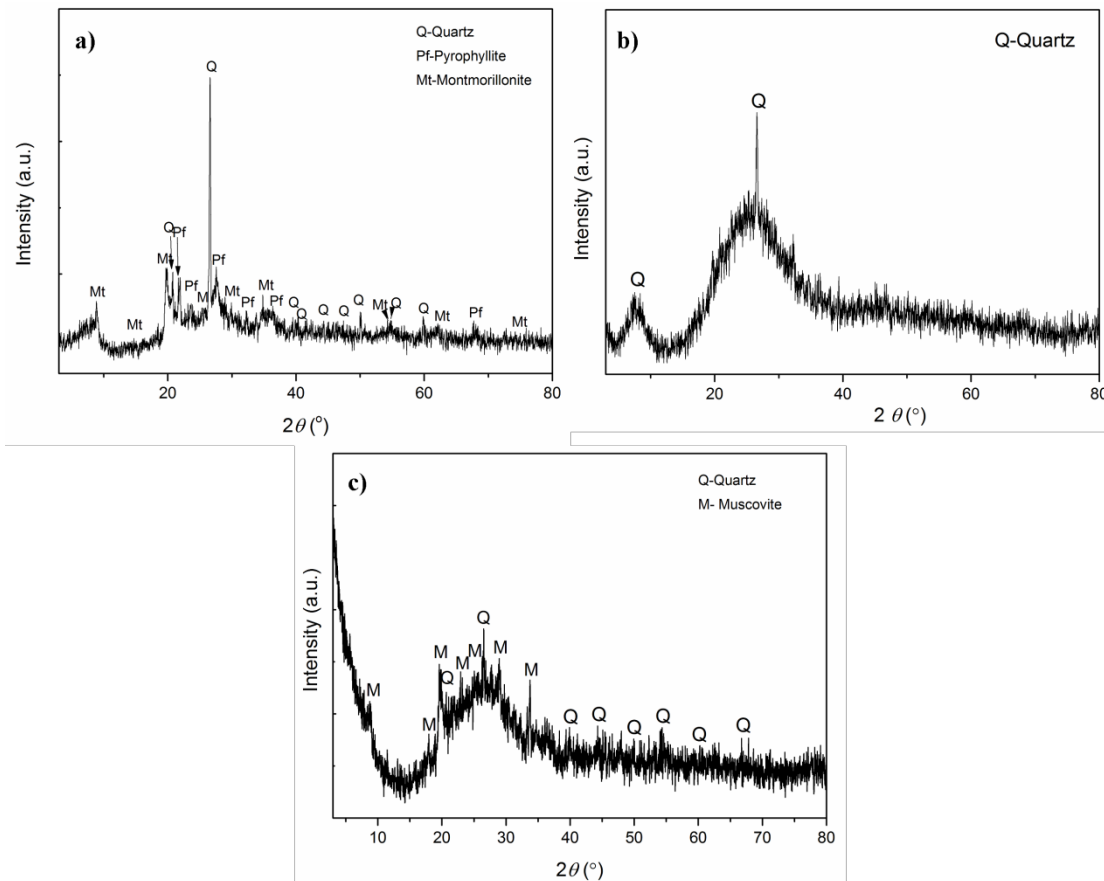


Fig. 2. XRD patterns of the geopolymer samples a) GPMK, C) GPMK D) GPMK.

3.2.2. SEM-EDS analysis

The SEM micrographs of geopolymers are shown in Fig. 3. All of the geopolymer samples (GPMK, GPMK, GPMK) were analyzed in a powder state. Uneven form of small particles grouped into agglomerates and individually arranged particles across the surface of large geopolymer plates, are visible on GPMK and GPMK samples (Fig. 3a and Fig. 3b). All particles were predominantly of different sizes and had smooth surfaces, as in previous observations from other studies [31]; silica is responsible for the particles of irregular size [32, 33]. Fig. 3c presents the SEM image of GPMK significantly different than the previous two. In this case, significant cross-linking is likely, creating a homogeneous surface with less capillary cracks and fewer individual and grouped particles on the surface. The important properties of diatomite are related to physical structures and an aggregate of fine particles perforated by a regular pattern of very small holes. The honeycomb silica structure gives diatomite useful characteristics such as unique particulate structure, chemical stability, low bulk density, high absorptive capacity, high surface area, and low abrasion. These

characteristics enable the material to be commercially applicable as a filter aid, absorbent [13, 19], anti-caking agent, thermal insulator, filler and extender, catalyst carrier, chromatographic support and additive for numerous other purposes [18].

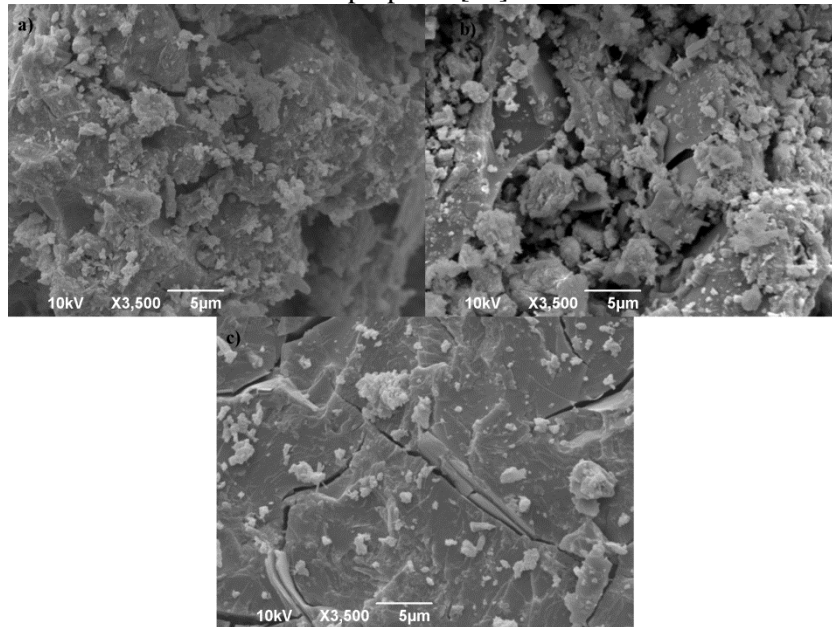


Fig. 3. SEM micrographs and EDS spectrum of a) GPMK b) GPMB c) GPMD.

The EDX analysis of geopolymers showed major elements of Si, Al and Na. The increase GP content increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The physical and chemical properties of geopolymers were a function of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios [30]. The geopolymer with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 2.06 and 13.35 (as shown in Fig. 3.) were observed by SEM photos to have the presence of a continuous and dense mass of geopolymer.

Table I presents the chemical composition acquired using EDS analysis on geopolymers solid surface samples.

Table I Elemental composition of investigated area of GPMK, GPMB and GPMD samples.

Element	GPMD	GPMB	GPMK
	Wt%	Wt%	Wt%
O	47.80	51.1	53.82
Na	10.44	11.75	7.87
Mg	-	0.66	12.37
Al	2.86	6.15	8.49
Si	38.90	25.75	16.98
K	-	0.59	0.47
Ca	-	0.58	-
Fe	-	3.42	-
Total:	100.00	100.00	100.00

The results of the analysis by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), showed that the bentonite exhibits smoothed particles surfaces with most of SiO_2 and Al_2O_3 with an average weight percentage respectively of 25.75 % and 6.15 %. There are also other constituents present such as carbon and its compounds given in Table I. It is clearly observed that non-dissolved spherical aluminosilicate particles or elongated perlite particles Fig. 3. are enclosed within an amorphous aluminosilicate matrix acting as a binder. Therefore, the geopolymeric materials are composed from solid particles chemically connected with an inorganic polymeric binder formed during the geopolymerization process. The mechanical strength of materials is strongly related to the strength of the chemical bonds formed on the interface of the solid particle/inorganic polymer. The interface is normally the surface where the geopolymeric materials fail.

SEM microphotographs presented in Fig. 3. at a magnification of 3500 times, show that samples synthesized from kaolin and bentonite have a more porous structure compared to SEM image of diatoms. The Si/Al ratio for geopolymer synthesized from metakaolin is 2.06, while the ratio for geopolymer synthesized from bentonite is two times higher, 4.19. Geopolymer synthesized from diatoms has the highest Si/Al ratio which is 13.35.

3.3. Contact angle measurement (water/ethylene – glycol)

The water contact angle is a parameter that determines the hydrophilicity/hydrophobicity of the material. This angle is related to the value of the contact angle between the water droplet and the solid. In general, geopolymers are cementitious materials with porous structures and display a wide range of pore variation, from nanometers to millimeters, including entrapped air voids, entrained air voids, capillary pores and nanoscale gel pores.

Tab. II Water/ethylene glycol contact angle.

Samples	Contact angle,° (H ₂ O)	Contact angle,° (ethylene-glycol)	γ_{sp} (mJ/m ²)	γ_{sd} (mJ/m ²)	γ_s (mJ/m ²)
GPMK	0	15.20	90.082	1.1557	91.238
GPMB	0	17.30	91.291	0.9564	92.248
GPMD	11.54	39.69	109.88	0.3582	110.23

Table II shows the results of the contact angle and free surface energy measurement obtained using water and ethylene - glycol as reference liquids. γ_s represents total free surface energy of the material, while γ_{sp} and γ_{sd} are polar and dipolar components respectively, according to the following equation (1):

$$\gamma_{sp} + \gamma_{sd} = \gamma_s \quad (1)$$

The most porous and lowest hydrophobicity geopolymer is synthesized from metakaolin (GPMK). Water wetting is complete (angle 0°) while ethylene - glycol shows a certain wetting angle of 15.2°. Polar component of the free surface energy ($\gamma_{sp} = 90.08 \text{ mJ/m}^2$) is significantly higher compared to the dipolar component ($\gamma_{sd} = 1.156 \text{ mJ/m}^2$), that further confirms the polar nature of the investigated geopolymer. Geopolymer synthesized from metabentonite (GPMB) has a higher value of contact angle with ethylene glycol compared to kaolin, while the water wetting is also complete. Polar component ($\gamma_{sp} = 91.29 \text{ mJ/m}^2$) is again significantly higher than dipolar ($\gamma_{sd} = 0.9564 \text{ mJ/m}^2$), which means GPMB is even more polar

material. This could be explained by the greater extent of cross-linking of Al and Si, as well as the much higher Si/Al ratio in synthesized geopolymer. This is confirmed by EDS analysis, which was expected considering that GPMB sample has Si/Al ratio slightly higher compared to GPMK. This was also confirmed in earlier studies using XRF method. The maximum value of contact angle and free surface energy has been achieved for geopolymer synthesized by diatoms (GPMD). The measured contact angle of water is 11.54° , and that of ethylene glycol is 39.69° . Introducing these values to Owens and Wendt model [34] indicates the value of the total free surface energy of 110.2 mJ/m^2 . It is higher than the values for the previous samples (GPMK, GPMB) and the difference between the polar (109.9 mJ/m^2) and dipolar (0.3582 mJ/m^2) energy components is even more pronounced, confirming that GPMD geopolymer is the most hydrophobic and the most adhesive among analyzed materials.

4. Conclusion

Physicochemical characterization of geopolymer materials in this research has confirmed that the more porous structure has a lower contact angle. FTIR analysis revealed a polymerization process of geopolymers from all three precursors (kaolin, bentonite and diatoms). Also, the structures of metabentonite, metakaolin and metadiatoms are observed as well as the spectrum shift. After 28 days FTIR spectra of aged geopolymers was recorded. Those samples were subjected to a contact angle measurement using water and ethylene glycol as reference liquids. SEM analysis showed that the structure of the geopolymers synthesized from metadiatoms is more compact. Contact angle measurement revealed that the contact angle values for ethylene-glycol are three times higher compared to water. These measurements have also confirmed that the geopolymers synthesized from metakaolin are the most porous, which can be explained by the smallest Si/Al ratio.

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Садржај: Циљ истраживања је одређивање хидрофобности геополимера, нових алумосиликатних материјала и утицаја односа Si/Al на њихова површинска својства. Поуздан индикатор хидрофобности је контактни угао који је одређен за геополимере. За мерење контактне угла као референтне течности употребљене су воду и етиленгликол. Три различита прекурсора су коришћена за синтезу геополимера: каолин, бентонит и дијатомеј. Структурна и микроструктурна карактеризација испитивана је следећим методама: XRD, FTIR, SEM/EDX. Потврђено је да геополимери синтетисани из метакаолина су најпорознији, што се може објаснити најмањим односом Si/Al. Максимална вредност контактне угла и слободне површинске енергије ($110,2 \text{ mJ/m}^2$) постигнута је за геополимере синтетисане од дијатомеја као прекурсора (GPMD). SEM микрграфија GPMD показује хомогену површину

геополимерног гела са уздужним шупљинама и значајно се разликује од микрографија узорка геополимера, GPMВ и GPMK.

Кључне речи: метакаолин; метадијатомеј, метабентонит; геополимер; контактни угао

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