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Investigation of nanoparticle use in geopolymer production

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Abstract: In this study, performance improvements of alumina nanoparticles of metakaolin based geopolymer samples were studied. It is aimed to develop a durable implant by combining the mechanical properties of inorganic polymers with the bioactive behavior of substances such as calcium hydroxide and calcium phosphate. This material, which is an example of high-tech engineering ceramics, has been calcined and it is use as an implant / prosthesis in biomedical fields as a result of improvement. It is foreseen that the production of biogeopolymer will provide hard / soft tissue and bone regeneration. One of the best ways to determine the bioactivity of biomaterials is to expose them to simulated body fluids. 7, 14 and 28-day cured sample surfaces were investigated using characterization of Scanning Electron Microscopy, X-Ray Diffraction and Fourier Transformed Infrared Spectrometry. As a result, in this study; the properties of alumina nanoparticles based metakaolin based geopolymer samples and their usefulness in the form of implant, bone substitutes as biocompatible materials were investigated and results were evaluated.

Keywords: Geopolymer, nanoparticle, alumina, metakaolen

1. Introduction

Nowadays, surgeons in medical practice areas increase the demand for new materials for application in cases of bone fractures or deficiencies caused by accidents, cysts, tumors and other bone diseases.(Korkusuz et al. 2011) These materials are produced from a variety of materials, such as organic or inorganic cements, with the main characteristics being biocompatibility, if possible, the ability to withstand bone regeneration and / or mechanical loading. In this study, it is aimed to develop a durable implant by combining the mechanical properties of inorganic polymers (geopolymers) with the bioactive behavior of substances such as calcium hydroxide and calcium phosphate. In order to increase the mechanical and biological performance of the synthesized geopolymer, alumina nanopowders was added. Geopolymer produced under the study will be expected to be used in biomedical areas as an implant / prosthesis after calcination.

Geopolymers are formed by mixing alkali or alkali-silica solutions of solid silicate-aluminate raw materials. (MacKenzie et al., 2007) The most important raw material is generally calcined clays, such as heat activated kaolin. (MacKenzie et al., 2010) Up to date, kaolinitic clays (Oudadesse et al., 2007), metakaolin, fly ash, blast furnace slag, fly ash-slag mixtures, metakaolin-fly ash mixtures, metakaolin slag mixtures, slag-red sludge mixtures, kaolin with fly ash and a kind of zeolite mineral Mixtures of non-calcined substances such as stilbite (Ros and Shima, 2013) have been used. (Mohamed et al., 2016) In this study, raw material, calcined kaolin clay, ie, metakaolin, were used as the main phase of geopolymer mortar.

Before the incorporation of calcium phosphate and calcium hydroxide compounds into the material, metakaolin must be activated for the synthesis of geopolymer. Sodium silicate solution with potassium hydroxide and sodium hydroxide salts for geopolymerization was used as activator.

2. Materials and Method

2.1. Raw materials and characterization studies

Chemicals used in material preparation; metakaolin clay, sodium hydroxide, potassium hydroxide, sodium silicate, pure water, calcium hydroxide, calcium phosphate, nano alumina powder, chitosan, acetic acid solution and hydroxy apatite. X-ray diffraction and Fourier transformed infrared spectroscopy instrumental characterization methods were applied to the metakaoline raw material supplied.

2.2. Preparation of Reference Geopolymer Samples

Metakaolin-based geopolymer samples containing calcium hydroxide and calcium phosphate powders were activated with the alkali salts of sodium and potassium hydroxide. Powdered chemicals containing metakaolin and calcium were first weighed. Weighing was continued with granular salts. At this stage, sodium and potassium hydroxide were weighed and then dissolved in some water. After activation of these materials with metakaolin, salt and sodium silicate, the appropriate amounts of calcium-containing components were added. Homogenization is essential here.

In the casting process, silicon molds with 30mm diameter and 20mm height are thoroughly cleaned and lubricated. The samples poured into the molds are compressed in the shaker to prevent air pockets. Samples that were kept at room temperature for 24 hours were kept in the curing pool for 3, 7, 28 days by removal from the mold.

Prepared geopolymer samples were named GP 1, 2, 3 and 4 according to their alkali salt and calcium content. GP1 and GP3 were activated with potassium hydroxide, GP2 and GP4 sodium hydroxide salt. GP1 and GP2 contain calcium hydroxide, GP3 and GP4 calcium phosphate. The x-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR) instrumental characterization methods were applied to these reference samples.

2.3. Strength Measurements

The compressive strength of geopolymer samples was tested with 3, 7, 14 and 28 days curing according to ASTM C109 and ASTM C191 (Annual Book of ASTM Standard, 2005) standards. Strength measurements were performed using a universal tensile compression device from Mohr Federhaff AG.

3. Results

The XRF results of the chemical composition of the metakaolin clay we use as raw material in all of the geopolymer samples are as follows.

Table 1. Chemical Composition of Metakaolin Clay

Percentage %					
SiO_2	**Al_2O_3**	**K_2O**	**Na_2O**	**Fe_2O_3**	**TiO_2**
59.80	35.20	0.7	0.6	1.2	1.5

The co-occurrence of reference geopolymer samples with the XRD analysis result for metakaolin is as follows. Either way, the upper spectrum is red and belongs to GP1 and GP2, respectively. The underlying spectrum is blue and belongs to metakaolin.

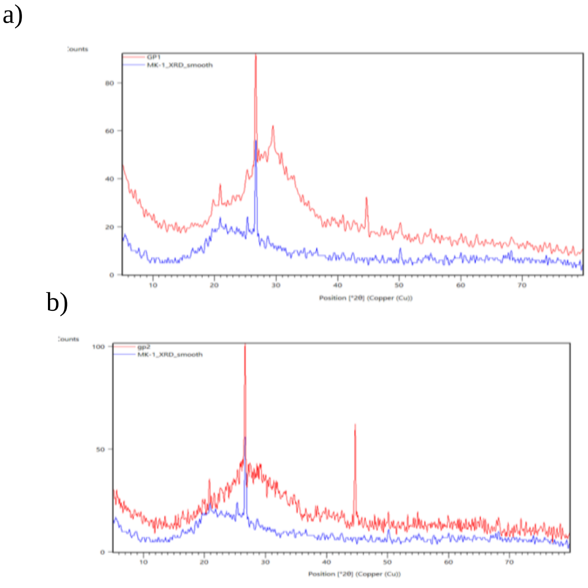

Figure 1. a) GP1 and Metakaolin XRD Spectrum, **b)** GP2 and Metakaolin XRD Spectrum

When evaluating the XRD analysis results, phase identification for the reference geopolymer samples was carried out.

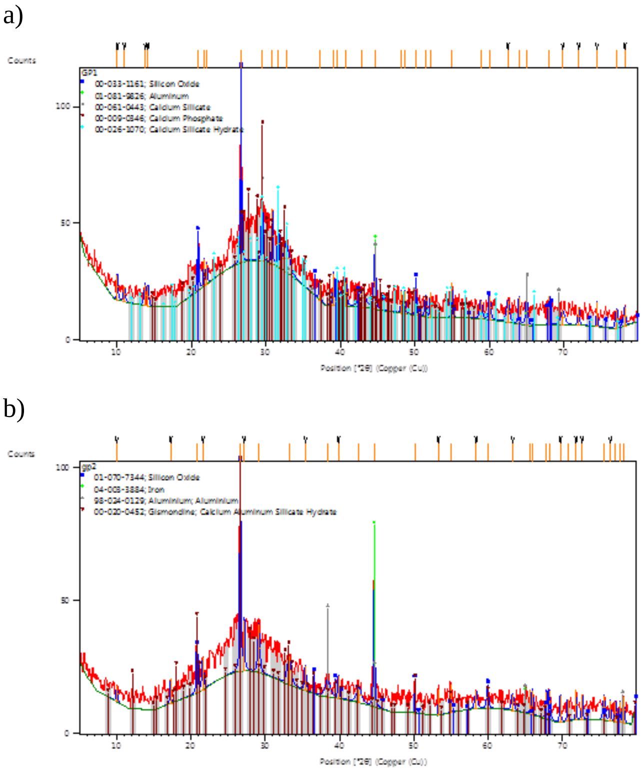

Figure 2. a) GP1 Phase identification, **b)** GP2 Phase identification

XRD spectra obtained from geopolymers including calcium components based on metakaolin and metakaolin are shown in Figures 1 a and b. In both ways, blue-colored spectra were observed in metakaolin clay and geopolymeric structure with red colored spectrum. When the spectra of metakaolin raw material and geopolymer samples were evaluated together, some phases were lost and it was observed that amorphous structure was formed with quartz. X-ray analysis parameters are 2θ and 10˚ - 80˚. The sloppy slope-shaped slope obtained from the analyzes shows that the metakaolin clay is an amorphous material (Barbosa et al., 2000). The amorphous structure of the metakaoline, which is used as the raw material, is closely related to the geopolymer amorphous structure. Therefore, it is not possible to say that the structure is a geopolitical structure. In order to support this finding, structural analyzes such as FTIR are needed.

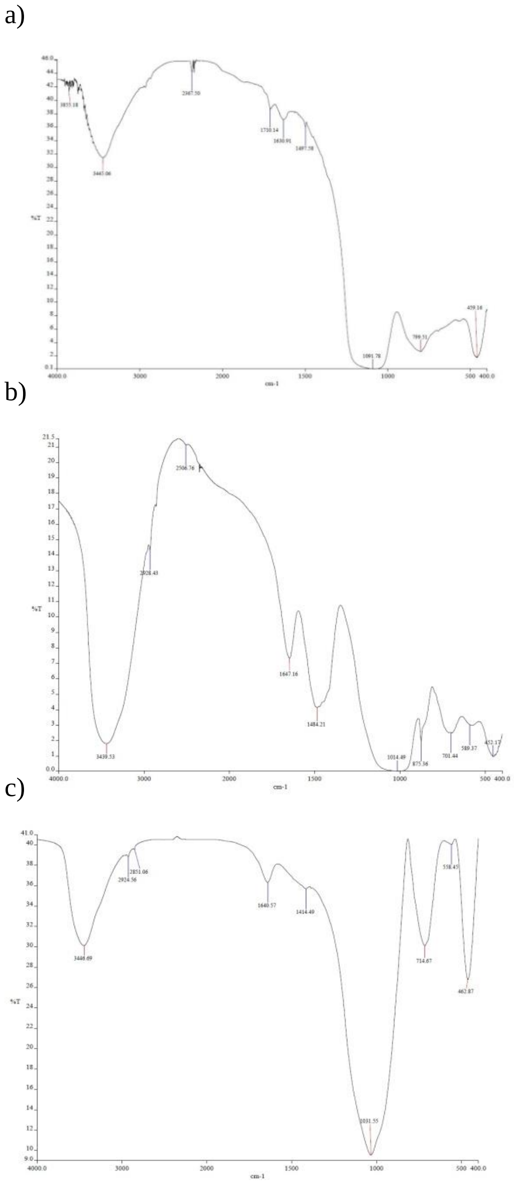

Figure 3. a) Metakaolin FTIR spectrum, **b)** GP1 (Non-calcined geopolymer sample) FTIR spectrum, **c)** GP2 (Calcined geopolymer sample) FTIR spectrum

FT-IR spectroscopy is used to identify the variety of metakaolin clay and geopolymer materials. Molecular structures containing Si–O–Si and Al – O bonds have been defined in geopolymeric structures. Metakolin and calcium containing references and FTIR analyzes of calcined geopolymers at 750° C are given in Figure 3 a, b and c, respectively.

The peaks of water added to the geopolymer material are shown in Figures 3 b and c. The bands in the 3300-3500 cm^{-1} wave number region are due to the structure-dependent water molecules. Geopolymerization increased water molecules. The peaks in the 1640-1650 cm^{-1} wave number indicate the H-O-H tendency (Lee and Van Deventer, 2002).

The peaks around the 700 cm^{-1} wave number represent the Si-O symmetric vibration band. The peaks around the 580-590 cm-1 wave number refer to Si-O-Si or Si-O-Al symmetric strain. Si-O-Si or Si-O-Al network structure is observed around 450 peaks.

Strength measurements; the reference geopolymer was carried out at 500° C and 750° C on calcined and fully cured samples. The average tensile strength of the samples tested is shown in Table 2.

Table 2. Tensile strength measurement results of geopolymer samples

TENSILE STRENGTH [MPa]			
SAMPLES	**Unheated**	**500 °C**	**750 °C**
Nano Al_2O_3 powder GP	3.10 (0.32)	1.99 (0.75)	0.80 (0.44)
Ca-hydroxide GP	4.35 (0.46)	0.68 (0.57)	0.97 (0.39)
Ca-phosphate GP	3.61 (0.42)	4.04 (0.85)	1.21 (0.65)

Samples with calcium hydroxide measured in 15 samples with the highest average strength among the reference samples followed by samples containing calcium phosphate and reference geopolymers (4.35, 3.61 and 3.10 MPa) respectively. The reference geopolymer resistance without calcium or nanoparticle having a tensile strength of 3.10 MPa is the lowest sample.

The lowest tensile strength (0.68 MPa) is the sample containing calcium hydroxide. The reason is that it has developed surface cracks before the test in the sample. Reference geopolymer samples were obtained with a tensile strength of 1.99 MPa. Samples containing calcium phosphate were obtained as 4.04 MPa. It describes the higher strength of the calcium phosphate containing sample in the alumina ceramics and the phosphate bonds known to occur in cements (Odler, 2000). It has been reported that phosphorus can be incorporated into the network structure of geopolymers and that geopolymers give higher strength (MacKenzie, 2003), (MacKenzie et al., 2007). Table 3 shows the tensile strength of other bioceramics and bone compared to one of the results measured in this study.

Table 3. Comparison of tensile strengths of bone and some bio-ceramic materials (MacKenzie et al., 2010)

MATERIAL	TENSILE STRENGTH (MPa)	REFERENCE
Bone	60 – 160	(Heimann, 2002)
Cancellous Bone	3	(Thompson and Hench, 1998)
Hydroxyl Apatite	80	(Thompson and Hench, 1998)
Bioglass ®	42	(Thompson and Hench, 1998)
Bioglass ®	5.54 (SD 0.529)	(Bresciani et al., 2004) †
Bioglass ® / Polyethylene *	10.15	(Thompson and Hench, 1998)
Bioglass ® / Polysulfone *	1.5	(Thompson and Hench, 1998)
Apatite – Wollastonite Glass - Ceramic / Polyethylene *	14.87	(Thompson and Hench, 1998)
Ca-Phosphate Geopolymer (500°C)	4.04	†
Nano Al_2O_3 Powder Geopolymer	3.10	†

†: Diametral compression testing

*: %40 ceramic, %60 polymeric phase

The direct comparison of the tensile strengths of the materials listed in Table 3 is not appropriate because of the non-constant parameters of the test methods. The result obtained from the unknown test method (Thompson and Hench, 1998) was much higher than the result obtained from the diameter compression test (Bresciani et al., 2004) (42 and 5.54 MPa, respectively).

All data obtained during mechanical experiments are the maximum load of the material. Tensile strength is calculated using the following formula:

$$\sigma = \frac{2P}{\pi D t} \qquad (1)$$

The applied load is P, D is diameter and t is the thickness of the sample. It is possible to determine the compressive strength by examining the relationship between compressive strength and tensile strength. Numerous empirical formulas have been proposed, many of which connect the following type of ft (tensile stress) and fc.

$f_t = k\,(f_c)^n$ (Ros and Shima, 2013), (Mohamed et al., 2016)

"k" and "n" are co-efficiency. "n" is between "½" and "¾" are used (Mohamed et al., 2016). The old value was used by the American Concrete Institute, but Gardner and Poon later found another value, in both cases the cylinder was used. In general, the most appropriate expression is:

$f_t = 0.3\,(f_c)^{2/3}$ (Gardner and Poon, 1976)

where "ft" (splitting force) and "fc" are both compressive strength of the cylinders as MPa. The graphs show the compressive strength of the empirical formula. According to the data obtained from the empirical formula given by the references, the graphical results were obtained by considering the compressive strength results and their relations with the tensile strength.

Table 4. Compression strength test results of 3, 7 and 28-day geopolymer samples

	NaOH		KOH		Al_2O_3 Nanopowder GP (MPa)
	CaOH GP (MPa)	$Ca_3(PO_4)_2$ GP (MPa)	CaOH GP (MPa)	$Ca_3(PO_4)_2$ GP (MPa)	
3 days	14.03	11.42	10.96	10.10	10.03
7 days	46.45	36.09	30.61	30.56	37.16
28 days	56.29	42.19	46.67	38.49	39.40

4. Conclusions

The conclusion for the geopolymer samples examined;

- Geopolymerization was performed for both calcium contents and using the FTIR method proved geopolymeric structure. Using two alkali activators had positive results in terms of geopolymerization and the XRD analysis helped to identify the phase for the minerals in the metakaolin composition.

- High strength values were obtained especially in samples activated with sodium hydroxide and added calcium hydroxide compound.

- Although geopolymer samples containing alumina nanoparticles showed low strength values compared to calcium containing geopolymers, they were relatively close and showed good strength compared to literature values.

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