Investigation of Mechanical Properties of Lithium-Based Geopolymer Composites Reinforced with Basalt Fibers

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ABSTRACT

Recently, geopolymer binders have been considered because of low cost, simple processes for synthesis and many raw materials in nature. Geopolymer with brittle nature does not have high strength and cannot be used alone for structural materials. Therefore, to use in different structures, the composite which is reinforced with fibers such as carbon, glass, basalt, etc hasbeen used. In this research, influence of different parameters such as firing temperature and weight fraction of continuous basalt fiber on strength of lithium-based geopolmer composites reinforced by basalt fibers was studied. Firstly, raw materials for geopolymer preparation were calcined. Then, geopolymer matrix with specific molar ratio was made with three different weight percent of basalt fiber. The Molds were put in an oven and after that the composites were taken out of the molds. Then the samples were cured at three different temperatures. After heat treatment, C-MOR of composites was tested and flexural strength and fracture energy for different samples were calculated. The results showed that basalt fiber composites at 200˚C had high strength, but by increasing temperature the strength decreased. Also, Fracture energy of composites at 200˚C was higher than other temperatures.

1. Introduction

Geopolymers or aluminosilicate mineral polymers are a group of 3-D polymers with mainly amorphous or semi-crystalline microstructures and are generally formed at room temperature or under 110ºC through polymerization of aluminate and silicate monomers and oligomers [1]. These amorphous materials are formed by reacting a solid aluminosilicate source such as dehydroxylated clay with an alkalisilicate or hydroxide solution under highly alkaline conditions [1]. Geopolymers exhibit characteristics such as low density, short production procedure and high resistance to acid attacks [2]. The synthesis of these materials needs a relatively low temperature, thus they release less carbon dioxide (CO_2) [2, 3]. The important advantage of geopolymers compared to organic polymers is higher heat and fire resistace.

Therefore, they can be used as an alternative for organic polymers in applications which require high heat resistance [4, 5].

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Depending on the silica/alumina ratio in their composition, geopolymers compromise three different monomeric units: polysialate, polysialatesiloxo and polysialatedisiloxo. Sialate is the abbreviated form of "silicon-oxo-aluminate" [6].

Over the past years, since pure geopolymer matrixes exhibit relatively low mechanical properties, various kinds of geopolymer-based composites reinforced by continuous and short fibers have been produced and their strength and fracture behavior have been investigated [7].

The main purpose of the fibers is to provide a control of cracking and to increase the fracture toughness of the brittle matrix through bridging action during both micro and macrocracking of the matrix [7, 8]. On the whole, geopolymer composites reinforced by fibers which can improve mechanical properties to a great extent, are used in different applications such as motor exhausts, offshore drilling platforms, pressure vessels and ship and aircraft cabins [2].

Dias et al. (2005, Brazil) studied the influence of volumetric fraction of basalt fibers on the fracture toughness of geopolymeric concretes reinforced by basalt fibers. They concluded that these composites have better fracture properties compared to conventional Portland cement reinforced by basalt fibers [7]. Also, recently several studies in China have been carried out by Li et al. to investigate the impact properties of basalt fiber reinforced Portland cements; these studies reveal that the addition of 1% (weight fraction) of basalt fiber increases the compressive strength of conventional Portland cement up to 20% and its energy absorption capacity up to 14% [4].

In the present study, the effect of parameters such as weight fraction of fibers and heat treatment at different temperatures on mechanical strength of lithium-based geopolymers reinforced by continuous basalt fibers as well as optimum conditions for application of these composites in various industries have been investigated. In the past, few studies have been carried out on the properties of lithium-based geopolymers and their composites.

Basalt fibers made from raw slag (containing basalt) has favorable physical and mechanical properties; therefore it has been recently used as a reinforcement material for cement; also, it is a suitable alternative for glass, aramid and other composite fibers [9].

In 2007, Kolousek et al. suggested an alternative to the conventional geopolymer synthesis route which involves solid-state reaction between a dehydrate clay mineral and the alkali hydroxide to give a hydraulically active product that sets upon the addition of a small amount of water [1, 10]. This solid-state method has successfully been adopted for synthesizing mineral polymers and was applied in the present research, too.

2. Materials and research methodology

The starting materials include halloysite, a New Zealand kaolin-type clay (Imerys Premium Grade) as an aluminosilicate source with 5µm particle size, lithium hydroxide as an alkaline activator (Merck Co., Germany) with more than 98% purity as basalt fiber as reinforcing material (Technobasalt Co., Ukraine). Table 1 shows chemical analysis (XRF) of halloysite and table 2 shows mechanical properties of the used basalt fibers. Also, SEM image of basalt fibers is shown in fig. 1.

Table1. Chemical analysis of halloysite

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	L.O.I
weight percent (wt%)	50.4	35.5	0.25	0.05	13.8

Table2. General characteristics of basalt fibers used in the research

Tensile strength	(Mpa)4250
Density	(gr/cm^3)2.6
Fiber diameter	(µm)8
Water absorption	(%)1

2-1. Calcination of primary materials

In this research geopolymer cement composition has molar ratios of

SiO2/Al2O3=2.41, Li2O/SiO2=0.47 and H2O/Al2O3=12. Prior to synthesis of geopolymer, halloysite and lithium hydroxide in proportions corresponding to the above mentioned molar ratios were mixed by a magnetic mixer for 10 minutes in order to obtain a homogeneous compound. The resulted composition was calcined at 650°C for 10 hours. The reason for doing so is the changing of kaolin into metakaolin and dehydrating it in order to obtain a solid composition and better solvability in water.

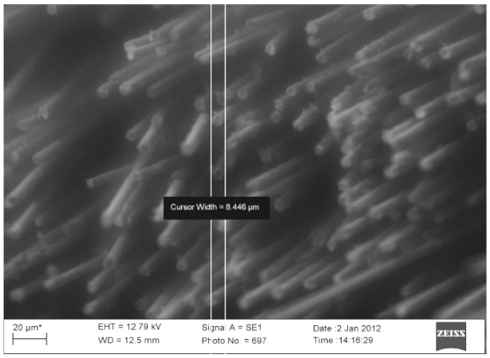

Fig.1. Scanning Electron Microscope (SEM) image of basalt fiber

After calcination, phase analysis of the resulted composition was performed by XRD; also, nuclei magnetic intensification pattern at magic angle (MAS-NMR) was taken from the composition.

XRD diffractometer was a product of Bruker Company, Germany (Model D8 ADVANCE) with copper target (Kα=1.5406°), stepsize=0.03° and 2θ=10-80°, as well as another diffractometer (Philips, Netherlands, Xpert) with copper target (Kα=1.5406°), stepsize=0.05° and 2θ=10-90°.

Nuclei magnetic intensification tests with spinning at magic angle (MAS-NMR) of 27Al and 29Si were performed by Bruker Advance500 spectrometer at 11.7T magnetic field. To identify 27Al-NMR spectrum, a Si3N4 probe with 4mm diameter and 10-12KHz spinning frequency was used and all chemical shifts in parts per million (ppm) were studied with reference to [Al(H2O)6]+3; for identifying 29Si-NMR spectrum, a zirconia probe with 4mm diameter and 6KHz spinning frequency was used and all chemical shifts were reported with reference to tetramethylsilane (TMS).

2-2. Synthesis of geopolymer composites

Synthesizing composite bodies involves several stages. In the first stage, for synthesis of geopolymer cement, the calcined composition is mixed with distilled water and vibrated for 10 minutes in order to prevent the formation of bubbles and porosity. 40 layers of basalt fibers with the length of forming molds (12cm) were prepared. The weight of each layer was 0.25gr. In the next stage, the composites consisting of two layers of geopolymer cement (each weighing 5gr) and a layer of basalt fiber were formed in Teflon molds. The first layer of cement was formed in the mold, then the fibers and after that the second layer of cement were placed on it. Following that, the sample was pressed by a punch with the size of the opening of the mold to obtain the junction between the cement layers and the fibers and to minimize the amount of porosities and vacant spaces. In the final stage, in order to prevent water loss of geopolymers, the molds were covered with a plastic film. The samples were prepared with different weight fractions of basalt fiber including one, two and three layers (2.5, 5 and 7.5 weight percent). Nine composite bodies were prepared according to the above mentioned stages and placed in an oven at 60°C for 24 hours. Three geopolymer bodies without fibers were also prepared for the purpose of comparison with the composites. Finally, after taking the samples out of the oven, the bodies were removed from the molds and were coded for heat treatment at different temperatures.

Fig. 2 shows the images of the stages for making the bodies. It should be added that the composition and the weight of geopolymer cement used in all samples was the same. Fig. 3 shows schematic of the shape and dimensions of the samples. As can be seen, the samples have the shape of cubic rectangles with 120mm length and 11mm width. Due to the number of fiber layers used for different composites, the samples have different thicknesses.

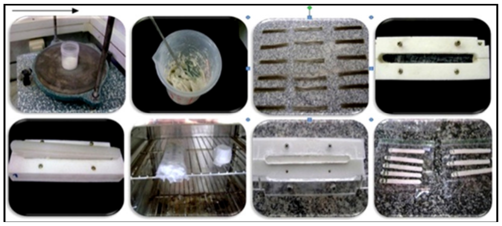

Fig.2. Different steps of geopolymer synthesis and preparation of basalt fiber composites

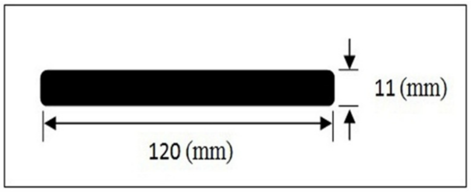

Fig.3. Schematic of the shape and dimensions of geopolymer and composite samples

2-3. Heat treatment of the samples

Heat treatment of nine composite bodies (with different weight fractions of fiber) and three geopolymer bodies was performed at 200, 500, and 700°C. The duration of curing each sample was 2 hours and the speed of oven temperature increase was 5°C/min. After they were taken out of the oven and cooled down, the samples were prepared for flexural strength test.

2-4. Cold flexural strength test

Prior to flexural strength test, which is also called three-point strength, the surface of the samples were smoothed by an abrasive paper so that force distribution would be the same all over the sample. The strength instrument used in this research was a universal testing machine with 2 tons capacity (H25KS, Hounsfield, England). In this test, the thickness of the upper jaw was 10mm and the two lower jaws were set 30mm apart. Also, the upper jaw displacement speed during the experiment was 0.5mm/min. Fig. 4 shows schematic of the mechanism of this instrument and the steps of performing three point strength test. The instrument has presented a force-displacement diagram for each sample during the experiment; by calculating maximum force and putting it in equation (1), flexural strength of the samples were obtained [11].

$$\sigma = \frac{3PL}{2bh^2} \qquad (1)$$

The variables in the equation are as follows:

σ= flexural strength $\left(\frac{N}{mm^2}\right)$ or (MPa)

P= force during fracture (N)

L= the distance between the two lower jaws (mm)

b= the sample width (mm) and h= the sample thickness (mm)

It should be mentioned that the width and thickness of each sample was measured at several points and their average which is presented in table 3 was put in equation (1). After measuring the strength of the samples, the area under the force-displacement diagram which shows fracture energy was calculated by equation (2) for different bodies [12].

The area under force-displacement diagram=

$$\int_a^b F.dL \qquad (2)$$

Where a is the primary displacement (which is zero for all the curves), b is the final displacement, F is the force and dL is variations of displacement.

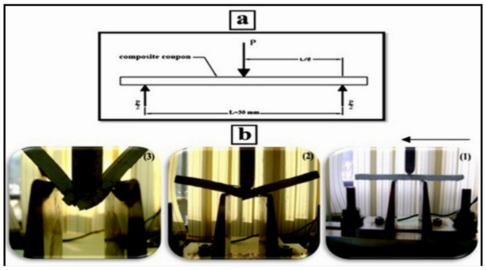

Fig.4.a) Schematic of the flexural strength mechanism, b) Steps of flexural strength test

2-5. Microstructure analysis

After specifying the results of flexural strength test, two samples with the highest and lowest strength were chosen from among the composites and the interface between geopolymermatrix and the fibers was analyzed by scanning electron microscope (SEM, Zeiss, Germany). Preparation of the samples was carried out by polishing the part where fracture had occurred and since the samples were not electrically conductive, they were coated by a thin film of gold before placing in the microscope.

Table3. Width and thickness of geopolymer and composite samples

average thickness $(\overline{h})$ (mm)	average width $(\overline{b})$ (mm)	sample code
5.82	10.63	200-*G
5.60	10.02	500-G
5.51	10.26	700-G
6.35	10.47	B1-200
6.47	10.57	B2-200
6.72	10.49	200-**B3
6.12	10.60	B1-500
6.27	10.15	B2-500
6.60	10.27	B3-500
6.25	10.17	B1-700
6.33	10.40	B2-700
6.80	10.61	B3-700

Note: *G-200 means geopolymer body cured at 200°C; **B3-200 means basalt fiber reinforced composite, three-layered, and cured at 200°C. The other samples have been coded in the same manner.

3. Results and discussion

3-1. Phase analysis of calcined composition

Fig. 5 shows XRD pattern for raw materials composition after calcinations. As can be seen, a broad amorphous peak in the range 2θ= 27-29° is observed in this pattern; this peak is the joint point of X-ray diffraction pattern of geopolymers [13, 14]. Also, semi crystalline phases such as lithium silicate, lithium aluminum silicate and eucryptite are present in the composition which are located on the amorphous peak. The sharp, narrow peaks in the pattern are related to the impurities in the primary materials. Fig. 6 shows MAS-NMR pattern of calcined raw materials composition. In the pattern corresponding to ^{27}Al-NMR some aluminum peaks in different chemical shifts are observed. By referring to the reference table [13, 15], it was concluded that the peak related to 56.4 chemical shift belonged to aluminum in IV-fold coordination (tetrahedral aluminum)and the other peaks in chemical shifts 1.8, 28.2, 66.3 and 78.9ppm belonged to aluminum in 6- and 8-fold coordinations. Therefore, in this composition, aluminum in various coordinations is present and since geopolymers are made up of tetrahedral AlO_4 and SiO_4 which are linked alternately [16, 17], it is expected that by polymerization process and geopolymer formation, only aluminums in IV-fold coordination would be present in the composition. In the pattern related to ^{29}Si-NMR, three silicon peaks in chemical shifts -68.2, -80.7 and -98.9ppm are present which are related to lithium compounds such as Li_4SiO_4 and Li_2SiO_3 [15] and confirm the presence of silicon in IV-fold coordination in the composition of raw materials.

Fig. 7 shows XRD pattern of geopolymer matrix after synthesis at 60°C. Careful observation of the pattern reveals that the sharp amorphous peak in the range 2θ= 27-29° (which was explained before) is still present in X-ray diffraction pattern of geopolymer and semi crystalline phases of quartz with higher intensity and lithium hydroxide and lithium aluminum silicate with lower intensity are observed on it.

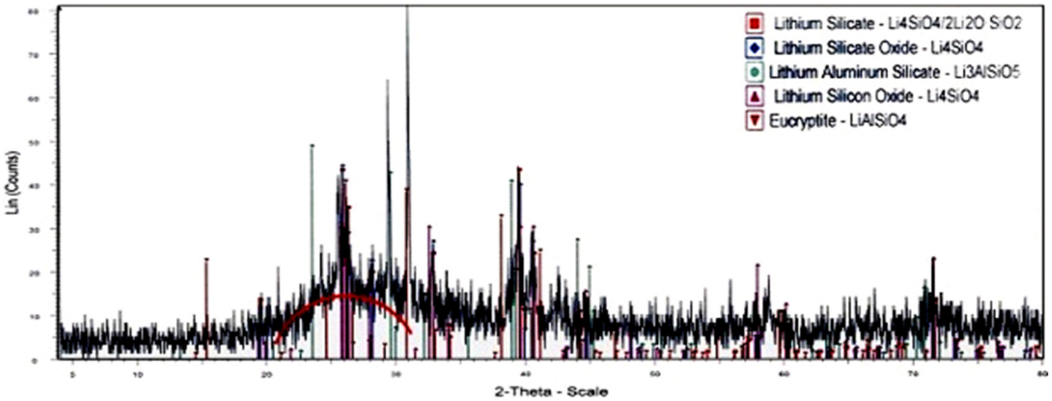

Fig.5. X-ray diffraction (XRD) pattern of calcined raw materials

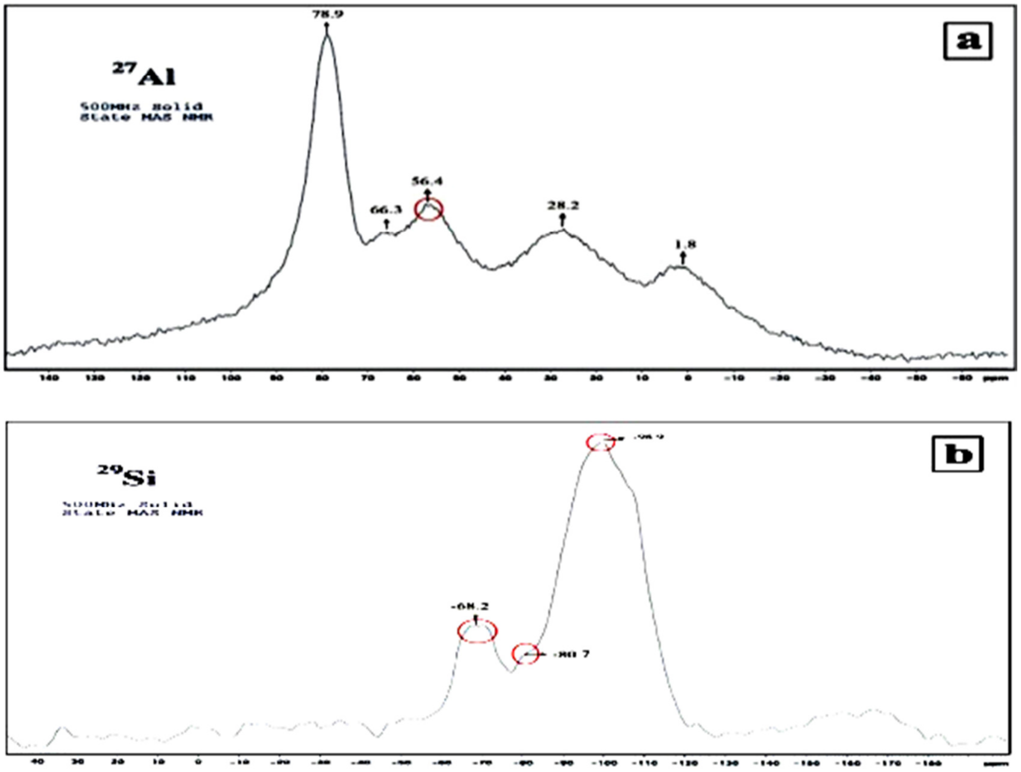

Fig.6. MAS-NMR pattern ofcalcined raw materials a) ^{27}Al-NMR pattern, b) ^{29}Si-NMR pattern

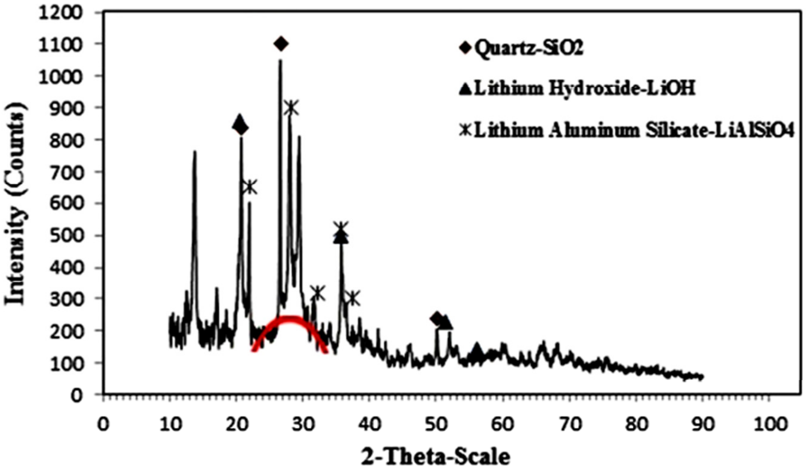

Fig.7. X-ray diffraction pattern of geopolymer after synthesis at 60˚C

Fig. 8 shows ^{27}Al-MAS-NMR pattern of geopolymer matrix after synthesis at 60°C. By comparing this pattern with ^{27}Al-MAS-NMR pattern of raw materials in fig.6-a, it is revealed that the only peak which is present here is related to tetrahedral aluminum in chemical shift 54.1ppm and the peaks related to Al in other coordinations have disappeared. Since the chemical shift of this peak is very close to the chemical shift of tetrahedral aluminum in geopolymers (55ppm), therefore the occurrence of polymerization and polymer formation is certain.

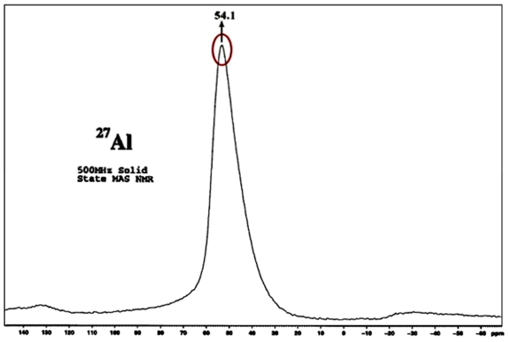

Fig.8. ^{27}Al-MAS-NMR pattern ofgeopolymer after synthesis at 60°C

3-3. Investigating the results of cold flexural strength test of bodies

Fig. 9 shows force-displacement diagram and results of flexural strength test of geopolymer bodies. In order to calculate the strength of each sample, maximum force at the moment of fracture is specified on the force-displacement diagram and by putting it in equation (1) the flexural strength of the sample is obtained. The results reveal that at 700°C with the evaporation of water and decrease of porosity, geopolymer has the highest strength, while at 500°C it has the lowest strength. But generally speaking, the strength of geopolymer at all temperatures is low and in applications where optimum strength is required, it cannot be used alone.

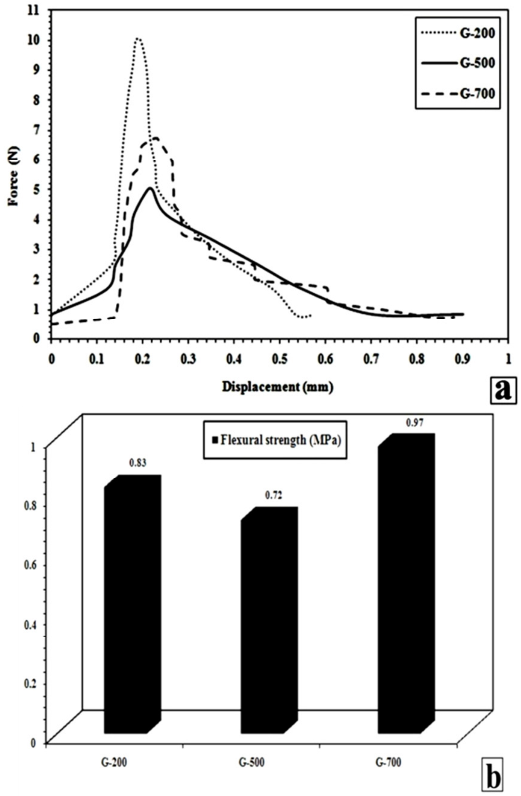

Fig.9. Results of the flexural strength of geopolymer bodies a) Force–displacement diagram, b) Comparison of the results

Fig. 10 shows force-displacement diagram and fig. 11 shows the results of flexural strength of composites with basalt fibers cured at different temperatures. In contrast to geopolymer bodies, the composites diagram consists of two parts. The first part is related to the composite fracture, and the second part is related to the fibers deformation. Therefore, for calculating strength, maximum force related to the first part of diagrams is considered.

At 200°C, the one-layered and three-layered samples with close strengths have a higher strength compared to the two-layered sample. Moreover, at this temperature, the strength of the composites with all three weight percents of fibers is higher than that of geopolymer bodies. At 500°C the strength of the composites has decreased compared to 200°C, but it is still higher than the strength of geoploymer bodies at this temperature. Also, it was observed that with increase of basalt fibers weight percent, the strength of composites increases, too. Therefore, at 500°C the one-layered sample has the highest strength and the three-layered one has the lowest strength. At 700°C, the strength of composites decreased dramatically. By observing the basalt fibers after the test it was revealed that the fibers are deformed and destroyed after heating at this temperature and their color changes from olive green to black. Therefore, the fibers lose their reinforcing property and cause the decrease of composite strength. This is confirmed by comparing the force-displacement diagram of composites at this temperature with force-displacement of geopolymer bodies and it was revealed that their tendency is similar and the fibers play no role at this temperature.

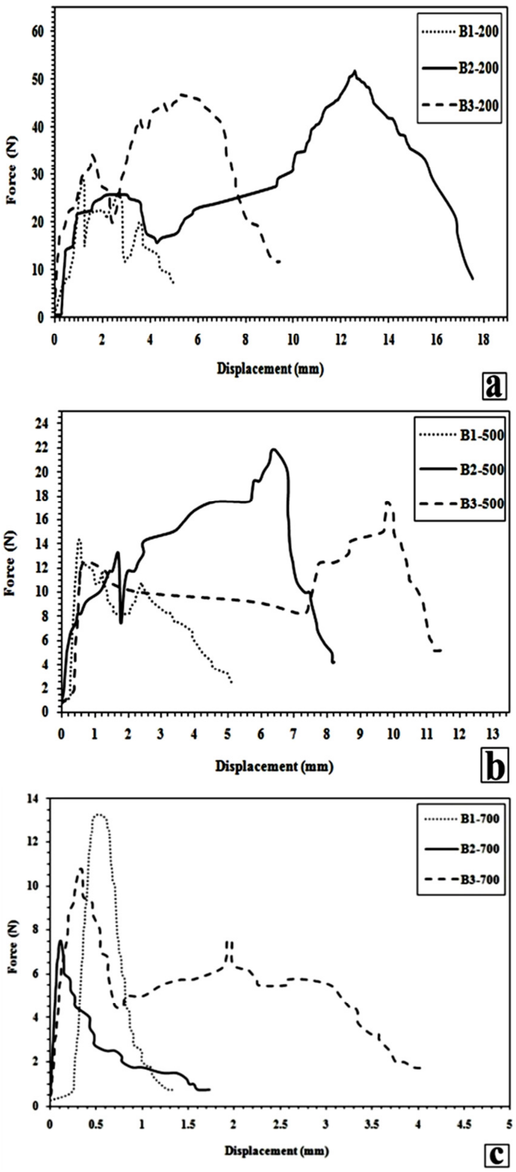

Fig.10. Force – displacement diagram of basalt fiber composites cured at a) 200˚C, b) 500˚C, c) 700˚C temperatures

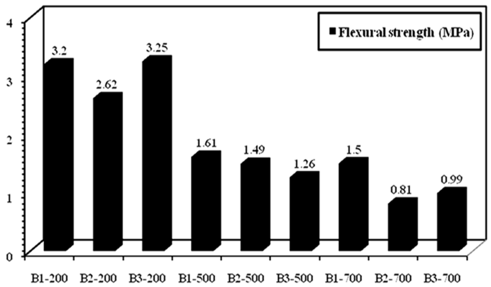

Fig.11. Comparison of the results of flexural strength of basalt fiber composites cured at different temperatures

3-4. Investigating the area under force-displacement diagram of the samples

By integration of the equation of the first part of diagram of each sample (through equation (2)) the area under force-displacement diagram which shows the energy required for fracture of the sample was determined. The results are shown in fig. 12. Like flexural strength in geopolymer bodies this parameter has increased with the increase of curing temperature, but on the whole due to ceramic properties of brittle geopolymer it has very low amounts. The composites have higher fracture energy because of the fibers and with a great difference from other temperatures, their fracture energy is the maximum at 200°C. Also, at 700°C fracture energy of composites is very low and is almost the same as geopolymer matrix. This is due to the damage and loss of properties of basalt at this temperature.

The area under force-displacement diagram (fracture energy) is proportional with the area under strain-stress diagram which shows the work per area unit or work of fracture [12]. Therefore, basalt fiber composites have higher fracture toughness at 200°C compared to other temperatures.

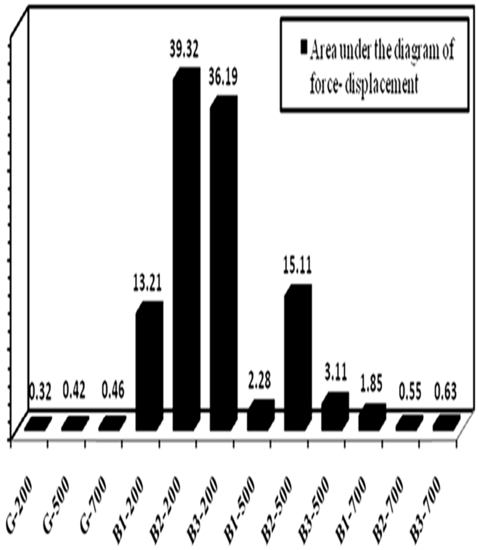

Fig.12. Comparison the results of area under the diagram of force- displacement for geopolymer and composite bodies cured at different temperatures

3-5. Investigating microstructure analysis of geopolymer matrix/basalt fibers interface

After flexural strength test, geopolymer cement/ basalt fibers interface of B3-200 and B2-700 samples with the highest and lowest strengths was studied by SEM. The images which were taken with about 300 magnification are shown in fig. 13. In the image related to B2-700 sample, a distance and vacant space is observed between geopolymer and basalt fibers and they are not properly joined. Also, basalt fibers are deformed and hence the composite strength has decreased dramatically. But in the image related to B3-200 sample, there is a better junction between geopolymer and basalt fibers and no distance is observed between them.

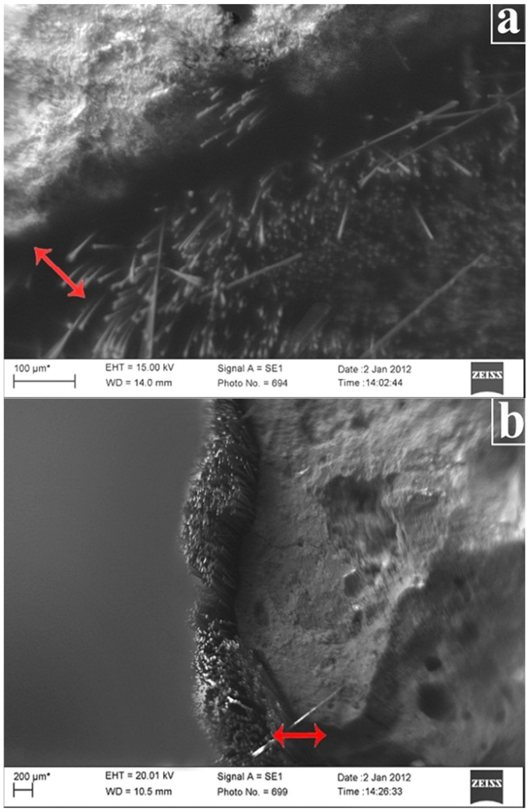

Fig.13.SEM images of geopolymer and basalt fiber in the interface a) B2-700 sample, b) B3-200 sample

4. Conclusion

1. ^{27}Al-MAS-NMR analysis of geopolymer matrix after synthesis confirmed the presence of tetrahedral aluminum in the composition as well as the occurrence of polymerization and geopolymer formation.
2. Results of flexural strength test of geopolymer bodies revealed that these bodies have the greatest strength at 200°C and the lowest strength at 500°C.
3. Results of flexural strength test of basalt fiber reinforced composites showed that increase of curing temperature has a negative effect on the strength of the bodies. Therefore, at 200°C the bodies have the greatest strength and at 700°C they have the lowest strength. Also, at 500°C with increase of basalt fibers weight percent, the strength of composites decreased.
4. Basalt fibers are damaged and deformed at 700°C; therefore they cannot play an effective role in increase of composite strength at this temperature. This was confirmed by SEM studies, too. Therefore, application of geopolymer composites reinforced by basalt fibers in different industries is possible in temperatures up to 700°C.

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