Construction and Building Materials 225 (2019) 909–926

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Influence of wetting-drying curing system on the performance of fiber reinforced metakaolin-based geopolymer composites

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HIGHLIGHTS

- Mechanical, durability and microstructural properties were studied in this investigation.
- Wetting drying curing method showed a certain improvement in terms of strength and morphology.
- The existence of fibers yielded a better performance in terms of fracture and thermal aspects.

ARTICLE INFO

Article history:
Received 3 March 2019
Received in revised form 18 June 2019
Accepted 19 July 2019
Available online 27 July 2019

Keyword:
Geopolymer
Metakaolin
Colemanite
Wetting-drying curing
Basalt fiber
Polyvinyl alcohol
Freezing-thawing

ABSTRACT

In this study, mechanical and durability properties of geopolymer composites prepared using metakaolin and colemanite binding materials with basalt and polyvinyl alcohol fibers were investigated under the influence of curing systems. For the 7 series prepared, two different curing conditions have been applied: wetting-drying and heat curing. The mechanical properties of geopolymer samples were investigated for 7 and 28 days strength and ultrasonic pulse velocity results, water absorption, unit weight and porosity. After the abrasion test, weight loss and length change were examined and after the high temperature tests of 200, 400 and 600 °C, the results of strength, ultrasonic pulse velocity and weight loss were found. The results showed that the residual strength values were high after high temperature tests. As a result of SEM, FT-IR and TGA-DTA analyzes, it was observed that high temperature post-geopolymer samples retained their stable structure. When the wetting-drying curing was applied, it was observed that the Si—O—Al bonds were higher in the FT-IR results. This showed a higher rate of geopolymerization and increased strength values. Similar behaviors were observed according to TGA-DTA results, and weight loss with temperature was found to be lower in samples applied to wetting-drying curing. Also, there was a positive effect on the strength results with the increase in basalt and polyvinyl alcohol fibers ratio. The main reason for this situation is the formation of a resistant layer with the effect of basalt and polyvinyl alcohol fibers. The compact structure of the geopolymeric matrix brings along a good degree of adhesion. This allows geopolymer samples to resist freezing-thawing. In geopolymer samples, despite the 90 cycles, the residual strength were high and the decrease in the ultrasonic pulse velocity rate results were limited.

1. Introduction

It is now accepted that geopolymer materials have a great potential for using in construction applications rather than Portland cement. In the future, the search for an alternative has accelerated due to the fact that the high amount of energy to be consumed during the production of Portland cement is not sustainable. In addition, the high amount of carbon dioxide produced by Portland cement production is another important factor affecting the search for an alternative [1]. To put it in numbers, approximately one tonne of CO_2 is released in production of one tonne of cement. As far as concrete production is concerned, 400 kg of carbon dioxide is released in 1 m^3 of concrete production [2]. In

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https://doi.org/10.1016/j.conbuildmat.2019.07.235
0950-0618/

addition, 12–15% of the energy consumed in the industrial field is in the cement production industry [3]. In the cement production process, the thermal energy consumed for grinding is estimated to be 2,72 GJ/tonne and the electrical energy consumed for incineration is 65 kWh/tonne [3]. Due to these situations, there is an urgent need for solutions for energy and carbon dioxide problems.

Geopolymer is an inorganic polymer material resulting from the reaction of the material such as an aluminosilicate source fly ash or metakaolin with alkaline solutions. As a result of the reaction of SiO_4 and AlO_4 by sharing oxygen atoms, the principal monomer unit of geopolymer called sialate (O l—Si—O—Al—O) occurs [4]. Geopolymer materials have been particularly interesting in recent years because they have both low carbon dioxide emissions and high mechanical and physical properties and excellent durability properties. These properties directly depend on the aluminosilicate material used in production and its properties. As an example of aluminosilicate used in the production of most geopolymers, fly ash, metakaolin, red mud, slag, bottom ash, rice husk ash, silica fume can be given. A large number of studies have been carried out on the evaluation of these materials, the investigation of the basic reactions, the study of mechanical and long-term stability properties [5–10].

Metakaolin is a binding aluminosilicate material with high pozzolanic properties produced by calcination of kaolin at high temperatures [11]. It has also a strong reaction with the solutions used as alkaline activators and forms high strength geopolymer samples [12–14]. Geopolimerization with metakaolin depends on the type and amount of activator and metakaolin and the curing system [15–17].

Turkey is the richest country in the world in terms of boron deposits and holds 72%. At the same time, approximately 2 million tons of boron minerals and compounds are produced in Turkey [18]. The most important ones are colemanite, ulexite and tincal. After the concentration of pure colemanite, which is a calcium borate mineral, a large number of byproducts are formed. Colemanite wastes are evaluated in different areas such as cement sector in order to prevent this damaging environment with waste material formation [18,19]. Kula et al. [20] investigated the mechanical properties of boron waste colemanite additive to Portland cement mortar as well as fly and bottom ash substitute materials. Using of colemanite waste up to 10% as substitution rate increases mechanical properties [21].

Rovnanik [22] tried different curing times when considering temperatures between 10 and 80 °C as the curing temperature for geopolymerization. The results were evaluated according to the results of compressive and flexural strengths, microstructural analysis and pore properties. In addition, it has been observed that the pore structure changes with the effect of the curing temperature and this situation affects the mechanical properties. In addition, the reaction process was followed by Infrared Spectroscopy method.

There is limited information in the literature for the pore structure of geopolymers [23]. More general information about the properties of Portland cement concrete is available. The pore structure of traditional concrete has a significant effect on the mechanical and durabiliy properties. Problems in pore structure negatively affect the compressive strength while facilitating diffusion of harmful substances such as sulphate, chloride and acid.

Burciaga-Díaz et al. [24] examined the behavior of geopolymer composites in the case of applying different curing temperatures to the mortar produced by mixing slag and metakaolin binders with silicate solution. They compared the strength and microstructural analysis of the mortars produced in the application of curing temperatures of 20, 60 and 70 °C. In long-term behavior, low temperatures were observed to be more effective.

Mangat et al. [25] applied three different curing conditions in water, room temperature and wet/dry to alkali activated mortars and Portland cement mortars. The most appropriate curing conditions for Portland cement mortars were curing in water, while the wet/dry curing method for alkali activated mortars was observed to be ideal. In addition, the retardant admixtures affect the pore structure and the strength properties of alkali activated mortars. It has been found that alkali activated mortars have lower porosity and this is a major factor affecting the strength.

Zhang et al. [26] exposed geopolymer samples obtained by using metakaolin and fly ash binders to the fire resistance test. A comparison of the results before and after high temperature was made. A product was presented by using thermogravimetric analysis and strength values according to the high temperature resistant.

Cai et al. [27] applied the freezing-thawing test to the alkali activated concrete produced using slag. Test results showed that the resistance of the samples was high and the resistance coefficient for the freezing-thawing test was close to 90%. Yunsheng et al. [28] produced geopolymer samples with polyvinyl alcohol additive for 20 cycles of freezing-thawing test. Impact strength and hardness tests showed no effect on the samples.

It is also possible to increase the mechanical properties of the sample due to the effect of fiber reinforcement. In the samples produced, the reaction process in the matrix is strengthened by the effect of fiber. Woven fabric, carbon, basalt and glass fibers have been reinforced by different studies [29–31]. Recently, different fibers have been used in geopolymer samples [32,33]. Dias and Thaumaturgo [34] observed the effect of basalt fiber on fracture toughness. It has been observed that the contribution of the fiber decreases the deformation by creating positive results in energy absorption. Li et al. [35] investigated geopolymer samples produced using the extrusion method and demonstrated that the effect of polyvinyl alcohol fiber increased matrix ductility and flexural strength and an appropriate toughness increase was achieved.

It is possible to use different number of substitute materials in metakaolin based geopolymer composites. In this study, different from the other studies, polyvinyl alcohol and basalt fibers were used with 0.8%, 1.6% and 2.4% by mass, with 10% substituted boron waste colemanite. In addition to the oven curing, wetting-drying curing method was used differently in this study. Water absorption, unit weight and porosity results were obtained with geopolymer samples 7 and 28 days ultrasonic pulse velocity, flexural strength, tensile strength and compressive strength results. Weight loss, flexural strength, ultrasonic pulse velocity and compressive strength results of geopolymer composites were evaluated after high temperature effect of 200, 400 and 600 °C. Similarly, the same properties were calculated after the freezing-thawing test consisting of 90 cycles. In addition, FTIR and TGA-DTA analyses of geopolymer samples before and after 600 °C were performed. Visual inspection of the samples was carried out after freezing thawing test consisting of 90 cycles and 600 °C high temperature test. Finally, after abrasion test, weight loss and length change were calculated.

2. Experimental

For this study, geopolymer products were formed by using colemanite waste and metakaolin as the binding material obtained from Eti Maden and Kaolin EAD companies, respectively. Metakaolin is a calcined binder with a very high pozzolanic activity of $Al_2O_3 + Fe_2O_3 + SiO_2$ 97.18%. The degree of geopolymerization bond in the reaction increases due to the fine-grained of metakaolin. The slag, which was taken from Bolu Cement Company and used in a constant ratio (13%) in the mixture, has a specific gravity of 2.88

g/cm^3. Metakaolin and boron waste colemanite have a specific gravity of 2.54 g/cm^3 and 2.38 g/cm^3, respectively. The different binders used have the chemical properties in Table 1. The abbreviations S, MK and C were used for slag, metakaolin and boron waste colemanite, respectively.

Rilem sand according to BS EN 196-1 has been taken from Trakya Limak Cement Company and has been added to the mixture at a fixed rate according to the binding material. A mixture of sodium silicate with Na_2O/SiO_2 = 1/3.29 ratio and sodium hydroxide (12 M) taken from Merck Company was prepared as activator.

In this study, the effects of polyvinyl alcohol and basalt fibers by participating in the mixture were investigated. Table 2 shows the properties of fibers used for freezing-thawing, high temperature and abrasion tests. PVA and B abbreviations were used respectively for polyvinyl alcohol and basalt fibers. The effect of fibers on weight loss and strength before and after experiments were examined.

In preparation of the geopolymer mixture, the binding materials of the colemanite and metakaolin were mixed with the activator mixture of sodium silicate and sodium hydroxide prepared one day before the mixing day by 1/1 ratio. One-third of the activator mixture consisted of sodium hydroxide and two-thirds of the activator mixture consisted of sodium silicate. Aggregate material (Rilem sand) was added to the mixture up to 2.5 times of the total binding material. In order to increase the calcium content, the high furnace slag was added to the mixture by 13% (fixed). The literature was used for the prepared mixture [24,36–39]. Table 3 shows the standard mix quantities.

A more detailed description of the geopolymer mortar mixture was followed: At first the sodium hydroxide solution (12 M) prepared prior to one day was allowed to cool under room conditions and mixed with sodium silicate before the mixture. Metakaolin (450 g), as the main binder material for the standard geopolymer mixture, was mixed using a stirrer drill with a total of 450 g of activator solution. A 1/1 ratio was used during this mixture. At a later stage, 13% blast furnace slag (60 g) was added to the mixture to increase the rate of calcium and shorten the setting time. Finally, Rilem sand was added by two and a half times of the binding material. Vibrations were applied to the samples placed on the molds.

Two different curing methods were applied. The initial stages of the two curing methods are same. After 2 h in the mold, the samples were kept under room temperature for 1 day. Samples placed in non-flammable oven bags were then kept in the oven at a temperature of 60 °C for 3 days (72 h) [40,41]. The purpose of using the non-flammable oven bag is to prevent the evaporation of the water present in the sample structure so that the reaction can continue thereafter. After this stage, two different methods were applied. In method 1, the samples were then held in plastic storage boxes until the day of the test. In the second method, the samples were subjected to 1 cycle wetting-drying test [25]. 1 cycle wetting-drying test includes keeping samples 3 days in water and then 3 days in the oven at 60 °C temperature. Subsequently, the samples in method 2 were similarly stored in plastic storage boxes until the day of the test.

Table 3
Standard geopolymer mortar mixing quantities (g).

Metakaolin	Sand	Slag	NaOH (12 M)	Na_2SiO_3
450	1125	60	150	300

Seven serial samples were produced for two different curing methods. As a control sample, the binder material consisted of 90% metakaolin and 10% colemanite [40,41]. Polyvinyl alcohol and basalt fibers were added to the control mixture as 0.8%, 1.6% and 2.4% by mass, respectively. The abbreviation H is used for only heat curing and for the wetting-drying curing WD is used. The amounts and abbreviations used in the mixture are shown in Table 4.

At the end of 28 days, water absorption, unit weight and porosity results of geopolymer samples produced were found. 7 and 28 day ultrasonic pulse velocity, flexural strength, tensile strength and compressive strength were determined. The compressive strength test was performed on the cube samples (ASTM C 109 [42]) while the flexural strength test was performed on prism samples (ASTM C 348 [43]). The tensile strength of the samples were also determined according to ASTM C1583 [44].

For the abrasion resistance test, 71 ± 1.5 mm cube samples were produced. The Bohme abrasion test was performed according to ASTM C779 [45]. Samples were kept in the oven at 105 °C for 1 day before the abrasion and high temperature test. For the high temperature test, the furnace's temperature rise rate was set at 1 °C/min and temperatures of 200, 400 and 600 °C were applied. After testing, the samples were allowed to cool in the furnace and then flexural and compressive strength, weight loss and ultrasonic pulse velocity tests were performed. Also FTIR and TGA-DTA analyzes were performed before and after high temperature effect.

90 cycles of freezing-thawing test were applied to the samples. 1 cycle of freezing-thawing test consisted of keeping 24 h at −20°and 24 h at + 20°. After the test, flexural and compressive strength, weight loss and ultrasonic pulse velocity tests were performed. Visual inspection of samples after freezing-thawing and high temperature tests was also carried out.

3. Results and discussion

3.1. Conclusion of flexural and compressive strength results

The results of the compressive and flexural strength tests are shown in Figs. 1 and 2. The results showed an increase in the 28-days in all of the mixtures according to the 7-days. In addition,

Table 1
The chemical composition of colemanite waste, slag and metakaolin.

Chemical properties %	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	B_2O_3	L.O.I.
MK	56.10	40.25	0.85	0.55	0.19	0.16	0.55	0.24	–	1.11
S	40.60	12.83	1.37	0.75	36.08	6.87	0.68	0.79	–	0.03
C	5.00	0.40	0.08	–	26.02	3.00	–	0.50	40.00	25.00

Table 2
The properties of fibers.

Fiber Type	Length (mm)	Diameter (μm)	Specific Gravity	Nominal Tensile Strength (MPa)
Basalt	12	20	2.73	4100
PVA	8	39	1.3	1620

Table 4
Geopolymer mortar mixing percentages (%).

Mix ID	Colemanite replacement ratio	MK
Control-H	10	90
PVA0.8-H	10	90
PVA1.6-H	10	90
PVA2.4-H	10	90
B0.8-H	10	90
B1.6-H	10	90
B2.4-H	10	90
Control-WD	10	90
PVA0.8-WD	10	90
PVA1.6-WD	10	90
PVA2.4-WD	10	90
B0.8-WD	10	90
B1.6-WD	10	90
B2.4-WD	10	90

there was a positive effect on the strength results with the increase in fibers ratio, while this is consistent with the previous results Based on the former findings in the same field and the latter explanation, the authors came up with a decision which states that using colemanite is beneficial to a certain extent. To be more specific, the performance of colemanite as a protecting layer and as voids filler -being used up to 10%- provides a certain improvement to the microstructure of the resulted matrix based on the fact that the geopolymeric matrix is a brittle and a relatively permeable matrix. [40,41].

Boron waste colemanite can be consumed to 10% in the geopolymer composites [20]. According to the studies, it was identified that a protective layer around cement particles is occured in the cementitious system with the effect of boron minerals and that cement particles and water contact is prevented with the effect of this layer. This influence affects directly hydration mechanism of cemented materials [46]. It has also been discovered that boron additives develop the strength properties for cement-based composites [47]. According to the literature, there is a critic threshold ratio for increasing strength with the colemanite. It is thought that some cations and anions, which result in unstable boron compounds for the system, interfere to the cement activation mechanism by using more than 10% colemanite. Due to this condition, it is thought that the decrease will be seen.

Petermann et al. [48] stated after exposing to wetting/drying curing method the AACM mortar had the highest strength and lowest porosity. At first wet curing helped producing more geopolymerisation, while the following dry curing developed increased compressive strength. Compared to exposing to dry and wetting/drying curing method, AACM mortar possessed a higher strength than wet curing in the equal porosity range. For example, in the most appropriate relationships, the compressive strengths with a porosity of 10% are 52.7 MPa and 61.2 MPa under wet and wetting/drying curing method respectively. This has an additional effect on porosity, which increases AACMs' strength with the dry curing. This can be because of the increased strength of the geopolymerisation products with dry curing, incorporating enhanced bonding with the geopolymer structure. Wet curing also supports hydration reactions of any high calcium compounds for the AACM binders. So, wetting/drying curing is the optimum curing method for strength-porosity relationship in AACMs.

In the 7-day's compressive strength results, the rates of increase compared to the control sample were between 6.48% and 18.17% for the only heat cured polyvinyl alcohol supplemented samples, while these rates were between 9.15% and 19.79% in the 28 days. The rates of increase in polyvinyl alcohol fiber were higher compared to the control and basalt fiber supplemented samples [5,41]. The increase rates of 7 day's compressive strength results were between 4.96% and 15.86% for the only heat cured basalt supplemented samples, while these rates were between 8.56% and 18.94% in the 28 days.

The results of flexural strength have shown similar to the results of compressive strength. In the 7-day's flexural strength results, the increase rates were between 16.73% and 25.50% for the only heat cured polyvinyl alcohol supplemented samples and these rates were between 17.23% and 25.41% in the 28-day results. The increase rates in the 7-day's flexural strength results were between 17.44% and 22.88% for the only heat cured basalt supplemented samples and these rates were between 16.26% and 22.01% in the 28-day results.

In the second stage, the series of the same samples exposed to the wetting-drying curing were produced. Through the wetting-drying curing, the continuation of geopolymerization and the formation of new crystalline geopolymerization products were

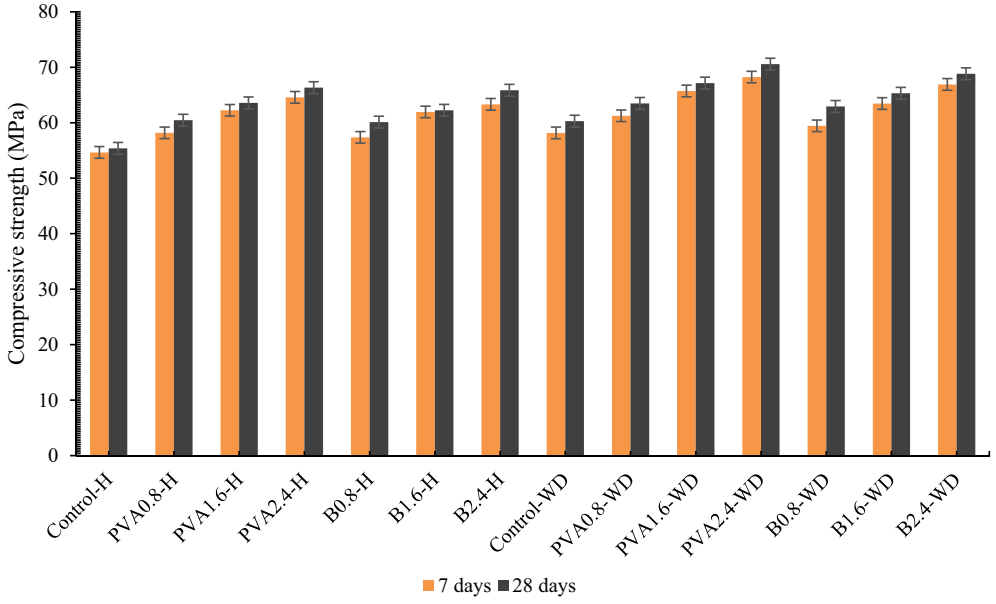

Fig. 1. Values of compressive strength for the mixes.

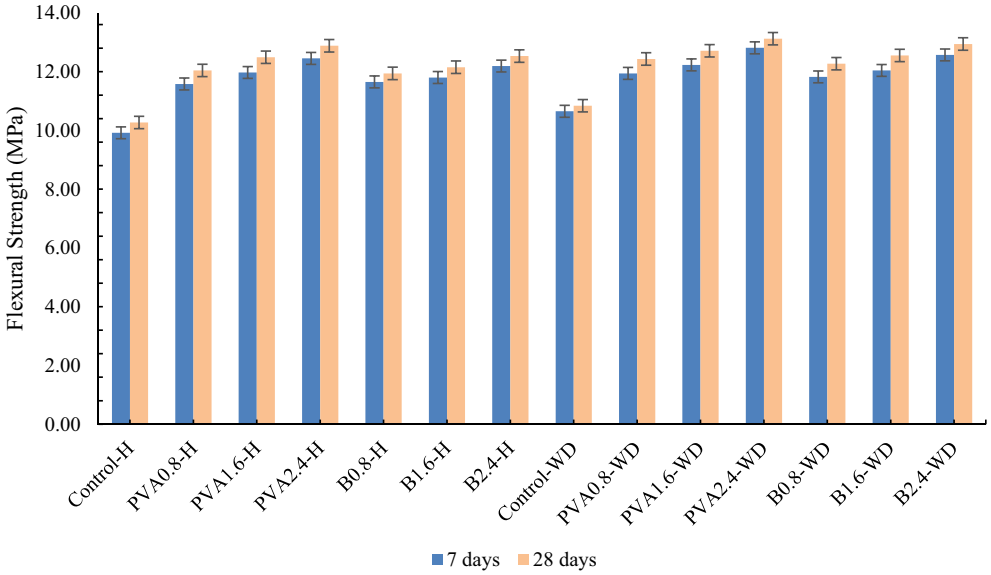

Fig. 2. Values of flexural strength for the mixes.

provided. This results in an increase in the strength results due to the wetting-drying curing [25].

In the 7-day's compressive strength results, the increase rates compared to the control sample were between 12.10% and 24.85% for the wetting-drying cured polyvinyl alcohol additive samples and these rates were between 14.63% and 27.41% in the 28-days. While the rates of increase in compressive strength of 7 days were found to be between 8.78% and 22.43% for the wetting-drying cured samples, these rates were between 13.63% and 24.30% in the 28-days.

According to the control sample, the increase rates in the 7 day's flexural strength results were between 20.36% and 29.13% for the wetting-drying cured polyvinyl alcohol additive samples while these rates were between 21.03% and 27.75% in the 28 days. The increase rates in the 7-day's flexural strength results were between 19.15% and 26.71% for the wetting-drying cured samples while these rates were between 19.47% and 26.00% in the 28 days.

3.2. Tensile strength results

The tensile strength results of geopolymer samples at 7 and 28 days are shown in Fig. 3. According to the results, the factors on the tensile strength are the presence of fibers and wetting drying curing method. Geopolymerization was ensured and the tensile strength increased with the wetting-drying curing effect. The presence of the fibers also increased the tensile strength results. The increase rates were higher in the results with the effect of polyvinyl alcohol [25].

With the effect of polyvinyl alcohol additive samples according to the control sample, the rates of increase on 7 days were between 8.59% and 31.25%, while this rates increased with the effect of wetting-drying curing and were between 21.61% and 42.97%. On the 28th day, the increase rates in polyvinyl alcohol supplemented samples were between 6.03% and 26.79% according to the control sample, while these ratios were 10.04% and 31.70% under the influence of wetting-drying curing.

In the samples with basalt fiber added according to the control sample, the rates of increase on the 7th day were between 4.69% and 24.48%, while this rate increased with the effect of wetting-drying curing and were between 14.58% and 34.90%. On the 28th day, the rates of increase in basalt fiber supplemented samples were between 2.46% and 16.52% according to the control sample, while this rates were between 7.14% and 22.32% under the influence of wetting-drying curing. The presence of the fibers also increased the tensile strength results.

As generally concluded from this investigation, wet/dry cycles directly affect the compressive strength while the impact of the fibers is directly obvious on the flexural strength. To show the impact of fibers and wet/dry cycles more obviously, a simple comparison could be made between the samples under normal conditions and the samples under combined effects (fibers and wet/dry cycles). To illustrate this comparison, control-H and PVA 2.4-WD could be compared in terms of compressive strength, flexural strength and tensile strength, respectively. The difference gained from this comparison is approximately 10 MPa in terms of compressive strength, 3 MPa in flexural strength and 2 MPa in tensile strength. This comparison states the fact that combining both effects yields in a certain improvement in mechanical properties.

3.3. Water absorption, voids ratio and unit weight

The effects of polyvinyl alcohol and basalt fibers additive and heat and wetting-drying curing methods on the physical properties of the colemanite additive metakaolin-based geopolymeric matrix are examined and the voids ratio, water absorption and unit weight are determined and shown in Table 5.

According to the results, there was a slight decrease in voids ratio and water absorption with the effect of fiber. The water absorption rate of polyvinyl alcohol and basalt fibers are high depending on their characteristics. Together with the fiber admixture, the water absorption ratio of the geopolymeric matrix has decreased as well as the voids ratio [41]. In the case of the application of the wetting-drying curing method, with the effect of water, more aluminosilicate gels are formed by the continuation of the reaction, thus reducing the voids ratio and the water absorption [25]. The unit weight values increased with the decrease in the water absorption and voids ratio.

Neville [49] showed that as the ratio of using basalt fiber enhances, the basalt fiber is the lightest as the component in the concrete mix, and the influence on the unit weight is not recognized and resulted in a slight increase in the unit weight. This is identical as the results obtained by Borhan [50], which shows that

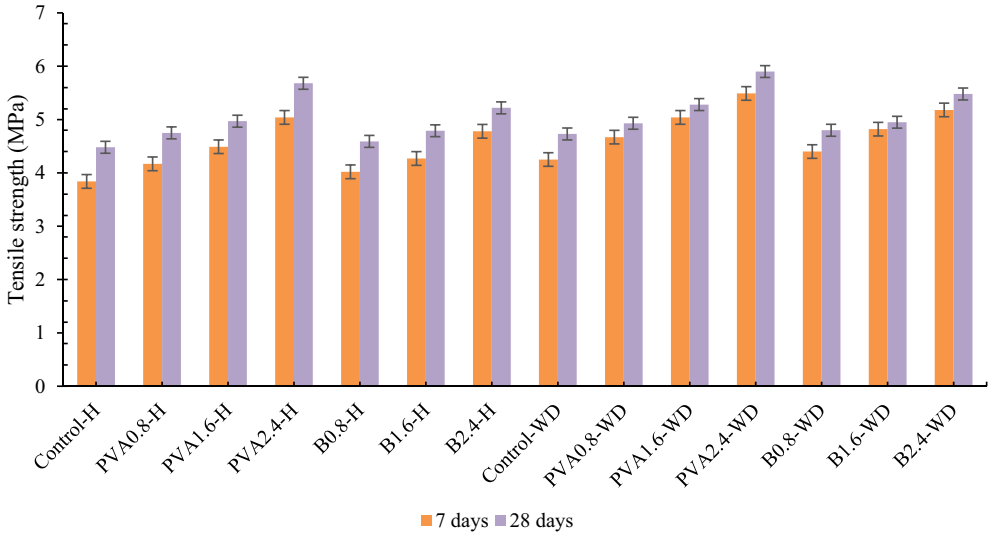

Fig. 3. Values of tensile strength for the mixes.

Table 5
Results of water absorption, voids ratio and unit weight.

	Unit weight (g/cm^3)	Water absorption (%)	Voids ratio (%)
Control-H	2.38	25.90	14.74
PVA0.8-H	2.41	24.23	14.29
PVA1.6-H	2.43	23.87	13.82
PVA2.4-H	2.46	23.25	13.56
B0.8-H	2.40	24.98	14.47
B1.6-H	2.42	24.56	14.03
B2.4-H	2.44	24.03	13.78
Control-WD	2.41	22.73	12.89
PVA0.8-WD	2.44	22.18	12.24
PVA1.6-WD	2.47	21.69	11.66
PVA2.4-WD	2.51	21.22	11.15
B0.8-WD	2.43	22.42	12.51
B1.6-WD	2.45	21.91	12.14
B2.4-WD	2.49	21.48	11.83

the basalt fibers have very low impact on the concrete's unit weight.

With the effect of polyvinyl alcohol fiber, the unit weight increase rates were between 1.26% and 3.36% and these rates increased with the effect of wetting-drying curing and were between 2.52% and 5.46%. In the case of basalt fiber, the unit weight increase rates were between 0.84% and 2.52% and these rates increased with the effect of wetting-drying curing and were between 2.10% and 4.62%.

With the effect of polyvinyl alcohol fiber, the water absorption decrease rates were between 6.45% and 10.23%, while these rates increased with the effect of wetting-drying curing and were between 14.36% and 18.07%. In the case of basalt fiber, the water absorption decrease ratee were between 3.55% and 7.22% and these rates increased with the effect of wetting-drying curing and were between 13.44% and 17.07%.

With the effect of polyvinyl alcohol fiber, the voids ratio decrease rates were between 3.05% and 8.01%, while these rates increased with the effect of wetting-drying curing and were between 16.96% and 24.36%. In the case of basalt fiber, the voids ratio decrease rates were between 1.83% and 6.51% and these rates increased with the effect of wetting-drying curing and were between 15.13% and 19.74%.

3.4. Ultrasonic pulse velocity results

The effect of polyvinyl alcohol and basalt fibers and curing conditions on the ultrasonic pulse velocity values of geopolymer samples were investigated. 7 and 28 day's ultrasonic pulse velocity results are shown in Table 6. There was an increase in ultrasonic pulse velocity results due to the effect of polyvinyl alcohol and basalt fiber. The increase in the results was higher with the effect of wetting-drying curing. In the ultrasonic pulse velocity results, the effective factor is the reduction of the voids ratio. The voids ratio decreases with the effect of fiber. Likewise, the voids ratio will be reduced by the action of wetting-drying curing. With the reduction of the voids ratio, the transition time of the ultrasound waves will be shortened and the transition velocity will increase [25,41].

In relation to the addition of fibers, the mixes' results were obtained near to each other, which is an indication that the matrix's compactness and homogeneity were not affected by the fibers. According to the findings, for the identical sample at different ages, as well as increased fiber content, a slight improvement can be seen. Al-mashhadani et al. also conducted a similar study and found a slight improvement for different fiber rates in the identical series and for the identical sample at different ages [5].

According to the control sample, with the effect of polyvinyl alcohol, the rates of increase were between 1.11% and 2.92% in the 7th day results and between 0.82% and 2.65% in the 28th day results. According to the control samples with the effect of the

Table 6
Results of UPV test (m/s).

	7 days	28 days
Control-H	3526	3553
PVA0.8-H	3565	3582
PVA1.6-H	3608	3619
PVA2.4-H	3629	3647
B0.8-H	3554	3589
B1.6-H	3582	3597
B2.4-H	3611	3624
Control-WD	3617	3645
PVA0.8-WD	3649	3668
PVA1.6-WD	3688	3713
PVA2.4-WD	3710	3734
B0.8-WD	3622	3652
B1.6-WD	3664	3683
B2.4-WD	3679	3705

wetting-drying curing, the rates of increase were between 3.49% and 5.22% in the 7th day results and between 3.24 and 5.09% in the 28th day results.

According to the control sample, with the effect of basalt fiber the rates of increase were between 0.79% and 2.41% in the 7th day results and between 1.01% and 2% in the 28th day results. According to the control samples with the effect of the wetting-drying curing, the rates of increase were between 2.72% and 4.34% in the 7th day results and between 2.79% and 4.28% in the 28th day results.

3.5. Abrasion resistance

Weight loss and length change rates are shown in Fig. 4. The effect of colemanite waste on abrasion was found to be positive by Mucteba et al. [40]. Similar to the strength results, abrasion behavior was observed. In this study, the effects of other factors on colemanite waste replacement control samples were investigated. When the results were examined, weight loss and length change were less than 16 g and 2 mm, respectively. As fiber content increased, there was an improvement in length change and weight loss. The main reason for this situation is the formation of a resistant layer with the effect of fiber. The results in this study are consistent with previous results [5,40,41]. In addition, it has been observed that resistance increased against abrasion as a result of geopolymerization reaction due to the effect of wetting-drying curing.

The findings for this study could be take into consideration according to previous studies [51]. In this paper, a research on the abrasion resistance with fracture energy for concrete with basalt fiber was invrstigated by Kabay. In this research, it was showed that the addition of basalt fiber significantly contributes

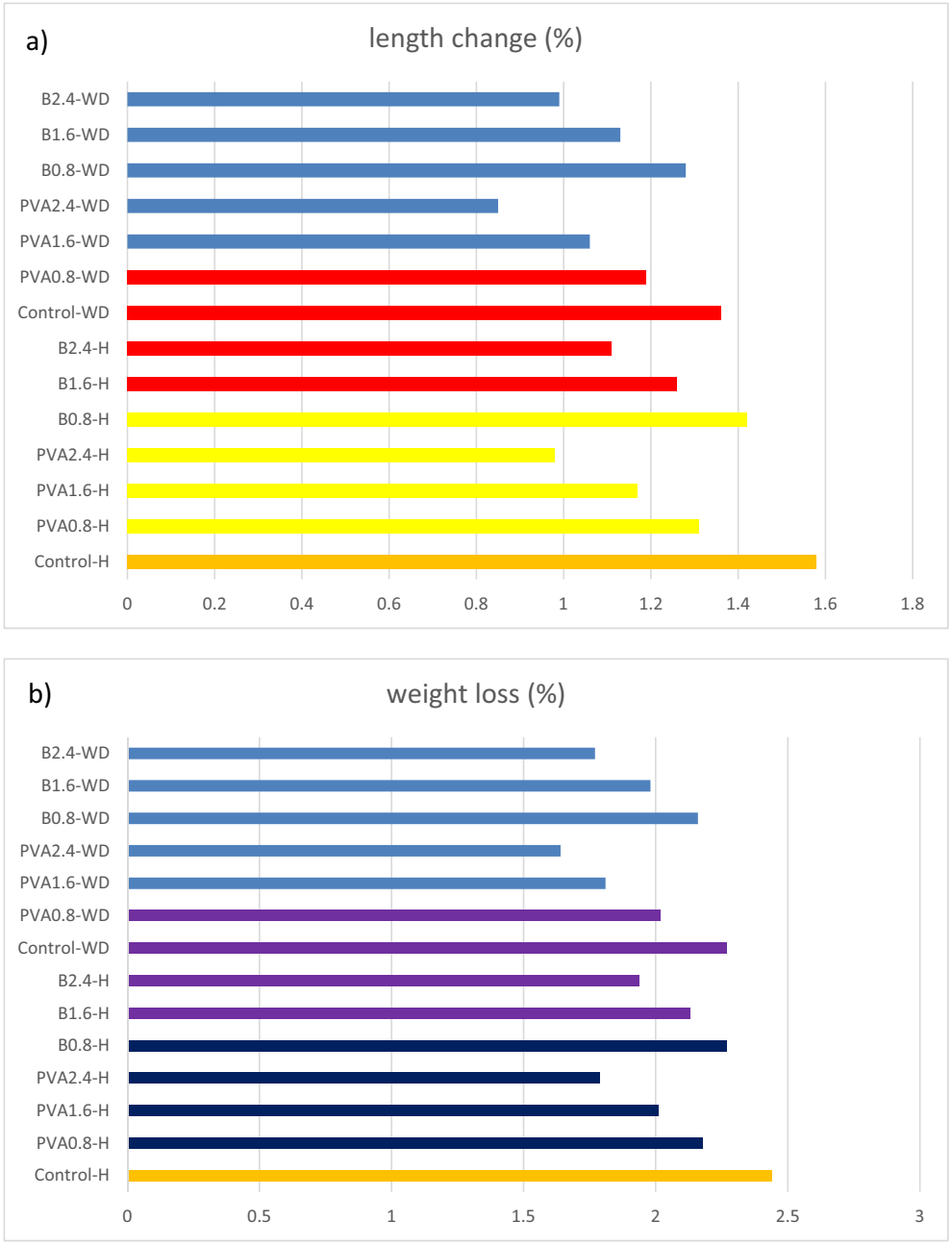

Fig. 4. Results of abrasion: a) length change b) weight loss.

to the abrasion resistance of the concrete. Basalt fibers also exhibited a decrease in the abrasive wear of the concrete between 18% and 2%. The increment in fiber content and length has also helped to abrasion resistance.

3.6. Correlation factors about the studied parameters

In this study, correlation factor was calculated using the test results to examine the conformity ratio of the results. The correlation factors between the compressive strength and UPV and between the flexural strength and weight loss were found. R^2 shows the correlation factor value, while this value is high, increases the degree of conformity. Values greater than 0.80 are satisfactory. Figs. 5 and 6 showed greater than 0.80 values in both correlations. The correlation factor between the compressive strength and UPV was 0.83 and between the flexural strength and weight loss was 0.82. The results are consistent with the results of previous studies [5,40,41].

For comparing the results of this study with previous findings, it is reported that there were accordance in terms of ultrasonic pulse velocity-compressive strength rate correlation and showed more relationship between abrasion resistance and flexural strength.

3.7. High temperature effect

3.7.1. Strength results

Physical and structural changes in geopolymer samples were examined after 200, 400 and 600 °C temperature tests. In addition, the role of polyvinyl alcohol and basalt fibers and curing conditions on the properties of colemanite waste-substituted control samples were investigated under the influence of the high temperature. The pre-test and post-test results were compared (Figs. 7 and 8). The reduction rates at the end of the test are shown in Tables 7 and 8.

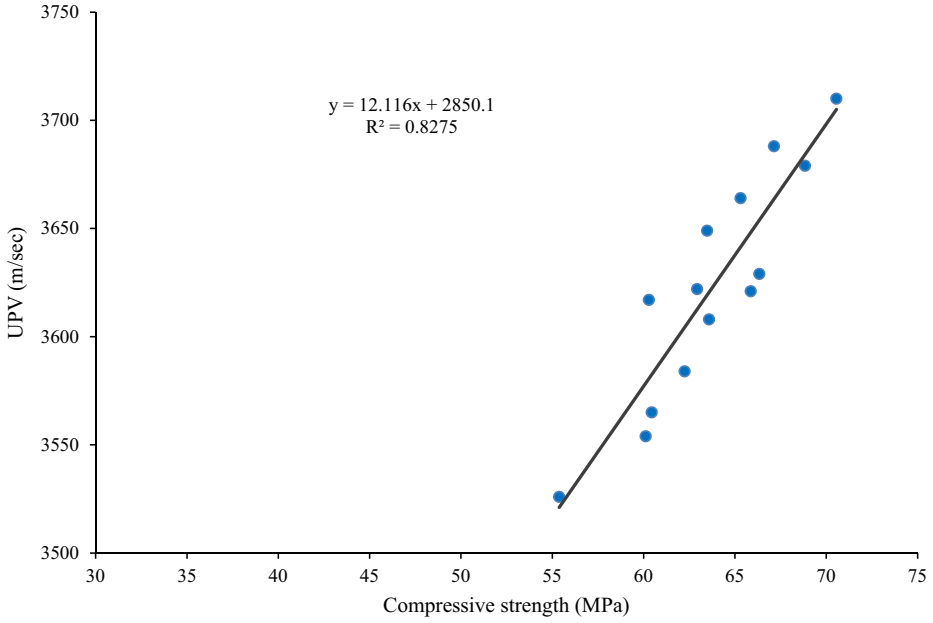

Fig. 5. The relation between compressive strength and UPV.

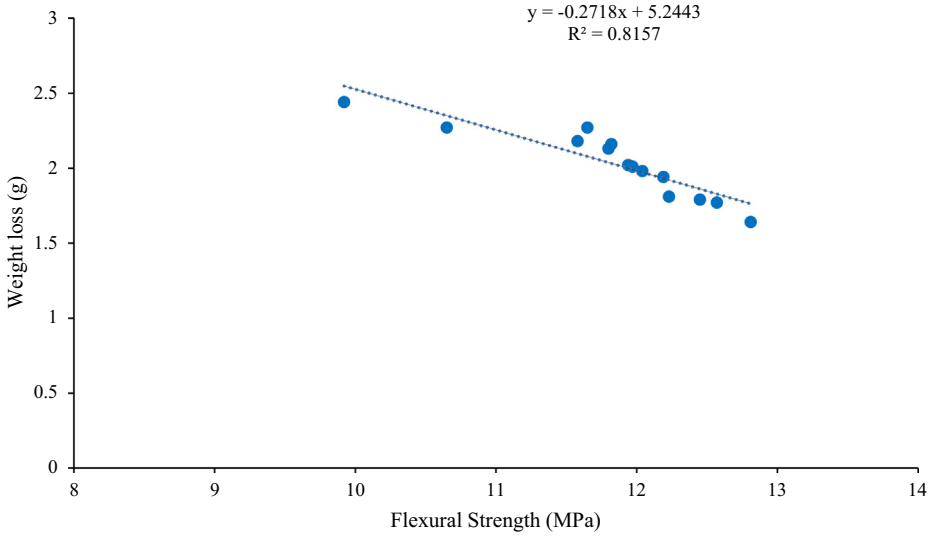

Fig. 6. The relation between flexural strength and weight loss.

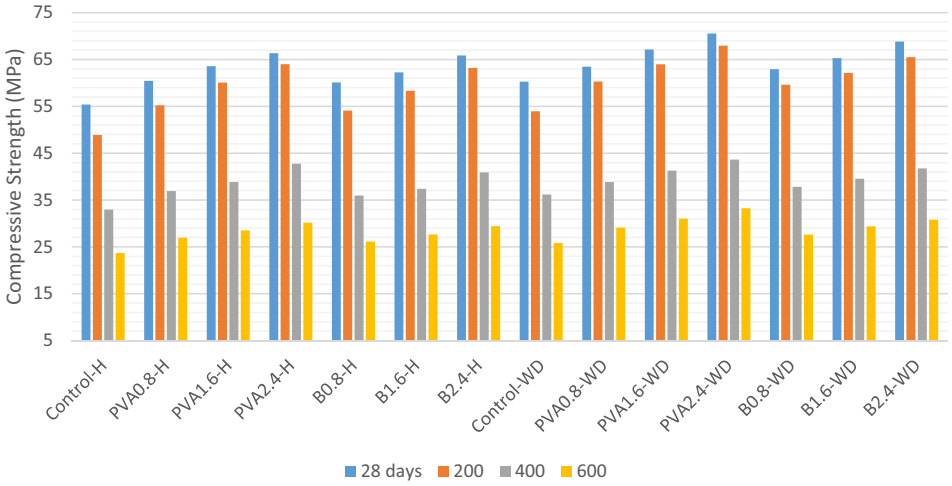

Fig. 7. Compressive strength results for high temperature effect.

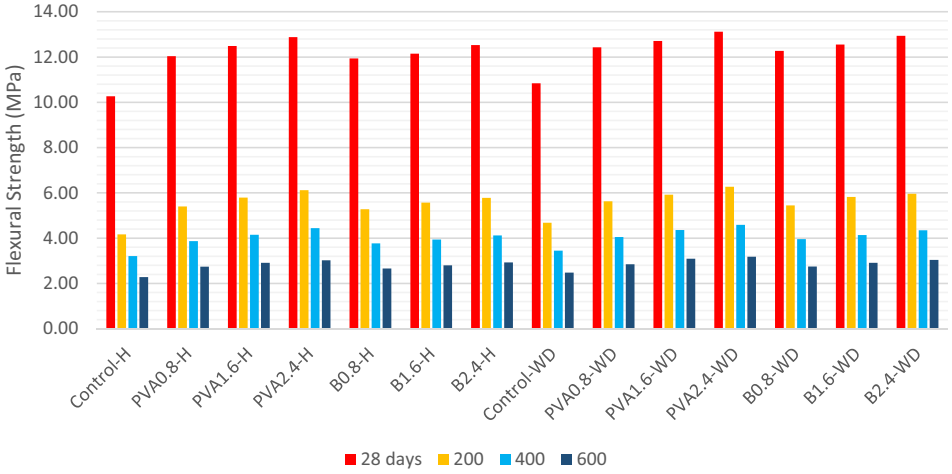

Fig. 8. Flexural strength results for high temperature effect.

Table 7
Compressive strength losses for high temperature effect (%).

	200 °C	400 °C	600 °C
Control-H	11.72	40.45	57.24
PVA0.8-H	8.64	38.94	55.42
PVA1.6-H	5.52	38.92	55.12
PVA2.4-H	3.50	35.53	54.52
B0.8-H	10.01	40.20	56.55
B1.6-H	6.30	39.94	55.55
B2.4-H	4.01	37.91	55.32
Control-WD	10.52	39.96	57.17
PVA0.8-WD	5.01	38.80	54.10
PVA1.6-WD	4.71	38.52	53.80
PVA2.4-WD	3.70	38.15	52.88
B0.8-WD	5.26	39.90	56.09
B1.6-WD	4.87	39.43	55.01
B2.4-WD	4.84	39.35	55.27

Table 8
Flexural strength losses for high temperature effect (%).

	200 °C	400 °C	600 °C
Control-H	59.40	68.74	77.80
PVA0.8-H	55.15	67.86	77.24
PVA1.6-H	53.64	66.77	76.70
PVA2.4-H	52.48	65.53	76.55
B0.8-H	55.78	68.43	77.72
B1.6-H	54.16	67.57	76.95
B2.4-H	53.87	67.12	76.62
Control-WD	56.83	68.17	77.12
PVA0.8-WD	54.71	67.42	77.07
PVA1.6-WD	53.42	65.70	75.69
PVA2.4-WD	52.21	65.02	75.76
B0.8-WD	55.58	67.73	77.59
B1.6-WD	53.63	67.01	76.81
B2.4-WD	53.94	66.38	76.51

Geopolymer samples experienced a loss of strength due to dehydration and evaporation of water in the matrix resulting from thermal reactions after 400 °C. The strength results were similar to the results before the effect of temperature. According to the control sample, basalt and polyvinyl alcohol fiber additive samples performed better. The main reason for this situation is the preservation of the mechanical integrity of the basalt and polyvinyl alcohol fibers under the influence of high temperature. The homogeneity and fine distribution of the crystalline phases of the fibrous materials have a positive effect on their physical and mechanical properties [41].

The wetting-drying curing improved the results of high temperature post-treatment through the formation of new crystalline geopolymerization products and the continuity of

geopolymerization [25]. When the flexural and compressive strength reduction ratios were examined, it was observed that the decrease in flexural strength results was higher. There is a greater tendency to the flexural strength against defects due to growth in porous structures and crack propagation with temperature [52].

The desired mechanical and physical properties of fibrated materials are referred to the homogenous and thin distribution of crystalline phases. This desirable microstructure can be provided with adding a nucleating agent such as P_2O_5, ZrO_2 or TiO_2. However, basalt rocks do not require a natural core material, such as Fe_3O_4, during melting, but produce it with the advantages over other fibers in order to obtain similar microstructure [53,54]. Kong et al., after exposing to high temperatures, examined the comparative behavior of the geopolymers with fly ash and metakaolin. They stated that the metakaolin based geopolymer suffered a loss of strength after exposure to 800 °C. Test results showed a 34% strength drop in samples synthesized with metakaolin at 300 °C [55].

These findings were evaluated according to the results of previous studies [5,30,56]. Almashhadani et al. researched the microstructural characterization and mechanical of fiber reinforced fly ash based geopolymer composites. They showed that geopolymers with PVA fibers increased 33.84% flexural strength in 28 days compared to the control mix amid other fibers. Natali et al. examined the bending behavior of metakaolin-based fiber-reinforced geopolymers involving various fibers. All fibers have improved the bending strength of geopolymers. The most remarkable PVA fiber reinforced geopolymers showed an increase of about 62% in the bending strength, and significant improvement in ductility after cracking [56]. Amuthakkannan et al. conducted a study to examine the influence of fiber length and content on the mechanical properties of polymer matrix composites with short basalt fibers. As a result of the research, it has been reported that bending strength increases significantly as fiber content enhanced [30]. Dias and Thaumturgo investigated the bending strength properties of the geopolymeric concrete reinforced with basalt fibers. For each increase in fiber content, they also reported an increase in bending strength, and adding basalt fiber as a volume ratio of 1.0% increased the bending strength of 23.80% compared to non-fiber specimens.

The decrease rates for geopolymer samples with polyvinyl alcohol additive were between 54.52% and 55.42% in the compressive strength results at 600 °C, while these rates decreased with the wetting-drying curing and were between 52.88% and 54.10%. While the reduction rates for geopolymer samples with polyvinyl alcohol additive were between 76.55% and 77.24% in the flexural strength results at 600 °C, these rates decreased and became between 75.69% and 77.07% due to the wetting-drying curing.

The decrease rates for geopolymer samples with basalt fiber additive were between 55.32% and 56.55% in the compressive strength results at 600 °C, while these rates decreased with the wetting-drying curing and were between 55.01% and 56.09%. While the reduction rates for geopolymer samples with basalt fiber additive were between 76.62% and 77.72% in the flexural strength results at 600 °C, these rates decreased and became between 76.51% and 77,59% due to the wetting-drying curing.

The results of compressive strength in polyvinyl alcohol additive samples exposed to 600 °C temperature were between 26.95 MPa and 30.17 MPa. Due to the wetting-drying curing, the results of the compressive strength at 600 °C increased and were in the range of 29.14 MPa and 33.25 MPa. The results of flexural strength in polyvinyl alcohol-supplemented samples exposed to 600 °C temperature were between 2.74 MPa and 3.02 MPa. Due to the wetting-drying curing, the results of the flexural strength at 600 °C increased and were in the range of 2.85 MPa and 3.18 MPa.

The results of compressive strength in basalt fiber additive samples exposed to 600 °C temperature were between 26.12 MPa and 29.43 MPa. Due to the wetting-drying curing, the results of the compressive strength at 600 °C increased and were in the range

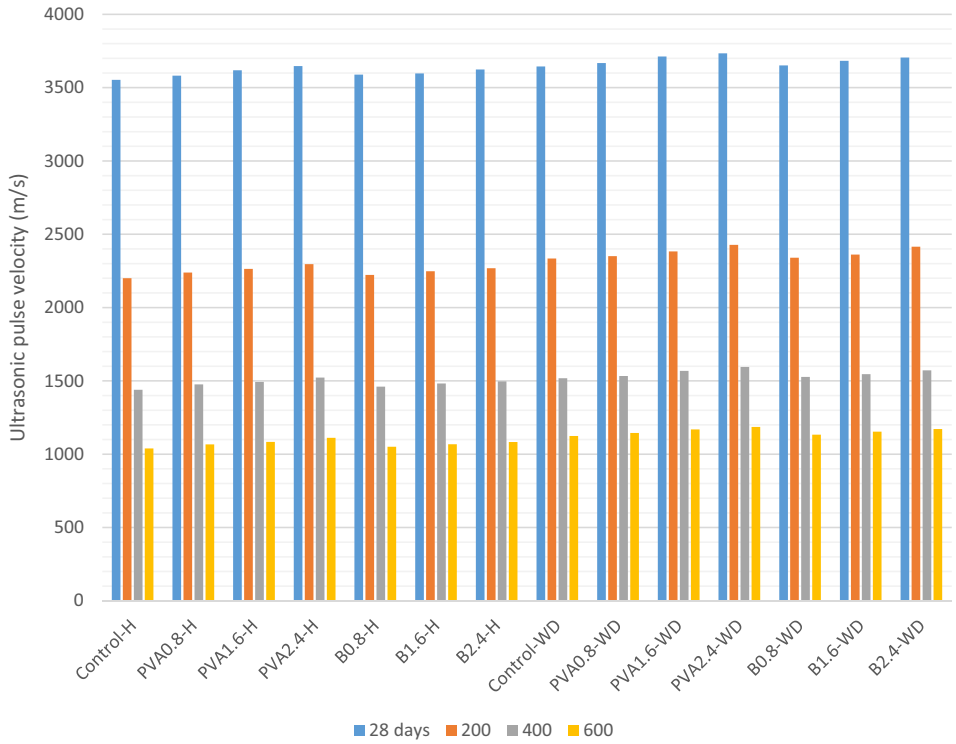

Fig. 9. Ultrasonic pulse velocity results for high temperature effect.

of 27.63 MPa and 30.79 MPa. The results of flexural strength in basalt fiber-supplemented samples exposed to 600 °C temperature were between 2.66 MPa and 2.93 MPa. Due to the wetting-drying curing, the results of the flexural strength at 600 °C increased and were in the range of 2.75 MPa and 3.04 MPa.

3.7.2. Ultrasonic pulse velocity results

In case of exposure to high temperature effect, additional voids are formed with the loss of mass due to the growth of the pore structure and the loss of water in the matrix. With the increase in the amount of voids, the transition time of the sound waves in the sample will increase and the ultrasonic pulse velocity will decrease [57]. The values and reduction rates of the ultrasonic pulse velocity at the end of the test are shown in Fig. 9 and Table 9.

The results of geopolymer mixtures after high temperatures effect show that basalt fiber geopolymer reinforced specimens behaved lightly better than other specimens. As temperature increases, all specimens exhibit similar behavior, and UPV values show significant changes up to 200 °C and then a big drop. According to Table 9, the geopolymer specimens showed a dramatic drop after 200 °C compared to the UPV results. The observation exhibits that the solid geopolimeric matrix has been severely suffered after 200 °C and is also consistent with the loss of bending and compressive strength values. Because of the formation of larger cracks under the influence of high temperature and the melting of fibers over 200 °C in geopolymer matrix composites, the propagation time of UPV has been delayed and lower UPV values have been obtained.

Table 9
Ultrasonic pulse velocity losses for high temperature effect (%).

	200 °C	400 °C	600 °C
Control-H	38.08	59.50	70.76
PVA0.8-H	37.49	58.79	70.21
PVA1.6-H	37.44	58.75	70.05
PVA2.4-H	37.04	58.24	69.51
B0.8-H	38.06	59.29	70.72
B1.6-H	37.50	58.80	70.31
B2.4-H	37.42	58.69	70.12
Control-WD	35.94	58.35	69.16
PVA0.8-WD	35.91	58.21	68.78
PVA1.6-WD	35.82	57.77	68.52
PVA2.4-WD	34.98	57.28	68.24
B0.8-WD	35.93	58.19	68.98
B1.6-WD	35.87	58.02	68.67
B2.4-WD	34.82	57.57	68.37

The decrease rates for geopolymer samples with polyvinyl alcohol additive were between 69.51% and 70.21% in the ultrasonic pulse velocity results at 600 °C, while these rates decreased with the wetting-drying curing and were between 68.24% and 68.78%. While the reduction rates for geopolymer samples with basalt fiber additive were between 70.12% and 70.72% in the ultrasonic pulse velocity results at 600 °C, these rates decreased and became between 68.37% and 68.98% due to the wetting-drying curing.

The results of ultrasonic pulse velocity in polyvinyl alcohol additive samples exposed to 600 °C temperature were between 1067 m/s and 1112 m/s. Due to the wetting-drying curing, the results of the ultrasonic pulse velocity at 600 °C increased and were in the range of 1145 m/s and 1186 m/s. The results of ultrasonic pulse velocity in basalt fiber-supplemented samples exposed to 600 °C temperature were between 1051 m/s and 1083 m/s. Due to the wetting-drying curing, the results of the flexural strength at 600 °C increased and were in the range of 1133 m/s and 1172 m/s.

3.7.3. Weight loss results

The weight loss rates in samples exposed to temperature are given in Fig. 10. Weight losses in polyvinyl alcohol additive samples were between 1.17% and 1.48% at 200 °C, between 2.78% and 3.09% at 400 °C and between 4.11% and 4.46% at 600 °C. Weight losses in polyvinyl alcohol additive samples with wetting-drying curing were between 1.02% and 1.29% at 200 °C, between 2.62% and 2.96% at 400 °C and between 3.99% and 4.26% at 600 °C. Weight losses in basalt fiber additive samples were between 1.29% and 1.67% at 200 °C, between 3.01% and 3.22% at 400 °C and between 4.23% and 4.48% at 600 °C. Weight losses in basalt fiber additive samples with wetting-drying curing were between 1.16% and 1.35% at 200 °C, between 2.74% and 3.03% at 400 °C and between 4.08% and 4.37% at 600 °C. Dehydration and

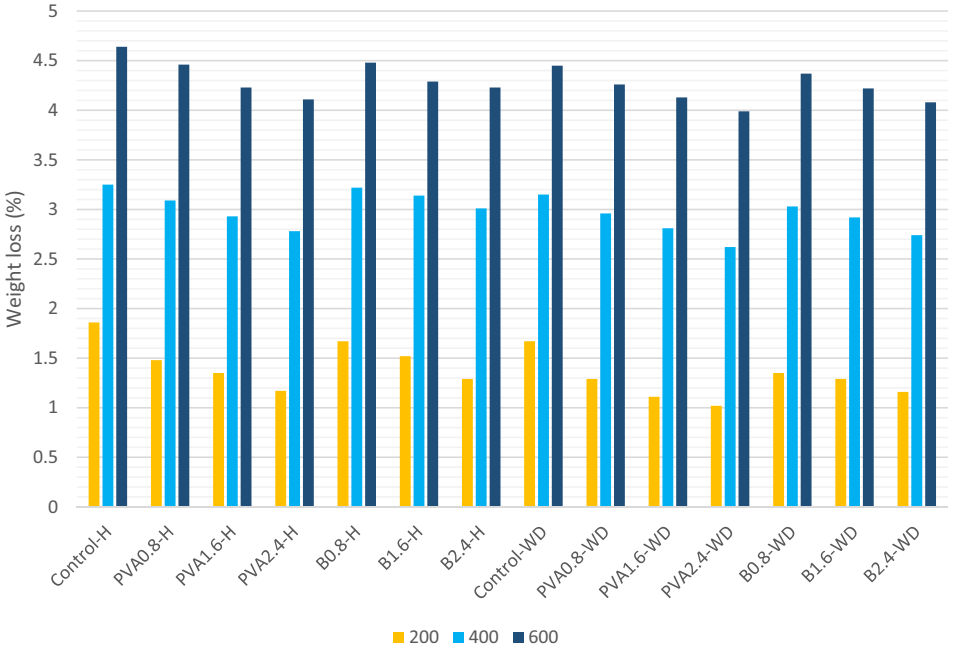

Fig. 10. Weight loss rates for high temperature effect.

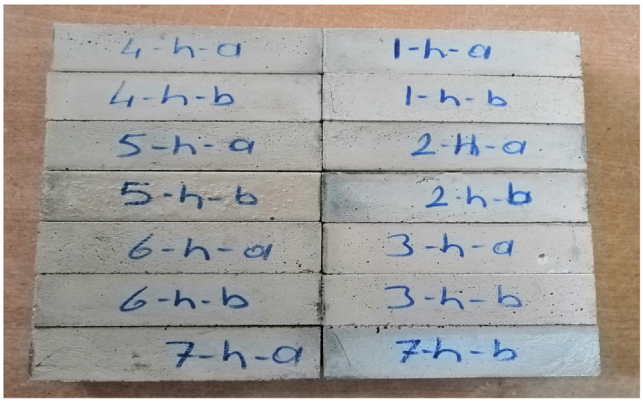

Fig. 11. Heat cured geopolymer samples for high temperature effect.

water evaporation in geopolymeric matrix due to high temperature effect create microstructure damage and weight loss [58].

When the results of all the mixtures were investigated, less weight loss was seen in the other samples than the control sample. This means that the fibers used show an important improvement in reducing weight loss. In addition, the increase in fiber length has been shown to have a positive effect on the performance of geopolymer mortars if exposed to high temperatures. Colemanite substitutions have reduced weight loss. As the temperature increases, a dehydration reaction happens in the geopolymer composites' structure and the existing moisture moves towards the surface of the sample and moves away. Because of this situation, internal damage to microstructure happens and provides an increase in weight loss. The main cause of weight loss before 600 °C is due to the evaporation of concentrated hydroxyl groups together with free water. Over 600 °C, weight loss was observed due to fiber and matrix interfacing reactions. Weight loss has increased due to significant fiber distortion. However, with the influence of fiber, weight loss was less than the control sample [55]. Thus, samples have shown that mechanical properties are reduced and fractures in a very brittle manner [59].

3.7.4. Analyses and visual inspection

Figs. 11 and 12 shows samples after 600 °C high temperature effect. Little color change was observed on the samples at 600 °C, the cracks were limited and the sample remained stable. The surface of the samples tended to be a little coarser [41].

The micrographs of SEM analyzes after the temperature effect of 200 and 600 °C are shown in Figs. 13 and 14. The general microstructure of homogenous and dense matrix consisting mainly of alumino-silicate gel before high temperature effect was protected after the test. It was understood that the microstructure of the sample did not appear to be significantly cracked after 200 °C temperature effect. An increase in crack formation was observed after a temperature of 600 °C [60,61]. However, it was understood that geopolymer samples were protected by good bonding and matrix continuity in geopolymerization.

Fig. 15 shows the FT-IR spectra before and after the temperature of 600 °C under two different curing conditions of the control mixture. Number 1 shows the only heat cured sample, while the number 2 shows the sample exposed to the wetting-drying curing. Likewise, the number 3 shows the only heat cured sample exposed to a temperature of 600 °C, while the number 4 shows the sample exposed to the wetting-drying curing and the 600 °C temperature. 975.5, 977.68, 968.32 and 977.54 cm^{-1} shows the wavelength for sample 1, sample 2, sample 3 and sample 4, respectively. These numbers indicates the presence of Si—O—Al bonds corresponding to asymmetric stretching vibrations.

In the samples applied to the wetting-drying curing, after the effect of the temperature, Si—O—Al bonds was self-preservation, but only a decrease was observed in the only heat cured samples. Furthermore, the presence of added water by the wetting-drying curing increases the intensity of the bands at about 3500 and 1650 cm^{-1} [62,63].

TGA and DTA curves are shown in Figs. 16–19 of the control samples produced in this study. Red curves show weight losses. In the Control-H sample, a decrease of 1.564% was observed in the TGA analysis before 600 °C temperature effect. After high

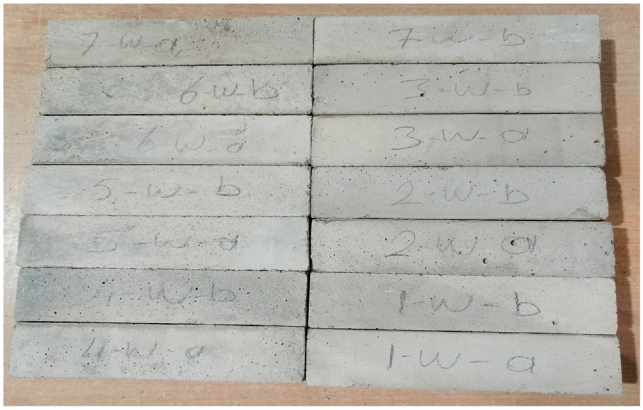

Fig. 12. Wetting-drying cured geopolymer samples for high temperature effect.

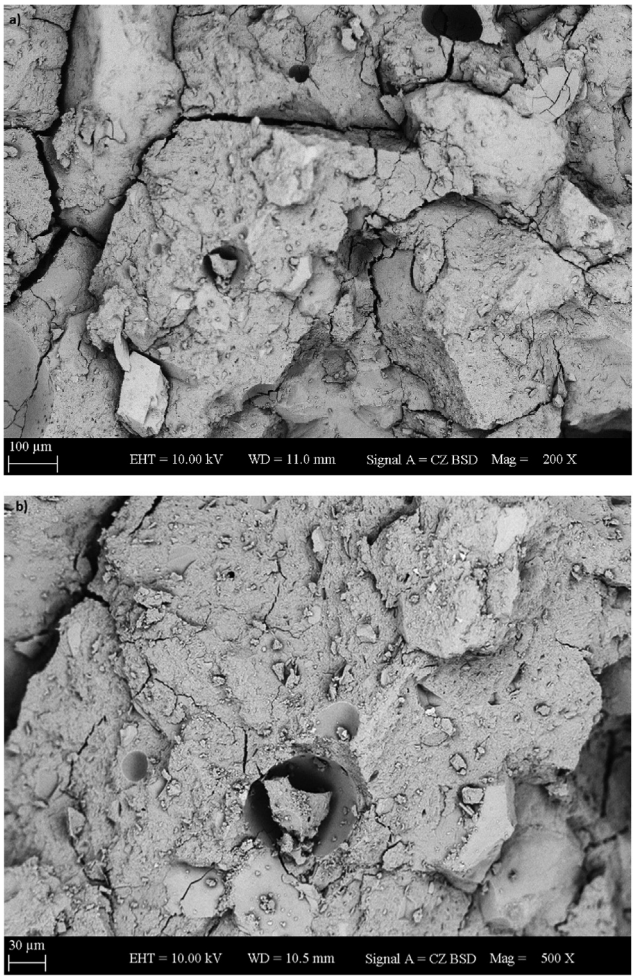

Fig. 13. SEM micrographs for control samples after 200 °C.

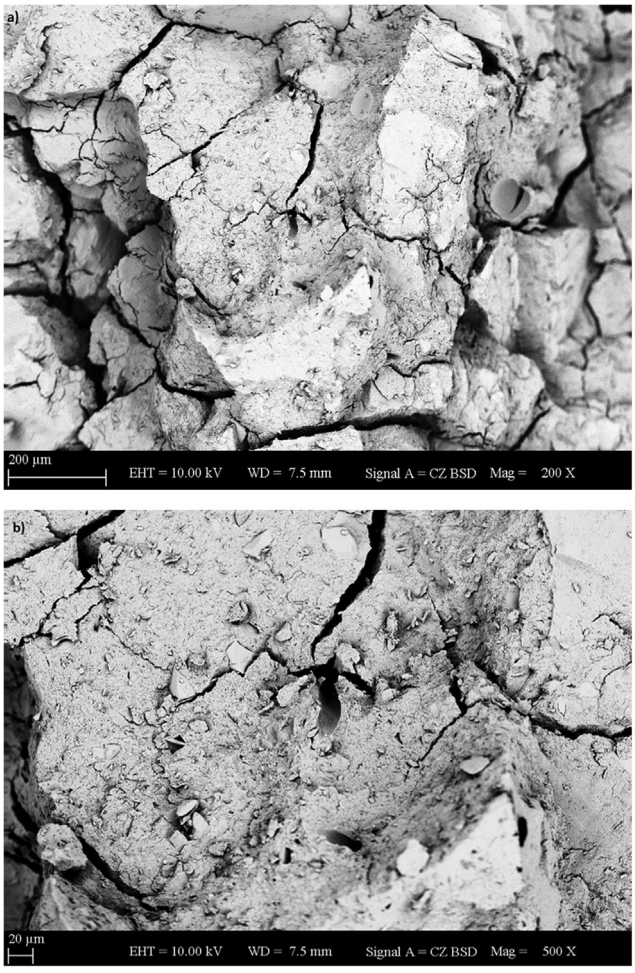

Fig. 14. SEM micrographs for control samples after 600 °C.

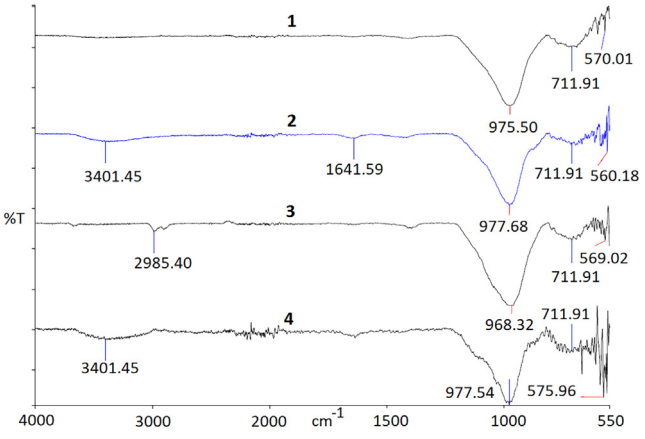

Fig. 15. FT-IR results of control-H and control-WD samples before and after 600 °C.

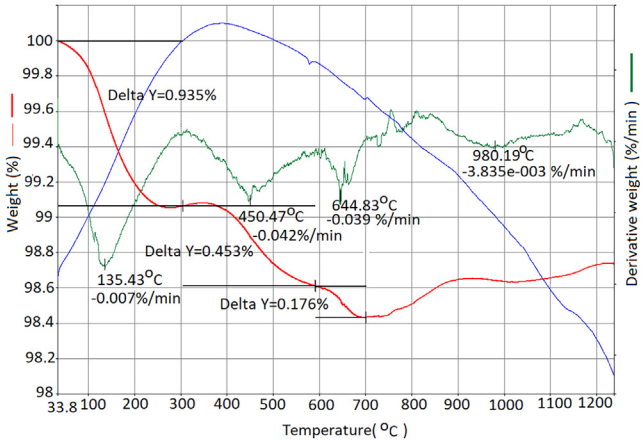

Fig. 16. TGA-DTA results of control-H sample before 600 °C.

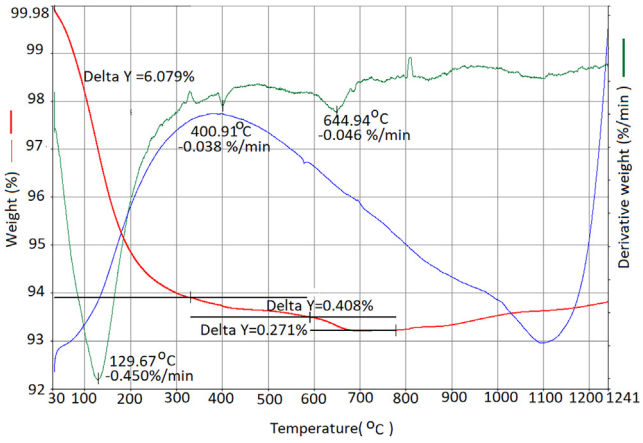

Fig. 17. TGA-DTA results of control-H sample after 600 °C.

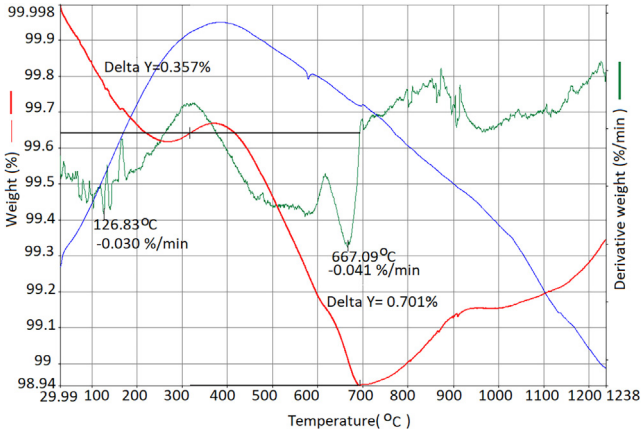

Fig. 18. TGA-DTA results of control-WD sample before 600 °C.

temperature effect, this rate increased and became 6.758%. In the control-WD sample, there was a 1.058% reduction in TGA analysis before the 600 °C temperature effect. After high temperature effect, this rate increased and became 3.896%. As can be seen, the increase in these rates after the high temperature effect was limited. This showed that geopolymer composites retained their stability. The amount of water in the matrix with the wetting-drying curing decreased the weight loss. While the high rate of weight loss was in the range of 0–300 °C, this was due to the evaporation of free and bound water in the matrix. The endothermic peaks formed in this range are seen in the DTA curves. Weight loss became stable after 700 °C. This is due to the evaporation of water chemically bound to the geopolymer and the hydroxyl groups, OH [64,65].

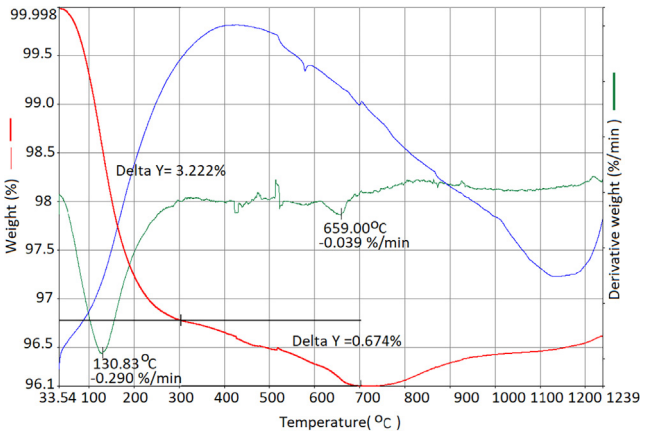

Fig. 19. TGA-DTA results of control-WD sample after 600 °C.

3.8. Freezing-thawing test

With the freezing-thawing test of 90 cycles, the results of the residual strength of the samples, ultrasonic pulse velocity and weight loss results were compared with the results of 28 days and are given in Figs. 20–23. The compact structure of the geopolymeric matrix brings along a good degree of adhesion. This allows geopolymer samples to resist freezing-thawing. In geopolymer samples, despite the 90 cycles, the residual strengths were high and the decrease in the ultrasonic pulse velocity rate results were limited. Due to the effect of polyvinyl alcohol and basalt fibers, the results of the strength and ultrasonic pulse velocity rates increased. The behavior of the fibers was similar to the behavior before the test. Weight loss was very limited.

The moist environment in which the experiment was conducted reduced weight loss. The results were consistent with the previous freezing-thawing tests [64,65]. The highest residual compressive strength after the freezing-thawing test was in the PVA2.4-WD sample with 51.56 MPa and the lowest residual strength was in the Control-H sample with 41.01 MPa. The highest flexural strength was in the PVA2.4-WD sample with 10.22 MPa, while the lowest flexural strength was in the Control-H sample with 8.16 MPa. The highest and lowest values for ultrasonic pulse velocity results were 3353 m/s and 3542 m/s, respectively.

Weight loss rates were highest in the Control-H sample with 0.79%, while the lowest was in the PVA2.4-WD sample with a ratio of 0.29%. Weight loss was reduced by the wetting-drying curing. Post-test visual inspection of samples are given in Figs. 24–25. No significant changes were observed in the external structure of the samples when visual inspection was performed after 90 freezing-thawing cycles.

The major event that occurred during the deterioration is the expansion of water in the permeable structure due to the freezing-thawing cycles. In the freezing phase, water will expand to 9% by volume and form a hydraulic pressure [66].

The air voids in the sample provide an area where the ice can expand. Even so, when the obtainable free space is filled, the freeze ice creates a pressure on the concrete matrix around it. When the strength exceeds the stress of the concrete, micro cracks occur and cause the concrete to deteriorate [67,68]. Due to the initial strength of geopolymer is higher, it can resist higher pressures than freezing water before micro cracks occur.

Microstructural researches have shown that geopolymer microcracks, due to capillary water expansion during the freezing-thawing cycles, appears in the interface between the aggregates and paste. These micro-cracks could contribute to the deterioration of the mortar. Crystals occur after exposing to freezing-thawing cycles. This is expectanted to reduce strength [69]. Mass loss after the freezing-thawing cycle was less than 1% for all the samples.

4. Conclusions

In this study, mechanical and durability properties of geopolymer composites prepared using metakaolin and colemanite binding materials with basalt and polyvinyl alcohol fibers were

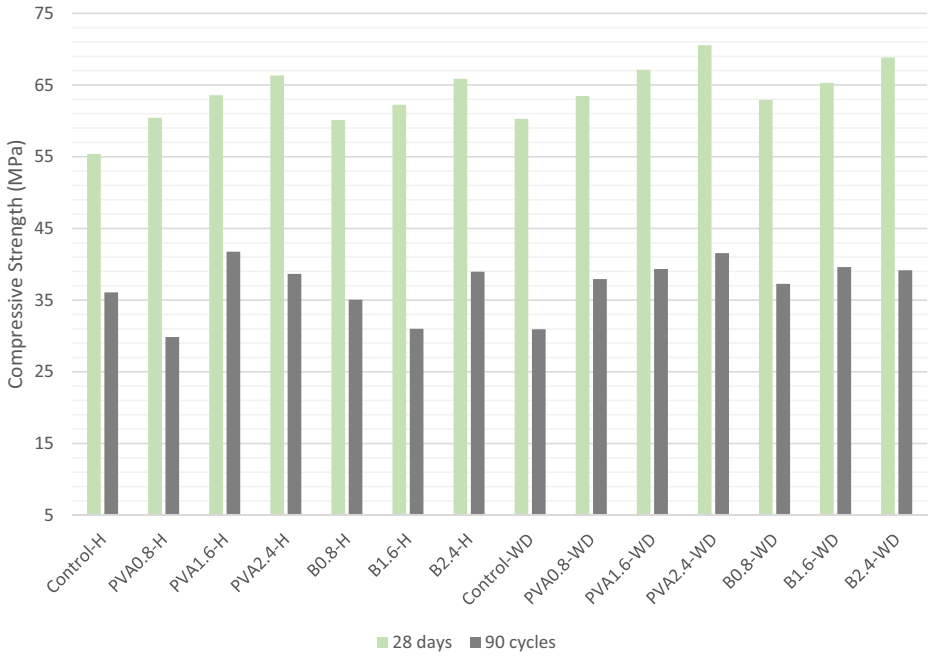

Fig. 20. Results of residual compressive strength for freezing-thawing test.

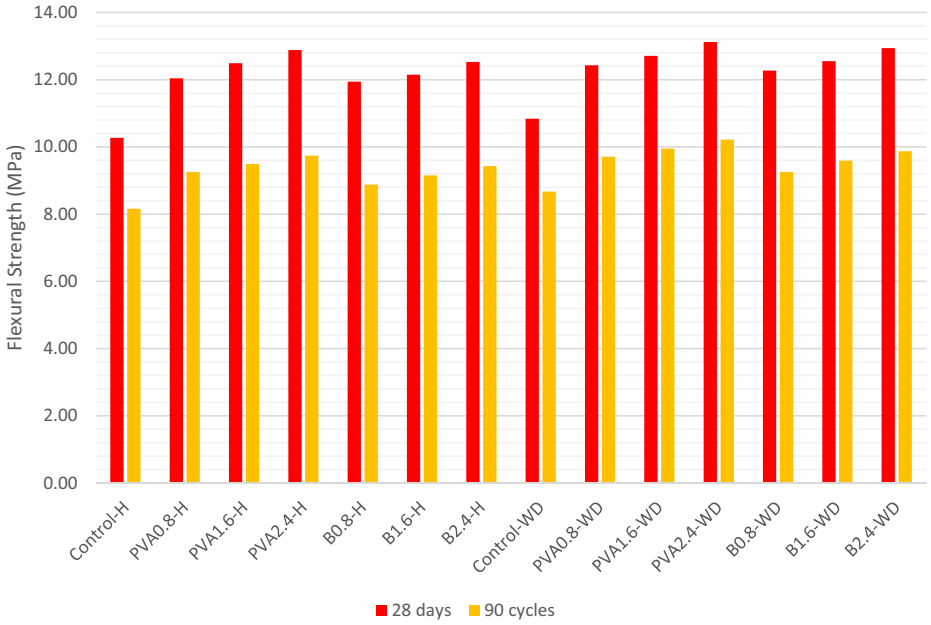

Fig. 21. Results of residual flexural strength for freezing-thawing test.

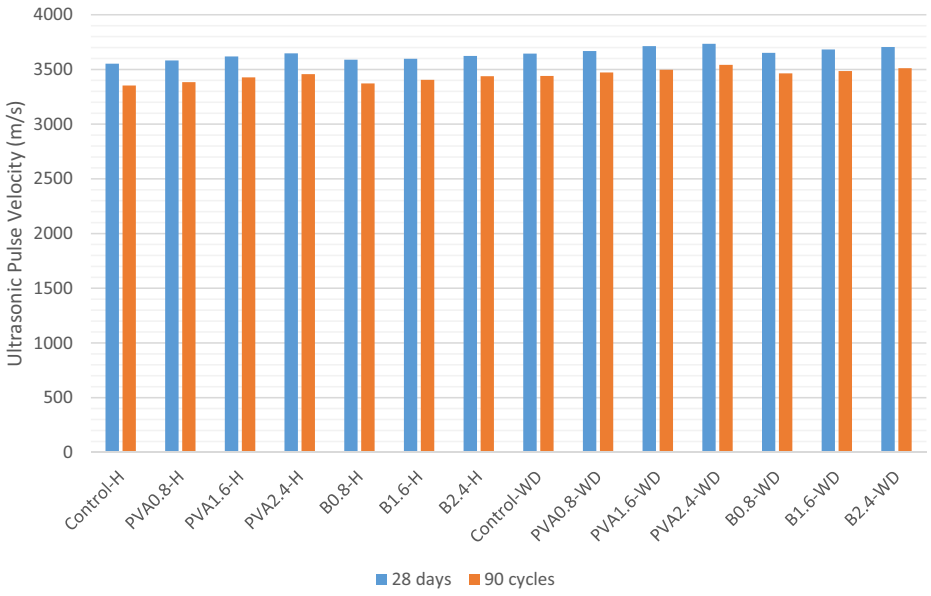

Fig. 22. Results of ultrasonic pulse velocity for freezing-thawing test.

investigated under the influence of wetting-drying curing and heat curing:

- The conducted research reveals the fact that the range of applications for this type of composites is wide due to the availability of many fiber types and due to the ease of application of fiber reinforced geopolymers. Metals manufacturing, nuclear energy stations, industrial high temperature furnaces, glass industry section, civil and military airports', and concrete reactor silos could be a promising application areas for the studied matrices since the main objective is to enhance the fracture properties of the resulted matrix such as tensile and flexural strength properties.
- The compressive and flexural strength results showed an increase in the 28-days in all of the mixtures according to the 7-days. In addition, there was a positive effect on the strength results with the increase in fiber ratio. Through the wetting-drying curing, the continuation of geopolymerization and the formation of new crystalline geopolymerization products were provided. This results in an increase in the strength results due to the wetting-drying curing.
- The factors on the tensile strength are the presence of fibers and wetting-drying curing method. Geopolymerization was ensured and the tensile strength increased with the wetting-drying curing effect. The presence of the fibers also increased the tensile strength results.

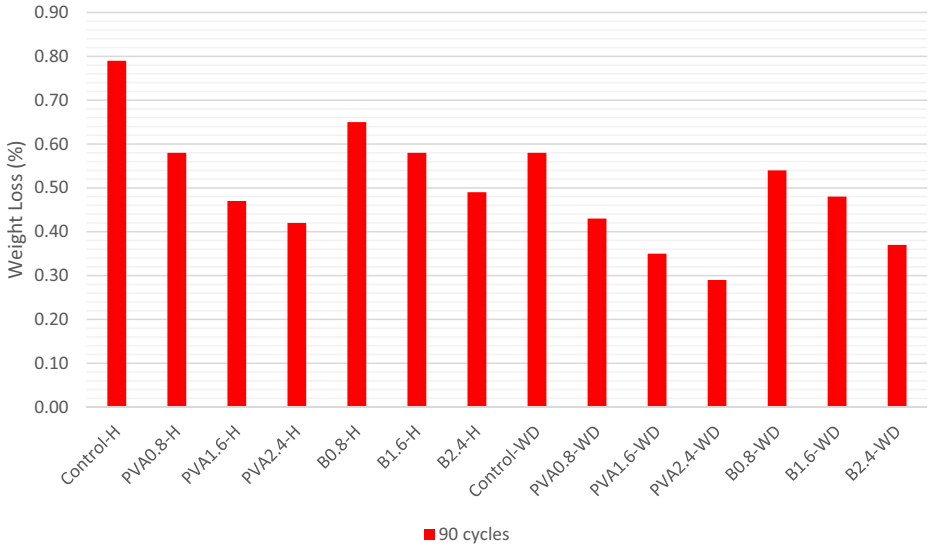

Fig. 23. Results of weight loss rates for freezing-thawing test.

Fig. 24. Freezing thawing test samples.

Fig. 25. Freezing thawing test samples-WD curing.

- In the case of the application of the wetting-drying curing method, with the effect of water, more aluminosilicate gels are formed by the continuation of the reaction, thus reducing the voids ratio and the water absorption. The unit weight values increased with the decrease in the water absorption and voids ratio. There was a slight decrease in voids ratio and water absorption with the effect of fiber. The water absorption rates of polyvinyl alcohol and basalt fiber are high depending on their characteristics.
- For the ultrasonic pulse velocity results, the effective factor is the reduction of the voids ratio. The voids ratio decreases with the effect of fiber. Likewise, the voids ratio will be reduced by the action of wetting-drying curing. With the reduction of the voids ratio, the transition time of the ultrasound waves will be shortened and the transition speed will increase. The correlation factor between the compressive strength and UPV was 0.83 and between the flexural strength and weight loss was 0.82. Values greater than 0.80 are satisfactory.
- When the abrasion results were examined, weight loss and length change were less than 16 g and 2 mm, respectively. As fiber content increased, there was an improvement in length change and weight loss. The main reason for this situation is the formation of a resistant layer with the effect of fiber.
- Geopolymer samples experienced a loss of strength due to dehydration and evaporation of water in the matrix resulting from thermal reactions after 400 °C. The wetting-drying curing improved the results of high temperature post-treatment through the formation of new crystalline geopolymerization products and the continuity of geopolymerization.

The general microstructure of homogenous and dense matrix consisting mainly of alumino-silicate gel before high temperature effect was protected after the test. It was understood that the

microstructure of the sample did not appear to be significantly cracked after 200 °C temperature effect. An increase in crack formation was observed after a temperature of 600 °C.

- The compact structure of the geopolymeric matrix brings along a good degree of adhesion. This allows geopolymer samples to resist freezing-thawing. In geopolymer samples, despite the 90 cycles, the residual strengths were high and the decrease in the ultrasonic pulse velocity rate results were limited. Due to the effect of polyvinyl alcohol and basalt fiber, the results of the strength and ultrasonic pulse velocity rates increased. The behavior of the fibers is similar to the behavior before the test.
- Microstructural researches have shown that geopolymer microcracks, due to capillary water expansion during the freezing-thawing cycles, appears in the interface between the aggregates and paste. These micro-cracks could contribute to the deterioration of the mortar. Crystals occur after exposing to freezing-thawing cycles. This is expectanted to reduce strength.

Declaration of Competing Interest

None.

Acknowledgment

This work was supported by research fund of the Yildiz Technical University, the authors would like to express their sincere gratitude to scientific research coordination unit for their financial support to the project (Project number: FBA-2017-3081).

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