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A survey on one year strength performance of reinforced geopolymer composites

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HIGHLIGHTS

- A combination of colemanite waste and metakaolin was utilized.
- Mechanical, durability and microstructural properties were studied until one year.
- The highest results were obtained with the wetting–drying curing method.
- The geopolymer composites resisted the high-temperature test performed after 1 year.

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ABSTRACT

Heat curing is a widely used method in geopolymer mortar production. While the heat curing shows an increase in strength values, the effect of this situation in the long term has not been examined sufficiently. In this study, the short-term and long-term effects of the curing conditions were examined together and a geopolymer sample with 90% metakaolin and 10% colemanite waste (by weight) was used. Also, polyolefin and polyamide fibers were used as 0.5%, 1.0%, and 1.5%, by volume. A wetting–drying method was applied for curing with heat curing. The Si-O-Al bonds were established to be stronger with wetting–drying curing. 14, 56, 90, and 365 days' flexural and compressive strengths results were determined. Also, the high-temperature test was applied after 365 days. SEM, TGA-DTA, and FTIR analyses were carried out pre and post the high-temperature test. When a comparison was done between the 14-day and the 90-day results, the 90-day results showed a reduction of strength according to 14-days. At the end of 365 days, these reductions fell and results were obtained close to 90 days of strength. The use of high-temperatures for curing was thought to contribute to the development of early-age strength by supporting the dissolution of solid binding materials and the formation of reaction products. On the other hand, due to the adverse effects on the quality and microstructure of the rapidly developing reaction products, strength decreases have been observed. Despite all these effects, the structure of the geopolymer has been preserved.

1. Introduction

Metakaolin is a popular resource binding material utilized in geopolymer production because it can solidify at room conditions and gives high results for compressive strength test [1–3]. Kaolin is converted to metakaolin with calcination at 550–800 °C and the optimum temperature of calcination for kaolin is 600 °C for 2 h [4–7]. Aygörmez et al. [8] investigated the curing conditions in detail on the production of metakaolin based geopolymer mortar. Different temperatures and durations were applied to find the ideal temperature for the curing. Three different periods (2, 24, 72 h) were applied for three different temperatures (40, 60, 80 °C). Besides, the effect of non-combustible furnace bag on curing conditions was investigated. Half of the samples were placed in the drying oven without a non-combustible furnace bag and half of them were placed with a non-combustible furnace bag. The highest results were obtained for samples cured at 60 °C for 72 h (59.65 MPa for compressive strength and 10.05 MPa for flexural strength). The results obtained at 40 °C were higher than those at 80 °C. The lowest results were obtained at 7.76 MPa for flexural strength and 25.14 MPa for compressive strength in samples cured at 80 °C for 2 h without non-combustible furnace bags. The benefit of using these bags was to decelerate the water evaporation con-

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tained in the sample's internal structure and to maintain the reaction. Mangat et al. [9] performed three dissimilar curing methods to alkali-activated and Portland cement mortars: Room temperature, water, and wet/dry. While the most suitable curing method for Portland cement mortars was water curing, wet/dry curing was found to be ideal for alkali-activated mortars. Moreover, it was observed that the curing temperature affected the mechanical properties by affecting the pore structure.

Previous studies have shown that colemanite wastes can be used to a certain extent. It was observed that it formed a protective layer and filled the voids by using 10%. Using this ratio (10%), it has been found that the geopolymer matrix provided an improvement in the microstructure with its relative brittleness and permeability [10]. Thus, it is suitable to use boron wastes at a rate of 10% in geopolymer composites [11]. It has been observed in previous studies that a protective layer around cement particles formed and prevented contact between cement particles and water by using boron minerals in cemented systems. This effect has been shown to directly affect the hydration mechanism [12]. Besides, the mechanical properties of cementitious systems improved [13]. When more than 10% of colemanite waste was used as a critical ratio, it was seen that some cations and anions formed by unbalanced boron compounds affected the cement activation mechanism. Thus, it was thought that it reduced mechanical properties.

The excellent degree of binding of geopolymers is related to the 3D "N-A-S-H" type gel, and this bond is defined as a network of alternative AlO_4 and SiO_4 tetrahedra [Q^4(Al)] bonded together by sharing O atoms [14–15]. The high-temperature test resulted in a high rate of chemical degradation when applied to OPC composites, and chemically bound water and interlayer water were lost due to the decomposition of CH and CSH [16]. When the difference in the thermal phases of the chemical structure was investigated, it was seen that geopolymers had a higher resistance to fire than OPC [17–19]. Zhang et al. [20] studied the high-temperature test on the geopolymer composites with fly ash and metakaolin. The results were compared before and after the high-temperature test. According to the test, a geopolymer product was presented with high compressive strength values. Celik et al. [21] investigated the high-temperature performance of metakaolin based geopolymer composites. They used four different types of fibers for producing geopolymer samples and showed that their stability was maintained even under the effect of 900 °C.

The evaluation of polyamide fibers leads to research in a potential field and supports preventing fracture of concrete. Jeon et al. investigated the engineering properties by using macro polyamide fiber [22]. Bending behavior and toughness of the concrete increased significantly with the polyamide fiber effect. Spadea et al. [23] researched on cement mortar produced using polyamide fibers. It was observed that toughness and energy absorption properties of concrete increased with fiber addition. It was also observed that tensile strength increased by 35% in the case of fiber addition and toughness increased by 13 times compared to the unreinforced material. Polyolefin fibers were used as additives in elastoplastic concrete production. When polyolefin fibers were used in concrete, it increased impact resistance, flexural toughness, and fatigue strength of concrete and reduced crack propagation. It can also be used for on-site applications such as asphalting, tunneling, mining, and the precast industry. Comprehensive studies have been conducted to investigate the mechanical behavior of these types of fibers on reinforced concrete structures [24–25].

Unlike the studies conducted so far, in this study, besides the short-term effect of the heat curing used in the production of geopolymer, the long-term effect was also examined. Thus, one year later, the changes of geopolymer mortars and how these changes behave in the case of high-temperature tests were investigated. Colemanite and metakaolin were used together for the prepared mixture (10% colemanite + 90% metakaolin by weight). Polyolefin and polyamide fibers were used as 0.5%, 1.0%, and 1.5%, by volume. A wetting–drying method was applied for curing in this study with heat curing. 14, 56, 90, and 365 days' flexural and compressive strengths results were determined for geopolymer samples. Also, the high-temperature test was conducted after 365 days. Thus, the long-term effects were investigated with a durability test. At the end of the high-temperature test consisting of 300, 600, and 900 °C, strength and weight loss results were checked. Also, SEM, FTIR, and TGA-DTA analyses with the effects of high-temperature were performed for sample 7-W which has the highest mechanical properties before and after the high-temperature test. Also, the correlation between weight-loss and flexural strength was examined after 900 °C.

2. Experimental program

2.1. Raw materials

Geopolymer composite samples were produced with boron waste colemanite (from the Eti Mine company) and the main binder material metakaolin (from Kaolin EAD company). The ratio of Fe_2O_3 + Al_2O_3 + SiO_2 in the content of metakaolin is 97.2% and it has a ratio of high pozzolanic activity. Also, its fine-grained structure increases the geopolymerization's degree that metakaolin creates. A fixed ratio (13%) of slag (from the Akçansa Company) was used as a source of calcium in the mixture. The properties of different raw materials are given in Table 1.

A blending of sodium hydroxide (12 M) and sodium silicate (SiO_2 / Na_2O = 3.29) was used. Rilem sand (from the Trakya Limak Company), following BS EN 196–1, was added to the mixture. The fibers used in this study were polyolefin and polyamide. Table 2 shows the fibers' properties. PA and PL were showed as abbreviations for polyamide and polyolefin fibers, respectively.

2.2. Preparation of geopolymer

Metakaolin, slag, boron waste colemanite, Rilem sand, sodium silicate, and sodium hydroxide were used for the preparation of geopolymer. The amount of standard mixture used in the geopolymer mixture is show in Fig. 1 for 450 g (10% colemanite + 90% metakaolin by weight). Slag was added at a constant rate (13% of the binding materials' mixture) for increasing the calcium content in the mixture. In preparing this mixture, the binder/activator ratio was considered as 1/1. The sodium hydroxide/sodium silicate ratio in the activator mixture was determined to be 1/2. The Rilem sand used as aggregate material was added to the mixture 2.5 times the binding materials' mixture.

The procedure followed in the geopolymer composite mixtures as described in more detail as follows: First, the NaOH solution (12 M) prepared before the day of the mixture and allowed to cool at room temperature was stirred with sodium silicate on the day of the mixture. In preparing the standard geopolymer composite mixture, the binder material with 405 g of metakaolin and 45 g of substitute material colemanite, was mixed with the activator (a total amount of NaOH and Na_2SiO_3 of 450 g) utilizing a stirrer drill. After this step, 60 g of slag was added at a rate of 13% of the binder materials' mixture for increasing the calcium content and reducing the setting time. Slag is formed by the melting of metal ore with a high Ca composition of 36% and has a high alumina and silica content. Slag has been used to illustrate the role of calcium in the hardening behavior of geopolymers. Also, slag is important for both early and late age characteristics. Although colemanite waste contains CaO at a rate close to the slag, it causes the setting time to be extended

Table 1
The raw materials' chemical composition.

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

Table 2
Properties of the fibers.

Fiber Type	Diameter (μm)	Length (mm)	Specific Gravity	Nominal Tensile Strength (MPa)	Aspect Ratios
PL	63	10	0.90	275	101.89
PA	55	10	1.14	900	115.5

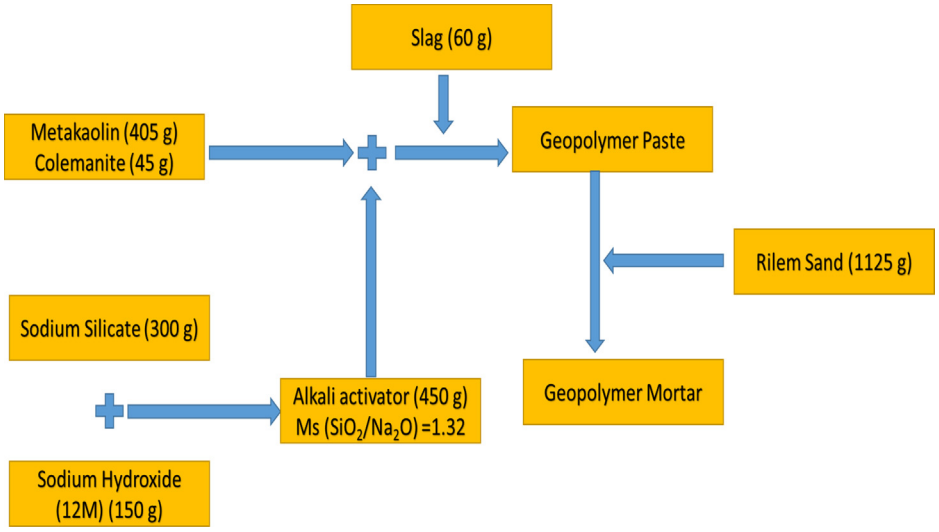

Fig. 1. Sample mixing procedure and contents (g).

due to its high B_2O_3 content. Increasing the soluble B_2O_3 concentration in the pore solution increases the initial solubility of CaO. However, over time, the Ca^{2+} cations and OH^- anions in the pore solution decrease to form CBH_6. Over time, CBH_6 covers the surface of the grains and the reaction slows down. The higher the B_2O_3 ratio, the slower the reaction. Similar reaction occurs between B_2O_3 and MgO. The result may be attributed to the combined effect of MgO and B_2O_3 increased setting time more than any single. Due to this situation, the setting time increases with the effect of colemanite, which has a high B_2O_3 ratio. To prevent this situation, slag has been added to shorten the setting time as a source of calcium [26]. In the matter of slag-based geopolymers, it is important to mention that different scientists make different suggestions on this subject. In the case of using slag, it is named AAM by various researches, while Davidovits [2–3] stated that a geopolymer will be obtained by using metakaolin and slag. Since there is no common decision in the scientific world, the geopolymer definition was preferred in this study. Also in this study slag was used at a very low rate. It is necessary to point out that even if the geopolymer technology and the concepts of alkali-activated materials are researched since the last mid-century, there is still confusion and no overall accepted consensus considering the terminology of these materials. The most common descriptions, which are found in literature, are "alkali-activated materials", "inorganic polymers" and "geopolymer". Many other nomenclatures are formed by combinations of these terms. However, still today, there is a disagreement in the research community, whether "geopolymer" can be considered as a subset of "alkali-activated binders". In the last step, Rilem sand was added at a rate of 2.5 times the binding materials' mixture. Unlike the fiberless mixture, polyolefin and polyamide fibers were added to the alkali mixture and mixed while preparing the fiber-reinforced mixes. The fibers were carefully added slowly to achieve a homogeneous distribution. The microfibers, which are particularly conjoined, were placed into small pieces. The mixture was visually checked to prevent agglomeration and mixing was continued until a homogeneous mixture was obtained. In this way, it was tried to create a uniform suspension and to overcome its weak distribution. Then the fiber activator mixtures were mixed with the binder material and aggregate, respectively. 0.5%, 1%, and 1.5% ratios were used by volume during the mixing of fibers. Then the geopolymer specimens were placed in the molds and subjected to vibration.

Since slag was used in the prepared samples, the specimen was removed from the mold after 2 h. The samples were then kept at room temperature conditions [23 ± 2 °C] and relative humidity of [90 ± 5%] for 24 h. This situation has been applied since it is known that the high relative humidity contributes to the improvement of strength and affects the shrinkage of the geopolymer mortar in the room conditions applied before the heat curing [27]. After keeping samples at room conditions for 24 h, samples were placed in the drying oven. Two dissimilar curing methods (wetting–drying curing and heat curing) were used when preparing the mixture. The curing methods' initial stages were the same. The samples were then placed in a non-combustible furnace bag and stored in the

oven at 60 °C for 72 h. The two methods then differed. In method 1 (heat curing), geopolymer specimens were stored in plastic boxes till the test day. For the second method (wetting–drying curing), in addition to method 1, specimens were exposed to a wetting–drying test curing method consisting of 1 cycle. The wetting–drying curing method, consisting of 1 cycle, involved keeping the samples in water for 3 days and then in the drying oven (using 60 °C) for 3 days. Then, the samples were stored in storage boxes similar to method 1 till the test day.

Seven geopolymer specimens were manufactured for each curing method. The control sample was produced with 90% metakaolin and 10% colemanite. The fibers were supplemented to the control mix as 0.5%, 1.0%, and 1.5% by volume, respectively. Sample 1 was the control sample, while samples 2, 3, and 4 were polyolefin reinforced samples with 0.5%, 1.0%, and 1.5% by volume, respectively. Samples 5, 6, and 7 were polyamide fiber reinforced samples with 0.5%, 1.0%, and 1.5% by volume, respectively. While the first 7 series were produced with heat curing, the second 7 series were manufactured with wetting–drying curing. The abbreviation W indicates that these samples were manufactured with the wetting–drying curing method.

2.3. Test procedure

Compressive and flexural strength results of 14, 56, 90, and 365 days were determined to see long term effects of geopolymer samples. ASTM C109 [28] was used for the compressive strength test of 50 mm cubic samples and the third-point loading test was applied for the flexural strength of 40x40x160 mm prism samples at 130 mm span length according to ASTM C348 [29]. These tests were carried out at a 0.5 mm/min loading rate. Three samples were used for each test. At the end of 365 days, 14 series were exposed to 300, 600, and 900 °C. One day before the test, the specimens were dried with 100 °C. The rate of temperature rise was 5 °C/min. After approaching the target temperature, the geopolymer specimens were maintained at a constant temperature for 1 h. To prevent thermal shock, the samples were kept in the oven with the door open state for 24 h. Strengths and weight loss were determined pre and post the high-temperature test. Also, the correlation between weight-loss and flexural strength was examined after 900 °C. A visual examination of the samples was performed after the tests. Also, SEM, TGA-DTA, and FTIR analyses were made pre and post the high-temperature test.

3. Results and discussion

3.1. Strength results

When the results of 14 mixes were examined, it was seen that fiber enhanced the compressive strength by 1%, and it decreased by 1.5%. The increase in compressive strength here was mainly due to the interaction of fibers with advancing cracks. As the compressive load increased, the lateral tension increased and so the cracks began to advance. The advancing crack formed the debonding at the matrix-fiber interface as it approached a fiber through tensile stresses perpendicular to the path it followed. As the advancing crack reached the interface, the fiber encountered a blunting process due to the debonding crack present. Thanks to the blunting process, the stress concentration at the crack-tip was reduced and the progression of the crack was prevented and even its path was changed. Such blunting, blocking, and further diverting of the crack allowed the mortar samples to withstand the additional compressive load, thereby increasing the compressive strength compared to non-fiber samples. This explained the situation was also supported by SEM micrographs (Fig. 2). SEM micrographs

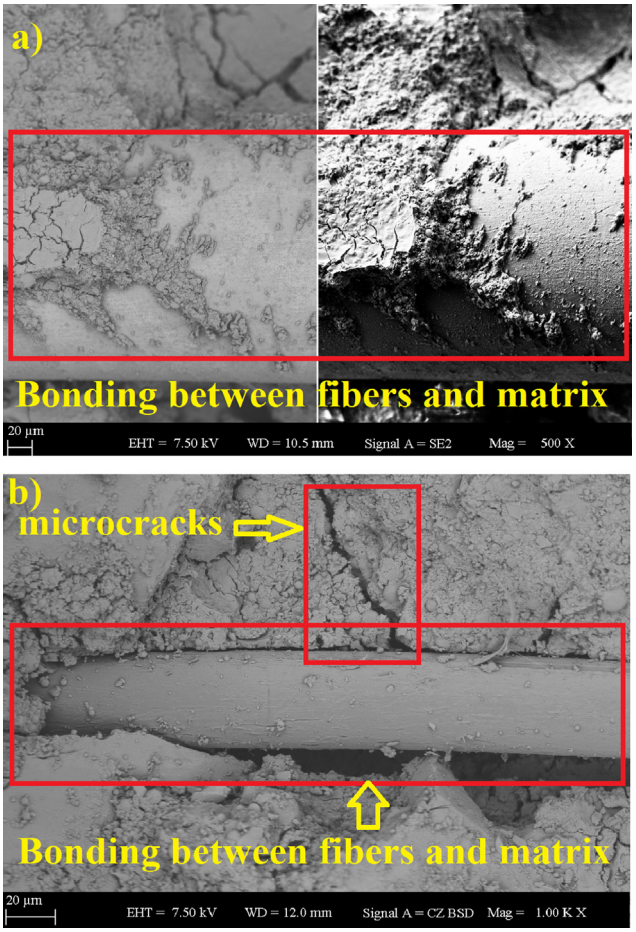

Fig. 2. SEM images for sample 7-W after 14 days.

show an acceptable degree of binding between the fiber and the matrix. Also, the formation of a good interface bond has been observed. Also, it is shown in SEM micrographs that the microcracks formed are stopped with fibers.

Furthermore, it was envisaged that these fibers appropriately dispersed in the mixing water and could disperse themselves better and thereby increased compressive strength. That was since polymeric fibers were well dispersed in the matrix, they helped to carry the applied stresses. Thus, the fibers and mortars could distribute the incoming compressive load utilizing the stress transfer mechanism at the fiber–matrix interface. Another possibility was that these fibers increased the plasticity of the composites so that they flowed under stress without breaking [30–32]. When the strength results were compared for two fibers, PA fibers provided better structural performance due to their higher tensile strength properties and good bonding formed by the geopolymeric matrix [21]. The compressive strength results decreased when the usage rate of the fibers was 1.5%. The reasons for this decrease were the fibers' low density and flocculation. This led to a decrease in the compressive strength and unit weight results and an increment in the water absorption results. Also, it has been seen that workability decreased with flocculation [33].

The addition of polyolefin and polyamide fibers to the composites significantly increased the ability of the cracks to stop, ie the cracking resistance, and retarded the macroscopic level of the microcracks [21]. The increase of fibers crossing the crack surface was one of the major reasons for increasing the mortar's flexural strength since it reduced the crack advancing. During loading, the microcracks were connected and formed larger cracks, while

the fibers connected both sides of the fracture surface and acted as bridges and increased the peak load. This means an improvement in load-bearing capacity after peak load and an increase in flexural toughness. The higher the fiber content ratio relative to the control sample, the greater the increase in response after cracking. For these reasons, as the fiber ratio increased, the flexural strength results increased [23–24].

When the results were analyzed, it was seen that the results of flexural and compressive strengths increased with the wetting–drying curing effect. This situation is consequent with other studies. Petermann et al. showed when this curing method was applied, the alkali-activated mortar had the lowest porosity and the highest strength value [34]. At first, geopolymerization occurred more when wet curing was applied, while in the next level dry curing enhanced compressive strength. According to wetting/drying and dry curing methods, the alkali-activated mortar had lower strength with equal porosity range in wet curing. For instance, in optimal relationships, the compressive strengths were obtained as 61.2 MPa and 52.7 MPa at a porosity of 10% in the wetting/drying and wet curing methods, respectively. Here, the dry curing portion had a distinct effect on the porosity and enhanced the strength results of the alkali-activated mortar, because the dry curing strengthened the binding property of the geopolymer structure and increased the strength of geopolymerization products. Wet curing enhanced the high calcium compounds' hydration reactions in AACM binders. For these reasons, it has shown that the wetting/drying curing is the ideal method in the alkali-activated mortar.

Figs. 3-4 show the 14, 56, 90, and 365-day results of compressive and flexural strengths. Comparing the 14-day results with the 56, 90, and 365-day results, the 90-day results showed a reduction according to the 14-day results. This decreased rate decreased in the following days and 365 days results were close to 90 days. This strength decrease was due to the use of high-temperatures for curing. In the wetting–drying curing, the decrease rate was lower over time because of the curing property. While curing, using high-temperature seemed to support the dissolution of solid binder materials and the formation of reaction products, this was thought to contribute to early-age strength development. It has been found that heat energy with optimum curing temperature controlled the geopolymerization reaction and hence strength development. However, the reaction thus developed had negative effects on the quality and microstructure of the reaction products. Puertas et al. [35] stated that diffusion was a factor that determined the rate of geopolymerization at high-temperatures and that the reaction products would be collected close to the grains of the binder materials. In the later stage, the microstructure gradually became inhomogeneous, leading to the reduction of continuous reactions during aging. In more detail for this phenomenon, the increasing temperature increased the dissolution of reactive species, ie, binding materials. This dense reactive process produced a larger quantity of products with a more heterogeneous and densely dispersed microstructure than the one obtained when the curing temperature was lower. This paste densification resulted in a delay in subsequent reactions, which made diffusion difficult at longer reaction times. Similar results were obtained when the effect of curing temperature on alkali activation was studied by other authors. Different studies have shown a decrease in strength after 28 days [36–37]. Here, gel chemistry has been shown to influence the long-term behavior of geopolymers.

When the 14-day compressive strength results were examined, the highest results with heat curing were obtained as 61.75 MPa and 62.99 MPa for samples 5 and 6, respectively. With the wetting–drying curing, these values increased and became 66.24 MPa and 67.75 MPa, respectively. When the 90-day results were examined, these results decreased. The results of samples 5 and 6 were obtained as 55.89 MPa and 56.73 MPa, respectively. These values increased with the wetting–drying curing and became 57.92 MPa and 58.44 MPa, respectively.

When the 14-day flexural strength results were examined, the highest results with heat curing were obtained as 12.36 MPa and 12.89 MPa for samples 6 and 7, respectively. With the wetting–drying curing, these values increased and became 12.79 MPa and

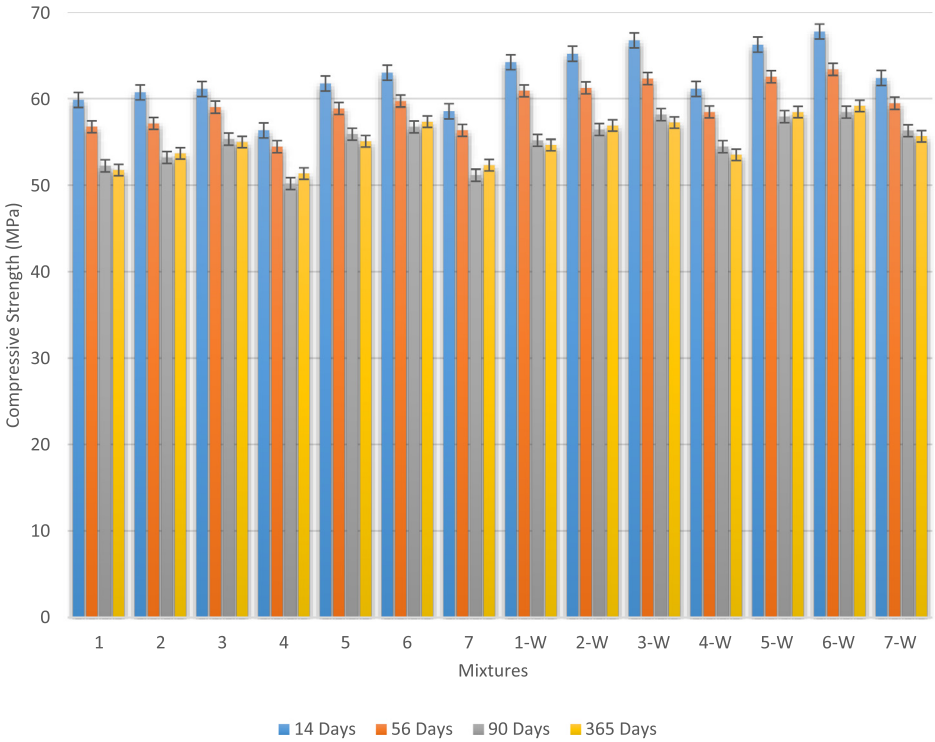

Fig. 3. The mixes' compressive strength values.

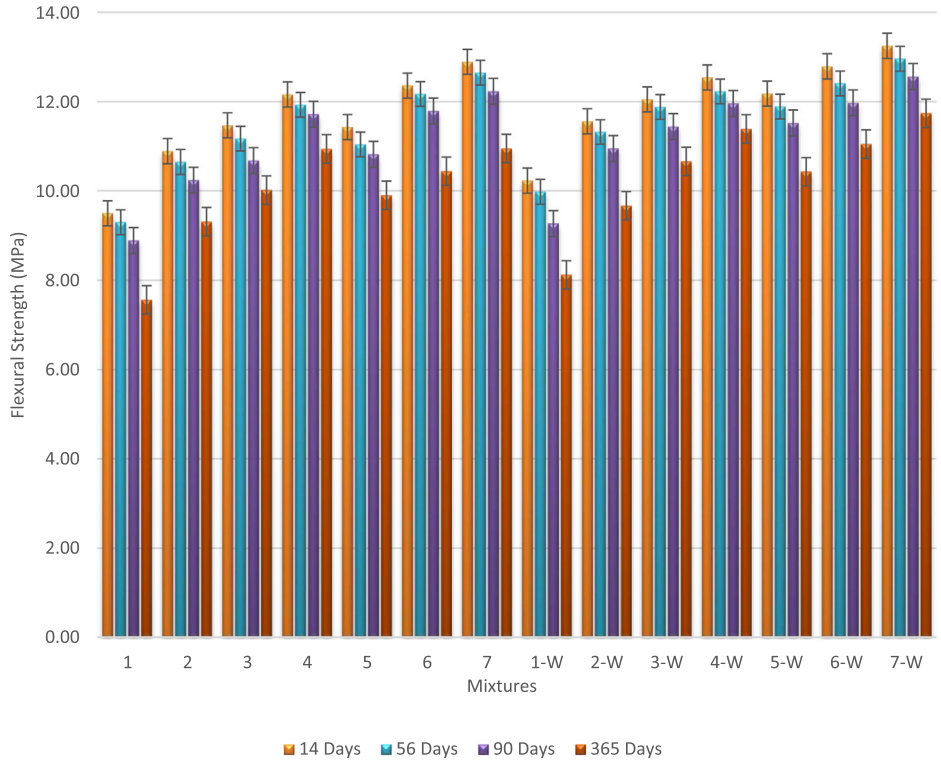

Fig. 4. The mixes' flexural strength values.

13.25 MPa, respectively. When the 90-day results were examined, these results decreased. The results of samples 6 and 7 were obtained as 11.79 MPa and 12.23 MPa, respectively. These values increased with the wetting–drying curing and became 11.97 MPa and 12.56 MPa, respectively.

To support the results found in this research, SEM analysis was performed 365 days after production to examine the microstructure of sample 7-W (Fig. 5). The purpose of this analysis is to examine the relationship between the results of strength and microstructure. When SEM micrographs were examined, it was seen that micro cracks around the geopolymer matrix began to occur later with aging due to the curing temperature effect. The spread of cracks was followed by the formation of air bubbles and pores. This situation explains the loss of strength with aging. However, it was observed that the continuity of the geopolymer matrix, where this situation was limited, was preserved [37].

3.2. High-temperature test

3.2.1. Analyzes and visual inspection

Changes in the geopolymer samples' surface after the test were examined (Figs. 6-7). Photographs were taken immediately after the samples were taken out of the oven. After exposed to 600 °C, the change in the color was seen in parallel with the decrease in compressive strength results. While the decrease in compressive strength continued to increase in the 600 °C-900 °C temperature range, the cracks began to be seen. With the effect of 900 °C, significant color changes were observed on the geopolymer samples' surfaces, but the surface cracks remained limited. This is compatible with the fact that the specimens retain their stability after high-temperature. The specimens had a slightly brittle structure and the surface tended to be a little coarser [21,38]. The main reason was the damage of the main chains (Si-O-Al) of the geopolymeric system by the effect of temperature.

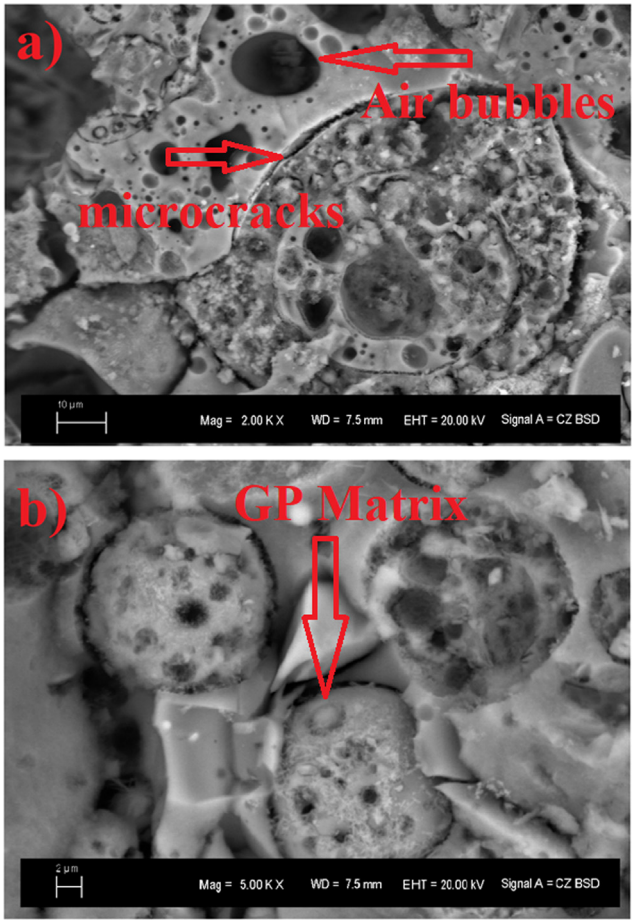

Fig. 5. SEM images for sample 7-W after 365 days.

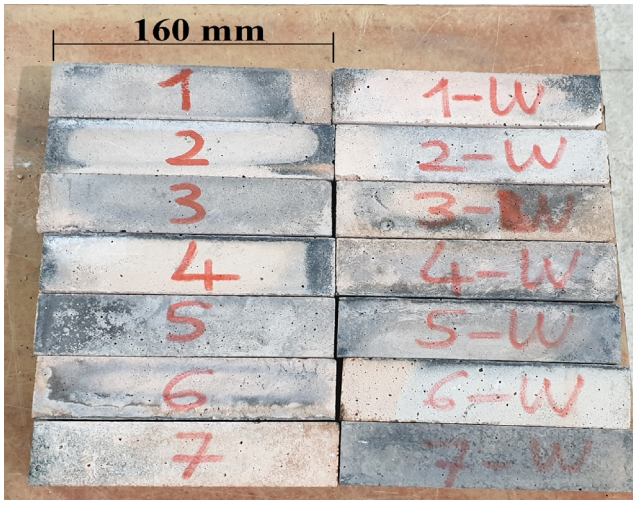

Fig. 6. Geopolymer samples after 600 °C.

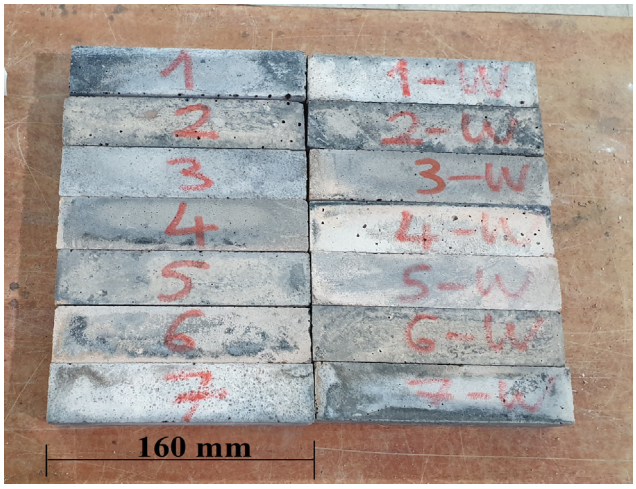

Fig. 7. Geopolymer samples after 900 °C.

The TGA-DTA curves are given in Figs. 8-9, before and after 600 °C for sample 7-W. Blue curves correspond to weight loss. For sample 7-W, TGA analysis showed a weight decrease of 0.1% before the 600 °C temperature effect. As can be seen, weight loss became very limited. After the high-temperature influence, this ratio increased to 6.38%. The results showed that the increase in the rates was limited after high-temperature. This showed that the stability of geopolymer composites was maintained despite the high-temperature effect. The majority of the weight loss changed from 0 to 300 °C, which was caused by the bound and free water's evaporation in the geopolymer matrix. Also, endothermic peaks can be seen in DTA curves. The weight losses were fixed after 700 °C. This was because of the water evaporation which was chemically bonded to the geopolymer and hydroxyl groups, OH [39–40].

Scanning electron microscopy (SEM) was performed on sample 7-W after exposure to a temperature of 600 °C to obtain information about the geopolymer matrix and its degree of bonding (Fig. 10). Also, when the microstructure analysis was examined in detail, it could be possible to provide an opinion about the relationships between the mechanical and microstructure properties of the geopolymer specimens after the high-temperature. The microstructure of the samples was maintained after 600 °C and no significant damage was observed. The main reasons for the microstructure to become more porous after the high-temperature were weight loss after 500 °C, matrix decomposition, and phase transformation. In Fig. 11, although the microstructural cracks and deformations appeared to some extent, it was seen that the microstructure did not change after the thermal attack. The reaction products formed on the geopolymer's silica-rich gels led to a high level of condensation and engendered the structure to fall after 600 °C, triggering a decrease in pore volume. Besides, the first condensation temperature has been found to decrease later than the increase in Si/Al ratio [41]. These factors led to a reduction in pore for the synthesized geopolymers. The decrease in the water loss and pore volume because of evaporation and dehydroxylation in the geopolymer after the thermal attack led to structural collapse or formation of condensed defects. Also, these effects caused a loss of strength. Also, the new crystal phases which were constituted by the redistribution of atoms because of uncontrolled diffusion were another cause of loss of strength. Despite these

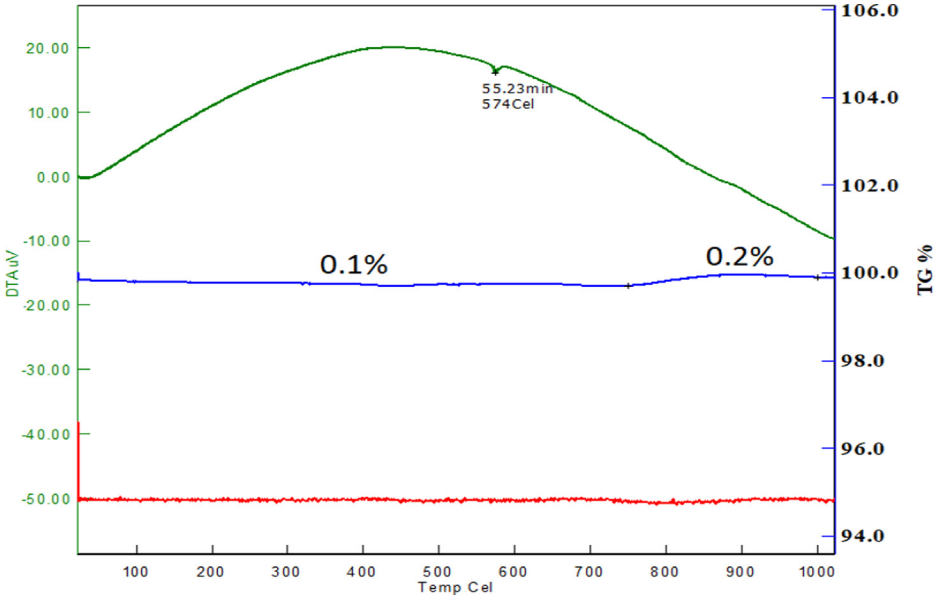

Fig. 8. TGA-DTA results for sample 7-W before the high-temperature effect.

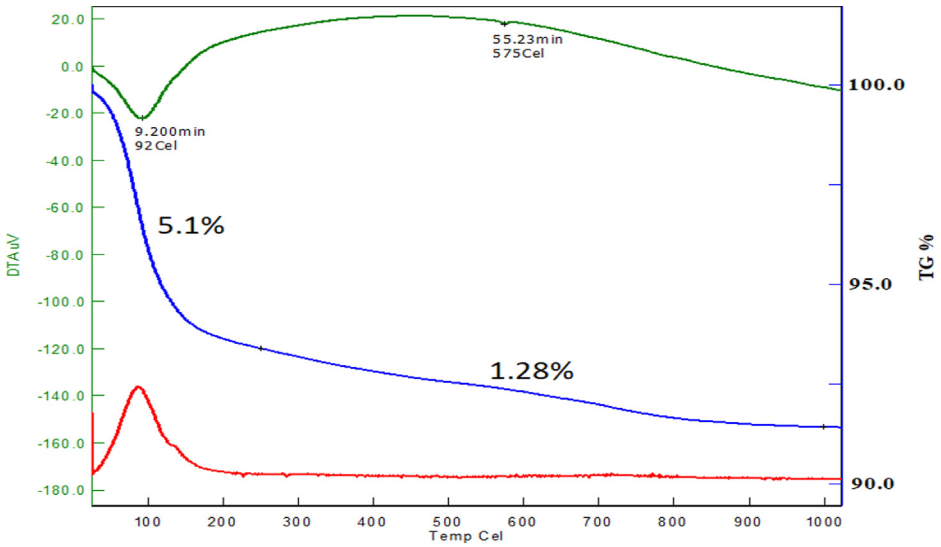

Fig. 9. TGA-DTA results for sample 7-W after 600 °C.

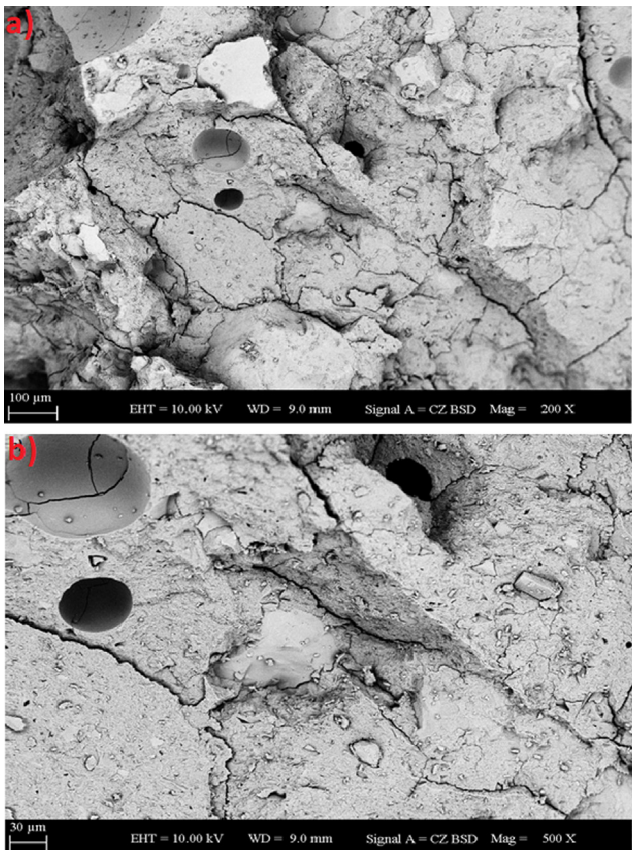

Fig. 10. SEM images for sample 7-W after 600 °C.

occurrences, the metakaolin-based geopolymers' basic structure has been maintained and low microstructural degradation has been observed at high-temperatures, and stability has been maintained [21,42]. However, it has been seen that matrix continuity and good bonding were maintained in geopolymerization occurring in geopolymer samples. It was observed that the overall microstructure of the homogeneous matrix formed in the alumino-silicate gel was preserved after testing, mainly in the geopolymer sample before high-temperature.

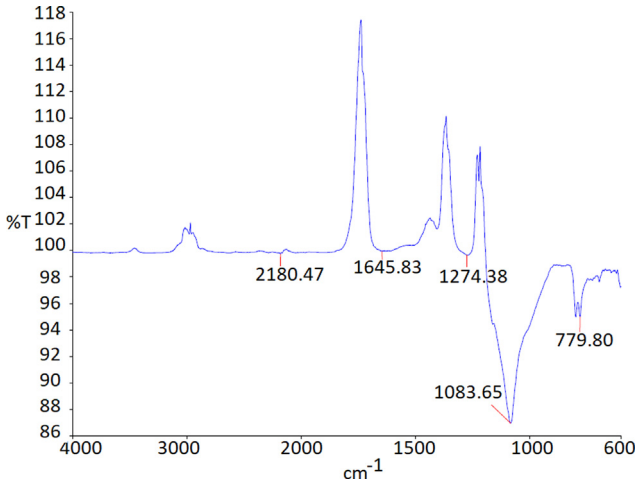

Fig. 11. FT-IR results of sample 7-W before the high-temperature effect.

Figs. 11-12 exhibit the FT-IR spectra of sample 7-W pre and post 600 °C. The wavelength before the 600 °C temperature was 1083.65 cm^{-1} while the wavelength after the 600 °C temperature

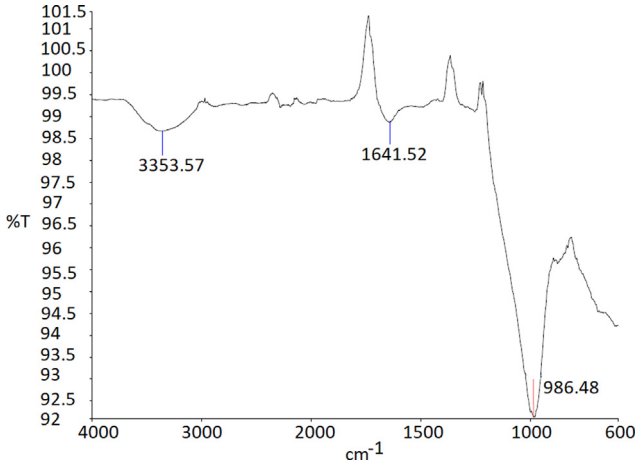

Fig. 12. FT-IR results of sample 7-W after 600 °C.

was 986.48 cm^{-1}. The Si - O - Al bonds correspond to the asymmetric stretching vibrations here, while the wavelengths here indicate this bond. Although Si-O-Al bonds exhibited a decrease compared to the pre-high temperature results, it was found that the sample retained the Si-O-Al bond structure. The band's intensity before the experiment was between 2180.47 and 1274.38 cm^{-1}, and then between 3353.57 and 1641.52 cm^{-1} [43–44].

3.2.2. Strength results

300, 600, and 900 °C temperatures were applied to determine the mechanical properties that occurred when high-temperature was applied to geopolymer samples. In this study, the temperatures were applied to the samples at the end of 365 days, not at the end of 14 or 28 days. Thus, the geopolymer samples' long term mechanical properties were determined and this study was supported by durability properties. Also, the roles of polyamide and polyolefin fibers and curing conditions were studied with high-temperature effects. The flexural and compressive strength values resulting from high-temperature effects were thus compared with the 365-day results at 23 °C (Figs. 13-14). After 500 °C, a significant reduction was observed when the strength results were examined. The results of geopolymer samples' compressive and flexural strengths were subject to reduction due to the free water evaporation caused by the thermal reaction mechanism present after 500 °C and the geopolymeric matrix's dehydration and the fibers' melting due to the high-temperature. In the process from 600 °C to 900 °C, these reduction rates started to increase [45]. Also, the flexural strength results of geopolymer samples were significantly affected by microstructural defects caused by problems such as the cracks' propagation at high-temperatures and growth in porous structures [46].

When heat curing was applied to the samples, the compressive strength losses were between 41.08% and 46.01% at 300 °C, between 67.47% and 69.77% at 600 °C and between 84.37% and 89.87% at 900 °C, respectively. When wetting–drying curing was applied to the samples, the compressive strength losses were between 38.95% and 43.78% at 300 °C, between 62.56% and 66.27% at 600 °C and between 82.10% and 84.90% at 900 °C, respectively. When heat curing was applied to the samples, the flexural strength losses were between 24.75% and 32.28% at 300 °C, between 53.61% and 62.57% at 600 °C and between 76.35% and 81.75% at 900 °C, respectively. While wetting–drying curing was applied to the specimens, the flexural strength losses were between 21.29% and 29.80% at 300 °C, between 55.02% and 59.88% at 600 °C and between 76.32% and 78.45% at 900 °C.

The main factor in adding fibers to cemented or geopolymer composite materials was to obtain higher results in flexural strength and increase flexural resistance [47]. It has been proven that polymer fibers were used to strengthen the composite structure and the fibers used in this way increased the flexural strength and toughness [48–50]. Celik et al. compared the flexural strength of the polyamide and polyolefin fiber-added samples concerning the control sample. The mechanical integrity of polyamide and polyolefin fibers was maintained to a certain extent under the high-temperature influence. The fibrous materials' crystalline phases had a good effect on the mechanical properties due to their homogeneity and fine distribution [22]. In this study, the performance observed before the high-temperature was also observed after high-temperature. The fiber additive was found to increase flexural strength results. But the compressive strength results showed a decrease in the use of 1.5% fiber. It was seen that as the fiber ratio increased, the bonds between the geopolymer or cement matrix and the fibers weakened, and the matrix was adversely affected [51–52]. This has been found to adversely affect pore characteristics and workability. It was thought that there was a loss in the compressive strength results because of this situation.

When the wetting–drying cure was performed, new crystalline geopolymerization products were formed and geopolymerization's continuity was ensured. This improved positively the results after high-temperature [9]. Arslan et al. compared the results of curing methods following the high-temperature test. The compressive strength results improved because wetting–drying curing reduced dehydration by providing additional water for geopolymerization [53].

In this study, the results of the compressive strength of polyamide-added samples after 600 °C were between 16.16 MPa and 18.65 MPa. The results increased with wetting–drying and were between 19.94 MPa and 22.15 MPa. The flexural strength results of polyamide-added samples after 600 °C were between 4.08 MPa and 5.08 MPa. The results increased with wetting–drying and were between 4.56 MPa and 5.24 MPa.

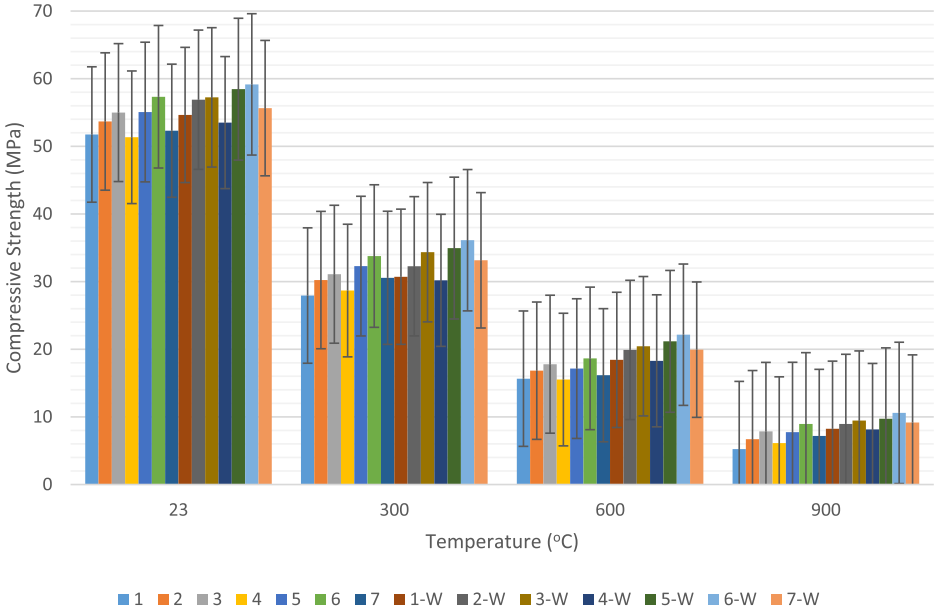

Fig. 13. Compressive strength results after the high-temperature effects.

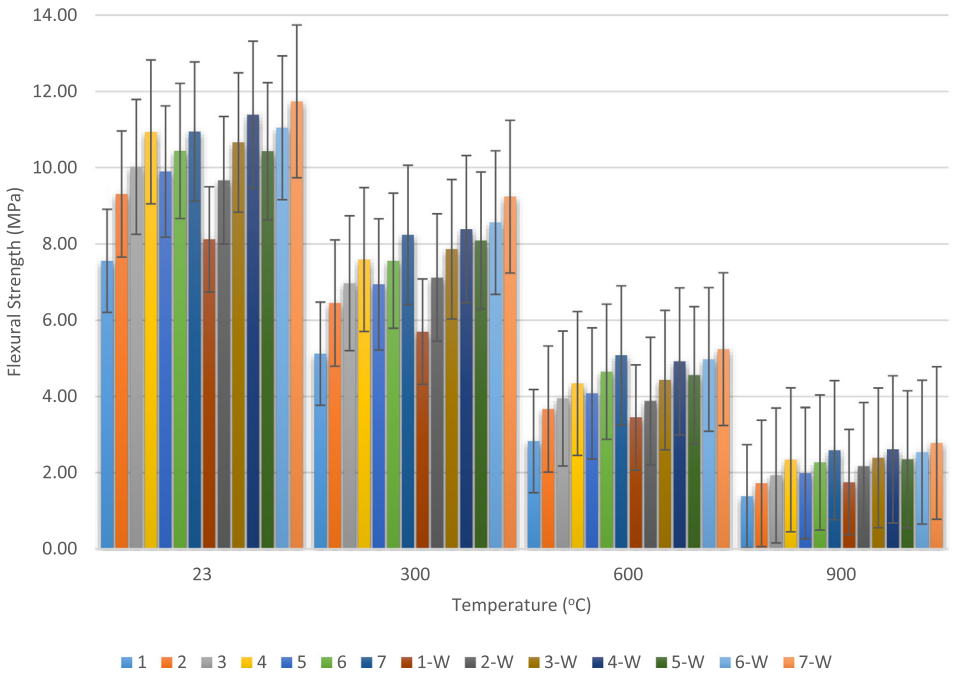

Fig. 14. Flexural strength results after the high-temperature effects.

In this study, the results obtained when the high-temperature test was applied to the geopolymer samples at the end of 365 days instead of 14 or 28 days did not change significantly due to the geopolymer sample's compact structure. In the long term, limited losses in the amount of strength did not prevent this compact structure [36].

3.2.3. Weight loss results

Following the high-temperature test, weight losses for samples are given in Fig. 15. The weight losses in polyamide-added samples changed from 2.02% to 2.35% at 300 °C, from 4.08% to 4.38% at 600 °C, and from 5.31% to 5.62% at 900 °C when heat cured. In the case of wetting–drying curing, the weight losses were reduced and changed from 1.77% to 2.16% at 300 °C, from 3.62% to 3.93% at 600 °C and from 5.08% to 5.43% at 900 °C. Microstructure damage occurred when the geopolymeric matrix was exposed to water evaporation and dehydration because of high-temperature effect and this resulted in weight loss [38]. When all results were evaluated, it was found that the weight loss for the fibrous specimens was less than the control specimen. Thus, a significant reduction was seen in weight loss with the fibers used. Also, it was shown that fiber length improved the performance in case of high-temperature. The addition of colemanite affected the metakaolin-based geopolymer structure in general and reduced weight loss. As a result of increasing temperature values, a reaction of dehydration occurred in the samples' structure and the sample's moisture escaped from the sample with moving to the outer surface. This caused internal damage to the microstructure and triggered weight loss in the samples. Before 600 °C, the major reason for weight loss was the co-evaporation of free water and concentrated hydroxyl groups. After 600 °C, interfacial reactions between fiber and matrix triggered weight loss. Significant fiber degradation increased weight loss. On the other hand, weight loss was reduced when the fiber was used [54]. Thus, the samples lost some of their mechanical properties, and fractures were brittle [55].

3.2.4. Correlation relationship between flexural strength and weight-loss

In this study, the correlation between flexural strength and weight-loss was investigated after 900 °C (Fig. 16). Thanks to this method, the state of consistency between the two specified features were determined. R^2 is a factor that shows the degree of correlation, and values higher than 0.80 correspond to a consistent result. The R^2 value in this study is 0.96 and shows a satisfactory result. The results obtained for this study are also compatible with the results in the literature [10].

4. Conclusions

For this study, geopolymer specimens' engineering properties after one year using metakaolin and colemanite waste with polyolefin and polyamide fibers were examined under the effect of heat curing method and wetting–drying curing method:

- When the results are analyzed in detail, it was seen that if the fibers were used at 1%, it increased the compressive strength results, while the use of more rates affected the situation negatively. The flexural strength results were different, and the highest flexural strength was obtained at the highest-fiber ratio. The fact that PA fibers had higher tensile strength than PL fibers and formed a stronger bonding degree in the geopolymeric matrix, provided higher results. It was observed that the results were higher than the heat curing with the wetting–drying cycle effect. This happened with the wetting–drying curing effect, which was made in addition to the heat curing. Hydration reactions were maintained by reacting the particles with wetting that did not react. With the drying curing method, the strength of geopolymerization products was increased and its binding property was increased.
- When the strength results on four different days were analyzed, it was seen that the 14-day results were the highest values and the decrease occurred in the following days (56, 90, and 365-day results). It was observed that the decrease ratio reduced after 90 days and the strength results of 365 days were close to 90 days. The main reason for this situation was the use of temperature for curing. Using a temperature of 60 °C supported the dissolution and reaction of solid binder materials. This situation provided early strength. However, this situation disrupted

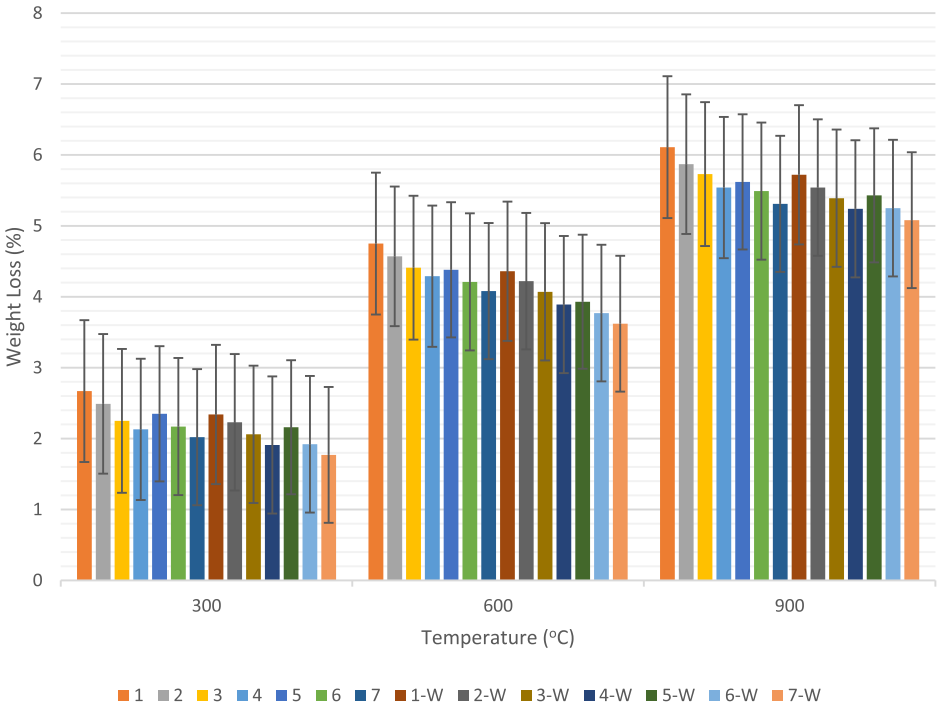

Fig. 15. Weight-loss rates after the high-temperature effects.

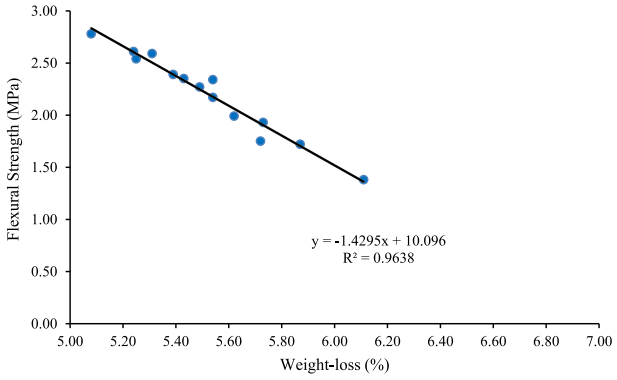

Fig. 16. Correlation relationship between flexural strength and weight-loss after 900 °C.

the homogeneity of the microstructure and the quality of the reaction products in the future and adversely affected the reaction. Thus, with aging, a decrease in strength occurred. This situation was lower with the application of wetting–drying curing.

- Also, unlike other studies, the high-temperature test was carried out after 365 days, not after 28 and 90 days. Thereby, unlike laboratory conditions, tests that are more suitable for real-life conditions were performed. Although the decreases in mechanical properties up to 365 days, the geopolymer compact matrix structure has been observed to maintain the stability of the samples after the high-temperature test.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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