



# Effect of Waste Filler Materials and Recycled Waste Aggregates on the Production of Geopolymer Composites

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## Abstract

In this research, the performance of fly ash/GGBS geopolymer mortars made with different quarry waste powder as filler materials by substituting the fine recycled aggregate (RS) with different ratios. Also, it was evaluated based on mechanical, physical, freeze–thaw, and microstructural analysis. Limestone waste (L), marble waste (M), and basalt waste powder (B) were used as filler materials developing eco-friendly and economical geopolymer from industrial waste as a promising sustainable area of research. Strength properties, ultrasonic pulse velocity, physical properties, freeze–thaw, XRD, and SEM analysis of geopolymer samples were investigated. The results revealed that using waste filler materials together with recycled aggregate effectively improves the mechanical properties of geopolymer composites substituting three different filling materials affected water absorption positively, strength properties, and freeze–thaw results. Current findings point to a potential solution. Successful use of fly ash, slag, recycled aggregate, and quarry waste has been achieved. The output of the study is expected to result in effective and environmentally friendly management of recycled wastes.

**Keywords** Geopolymer · Fly ash · Ground granulated blast furnace · Freezing–thawing · Recycled aggregate · Waste filler materials

## 1 Introduction

The cement industry is not included in an environmentally friendly production process class. The cement industry is recognized as one of the leading causes of CO<sub>2</sub> emissions. Cementitious binders were partially or fully replaced with waste materials and industrial by-products to transform the construction industry into sustainable applications [1, 2]. It has been proven that the strength, durability, and workability of concrete and mortars can be increased by using recycled materials. Today's common cement substitutes are binders such as fly ash, slag, and silica fume [3, 4].

A significant amount of energy is used with the quarry and refining activities to obtain aggregates. Mining operations in aggregates production have become one of the leading environmental problems due to both esthetic and energy

problems. For these reasons, recycled aggregates have been an exciting field [5–7]. In addition to energy and environmental problems, the cost of river sand has accelerated the search for alternative sands. Recycled aggregates are obtained due to demolition structures such as bridges, buildings, and pavements. Therefore, recycled concrete has been evaluated as source material to reduce natural aggregate consumption [8]

Fly ash is a common and available material worldwide. The fact that fly ash is a by-product with pozzolanic properties plays an essential role in the construction industry. Due to the importance of fly ash, many geopolymer researchers have studied [9–12] durability, mechanical properties, and microstructure. Fly ash has emerged as an alternative to Portland cement due to its low carbon footprint, good mechanical properties and superior durability. Fly ash, mainly Class F fly ash, is a good candidate for geopolymer materials.

Basalt is a hard and dense igneous rock. Basalt stone can be used as aggregate, curbstone, paving stone, airfield, and railway ballasts [4, 13, 14]. When basalt stone is used in crushed form, it provides high abrasion resistance. It creates a tight grain structure and reduces water absorption and abrasion loss rates. Due to its dense structure, it also contributes to the increase in specific gravity [15]. Previous studies [16, 17]

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investigated geopolymer mortars' mechanical and durability properties produced with recycled fine aggregate and basalt sand. Researchers have shown that basalt sand with recycled aggregate significantly increases the strength of the mortars. The study also stated that basalt sand effectively maintained the strength of mortars under the influence of high temperatures. Venyite et al. [18] investigated the effects of combined metakaolin and basalt powder additives on laterite-based geopolymers activated with rice husk ash/NaOH solution. The research revealed that basalt powder did not contribute to geopolymerization at room temperature or contributed insignificantly. The use of basalt powder reduced the strength of the samples in the study but improved the microstructure and hardening times.

A large amount of marble dust waste is generated from industrial activities such as the processing and mining marble stones. Marble dust waste spreads due to winds and causes adverse environmental effects. For this reason, in recent years, marble dust waste has been used as a natural aggregate substitute or cement substitute to produce concrete mixes [19]. Marble wastes are green materials that do not contribute to CO<sub>2</sub> emissions. It is stated that geopolymer materials (brick, cladding tiles, block wall elements) produced with marble waste can be a great environmentally friendly material [20]. Khyaliya et al. [21] investigated mortars' strength and durability properties produced with Portland cement, river sand, and marble dust waste. The results revealed that the substitution of marble powder to fine aggregate improved the mechanical and durability properties of the mortars. Khodabakhshian et al. [22] investigated the durability properties of ordinary Portland cement concrete with partial replacement of marble dust waste and silica fume. The study revealed that 5% replacement of ordinary Portland cement with marble powder increased the compressive strength by 4%, and the weight loss of the samples exposed to sulfuric acid attack decreased with the increase in marble powder replacement. Saloni et al. [23] investigated the strength and durability properties of fly ash-based and marble aggregate alkali-activated concrete. It has been reported that the addition of marble aggregates up to 50% in the mixture increases the flexural, compressive, split tensile, and modulus of elasticity values. However, it has been stated that more than 50% marble substitution causes lower strength values due to the non-homogeneous mixture. The resistance increased with replacing waste marble aggregate in the mixtures. Researchers have revealed that penetrability decreases with waste marble aggregate replacement. The use of marble wastes resulting from marble production as a substitute for aggregate is essential in solving the existing problems.

On the other hand, limestone is an important raw material for producing binders with a low environmental footprint and is a common and readily available raw material. According to

international standards, it is stated that limestone can be used as a substitute for Portland cement up to 35% [24]. The use of limestone in Portland cement systems has demonstrated many advantages [25]. As in Portland cement systems, limestone is also used in geopolymer systems.

Qian et al. [26] investigated the effect of limestone waste on the fresh and hardened properties of metakaolin-based geopolymers. Researchers used limestone as filling material from 10 to 30%. The results showed that the addition of extra limestone resulted in better particle distribution, thus a better improvement in rheology and strength. Cwirzen et al. [27] replaced limestone with metakaolin at 30, 50, and 70 percent in geopolymer production. In addition, the researchers cured the samples at 30 and 50 degrees. The binders are activated with 3 and 5 molar sodium hydroxide. The results showed that the compressive strength of geopolymer pastes decreased when three molar sodium hydroxide was used. It was observed that the compressive strengths increased in the 30 and 50% replacement of limestone in the activation of 5 molar sodium hydroxide. Rakhimova et al. [28] investigated the effects of limestone fineness, concentration, and chemical–mineralogical composition on various properties of slag-based alkali-activated mortars. In the study, compressive strength of 26.2–48.8 MPa was obtained up to 60% limestone content in the 28-day strength of alkali-activated slag mortars. The satisfactory bond strength of the binder gel and limestone led to an improvement in the physical structure and compressive strength of the alkali-activated slag mortars.

While low calcium fly ash and slag have been extensively investigated as raw material for the synthesis of geopolymers in recent years, the study of using different waste fine filler material producing fly ash–slag-based geopolymer with recycled aggregate is limited. This study evaluates unusable industrial waste materials (Marble, Basalt, Limestone) with recycled aggregates and offers high performance and green geopolymer. In order to investigate the effect of filler materials at different ratios, flexural, compressive, split tensile strength, ultrasonic pulse velocity (UPV) tests, scanning electron microscopy (SEM), and X-ray diffraction analysis (XRD) analysis were performed. In addition, the freeze–thaw properties of geopolymer mortars were tested for 180 cycles. This research aimed to understand the performance of fly ash–slag mortars using different quarry waste aggregate/recycled aggregate and to provide a comprehensive and practical database for guideline modification, engineering purposes, and further investigations on the field of geopolymers and alkali-activated mortars.



## 2 Materials and Methods

### 2.1 Binders

In the experimental studies, class F fly ash was used to produce geopolymer mortar. FA was supplied from Zonguldak/Turkey, while ground granulated blast furnace slag (GGBS) was supplied from the cement factory in Bolu/Turkey. The chemical composition of the binder materials is shown in Table 1.

### 2.2 Chemicals

Sodium silicate  $\text{SiO}_2/\text{Na}_2\text{O} = 3.29$  M and sodium hydroxide 12 M were used as alkali activator. Chemicals are provided from AS Chemistry Company in Turkey.

### 2.3 Filler Materials

Recycled aggregate (RS) was used as fine aggregate in the control series. The particle diameter of the recycled aggregate is smaller than 2 mm and is provided following the TS706 EN-12620 [29] standard. In three categories, limestone powder (L), waste marble powder (M), and waste basalt powder (B) were partially replaced with recycled aggregate in different ratios as a fine aggregate. Limestone powder was provided from Gebze Rock Quarry/Turkey, basalt powder was provided from INCI Group Company Sakarya/Turkey,

and marble powder was obtained from Alibeykoy/Istanbul. Limestone's specific gravity is 2.7, and its water absorption value is 4.6%. The specific gravity value of Marble powder is 2.61, the water absorption is 0.05% and the Blaine fineness ratio is  $4372 \text{ cm}^2/\text{g}$ . Basalt powder has a specific gravity value of 2.99 and a Blaine fineness ratio of  $3500 \text{ cm}^2/\text{g}$ . SEM images of filler materials are shown in Fig. 1. In addition, the chemical compositions and physical properties of fillers are shown in Table 2.

### 2.4 Mix Proportioning and Testing Methodology

Geopolymer mortars were synthesized using class F FA and GGBS at a constant rate in all mixtures. The binder materials were dissolved in an alkali silicate solution. Sodium hydroxide solution was prepared by adding 480 g (12 M)–1 L of distilled water. The sodium hydroxide solution was kept at room temperature for 24 h before production. One-third of the activator mixture consisted of sodium hydroxide, and two-thirds consisted of sodium silicate. The binder FA's weight ratio to aggregate materials was constant at 1:2. The activator to binder ratio for this mixture was taken at 0.75:1. Mixture compositions of geopolymer mortars are shown in Table 3. After the fly ash and slag, chemical activators were mixed so that they became homogeneous, the desired amount of filling material was added to the mixture. The obtained mixture was then cast into molds to avoid the entrapped air and voids from the sample molds on the vibrator. One hour after

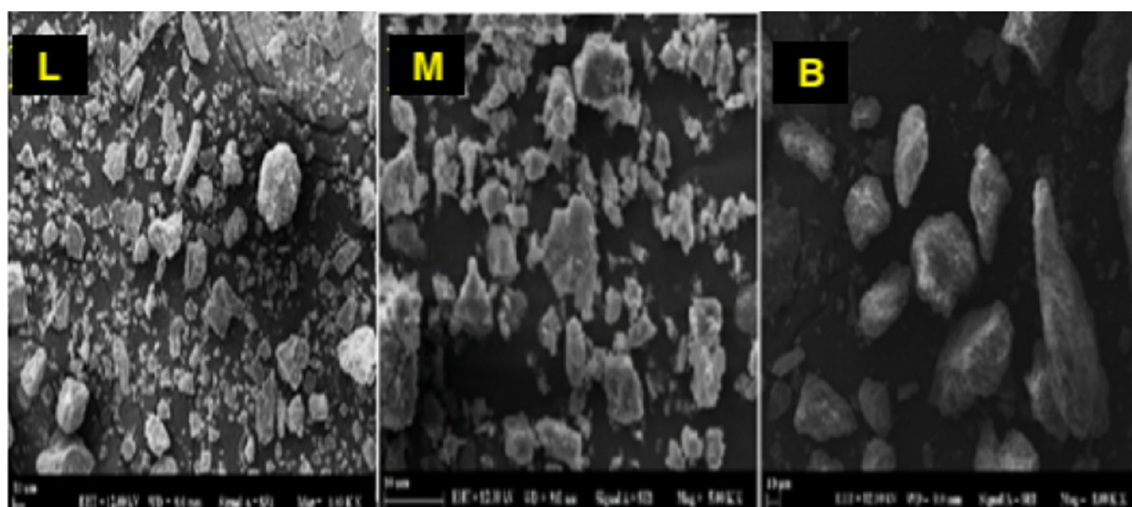


Fig. 1 SEM images of the L, M, and B

Table 1 Chemical composition of FA and GGBS

| Oxides             | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | $\text{CaO}$ | $\text{MgO}$ | $\text{SO}_3$ | $\text{Na}_2\text{O}$ | free CaO | Cl -   | LOI  |
|--------------------|----------------|-------------------------|-------------------------|--------------|--------------|---------------|-----------------------|----------|--------|------|
| FA % (by weight)   | 54.08          | 26.08                   | 6.681                   | 2.002        | 2.676        | 0.735         | 0.79                  | 0.11     | 0.092  | 1.36 |
| GGBS (% by weight) | 40.55          | 12.83                   | 1.10                    | 35.58        | 5.87         | 0.18          | 0.79                  | —        | 0.0143 | 0.03 |



**Table 2** Chemical compositions and physical properties of filler materials

| Materials                      | L %   | M %   | B %  | RS % |
|--------------------------------|-------|-------|------|------|
| SiO <sub>2</sub>               | 4.93  | 0.70  | 56.9 | 96.7 |
| Al <sub>2</sub> O <sub>3</sub> | 0.82  | 0.29  | 17.6 | 1.05 |
| Fe <sub>2</sub> O <sub>3</sub> | 0.58  | 0.12  | 8.1  | 0.56 |
| TiO <sub>2</sub>               | –     | –     | 0.9  | –    |
| CaO                            | 51.97 | 55.49 | 8.15 | 0.08 |
| MgO                            | 0.58  | 0.23  | 2.1  | –    |
| K <sub>2</sub> O               | –     | 1.80  | 1.9  | 0.12 |
| Na <sub>2</sub> O              | –     | 2.44  | 3.8  | 0.12 |
| SO <sub>3</sub>                | –     | –     | –    | –    |
| Loss of Ignition               | 40.40 | 42.83 | –    | 0.29 |
| P <sub>2</sub> O <sub>5</sub>  | –     | –     | 0.2  | –    |
| MnO                            | –     | –     | 0.1  | –    |
| Specific Gravity               | 2.79  | 2.71  | 2.76 | 2.63 |
| Blaine (cm <sup>2</sup> /g)    | 2500  | 8888  | 6285 | 3500 |

**Table 3** Mixing compositions of produced geopolymer mortars (kg/m<sup>3</sup>)

| Mix ID  | Fly ash | GGBS  | Na <sub>2</sub> SiO <sub>3</sub> | NaOH   | Recycled Aggregate | Filler Material (L or M or B) |
|---------|---------|-------|----------------------------------|--------|--------------------|-------------------------------|
| Control | 496.66  | 64.57 | 283.10                           | 139.07 | 993.32             | 0.00                          |
| 25 L    | 496.66  | 64.57 | 283.10                           | 139.07 | 773.46             | 248.33                        |
| 50 L    | 496.66  | 64.57 | 283.10                           | 139.07 | 553.61             | 496.66                        |
| 75 L    | 496.66  | 64.57 | 283.10                           | 139.07 | 333.76             | 744.99                        |
| 25 B    | 496.66  | 64.57 | 283.10                           | 139.07 | 771.08             | 248.33                        |
| 50 B    | 496.66  | 64.57 | 283.10                           | 139.07 | 548.83             | 496.66                        |
| 75 B    | 496.66  | 64.57 | 283.10                           | 139.07 | 326.59             | 744.99                        |
| 25 M    | 496.66  | 64.57 | 283.10                           | 139.07 | 766.98             | 248.33                        |
| 50 M    | 496.66  | 64.57 | 283.10                           | 139.07 | 540.64             | 496.66                        |
| 75 M    | 496.66  | 64.57 | 283.10                           | 139.07 | 314.30             | 744.99                        |

casting, the samples were left in the oven at 80 degrees for 24 h. Samples were stored under laboratory conditions until scheduled testing. After the mixing procedures were completed, 50 mm cube molds were used for the compressive strength tests, 40 × 40 × 160 mm prisms for the flexural strength and UPV tests, and cylindrical molds with a diameter of 100 mm and a height of 200 mm were used for the split tensile strength test. The compressive strength test was obtained consecutively after 7, 28, and 56 days, according to ASTM C109/109 M [30]. A flexural strength test was also obtained after 7, 28, and 56 days consecutively conducted according to ASTM C348-20 [31]. Ultrasonic pulse velocity test was carried on before the flexural testing on prismatic specimens to check the quality of manufactured geopolymer specimens. The split tensile strength test of the geopolymer specimen was determined by ASTM C 496 [32]. After 28 days, the freeze–thaw performances of the geopolymer composites were tested. Compression, flexural and UPV

tests were performed with 180 cycles of freeze–thaw. In addition, weight changes were calculated after the freeze–thaw test.

XRD and SEM analyzes were applied for the series with the highest strength result of the geopolymer samples. Since the geopolymer samples are not conductive, the surface of the samples obtained from the study was coated using a micro-palladium spray coating. It was ensured that there were no scratches or image instability during the image acquisition with the coating. The samples were coated with a conductive layer by the spray device. The XRD test, on the other hand, works according to the principle of finding the mineralogical composition of the crystal grains by using the X-ray powder diffraction measurement method.

**Table 4** Physical properties of the investigated mixtures

| Mix ID | Water absorption (%) | Unit weight (gr/cm <sup>3</sup> ) | Void ratio (%) |
|--------|----------------------|-----------------------------------|----------------|
| RS     | 13.7                 | 2.3                               | 20.3           |
| 25 L   | 13.4                 | 2.3                               | 19.7           |
| 50 L   | 12.5                 | 2.3                               | 18.5           |
| 75 L   | 12.3                 | 2.6                               | 20.2           |
| 25 M   | 13.2                 | 2.3                               | 18.9           |
| 50 M   | 13.8                 | 2.2                               | 19.6           |
| 75 M   | 15.2                 | 2.2                               | 21.0           |
| 25 B   | 11.5                 | 2.3                               | 16.7           |
| 50 B   | 12.1                 | 2.3                               | 17.7           |
| 75 B   | 10.8                 | 2.3                               | 16.0           |

### 3 Result and Discussion

#### 3.1 Physical Properties

Table 4 shows the physical properties of the produced geopolymer composites. Water absorption tests were carried out by ASTM C1585-20 [33] standard and were performed with 50 mm cube specimens. In general, the water absorption values of the geopolymer samples (L, B and M) with filler material produced in the study showed a lower water absorption value than the reference series. Substitution of the filler material to recycled aggregate improved the water absorption values [34–36]. For example, while the water absorption value increased by 2% in the series with 25% L waste replacement, this value increased to 10% in the series with 75% L waste. For M waste, the situation was different, and an increase in water absorption values was observed with the increase in M waste substitution. It is seen that the mixtures produced with BS waste improve the water absorption values much better than the other mixtures compared to the control mixture. For example, the 75B series has 20% less water absorption than the control mixture. In addition, it was revealed that there was a good correlation between the water absorption values of the samples and the void ratio values.

#### 3.2 Compressive Strength

Figure 2 shows the compressive strength (CS) results of geopolymer composites. Also, Fig. 3 shows the rate of improvement compared to the control mix according to the substitution rate of the filler material. As shown in Fig. 3, as the L and B waste replacement ratio increased, the improvement in compressive strength further increased. It was revealed that the highest growth rate and the highest compressive strength values were obtained from L waste

mixtures. The rate of improvement of the geopolymer composites produced with L waste compared to the control mixture varied between 15 and 39%. This value varied between 15 and 34% in geopolymer composites produced with B waste. In the mixtures produced with M waste, the growth rate did not show a linear improvement as in the mixtures produced with the other two filling materials. While the highest growth rate and compressive strength were obtained at a 50% replacement rate in M waste, the strength values decreased at 25% and 75%. With the use of L, apart from the role of filler, its dissolution in an alkaline environment, being rich in calcium oxide, and reacting with the primary geopolymer gels improved the compressive strength values.

The use of limestone as a filler makes it possible to fill the pores inside the matrices and clarifies the important effects of limestone in packing the particles in the geopolymer matrix [26]. Studies [21, 27, 28] on alkali-activated concrete produced with fly ash binder and waste marble aggregate in the literature are the same as the trend of compressive strength in marble powder obtained in this study. The main chemical compositions of marble powder are alumina, silica, calcite, and dolomite. The silica in the marble powder reacts with  $\text{Ca}(\text{OH})_2$  and causes an increase in the compressive strength. Saloni et al. [23] reported improvements in the mechanical properties of geopolymer composites up to 50% marble dust waste replacement. It is thought that the decrease in compressive strength caused by the increase in the substitution rate of marble dust is due to factors such as loss of workability and high-water demand of marble dust waste due to the vicious structure of the alkaline solution [37]. The reasons mentioned have affected the pore structure of the mixtures and caused a decrease in the compressive strength. Although the marble dust waste is not a pozzolanic material, the presence of CaO in its structure caused the formation of CSH, CASH, and NASH by entering the reaction with the alkaline solution [38]. In addition, if the marble dust waste exceeds 50%, it is expected that there will be excessive hydration heat, which causes higher water consumption. Due to the excessive heat generated, cracks appear that prevent the development of a homogeneous and dense matrix structure. In this case, it is thought to be among the factors that reduce the compressive strength [23]. Binici et al. [15] studied the addition of basalt powder to concrete in a previous study and showed that basalt used in both powder and coarse aggregate had a positive effect on the strength and abrasion of concrete.

#### 3.3 Ultrasonic Pulse Velocity (UPV)

UPV test, one of the non-destructive testing methods, was carried out on geopolymer samples to recognize the discontinuities and quality of the samples and to identify possible defects. Figure 4 shows the UPV results of geopolymer composites. Also, the correlation between compressive strength



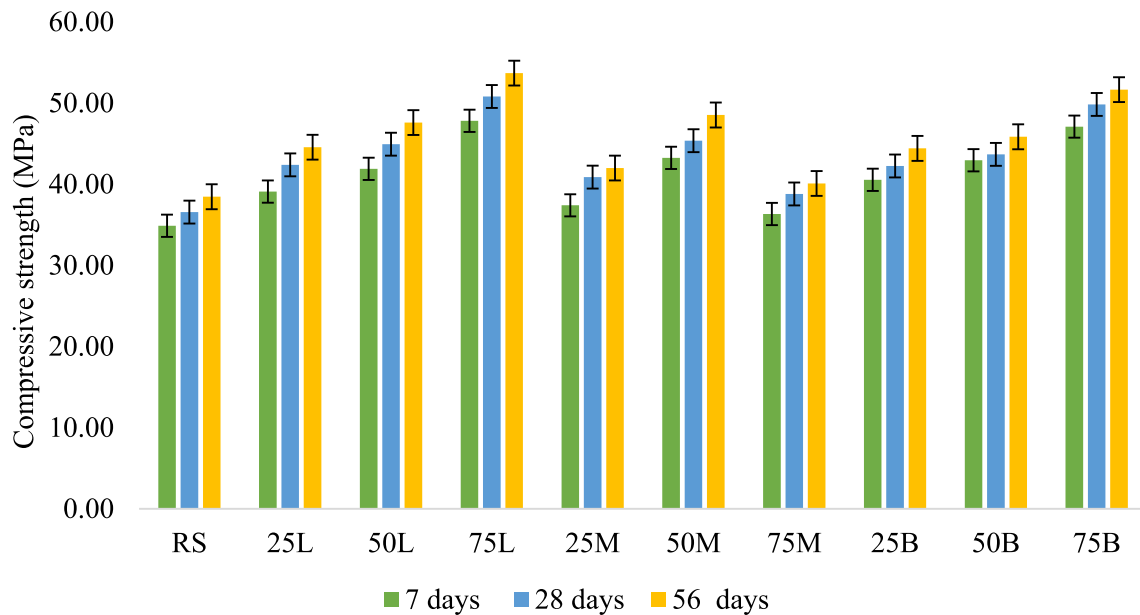


**Fig. 2** Compressive strength results of investigated composites

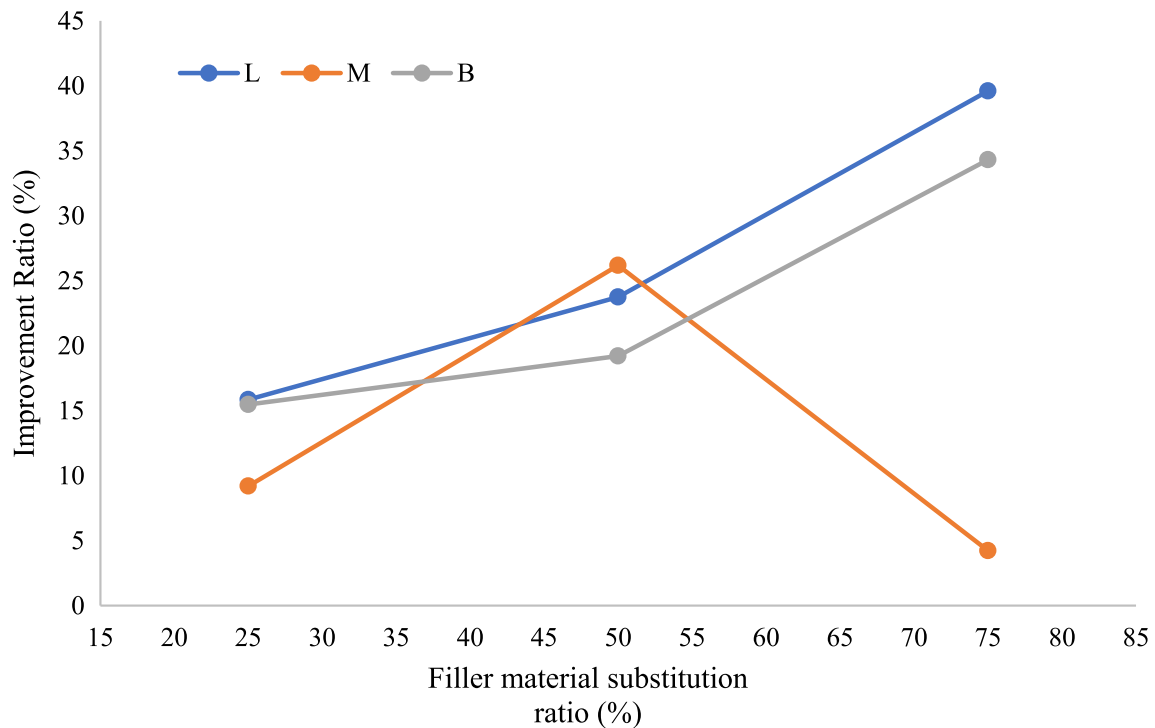


**Fig. 3** Improvement ratios were relative to the control mixture according to the substitution rate of the fillers

and UPV values is shown in Fig. 5. Although there were no significant differences in the geopolymer samples' 7, 28, and 56-day UPV values, the improvement of these values was slight. The test results reveal that UPV and compressive strength values are strongly related. UPV and compressive strength results revealed a similar growth pattern. More specifically, combining the test results revealed a correlation

coefficient of 0.95. It was concluded that the compressive behavior of geopolymer composites could be predicted by performing the UPV test. The 56-day average UPV value of geopolymer composite mixtures is 3228, and these values have increased or decreased proportionally with the trends in compressive strength. Compared to the control series, the UPV values of all mixture series are improved. The results

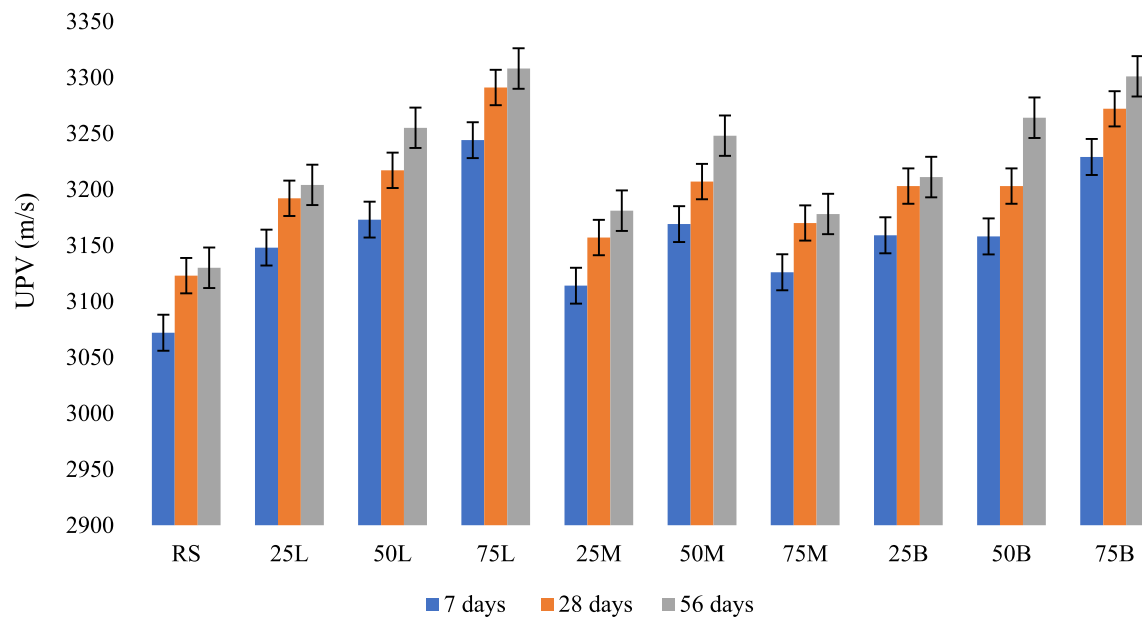


**Fig. 4** Ultrasonic pulse velocity values of the investigated mixes

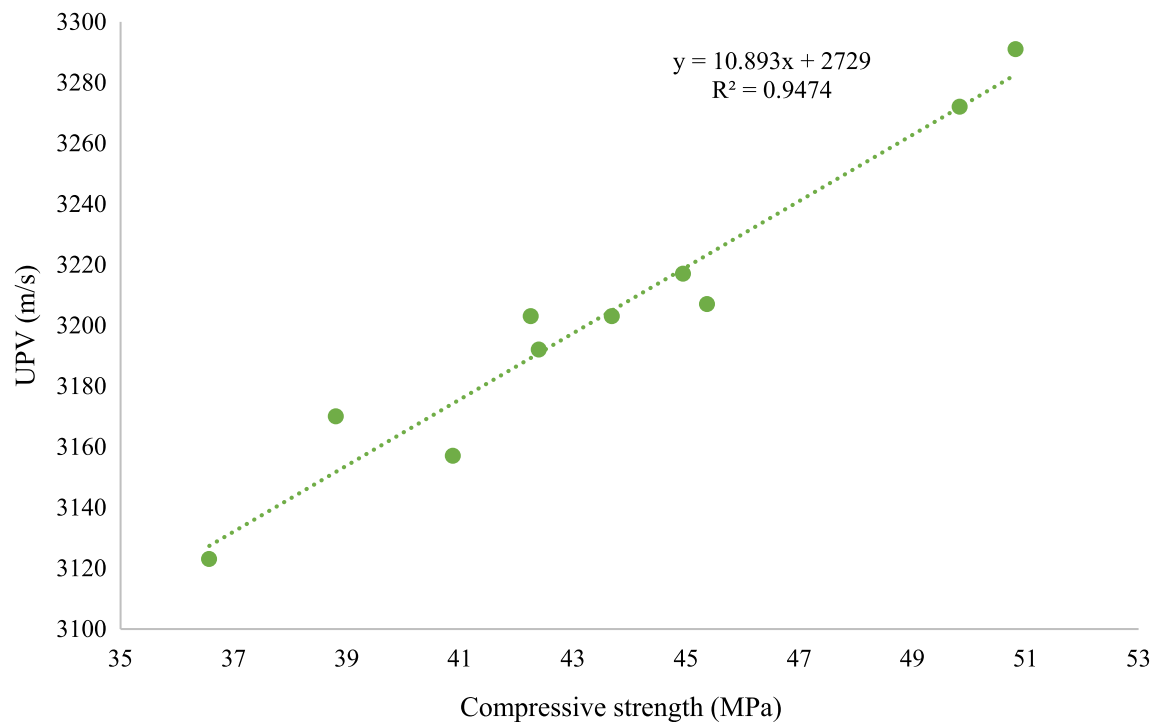


**Fig. 5** The correlation between UPV and compressive strength

agree with previous results presented by Tammam et al. [39]. Binici et al. [15] stated that the use of filling materials in the mixture reduces water absorption and porosity, and therefore, the ultrasonic pulse velocity increases with the decrease in the void values.

### 3.4 Flexural Strength

Figure 6 shows the flexural strength (FS) results of geopolymer composites. In addition, in Fig. 7, the improvement rates were obtained according to the replacement rate of the filler material and compared to the control series. In general, it was observed that the filling material substitution



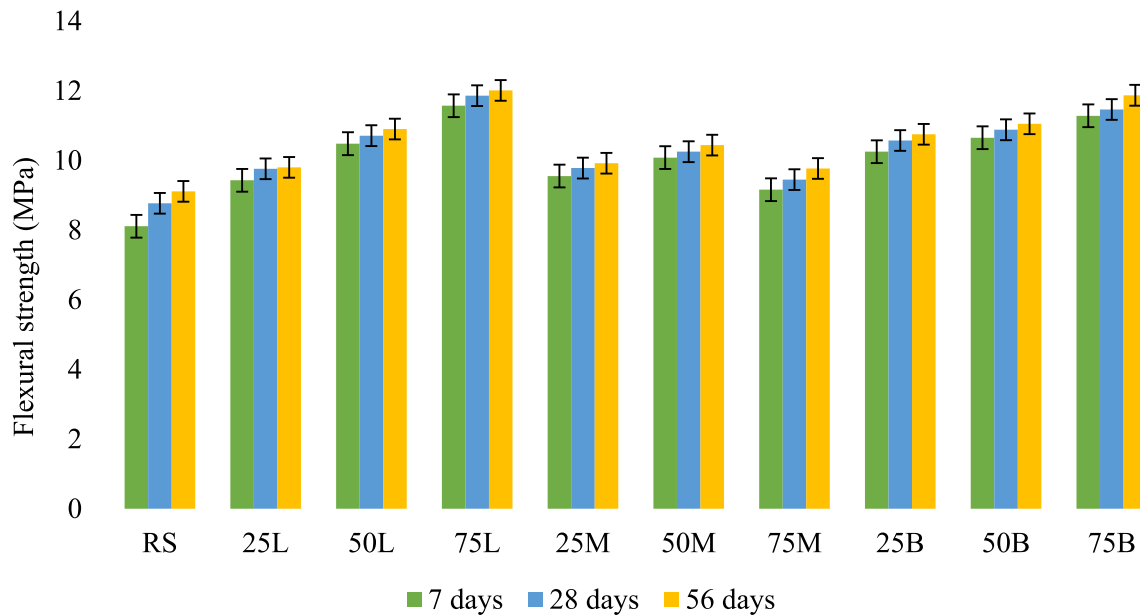


**Fig. 6** Flexural strength result of the manufactured composites

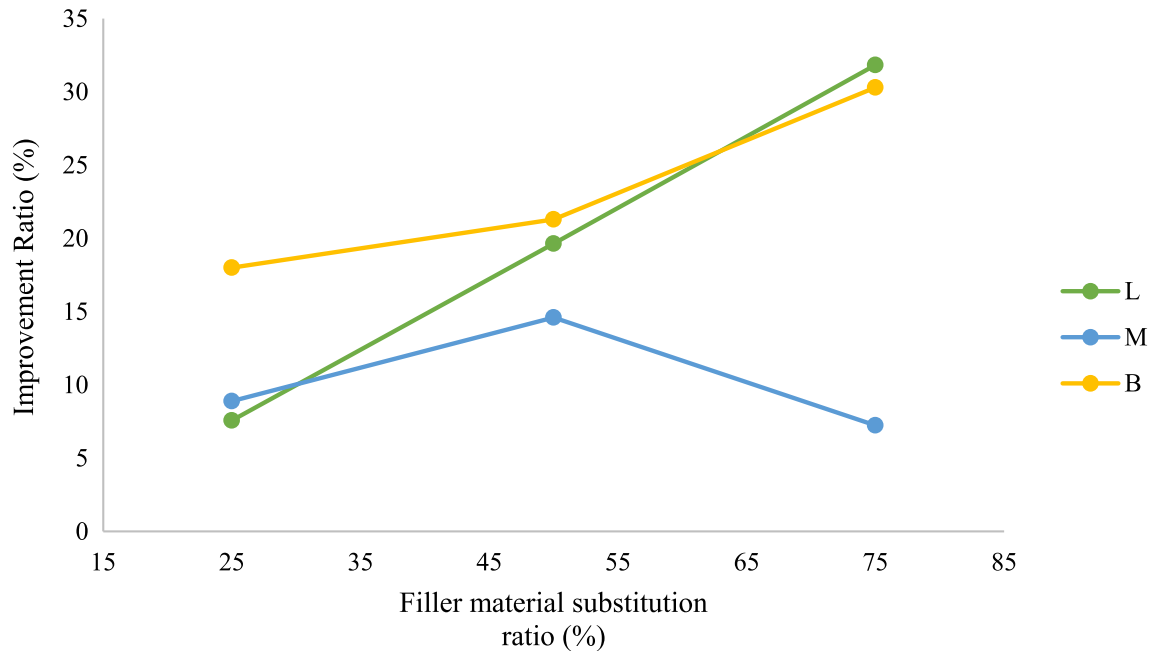


**Fig. 7** Improvement ratios are relative to the control mixture according to the substitution rate of the fillers in flexural strength

had a positive effect on all mixture series. While the rate of improvement in the series of mixtures with basalt and limestone waste substituted increases as the substitution rate increases, the improvement rate in the series of mixtures with the replacement of marble waste was up to 50%, as in the results of compressive strength. The flexural strength of the geopolymer composites ranged from 9 to 12 MPa. The highest flexural strength value of 12 MPa was obtained from the series with 75% L waste replacement. The lowest flexural

strength value was obtained from the control RS series with recycled concrete waste with 9 MPa. It can be said that L and B are more effective than M in promoting hydration in the fly ash/GGBS matrix. The decrease in flexural strength with the use of more than 50% of M powder is attributed to the high-water requirement due to excessive CaO in the matrix, improper hydration, and polymerization, as mentioned in the compressive strength [23]. Due to its partial dissolution in an

alkaline environment, limestone added to the geopolymerization reaction enabled the expansion of the basic system of geopolymeric binders. The use of limestone as a filling material made it possible to fill the pores in the matrix [39]. Limestone made it possible to expand the structural network of geopolymeric binders and thus contributed to the geopolymerization reaction. Up to 75% limestone content increased the reactive phase and mechanical properties and reduced water absorption. The use of limestone as an additive material reveals the beneficial effects of limestone in packaging the particles in the matrix, thus making it possible to fill the pores in the matrix [40].

Studies [34, 36, 41] in the literature indicate that using limestone in geopolymer mortars improves mechanical properties. In the studies [4, 16] on concrete and mortar in the literature, it has been stated that the use of Basalt additive has a positive contribution to properties such as strength and abrasion. It is thought that the contribution of basalt in powder form to fill the voids in the composite increases the strength values with the increase in the basalt substitution rate.

Colangelo et al. [42] investigated lightweight geopolymer composites' mechanical and thermal properties in their study using marble powder as inert filling material. Like the results obtained in this study, significant increases were observed in both compressive and flexural strengths by adding marble powder to geopolymers. The increase in mechanical properties with marble dust is attributed to the amount of silica. Interfacial bonding occurs between silica and marble grains and binding materials (slag, fly ash) [20].

### 3.5 Split Tensile Strength

The split tensile strength results of geopolymer composites are shown in Fig. 8. In addition, the rate of improvement of split tensile strengths according to the control series of three different filler materials is shown in Fig. 9. It is seen that the development trends in compressive and flexural strength are also valid in split tensile strength values. As the substitution rate of the L waste substituted series increased, the split tensile strengths increased even more. Likewise, with the B waste replacement rate increase, the split tensile strength values showed a remarkable increase. For example, while the 25L series showed a 20% increase in strength, the 75L increased this value to a remarkable 48%. Again, while the improvement rate was 6% in the 25B series, this value increased to a remarkable 38% in the 75B series. A different situation emerged from the other two filling materials for the M powder waste replacement. While 25% substitution of M powder waste caused 7% flexural strength loss compared to the control series, this loss increased to 16% at a 75% substitution rate. On the contrary, 50% marble dust waste substitution showed a remarkable improvement in split

tensile strength of 26% compared to the control series. In general, the tensile strength trend is split for M waste was similar to that observed for other strength values.

The split tensile strength results for the marble powder substituted geopolymer mortars seem to be similar to the compressive strength. Factors in compressive strength are also thought to be responsible for improving splitting tensile strength. In marble series, an increase in splitting tensile strength up to a certain value may result in hydrated calcium silicate gel formation between  $\text{CaCO}_3$  and silica [23].

## 3.6 Freeze–Thaw Tests

### 3.6.1 Strength Properties

The effect of filling materials on the compressive and flexural strength of the produced geopolymer samples was determined by the freeze–thaw effect. The values are shown in Figs. 10 and 11. In addition, 28-day compressive and flexural strength values and the values obtained after the freeze–thaw test are compared in Table 5. The compressive and flexural strength values of all produced geopolymer mixtures decreased compared to the 28-day mechanical values after the freeze–thaw test. According to the 28-day compressive and flexural strength values, the greatest compressive and flexural strength loss occurred in the control series. With the substitution of L and B waste, it is seen that the losses decrease as the replacement rate increases in both strength types. For example, while the flexural strength loss in the 25L mixture series was 15%, the loss in the 75L series decreased to 11%. In both strength types, the difference between the losses is not large and cannot be considered.

On the other hand, when the mixtures are compared to the control series after 180 cycles of freezing test, they show very effective results. After the freeze–thaw test, the mixtures showed an average improvement of 24% in both compressive strength and flexural strength compared to the control series. As in the mechanical properties, the strength development in the series with L and B waste substitutes increased with the increase in the substitution rate. M waste substituted series still maintained its trend in mechanical properties and gave the highest result at a 50% substitution rate. The compact matrix and high strength of the geopolymer samples help resist the stresses caused by the freeze–thaw effect until micro-cracks are formed due to the hydraulic pressure created by the expansion of the water present in the matrix [43]. In addition, air voids in the sample cause a decrease in strength properties compared to normal conditions, as the leading cause of micro-cracks and deterioration [44].



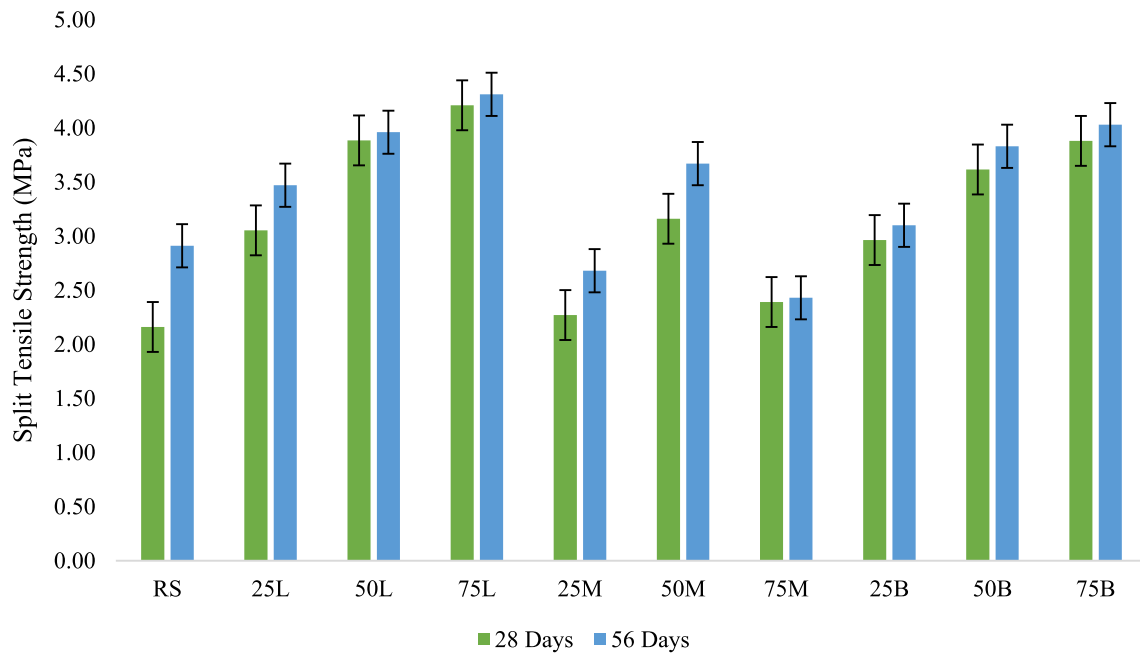


**Fig. 8** Split tensile strength values of the investigated mixes

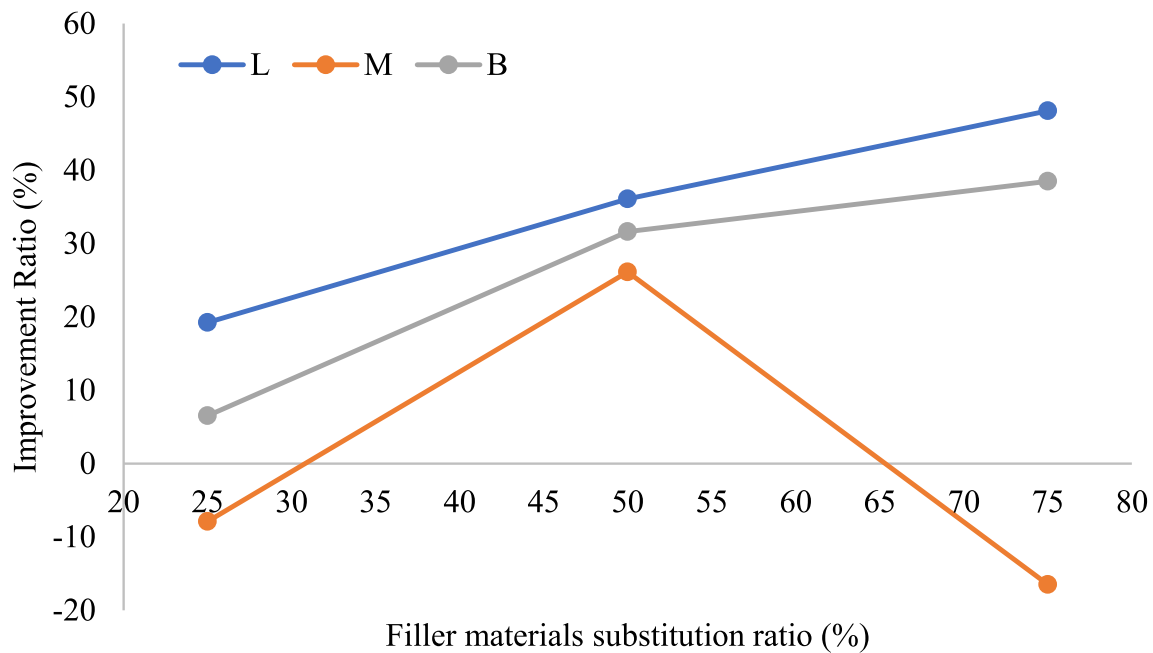


**Fig. 9** Improvement ratios relative to the control mixture according to the substitution rate of the fillers in 56-day split tensile strength

### 3.6.2 UPV Test

In Fig. 12, the UPV values of 28 days and the UPV values obtained after 180 cycles of the freeze–thaw test were compared. In addition, the correlation between the compressive strength values obtained after freeze–thaw and the UPV values is shown in Fig. 13. A decrease similar to the trend in the

compressive strength results was observed in the UPV values obtained after freezing and thawing. It was found that the UPV values of all mixture series were higher than the control series. For this reason, it can be said that the series with filler material has a more continuous matrix structure. The correlation coefficient between the compressive strengths obtained after freezing–thawing and the UPV values was obtained as 0.92, which indicates a strong correlation between them. The

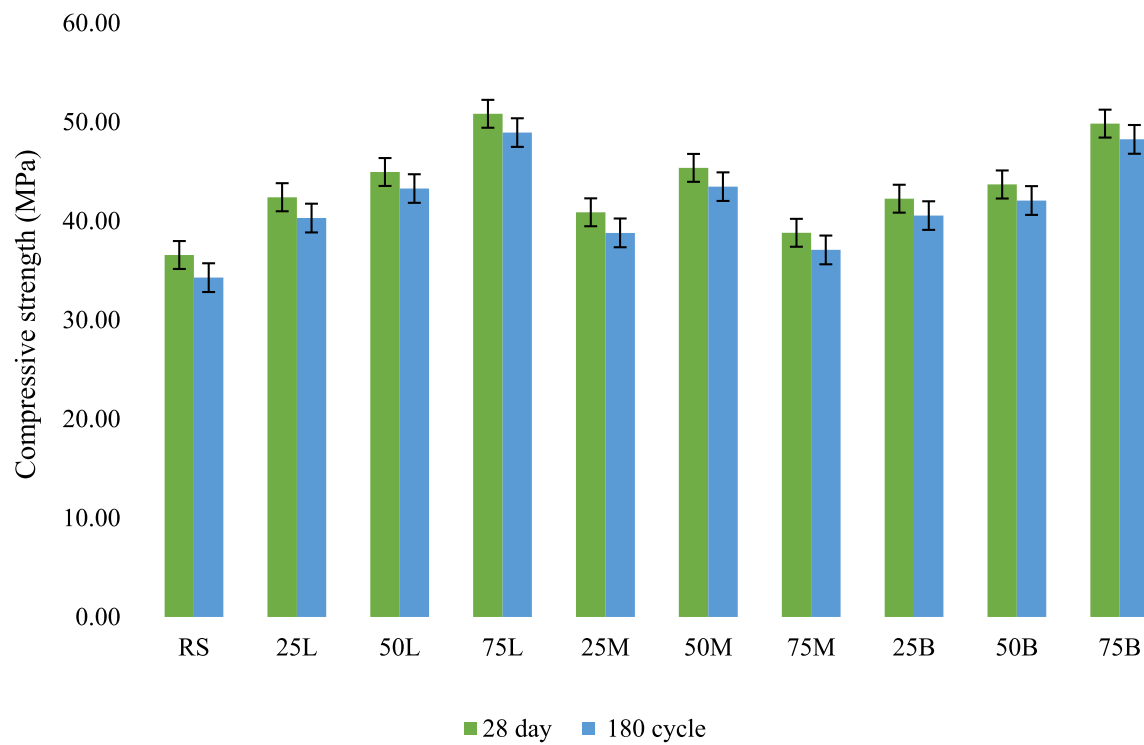


**Fig. 10** Compressive strength results after freeze–thaw tests

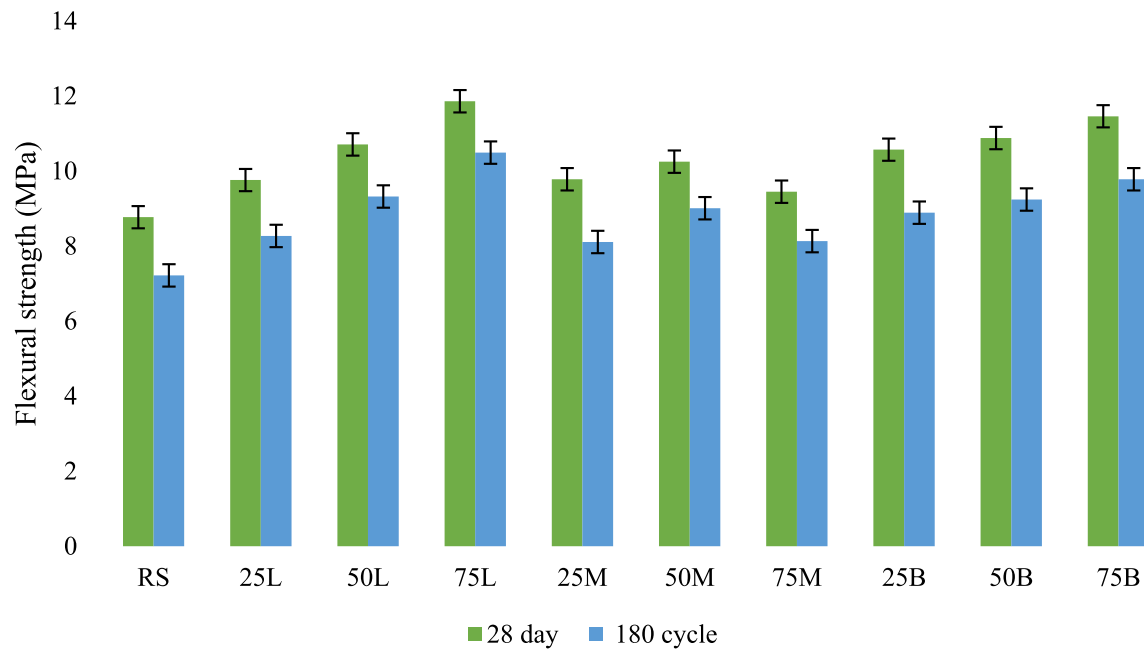
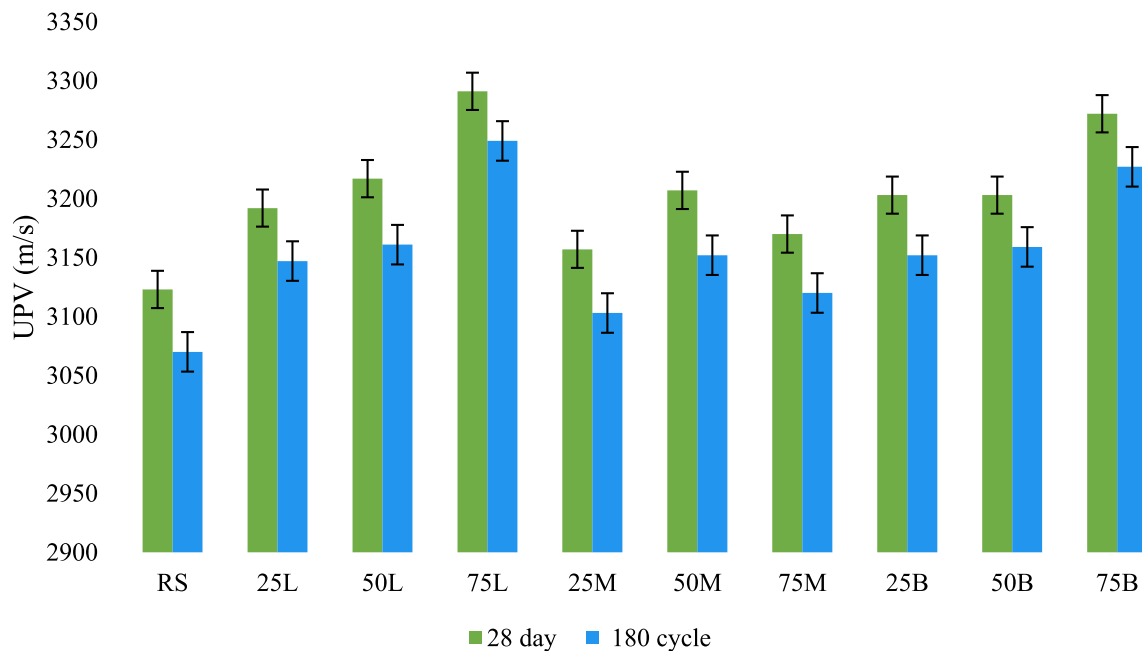


**Fig. 11** Flexural strength results after freeze–thaw tests

**Table 5** Comparison of the 28-day compressive and flexural strength values with the values after the freeze–thaw test

| Mix ID | 28-day CS (MPa) | CS after 180 cycles (MPa) | I.R of CS % | 28-day FS (MPa) | FS after 180 cycles (MPa) | I.R of FS% |
|--------|-----------------|---------------------------|-------------|-----------------|---------------------------|------------|
| RS     | 36.57           | 34.28                     | – 6.26      | 8.77            | 7.22                      | – 17.67    |
| 25L    | 42.40           | 40.3                      | – 4.95      | 9.76            | 8.27                      | – 15.27    |
| 50L    | 44.95           | 43.28                     | – 3.72      | 10.71           | 9.32                      | – 12.98    |
| 75L    | 50.83           | 48.93                     | – 3.74      | 11.86           | 10.49                     | – 11.55    |
| 25 M   | 40.88           | 38.8                      | – 5.09      | 9.78            | 8.11                      | – 17.08    |
| 50 M   | 45.37           | 43.47                     | – 4.19      | 10.25           | 9.01                      | – 12.10    |
| 75 M   | 38.81           | 37.08                     | – 4.46      | 9.45            | 8.13                      | – 13.97    |
| 25B    | 42.26           | 40.55                     | – 4.04      | 10.57           | 8.89                      | – 15.89    |
| 50B    | 43.69           | 42.07                     | – 3.71      | 10.88           | 9.24                      | – 15.07    |
| 75B    | 49.84           | 48.25                     | – 3.19      | 11.46           | 9.78                      | – 14.66    |

**Fig. 12** Ultrasonic pulse velocity values of the investigated mixes after the freeze–thaw test

results agree with previous results presented by Chakkor et al. [13].

### 3.6.3 Weight Loss

Figure 14 shows the weight loss results after the freeze–thaw test in geopolymer composites. The mixtures exhibited an average weight loss of 3.36%. It was found that the weight loss rates with filler replacement were less than in the control series. However, it can be said that these values are not significant differences. The lowest weight loss result was obtained from the B waste substituted series, while the highest loss result was obtained from the control series. It is seen that the weight loss values are further reduced with the B waste substitution. Although the values are close to each other, it

has been revealed that 50% substitution is more effective in the series with M and L waste substitutes. In the later stages of the freeze–thaw cycle of the geopolymer samples, weight loss was observed due to flaking on the surface of the samples. The compact structure of the geopolymer samples caused the weight loss to be low [45].

### 3.7 XRD Analysis

The XRD analysis could be used for compound analysis. It was performed on 50 M and 50L samples. The main noticed compounds of the geopolymerization progress were quartz, mullite, and calcite in the L and M specimens. Moreover, the peaks between  $20^\circ$  and  $30^\circ$   $2\theta$  in all the series studied indicate satisfactory geopolymerization. Meanwhile, XRD

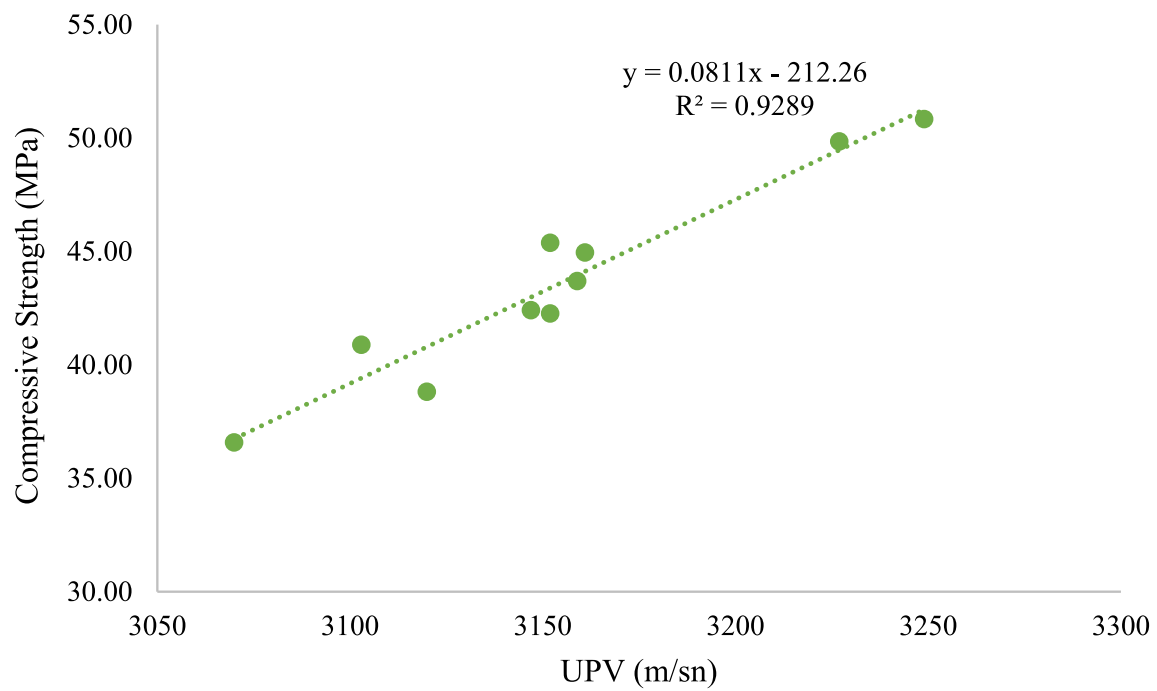


**Fig. 13** Correlation between compressive strength and UPV after 180 cycles freeze–thaw test

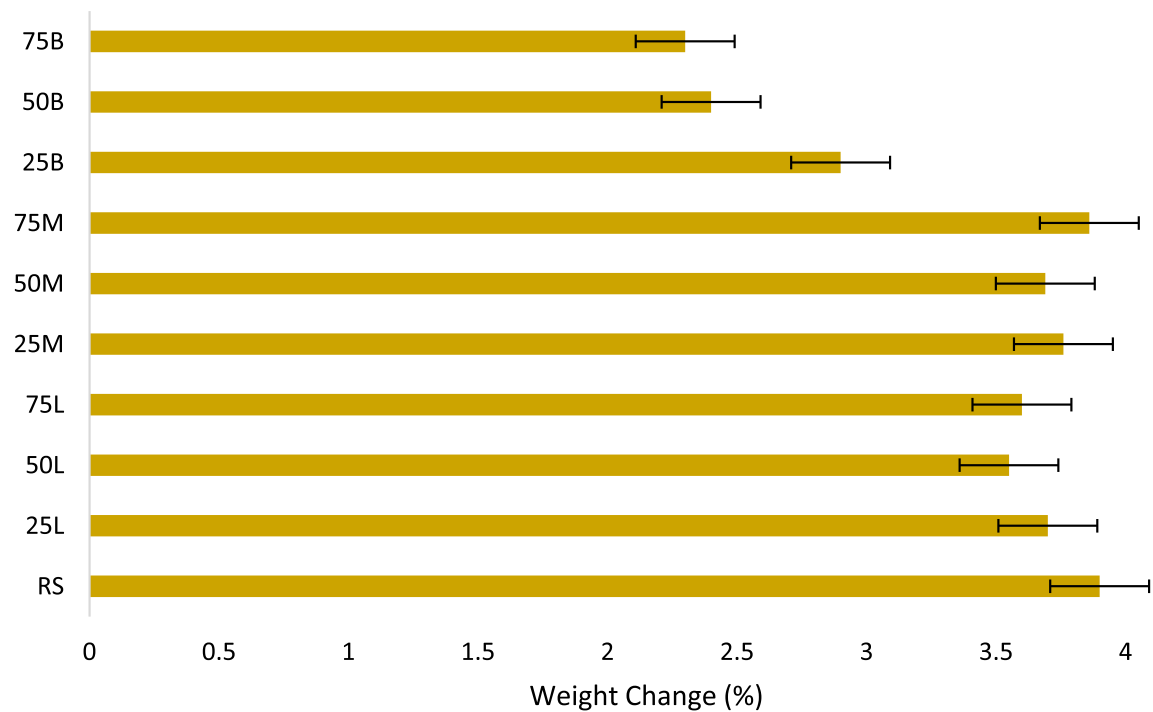
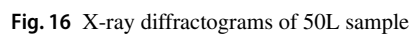
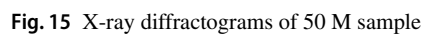


**Fig. 14** Weight loss rates after freeze–thaw test



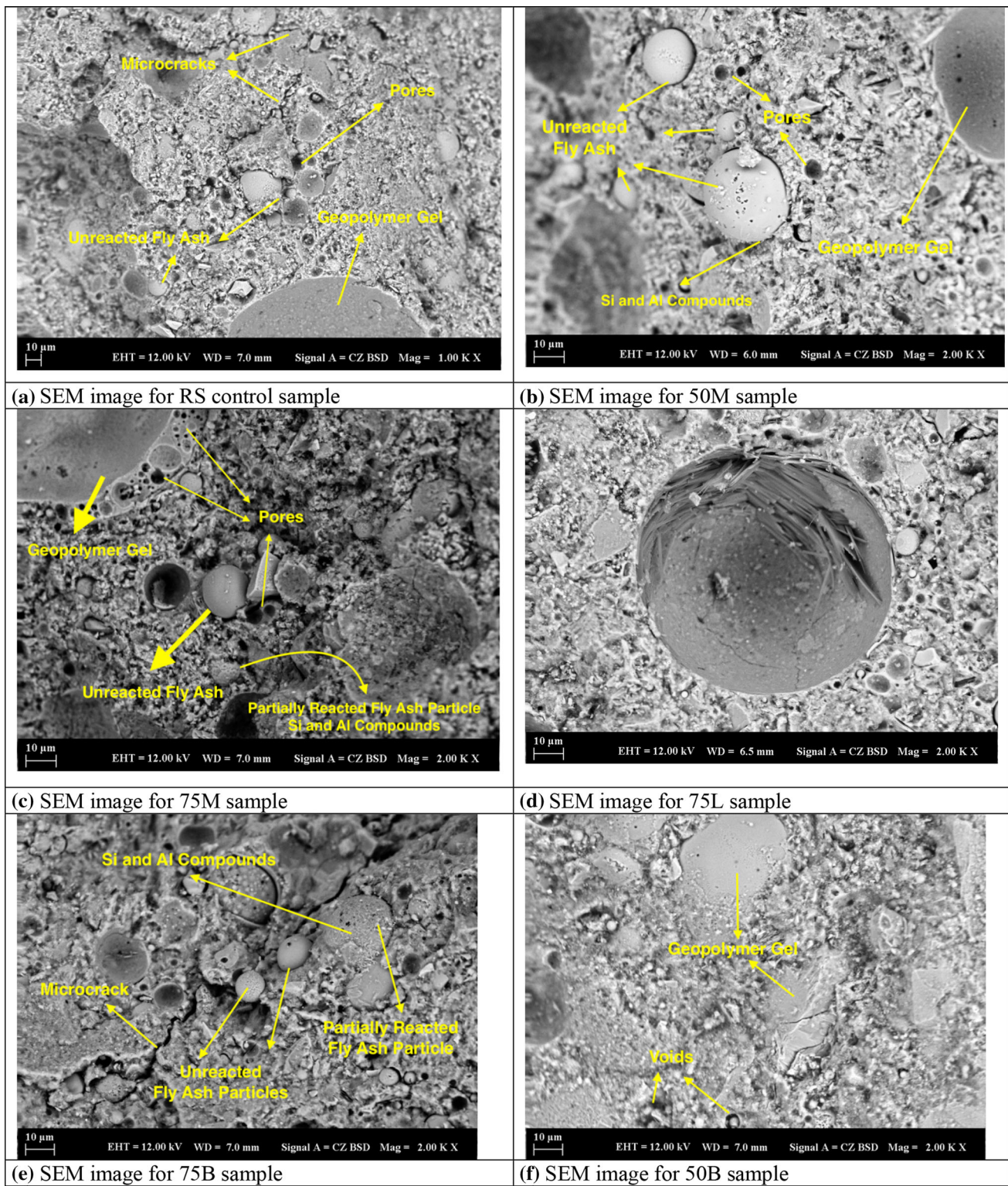


Fig. 17 SEM images of investigated mixes



results of control, 50 M, and 50L geopolymer samples are shown in Fig. 15–16. Considering the XRD results, the presence of quartz in the peaks was detected in the geopolymer samples containing various filler materials. This is mainly due to the high content of crystalline silica in the fly ash binder material. The most intense region where quartz peaks were observed was between  $20^{\circ}$ – $30^{\circ}$  ( $2\theta$ ), which means that the hump is attributed to the vitreous phase of the original ash, slightly shifted from  $20$ – $30^{\circ}$  values. The patterns in the XRD results mainly agree with the observations of Uysal et al. [46], Provis et al. [47], and Al Mashadani et al. [48]. The patterns mainly show the crystal phase of the produced samples. This phase is observed with quartz peaks in the range of  $25$ – $31^{\circ}$ . The sharp peaks in the patterns are believed to be related to the presence of unreacted fly ash particles. In the M and L geopolymer series, small amounts of mulite and calcite were detected besides quartz. In the results of the marble powder-filled geopolymer mortars, low calcite peaks were observed. The different characteristic peaks may depend on the geopolymer composite mixture designs, aluminosilicate source type, filler type, alkali activator type, unreacted alumina or silica, and other unreacted elements impurities. The higher compressive strengths of the blends confirm the microstructural analysis for the formation of geopolymer phases in the prepared mixes.

### 3.8 SEM

Figure 17 shows SEM images. As seen in many micrographs, many unreacted fly ash particles were detected. The samples showed good strength behavior as the presence of unreacted fly ash in the geopolymer matrix particles positively affected the bonding pattern of the produced samples [48]. The micrographs in Figs. 17b, c, e show fly ash particles reacting with prism-shaped columns composed mainly of Si and Al components. This ultimately means that there are Si–O and Al–O bonds, in line with the results of Zhang [49], Al Mashadani et al. [48], Tammam et al. [39]. The homogeneity of geopolymer composites changed with the addition of different wastes in terms of morphological behavior. With the increase in marble and basalt waste, it has been observed that geopolymer composites are not homogeneous compared to mixtures with less added marble and basalt. It can be said that limestone added geopolymer composite has more homogeneous phases in accordance with the mechanical and durability results [10]. Many researchers [50, 51] have demonstrated that the limestone particle can fill the pores between the hydration products and relatively reduce the porosity in the matrix. The nucleation effect of limestone can improve the degree of hydration of the binder and give more hydration products [39].

## 4 Conclusions

Mechanical properties, freeze–thaw effect, and microstructural analyzes of geopolymer mortars were investigated. Recycled waste concrete has been substituted for different quarry waste filler materials. The study results are as follows:

- Filler material substitution improved the void ratio and water absorption values of geopolymer composites.
- Using filling materials with recycled concrete aggregate significantly improved the compressive strength values. Remarkable strength improvements of up to 39% in the use of limestone waste, 26% in marble dust waste, and 34% in basalt waste were found.
- Flexural strength values have improved strongly with the use of filler materials. Limestone waste and basalt waste were found to be very effective. All mix series showed satisfactory results with an average improvement of 17%.
- While limestone and basalt waste from filling materials effectively developed split tensile strengths, marble dust waste was able to develop at a certain replacement rate.
- In general, recycled concrete aggregate and waste filler materials in mechanical properties have shown remarkable results.
- The correlation between mechanical properties and UPV values is quite strong.
- It turns out that the mechanical properties obtained after the freeze–thaw test are lower compared to the 28-day mechanical properties. While this decrease in compressive strength was 4%, the average decrease in flexural strength was 14%.
- After the freeze–thaw test, the waste filler material series showed more effective mechanical properties than the control series.
- After the freeze–thaw test, the series lost weight. Although the waste filler material series shows less weight loss than the control series, the differences are insignificant.
- According to the SEM image, the geopolymerization mechanisms of the fly ash and alkaline solution were good for all the categories and the control sample. Furthermore, the internal characteristics and bonding between the geopolymeric matrix and the filler material were good.
- Research results show that industrial quarry waste materials can be successfully used with recycled aggregate. This research can create geopolymer composite materials by an eco-friendly process that is economically viable and eco-friendly.



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