

## Investigation of Physical and Mechanical Properties of Polyester Matrix Polymer Composites Containing Walnut Shell Waste and CEN Sand

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### Abstract

The aim of this study is to investigate the potential of using walnut shells, an agricultural waste product, in polymer composites to reduce the environmental impacts and contribute to the production of sustainable materials. To this end, Flame Retardant Polyester (FRP) was used as a binder in the production of composite materials, while standard CEN sand and Waste Walnut Shells (WWS) were used as filler materials. While creating composite mixture groups, FRP was preferred at 50% and filler ratio was also maintained at 50%. Then, the WWS was replaced by standard CEN sand at volume proportions of 25%, 50%, 75% and 100%. The apparent density, water absorption, porosity, ultrasonic pulse velocity (UPV) and compressive strengths of the produced polymer composites were investigated. In the specimens where WWS was replaced by 100% with standard CEN sand, a decrease of 27%, 20% and 28% was detected in compressive strengths, UPV and apparent density values, respectively, compared to the control specimen. The most negative behavior in terms of water absorption was observed in the specimen coded WS75 with a water absorption rate of 0.80%. The use of WWS in polymer composite production is evaluated as an economical raw material source, contributes to the prevention of environmental pollution and is also important with its potential to be recycled into the economy.

**Keywords:** Polymer composite, Waste walnut shell, CEN sand, Mechanical properties, Physical properties

## Ceviz Kabuğu Atığı ve CEN Kumu İçeren Polyester Matrisli Polimer Kompozitlerin Fiziksel ve Mekanik Özelliklerinin İncelenmesi

### Öz

Bu çalışmanın amacı, tarımsal atık olan ceviz kabuklarının çevresel etkilerini azaltmak ve sürdürülebilir malzeme üretimine katkı sağlamak amacıyla polimer kompozitlerde kullanım potansiyelini araştırmaktır. Bu doğrultuda kompozit malzeme üretiminde Alev Geciktiricili Polyester (AGP) bağlayıcı olarak kullanılırken standart CEN kumu ve Atık Ceviz Kabukları (ACK) dolgu malzemesi olarak kullanılmıştır. Kompozit karışım grupları oluşturulurken AGP %50 ve dolgu %50 oranlarında tercih edilmiştir. Daha sonra AGP oranı sabit tutularak ACK hacimce %25, %50, %75 ve %100 oranlarında standart CEN kumu ile yer değiştirmiştir. Üretilen polimer kompozitlerin görünür yoğunluk, su emme, porozite, ultrases geçiş hızı (UGH) ve basınç dayanımları incelenmiştir. Standart CEN kumu ile ACK'nın %100 yer değiştirdiği numunelerde basınç dayanımları, UGH ve görünür yoğunluk değerlerinde kontrol numunesine göre sırasıyla %27, %20 ve %28 oranlarında azalma tespit edilmiştir. Su emme açısından en olumsuz davranış %0.80 su emme oranıyla WS75 kodlu numunede gözlenmiştir. ACK'nın polimer kompozit üretiminde kullanılması, ekonomik bir ham madde kaynağı olarak değerlendirilerek, çevre kirliliğinin önlenmesine katkı sağlamakta ve aynı zamanda ekonomiye geri kazandırılma potansiyeliyle önem taşımaktadır.

**Anahtar Kelimeler:** Polimer kompozit, Atık ceviz kabuğu, CEN kumu, Mekanik Özellikler, Fiziksel Özellikler

## 1. Introduction

Polymer composites are economically disadvantageous materials despite their high strength and chemical resistance [1]. However, the economically disadvantageous situation can be avoided by using agricultural wastes such as sunflower stalks, corn cobs, rice husks, wheat husks etc. as reinforcement materials in polymer composites. The use of agricultural wastes in the production of composite materials has the potential to directly improve environmental sustainability. The use of agricultural wastes as reinforcement materials in polymer composites both enables the recycling of wastes and offers an alternative to petrochemical-based materials [2–4]. Agricultural wastes contribute to the reduction of the density of polymer composites due to their light weight and contribute to the improvement of the mechanical properties of composites due to their natural fibrous structure. [5,6]. Agricultural wastes are frequently preferred by researchers in composite production. Agricultural wastes such as jute [7] and hemp [8], [9], [10] have been extensively studied as reinforcement materials in cement-bonded composites. In composites with a lime binder, materials such as hemp stalk [11–13] and wheat husk [14] have been utilized. Similarly, for composites with a polymer binder, jute [15–20], hemp [21–23] etc. have been employed. In addition to the agricultural products mentioned above, another agricultural product that has the potential to be used is walnut shells.

According to Turkish Statistical Institute data, 360.000 tonnes of walnuts were produced in Turkey in 2023. Yaman [24] reported that the average waste amount of seven different walnut species produced in Turkey is 48%. Based on these data, it can be concluded that there are 172.800 tonnes of waste walnut shells in Turkey for 2023. The utilisation of walnut shells in composite materials promotes environmental waste reduction. Therefore, the use of walnut shells in polymer composites contributes to environmental sustainability goals. Walnut shells are generally a low-cost and readily available material. The use of these products can reduce production costs and make the cost of final products competitive [25]. Walnut shells have a structure containing natural fibres. These fibres can increase the mechanical properties of the composite material when combined with the polymer matrix. Based on this data, walnut shells are expected to contribute to the production of more durable and lightweight products. Walnut shell has superior technical properties compared to other agricultural wastes [26,27]. The authors state that its strength and resistance to decay are much higher than other agricultural waste materials. According to Beskopylny et al. [25], walnut shell contains 50.3% lignin, 23.9% cellulose, 22.4% hemicellulose and 3.4% ash. Kolak [4] stated that materials with high lignin content exhibit hydrophobic behavior. Due to its high lignin content, walnut shell is expected to show lower water absorption behaviour compared to other agricultural products. Furthermore, the biodegradability and low density of walnut shells may offer significant advantages for certain applications (lightweight building elements, insulation materials, etc.). Abdulwahid et al. [27] investigated the use of walnut shells as fillers in insulation materials. They stated that walnut shell has good thermal properties and can be used as insulation material. Balcıoğlu et al. [28] examined the wear resistance of polyester resin based walnut shell reinforced polymer composite and stated that the amount of wear increased as the walnut shell ratio increased. Beskopylny et al. [25] investigated the physical and mechanical properties of

the composite containing waste walnut shells. They stated that the properties of concrete improved and the density decreased with the addition of walnut shell at low rates.

Pradhan and Satapathy [29] investigated the mechanical and thermal properties of walnut shell filled polyester based composite. They emphasised that walnut shell substitution increased the compressive strength while decreasing the thermal conductivity and density. Talikoti et al. [30] reported that the flexural, tensile and compressive strengths of the composite with epoxy binder to which walnut shell powder was added increased in their study. It was stated that there was a 42% increase in compressive strength with walnut shell powder-epoxy substitution. Ahlawat et al. [31] examined the flexural, tensile and tribological properties of polyester binder composite produced using walnut shell powder brought to 75-250 micron size. It was stated that the flexural and tensile strengths decreased as the walnut shell content increased. Despite the increase in the load applied to the composites, a decrease in wear resistance was observed, while a partial increase in friction coefficients was observed.

Obidiegwu et al. [32] produced 0.10, 0.20 and 0.30 mm walnut shell powder filled polypropylene based polymer composites. In the study, walnut shell powder was used at 0%, 5%, 10%, 15% and 20%. It was reported that as the proportion of walnut shell powder increased in the composite mixtures, flexural, compressive and elongation at break values decreased, while water absorption and flame spread rates increased. Pączkowski [33] used walnut shell powder and unsaturated polyester resin in the size of 0.10-0.25 m. Walnut shell powder used at 2, 5, 7 and 10 wt%. The authors stated that as the amount of filler increases, flexural strength decreases and water absorption increases.

In this study, flame retardant polyester was used as binder while standard CEN sand and waste walnut shells were used as fillers. Flame retardant polyesters were preferred because they prevent flame formation by forming a char layer on the composite surface during fire. Walnut shell was used in 0, 25, 50, 75 and 100 % by volume replacement with standard CEN sand. The composite specimens were subjected to apparent density, porosity, water absorption, UPV, compressive strength and UL94 vertical combustion tests. Since the studies on waste walnut shell reinforced/filled composites are limited in the literature, this study aims to make an important contribution to the literature.

## **2. Material and Method**

### **2.1. Material**

Flame Retardant Polyester, one of the components of the polymer matrix, was obtained from İlkalem A.Ş. Methyl Ethyl Ketone Peroxide (MEKP) was used as hardener and cobalt octoate was used as accelerator. While standard CEN sand was used as filling material, walnut shells grown in Bingöl region were substituted with CEN sand.

MEKP is a mixture product and contains methyl, ethyl, ketone and peroxide. This mixture is used to initiate the polymerisation reaction of polyester resins. In the presence of a cobalt

accelerator, it can be applied at room temperature or at elevated temperatures. Technical properties of MEKP are given in Table 1.

**Table 1.** MEKP technical specifications

<b>Properties</b>	<b>Value</b>
Density g/cm <sup>3</sup>	1.16
Colour	Colourless
Active Oxygen Content (%)	9.4-9.6
Peroxide Content (%)	40

Cobalt octoate was used to accelerate the polymerisation reaction. Technical specifications of the product are given in Table 2.

**Table 2.** Cobalt octoate technical specifications

<b>Properties</b>	<b>Value</b>
Density g/cm <sup>3</sup>	0.93
View	Liquid
Colour	Violet blue
Metal content (%)	5.9-6.1
Total solid content (%)	30±2

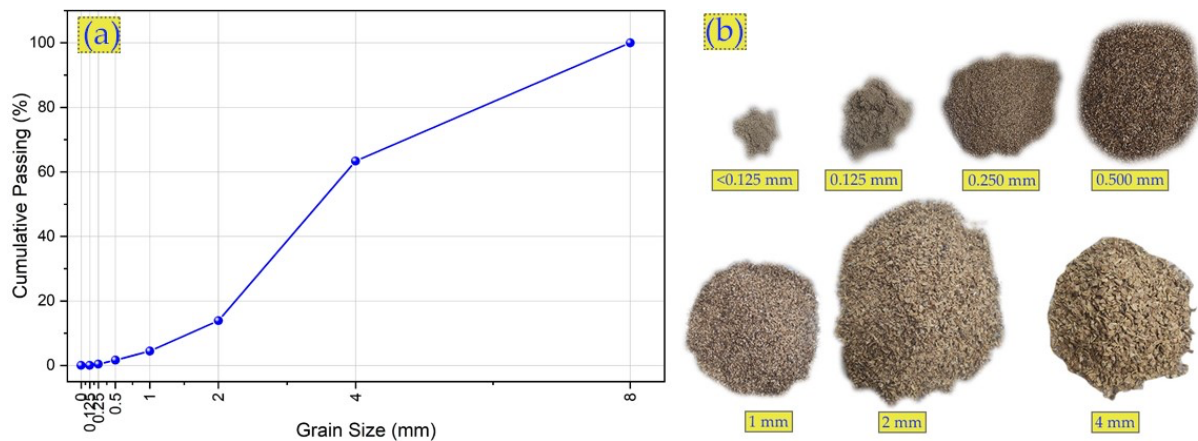
In order to minimise the effect of the filler material on the polymer composite, standard CEN sand was preferred as filler material. In addition, walnut shells obtained from local walnut species grown in Bingöl province were used as filling material (Figure 1).



**Figure 1.** (a) unground and (b) grounded walnut shells

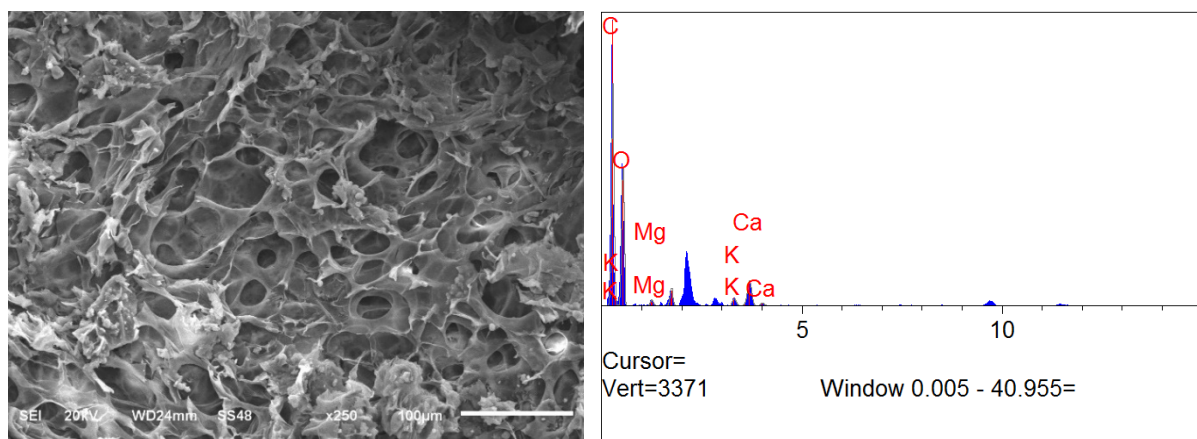
Walnut shells to be used in the study were sieved and granulometry was determined. The particle size distribution of walnut shells is shown in Figure 2a and the sieved walnut shells are shown in Figure 2b. In the study, walnut shells smaller than 8 mm in diameter were preferred to ensure a more homogeneous dispersion. Due to their larger surface area, small particles allow a stronger interfacial bonding with the polymer. In addition, these sizes can be more easily processed during the manufacturing process and increase the consistency of the physical

properties of the composites. In this way, walnut shells can be used more efficiently and effectively as reinforcement material.



**Figure 2.** (a) grain size distribution of walnut shells, (b) sieved walnut shells

The porous structure of the walnut shell used as filler in the study was visualised by scanning electron microscope (SEM) (Figure 3a). Elemental analysis was performed by X-ray spectroscopy (EDX) (Figure 3b). The walnut shell was coated with gold and palladium prior to SEM imaging. It was then imaged in a scanning electron microscope under 20 kV voltage at 250 times magnification. Figure 3a clearly shows the porous structure of the walnut shell. The elements O, C, Ca, Si, K and Mg were detected in the walnut shell by EDX at 50.551%, 44.720%, 2.308%, 1.199%, 0.657% and 0.566% by weight, respectively.

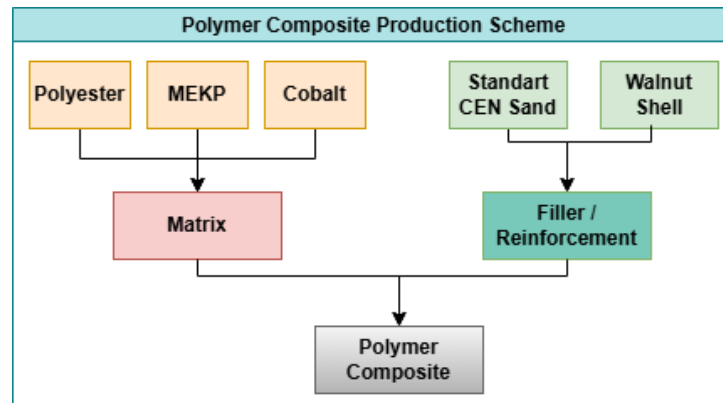


**Figure 3.** (a) SEM and (b) EDX image of walnut shell

## 2.2. Production of Polymer Composites

In the production of polymer composites, the matrix was produced first. While producing the matrix, 2 wt% MEKP was added to FRP and mixed for 90 seconds. Then 0.2 wt% cobalt octoate was added and mixed for another 90 seconds to obtain a homogenous mixture. Then, standard CEN sand and ground walnut shells passed through 8 mm sieve were added to the prepared polymer matrix by mixing for 90 seconds in the mixer. The prepared filler and polymer matrix mixture was mixed in a mixer for 180 seconds at a constant speed of 140 rpm, then placed in

moulds and kept under laboratory conditions ( $23\pm 2^{\circ}\text{C}$  and  $45\pm 5\%$  relative humidity) for 24 hours. The polymer composite production scheme is shown in Figure 4.

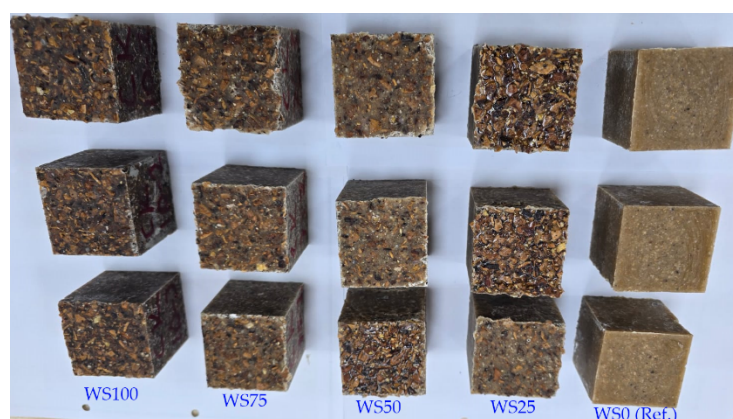


**Figure 4.** Polymer composite production scheme

The blend ratios of the polymer composite groups are shown in Table 3 and the specimens produced using these ratios are shown in Figure 5. FRP/filler was preferred at a ratio of 1:1 when forming the mixture groups. Walnut shell was used by replacing with standard CEN sand at 0, 25, 50, 75 and 100 % by volume. The mixture group in which only standard CEN sand was used as filler was coded as control specimen (Ref.). Other mixture groups were coded depending on the proportion of walnut shell used. For example, in the specimen coded WS25, walnut shell was used by replacing 25% by volume with standard CEN sand.

**Table 3.** Composite mix ratios

Mix Code	Mix Ratios (% by vol.)		
	Matrix FRP	Filler	
		CEN sand	Walnut Shell
Ref.	50	50	0
WS25	50	37.5	12.5
WS50	50	25	25
WS75	50	12.5	37.5
WS100	50	0	50



**Figure 5.** Produced composite specimens

### 2.3. Experimental Procedure

Archimedes balance was used for apparent density, porosity and water absorption tests of the produced polymer composites. The specimens used in the Archimedes balance experiment were dried in an oven at  $105\pm 5^\circ\text{C}$  and mass measurements were made. Then, the specimens were kept in water until they were completely saturated with water. The surface of the saturated specimens was dried with a damp cloth and the saturated dry surface mass was measured. In the final stage, the masses of the specimens immersed in water were determined on the Archimedes balance and using these data, the apparent density, water absorption and porosity values of the specimens were calculated using the equations given below.

$$\text{Apparent density} : M_0/(M_0-M_1) \quad (1)$$

$$\text{Water absorption} : (M_2-M_0)/M_0*100 \quad (2)$$

$$\text{Porosity} : (M_2-M_0)/(M_2-M_1)*100 \quad (3)$$

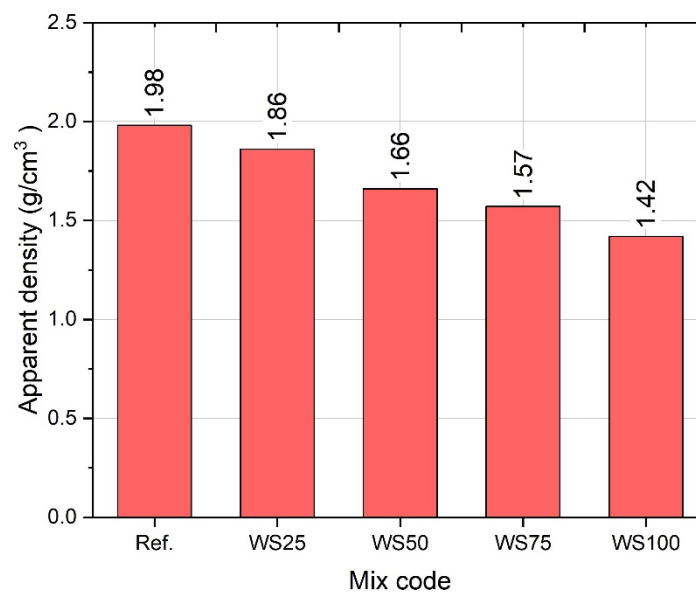
Here,  $M_0$ : oven dry mass,  $M_1$ : mass in water,  $M_2$ : saturated dry surface mass.

Three specimens of 5x5x5 cm each were used to determine density, water absorption, porosity, UPV and compressive strength values. The UPV test was performed according to ASTM C597-16 (2016) [34] and the compressive strength test was performed according to TS EN 12390-3 (2021) [35]. UL94 vertical combustion test was performed according to TS EN 60695-11-10 (2014) [36].

## 3. Results and Discussion

### 3.1. Apparent Density Test Results

The apparent density test results of the composite mixture groups are given in Figure 6.

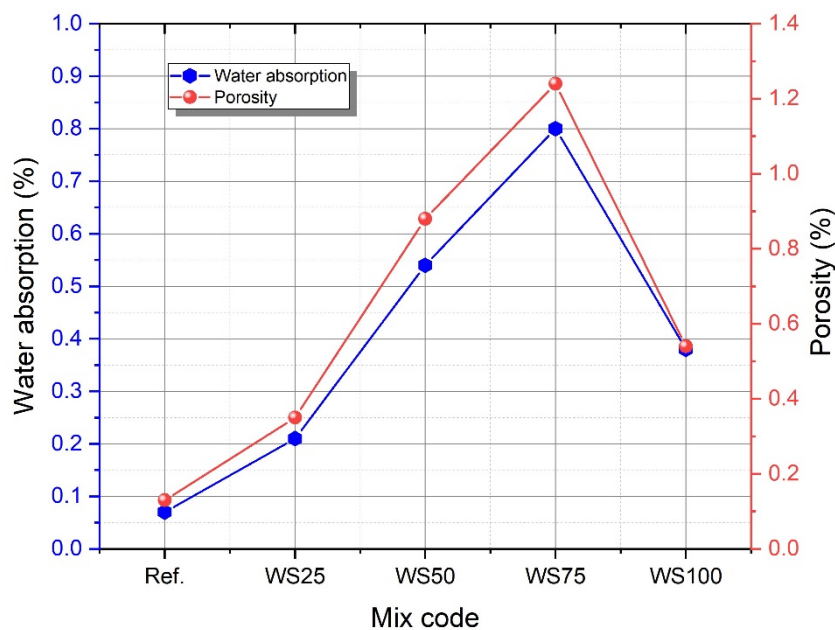


**Figure 6.** Apparent Density Test Results

While the apparent density of the control specimen was  $1.98 \text{ g/cm}^3$ , a decrease in apparent density was observed with walnut shell substitution. The lowest apparent density was determined as  $1.42 \text{ g/cm}^3$  in the specimen coded WS100. The increase in the amount of walnut shell caused a decrease in the apparent density of the composites. Compared to the control specimen, the apparent densities decreased by 6%, 16%, 21% and 28% with walnut shell-standard CEN sand substitutions of 25%, 50%, 75% and 100% by volume, respectively. In previous studies, researchers [25,29] reported that composite densities decreased with an increase in the amount of porous material.

### 3.2. Water Absorption and Porosity Test Results

Water absorption and porosity test results of the mixture groups are shown in Figure 7. The lowest water absorption value was reached in the control specimen with 0.07%. When CEN sand was used up to 75% in place of walnut shells, higher water absorption values were seen. When compared to the control specimen, an increase in water absorption values was observed at 100% displacement. However, a decrease was observed when compared to 50% and 75% displacement. The changes in the water absorption values of WS25, WS50, WS75 and WS100 coded specimens compared to the control specimen were determined as 200, 671, 1043 and 443%, respectively. Although the exchange rates are high compared to the control specimen, the water absorption is low. The highest water absorption was measured as 0.80% in the specimen coded WS75. The low water absorption values of the composite mixture groups were attributed to the low water absorption properties of polyester resin as stated in previous studies. Since polyester resin was used at 50% by volume, it affected the water absorption behaviour of the composite. The partial increase in water absorption due to the increase in walnut shell content was attributed to the fact that walnut shell exhibited more water absorption behaviour than CEN sand. In previous studies, researchers [32,33] stated that water absorption increased due to the increase in walnut shell content.



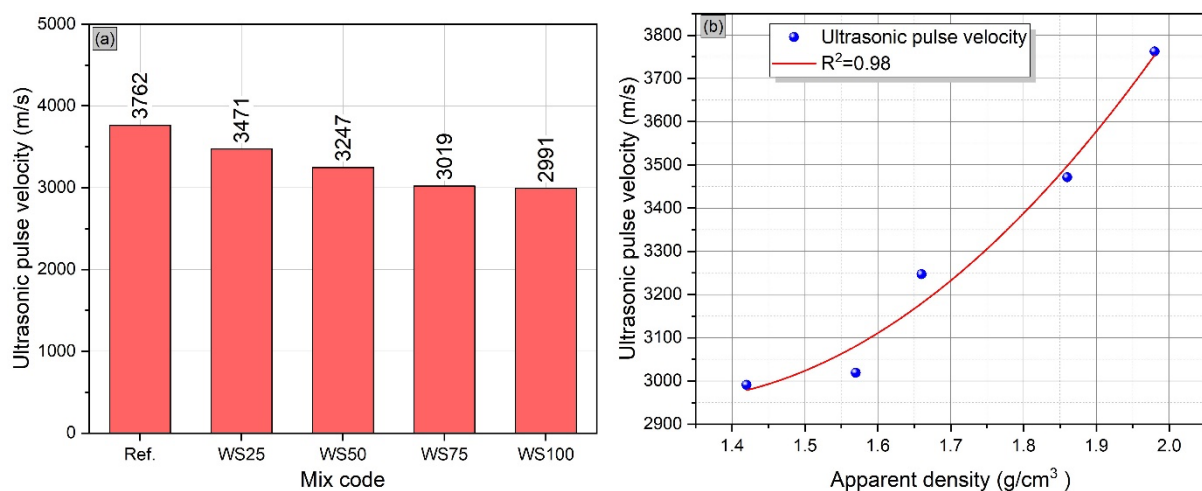
**Figure 7.** Water Absorption and Porosity Test Results



Since the walnut shells used have a more porous structure than the standard CEN sand, an increase in the porosity ratios of the composite was observed as the walnut shell ratio increased in the mixture groups compared to the control specimen. The lowest porosity value was 0.13% in the control specimen, while the highest porosity value was 1.24% in the specimen coded WS75. The fact that the water absorption and porosity values of the specimen coded WS100 are partially lower compared to the specimens coded WS50 and WS75 is thought to be related to the absence of CEN sand in this specimen and the better coating of the walnut shell with the matrix.

### 3.3. Ultrasonic Pulse Velocity Test Results

UPV test results are given in Figure 8. When Figure 8a is analysed, it is seen that the UPV values decrease as the walnut shell ratio increases in the mixture groups. While the UPV value of the control specimen (Ref.) was 3762 m/s, the UPV values of the specimens coded WS25, WS50, WS75 and WS100 were determined as 3471, 3247, 3019 and 2991 m/s, respectively, depending on the increase in walnut shell ratio. In previous studies have also reported a decrease in UPV values due to an increase in the porous filler ratio [37–39].



**Figure 8. (a) UPV Test Results and (b) Relationship with Apparent Density**

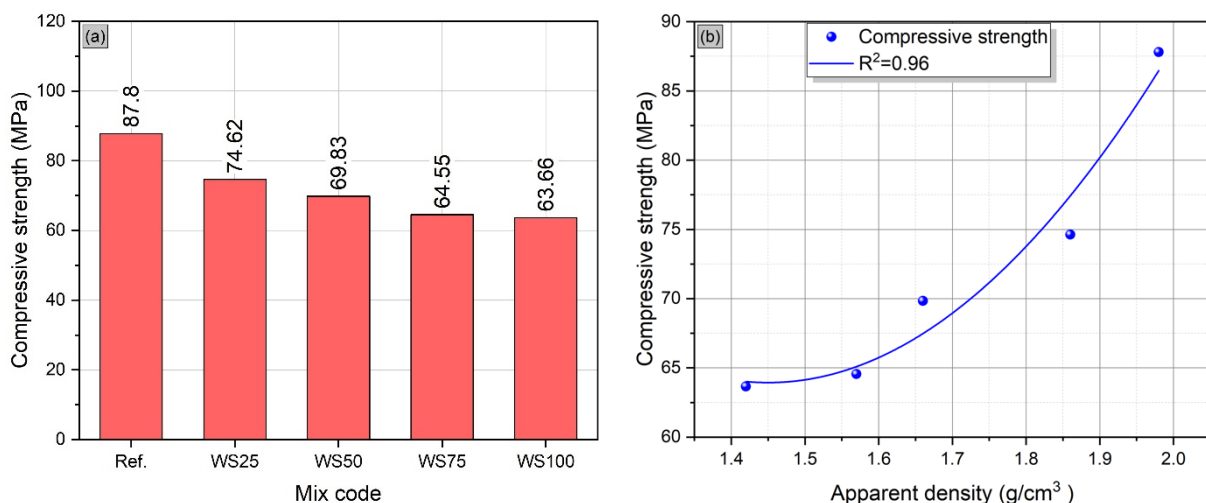
The relationship between UPV and apparent density is shown in Figure 8b. As can be seen from the figure, as the apparent density increases, UPV values also increase. There is a positive non-linear polynomial relationship between apparent intensity and UPV values. The correlation coefficient of this relationship was determined as  $R^2=0.98$ . Correlation coefficients above 0.95 indicate a strong relationship between the parameters. From this point of view, it can be said that there is a strong relationship between visible density and UPV.

### 3.3. Compressive Strength Test Results

The compressive strength test results are presented in Figure 9a. According to these results, the compressive strength of the control specimen consisting of FRP matrix and CEN sand was determined as 87.80 MPa. Compared to the other specimens, the control specimen exhibited the highest compressive strength. The compressive strengths of specimens coded WS25, WS50,

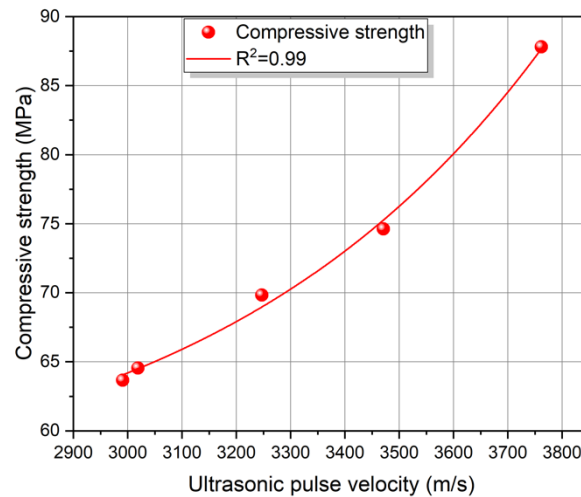
WS75 and WS100 were determined as 74.62 MPa, 69.83 MPa, 64.55 MPa and 63.66 MPa, respectively. These data clearly show that the compressive strength decreases with increasing walnut shell content. In particular, the lowest compressive strength was observed in the WS100 specimen where the walnut shell ratio reached 100%. The decrease in compressive strength as the walnut shell ratio increases in the mixture groups may be due to the fact that walnut shell has a more porous structure. In previous studies, it has been reported that the compressive strength of composite materials generally decreases as the porous material ratio increases [39,40]. In this study, it is thought that the homogeneous distribution of walnut shell in the matrix and the structural properties of walnut shell cause a decrease in compressive strength. However, the compressive strength of the composites produced showed a level of performance that can be used in structural elements despite the walnut shell substitution. Compared to the control specimen, the rates of decrease in compressive strength with walnut shell substitution were determined as 15%, 20%, 26% and 27%, respectively. These results show that there is a gradual decrease in compressive strength with the increase in walnut shell ratio.

The relationship between compressive strength and apparent density is shown in Figure 9b. As can be seen from the graphs, as the apparent density increases, a significant increase in compressive strength is observed. There is a non-linear polynomial relationship between apparent density and compressive strength and there is a positive correlation between these two parameters. The correlation coefficient greater than 0.95 ( $R^2=0.96$ ) shows that the relationship between apparent density and compressive strength is quite strong. These findings reveal that the mechanical properties of composite materials are directly related to the density and porous materials such as walnut shells significantly affect this relationship. The results show that walnut shell substitution significantly reduces the compressive strength of composite materials, but still these materials exhibit sufficient mechanical performance to be used in structural elements.



**Figure 9.** (a) Compressive Strength Test Results and (b) Relationship with Apparent Density

The relationship between UPV and compressive strength is shown in Figure 10. As can be seen from the figure, as the UPV increases, the compressive strength values also increase. There is a positive polynomial relationship between UPV and compressive strength values. It can be said that there is a strong relationship between UPV and compressive strength ( $R^2=0.99$ ).



**Figure 10.** Relationship between compressive strength and UPV

The type and proportion of binder material used can improve the mechanical performance of composites. Increasing the amount of binder polyester can increase the strength of walnut shell reinforced composites. In addition, applying alkaline surface treatment to walnut shell can improve the strength of composites. Reducing the size of walnut shell can improve the mechanical properties due to its better wettability associated with increased surface area. Finally, the combination of walnut shell with other reinforcing materials or hybrid composites can increase the compressive strength.

Although there is a reduction in strength values, there are significant benefits in terms of environmental sustainability, economic costs and innovation potential. Especially for environmentally sensitive industries and sectors looking for low-cost, sustainable solutions, walnut shell offers a strong alternative. The reduction in mechanical performance can be offset by performance that is often sufficient for lighter weight and affordable applications, which is one of the reasons why the use of walnut shell is favoured.

Investigations on the mechanical properties of the binder materials used in this study can form the basis for future research. In particular, studies on how biodegradable polymer binders provide better interaction with organic wastes such as walnut shells can be advanced. Improvements on binder type and ratio can improve the performance of composites.

The findings of this research shed light on future studies and contribute to the production of more efficient, environmentally friendly composite materials. The present research has helped us to understand the potential of walnut shell and improvements can be made in different aspects to improve the utilisation of this material.

### 3.4. UL94 Vertical Burning Test Results

All of the specimens ignited in the UL94 vertical combustion test of the produced composites, but when the flame source was removed from the environment, the flame on the specimen surfaces extinguished spontaneously within 2-4 seconds. The first ignition occurred at the 10th second in the specimen coded WS100 and the flame was extinguished spontaneously within 4

seconds when the flame source was removed. Aluminium Hydroxide- $\text{Al}(\text{OH})_3$  in the FRP used in the study prevents flame propagation by forming a char layer on the specimen surface during combustion. This has also been reported in previous studies [41,42]. Flame retardants enter early degradation and form a protective shell on the material. This shell slows down the combustion process by cutting the contact between the material and oxygen [43]. Since no flame propagation was observed on the material surface, no flaming droplet formation occurred and no flame-induced combustion occurred in the cotton under the experimental setup. According to the results of the UL94 vertical combustion test, all specimens were evaluated in class  $V_0$ .

### 3.5. Statistical Analyses

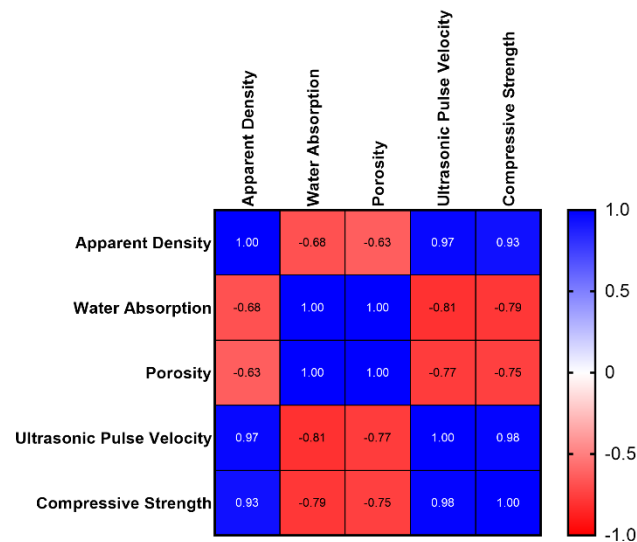
In order to test the response of the obtained material under different conditions, apparent density, water absorption, porosity, ultrasonic pulse velocity and compressive strength values were determined and included in the research (Table 4).

**Table 4.** Values of the material under different test conditions

<b>Mix Code</b>	<b>Apparent Density (<math>\text{g}/\text{cm}^3</math>)</b>	<b>Water Absorption (%)</b>	<b>Porosity (%)</b>	<b>Ultrasonic Pulse Velocity (m/s)</b>	<b>Compressive Strength (MPa)</b>
<b>Ref.</b>	1.98	0.07	0.13	3762	87.80
<b>WS25</b>	1.86	0.21	0.35	3471	74.62
<b>WS50</b>	1.66	0.54	0.88	3247	69.83
<b>WS75</b>	1.57	0.80	1.24	3019	64.55
<b>WS100</b>	1.42	0.38	0.54	2991	63.66

According to the results of the correlation analysis, there is a negative correlation between apparent density and water absorption and porosity, while there is a positive correlation between apparent density and UPV and compressive strength. A positive relationship was found between water absorption and porosity, but water absorption shows a negative relationship with UPV and compressive strength. Likewise, porosity has a negative relationship with UPV and compressive strength. On the other hand, a positive relationship was found between UPV and compressive strength (Figure 11).

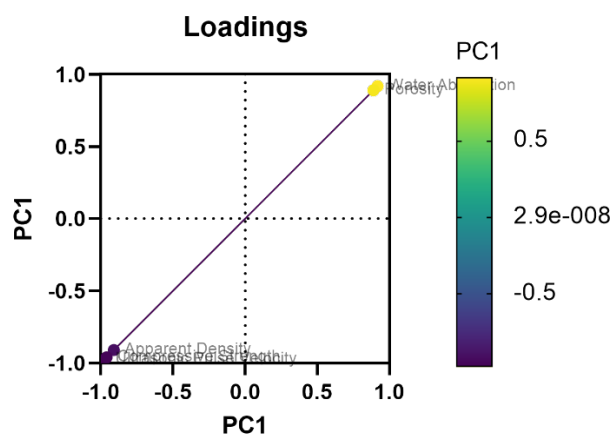
Following the correlation analysis, principal component analysis (PCA) was performed to determine the direction of the relationship between the data. As a result of the analyses, a negative correlation was observed between apparent density, compressive strength and ultrasound transmission rate, while a positive correlation was observed between water absorption and porosity (Table 5, Figure 12).



**Figure 11.** Pearson r Correlation Data

**Table 5.** Principal Component Analysis Results

PC summary	PC1	PC2	PC3	PC4
Eigenvalue	4.332	0.6142	0.05097	0.003157
Proportion of variance	86.63%	12.28%	1.02%	0.06%
Cumulative proportion of variance	86.63%	98.92%	99.94%	100.00%



**Figure 12.** Basic Component Analysis

Correlation and basic component analyses showed that there are significant relationships between the physical properties of the materials. There are positive correlations between apparent density and compressive strength and ultrasonic transmission rate. In addition, there are negative correlations between apparent density and water absorption and porosity. This shows that it has a significant effect on the durability and structural properties of the material. As a result, it is understood that the performance properties of materials are interrelated and these relationships should be optimised.

#### 4. Conclusion

In this study, the potential of using flame retardant polyester resin, CEN sand and walnut shell, an agricultural waste, in polymer composites was investigated. Within the scope of the research, the physico-mechanical performances of the composites were examined in detail and the changes in mechanical, physical properties and combustion behaviour were evaluated by adding walnut shell to the composites. The results obtained show that walnut shell substitution improves the environmental sustainability of composite materials and has significant effects on mechanical and combustion properties. The results are listed below:

- Walnut shell substitution reduced the apparent densities of the composites.
- Water absorption and porosity ratios increased in parallel with the increase in the amount of walnut shell, but these ratios remained at low levels due to the high amount of polymer. The highest water absorption was determined as 0.80% in specimen WS100.
- A decrease in ultrasonic pulse velocity (UPV) values was observed with increasing walnut shell content in the composites. This decrease is related to the porous structure of walnut shell. Water absorption and porosity test results also support this situation.
- The compressive strength of the composites decreased depending on the amount of walnut shell used. This decrease is due to the structural porosity of walnut shell. The highest compressive strength was obtained as 87.8 MPa in the control specimen, while the lowest compressive strength was determined as 63.66 MPa in the specimen coded WS100.
- The polymer based composites produced exhibited favourable performance in terms of fire resistance.

In conclusion, the data obtained in this study show that walnut shell substitution significantly reduces the compressive strength of composite materials, but despite this reduction, the materials exhibit sufficient mechanical performance to be used in structural elements. The use of walnut shell in composites increases environmental sustainability

Future research may enable the production of more sustainable and environmentally friendly composites through the use of biodegradable polymer binders. Further investigation of the compatibility of these binders with agricultural wastes and their effects on performance properties such as mechanical and thermal properties of composites may make it possible to make biodegradable materials more efficient and durable for industrial applications. Furthermore, a comprehensive assessment of the environmental impact of such composites through life cycle analyses (LCA) could be an important focus area for future research.

#### References

- [1] L. Thomas, J. Sebastian, A. Santhosh, R. Vijay, V.N. Ajukumar, M.T.B.H. Hameed Sultan, M. Mubarak Ali, Physicochemical Modifications on Fibre Reinforced Polymer Composites for Mining Applications, *J. Mines, Met. Fuels* (2023) 2545–2553. <https://doi.org/10.18311/jmmf/2023/36535>.
- [2] R. Phiri, S. Mavinkere Rangappa, S. Siengchin, O.P. Oladijo, H.N. Dhakal, Development of sustainable biopolymer-based composites for lightweight applications from

- agricultural waste biomass: A review, *Adv. Ind. Eng. Polym. Res.* 6 (2023) 436–450. <https://doi.org/10.1016/j.aiepr.2023.04.004>.
- [3] Y. Karaduman, Viscoelastic properties of natural fiber reinforced cork based sandwich composites, *Pamukkale Univ. J. Eng. Sci.* 24 (2018) 1257–1261. <https://doi.org/10.5505/pajes.2018.56492>.
- [4] M.N. Kolak, Polimer esaslı kenevir, ketencik ve perlit içeren kompozitlerin fiziko-mekanik ve termal özelliklerinin incelenmesi, Atatürk Üniversitesi, 2023.
- [5] S.H. Kamarudin, M.S. Mohd Basri, M. Rayung, F. Abu, S. Ahmad, M.N. Norizan, S. Osman, N. Sarifuddin, M.S. Desa, U.H. Abdullah, I.S. Mohamed Amin Tawakkal, L.C. Abdullah, A Review on Natural Fiber Reinforced Polymer Composites (NFRPC) for Sustainable Industrial Applications, *Polymers (Basel)*. 14 (2022). <https://doi.org/10.3390/polym14173698>.
- [6] S. Rajaram, T. Subbiah, F.S. Arockiasamy, J. Iyyadurai, Transforming Agricultural Waste into Sustainable Composite Materials: Mechanical Properties of Tamarindus Fruit Fiber (TFF)-Reinforced Polylactic Acid Composites, in: *Int. Conf. Process. Perform. Mater. (ICPPM 2023)*, MDPI, Basel Switzerland, 2024: p. 32. <https://doi.org/10.3390/engproc2024061032>.
- [7] M.T. Ferrandez-García, C.E. Ferrandez-Garcia, T. Garcia-Ortuño, A. Ferrandez-Garcia, M. Ferrandez-Villena, Study of waste jute fibre panels (*Corchorus capsularis* L.) agglomerated with portland cement and starch, *Polymers (Basel)*. 12 (2020) 599. <https://doi.org/10.3390/polym12030599>.
- [8] N. Stevulova, J. Cigasova, I. Schwarzova, A. Sicakova, J. Junak, Sustainable bio-aggregate-based composites containing hemp hurds and alternative binder, *Buildings* 8 (2018) 25. <https://doi.org/10.3390/buildings8020025>.
- [9] V. Barbieri, M. Lassinantti Gualtieri, T. Manfredini, C. Siligardi, Lightweight concretes based on wheat husk and hemp hurd as bio-aggregates and modified magnesium oxysulfate binder: Microstructure and technological performances, *Constr. Build. Mater.* 284 (2021) 122751. <https://doi.org/10.1016/j.conbuildmat.2021.122751>.
- [10] M. Charai, H. Sghiouri, A. Mezrhab, M. Karkri, Thermal insulation potential of non-industrial hemp (*Moroccan cannabis sativa* L.) fibers for green plaster-based building materials, *J. Clean. Prod.* 292 (2021) 126064. <https://doi.org/10.1016/j.jclepro.2021.126064>.
- [11] P. Brzyski, M. Gładdecki, M. Rumińska, K. Pietrak, M. Kubiś, P. Łapka, Influence of hemp shives size on hygro-thermal and mechanical properties of a hemp-lime composite, *Materials (Basel)*. 13 (2020) 5383. <https://doi.org/10.3390/ma13235383>.
- [12] J. Williams, M. Lawrence, P. Walker, The influence of constituents on the properties of the bio-aggregate composite hemp-lime, *Constr. Build. Mater.* 159 (2018) 9–17. <https://doi.org/10.1016/j.conbuildmat.2017.10.109>.
- [13] M. Degrave-Lemeurs, P. Glé, A. Hellouin de Menibus, Acoustical properties of hemp concretes for buildings thermal insulation: Application to clay and lime binders, *Constr. Build. Mater.* 160 (2018) 462–474. <https://doi.org/10.1016/j.conbuildmat.2017.11.064>.

- [14] V. Barbieri, M. Lassinantti Gualtieri, C. Siligardi, Wheat husk: A renewable resource for bio-based building materials, *Constr. Build. Mater.* 251 (2020) 118909. <https://doi.org/10.1016/J.CONBUILDMAT.2020.118909>.
- [15] M.I. Reddy, M.A. Kumar, S.A. Reddy, P.V.K. Raju, Thermo physical properties of Jute, Pineapple leaf and Glass fiber reinforced polyester hybrid composites, *Materials Today-Proceedings* 5 (2018) 21055–21060.
- [16] J. Militký, A. Jabbar, Comparative evaluation of fiber treatments on the creep behavior of jute/green epoxy composites, *Compos. Part B Eng.* 80 (2015) 361–368. <https://doi.org/10.1016/j.compositesb.2015.06.014>.
- [17] H. Ahmad, M. Islam, M. Uddin, Thermal and Mechanical properties of epoxy-jute fiber composite, *J. Chem. Eng.* 27 (2014) 77–82. <https://doi.org/10.3329/jce.v27i2.17807>.
- [18] D. Djeghader, B. Redjel, Effect of water absorption on the Weibull distribution of fatigue test in jute-reinforced polyester composite materials, *Adv. Compos. Lett.* 28 (2019) 096369351985383. <https://doi.org/10.1177/0963693519853833>.
- [19] B. V. Subrahmanyam, S. V. Gopala Krishna, R. Jithendra Kumar, S.B.R. Devireddy, Experimental and micromechanical thermal characteristics of jute fiber reinforced polyester composites, in: *Mater. Today Proc.*, Elsevier Ltd, 2019: pp. 350–356. <https://doi.org/10.1016/j.matpr.2019.06.311>.
- [20] F. Rahman, A. Eiamin, M.R. Hasan, S. Islam, M.M. Haque, M.A. Gafur, S.A. Dhar, Effect of Fiber Loading and Orientation on Mechanical and Thermal Properties of Jute-Polyester Laminated Composite, *J. Nat. Fibers* 19 (2022) 1741–1755. <https://doi.org/10.1080/15440478.2020.1788485>.
- [21] N.V. Subba Raju, M.I. Reddy, M.A. Kumar, K. Ramji, Study on thermo physical properties of hemp, jute and glass fiber reinforced polyester composites, *Mater. Today Proc.* 5 (2018) 5918–5924. <https://doi.org/10.1016/j.matpr.2017.12.191>.
- [22] H. Dhakal, Z.T. Zhang, M. Richardson, Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites, *Compos. Sci. Technol.* 67 (2007) 1674–1683. <https://doi.org/10.1016/j.compscitech.2006.06.019>.
- [23] A. Vinod, J. Tengsuthiwat, Y. Gowda, R. Vijay, M.R. Sanjay, S. Siengchin, H.N. Dhakal, Jute/Hemp bio-epoxy hybrid bio-composites: Influence of stacking sequence on adhesion of fiber-matrix, *Int. J. Adhes. Adhes.* 113 (2022) 103050. <https://doi.org/10.1016/j.ijadhadh.2021.103050>.
- [24] K. Yaman, Bitkisel atıkların değerlendirilmesi ve ekonomik önemi, *Kastamonu Üniversitesi, Orman Fakültesi Derg.* 12 (2012) 339–348.
- [25] A.N. Beskopylny, S.A. Stel'makh, E.M. Shcherban', L.R. Mailyan, B. Meskhi, A.A. Shilov, A. Chernil'nik, D. El'shaeva, Effect of Walnut-Shell Additive on the Structure and Characteristics of Concrete, *Materials (Basel)*. 16 (2023). <https://doi.org/10.3390/ma16041752>.
- [26] H. Marey, G. Kozma, G. Szabó, Effects of Using Green Concrete Materials on the CO2 Emissions of the Residential Building Sector in Egypt, *Sustainability* 14 (2022).



- <https://doi.org/10.3390/su14063592>.
- [27] M.Y. Abdulwahid, A.A. Akinwande, M. Kamarou, V. Romanovski, I.A. Al-Qasem, The production of environmentally friendly building materials out of recycling walnut shell waste: a brief review, *Biomass Convers. Biorefinery* (2023). <https://doi.org/10.1007/s13399-023-04760-2>.
- [28] H.E. Balcıoğlu, Ö. Yeşil, M. Aktaş, Ceviz Kabuğu Takviyeli Polyester Reçinenin Aşınma Dirençlerinin Belirlenmesi, 1, *Ulus. Geri Kazanım Kongre ve Sergisi* (2012) 2–4.
- [29] P. Pradhan, A. Satapathy, Physico-mechanical characterization and thermal property evaluation of polyester composites filled with walnut shell powder, *Polym. Polym. Compos.* 30 (2022) 09673911221077808. <https://doi.org/10.1177/09673911221077808>.
- [30] C.B. Talikoti, T.T. Hawal, P.P. Kakkamari, M.S. Patil, Preparation and characterization of epoxy composite reinforced with walnut shell powder, *Int. Res. J. Eng. Technol.* 2 (2015) 721–725.
- [31] V. Ahlawat, S. Kajal, A. Parinam, Experimental analysis of tensile, flexural, and tribological properties of walnut shell powder/polyester composites, *Euro-Mediterranean J. Environ. Integr.* 4 (2018) 1. <https://doi.org/10.1007/s41207-018-0085-6>.
- [32] M.U. Obidiegwu, S.C. Nwanonyi, I.O. Eze, I.C. Egbuna, The effect of walnut shell powder on the properties of polypropylene filled composite, *Int. Asian Res. J.* 2 (2014) 22–29.
- [33] P. Paçzkowski, Properties of Eco-Friendly Composites Based on Post-Consumer Recycled Resin Filled with Walnut Shell Powder, *Polymers (Basel)*. 15 (2023) 4389. <https://doi.org/10.3390/polym15224389>.
- [34] ASTM C597-16, Standard Test Method for Pulse Velocity through Concrete., American Society for Testing Materials, Philadelphia., 2016.
- [35] TS EN 12390-3, Testing hardened concrete - Part 3: Compressive strength of test specimens, Turkish Standards Institution, Ankara, 2019.
- [36] TS EN 60695-11-10, Fire hazard testing -- Part 11-10: Test flames - 50 W horizontal and vertical flame test methods, 2014.
- [37] H. Polat, İ. Üstün, A. Şafak, A.N. Çakılcıoğlu, Utilization of waste brick powder as admixture in polymer concrete: Investigation of mechanical properties, *Recep Tayyip Erdogan Univ. J. Sci. Eng.* 4 (2023) 76–86. <https://doi.org/10.53501/rteufemud.1306484>.
- [38] H. Polat, B. Demirel, M.N. Kolak, M. Oltulu, Investigation of the use of barite mineral in polymer concrete, *Bingol Univ. J. Tech. Sci.* 1 (2020) 25–32. <https://dergipark.org.tr/en/download/article-file/2039838>.
- [39] V. Akyuncu, F. Sanliturk, Investigation of physical and mechanical properties of mortars produced by polymer coated perlite aggregate, *J. Build. Eng.* 38 (2021) 102182.

<https://doi.org/10.1016/j.jobe.2021.102182>.

- [40] M.N. Kolak, M. Oltulu, Investigation of thermal conductivity properties of polymer based composites containing waste materials, *Int. J. Eng. Res. Dev.* 13 (2021) 310–320. <https://doi.org/10.29137/umagd.822265>.
- [41] M. Kaya, Alev Geciktirici Ve Duman Bastırıcı Katkı Maddeleri, *Eskişehir Osmangazi Üniversitesi Mühendislik ve Mimar. Fakültesi Derg.* 11 (1998) 77–88. <https://dergipark.org.tr/en/download/article-file/327266>.
- [42] N.A. Isitman, C. Kaynak, Effect of partial substitution of aluminum hydroxide with colemanite in fire retarded low-density polyethylene, *J. Fire Sci.* 31 (2012) 73–84. <https://doi.org/10.1177/0734904112454835>.
- [43] B. Aydoğan, N. Usta, Nanokil ve kabaran alev geciktirici ilavesinin rijit poliüretan köpük malzemelerin ısı bozunma ve yanma davranışlarına etkilerinin incelenmesi, *Gazi Üniversitesi Mühendislik-Mimarlık Fakültesi Derg.* 30 (2015) 9–18. <https://doi.org/10.17341/gummfd.50725>.