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Investigation of the Effect of Alkalinization Process on the Tribological Performance of Lignocellulosic Waste Reinforced Eco-Composite Materials

Safeer Ansari [1], **Aung Htet Moe** [1], **Sena Kabave Kılınçarslan** [1], **M. Salih Gül** [1], **Enes Kılınçarslan** [1]

[1] *Karabük Üniversitesi, Karabük, TÜRKİYE*

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Abstract
In this study, particles obtained from walnut and hazelnut shells, which are lignocellulosic agricultural wastes, were used as reinforcement in the production of composite materials. After the grinding and sieving processes, the shells were subjected to heat treatment in order to remove the moisture from their content. Then, surface modification processes were carried out with the alkalization method. Four different composite samples with both walnut and hazelnut shell fillings were produced as neat polymer, untreated, heat-treated, and surface-modified reinforcement. The samples were subjected to hardness and tensile tests, and their mechanical behaviors were determined. Then, wear tests were carried out on the ball-on-flat device. Weight loss and friction coefficient data were obtained as a result of the wear tests. In addition, wear marks were examined morphologically with SEM and EDX analysis methods. As a result of the study, it was determined that the surface modification process increased the mechanical and tribological performance for both fillers. This shows that surface modification processes must be carried out before using lignocellulosic agricultural wastes as reinforcement.

Key Words
Lignocellulosic Waste, Natural Reinforcements, Eco-composites, Wear Performance.

Öz
Bu çalışmada, lignoselülozik tarımsal atık olan ceviz ve fındık kabuklarından elde edilen parçacıklar kompozit malzeme üretiminde takviye olarak kullanılmıştır. Öğütme ve eleme işlemlerinin ardından kabuklar, içeriğindeki nemin uzaklaştırılması amacıyla ısıl işleme tabi tutuldu. Daha sonra alkalizasyon yöntemi ile yüzey modifikasyon işlemleri gerçekleştirilmiştir. Ceviz ve fındık kabuğu dolgulu; saf polimer, işlemsiz, ısıl işlemli ve yüzey modifikasyon işlemli olarak dört farklı kompozit numune üretilmiştir. Numunelere sertlik ve çekme testleri uygulanarak mekanik davranışları belirlenmiştir. Daha sonra ball-on-flat cihazında aşınma testleri gerçekleştirilmiştir. Aşınma testleri sonucunda ağırlık kaybı ve sürtünme katsayısı verileri elde edilmiştir. Ayrıca aşınma izleri SEM ve EDX analiz yöntemleri ile morfolojik olarak incelenmiştir. Çalışma sonucunda, yüzey modifikasyon işleminin her iki dolgu malzemesi için de mekanik ve tribolojik performansı artırdığı belirlenmiştir. Bu durum, lignoselülozik tarımsal atıkların takviye olarak kullanılmasından önce mutlaka yüzey modifikasyon işlemlerinin gerçekleştirilmesi gerektiğini göstermektedir.

Anahtar Kelimeler
Lignoselülozik Atık, Doğal Takviyeler, Eko-kompozitler, Aşınma Performansı.

1. Introduction

Environmental pollution is increasing day by day worldwide, and a large part of this pollution consists of polymer waste. Increasing environmental concerns and sustainability goals have made green production mandatory for material production technologies. The green production approach targets not only sustainable final products but also raw material selection, energy consumption, toxicity control, and waste reduction. In this direction, environmentally friendly production can be achieved by using agricultural waste instead of synthetic reinforcement components in polymer composite production. These waste materials contribute to both the cost and the reduction of carbon emissions to the environment (Sanjay et al. 2018). Therefore, the production of green polymer composite materials is significantly important as they minimize environmental waste and enhance resource efficiency (Rogovina 2016).

***Corresponding Author:** *senakilincarslan@karabuk.edu.tr*

Natural fiber reinforcements, including coir, bamboo, and sisal, can improve the mechanical strength and modulus of polymer composites. Barbhuiya et al. illustrated that the flexural modulus of epoxy composites elevates with fiber loading, attaining optimal values at particular weight percentages (Hussain Barbhuiya, Uddin Choudhury, and Ismail 2016). Moreover, research by Jariwala and Jain demonstrated that chemical treatments can markedly enhance the interfacial strength between fibers and the polymer matrix, thereby directly influencing mechanical performance (Jariwala and Jain 2019). These treatments are essential for reducing moisture absorption and improving the durability of composites, particularly for outdoor applications (Prasad et al. 2021). The tribological characteristics of these composites are a crucial factor in their performance, particularly in applications requiring wear resistance. A study examining the tribological performance of various natural fibers revealed that fiber pre-treatment enhances their adhesion to the polymer, thereby improving wear properties (Paul, Mahakur, and Bhowmik 2024). Nallusamy's research on Roselle fibers underscored their appropriateness for mechanical reinforcement and applications necessitating excellent wear resistance, highlighting the potential for economical material recycling from agricultural waste (Nallusamy 2016). Mechanical testing of these composites generally encompasses evaluations of tensile strength, flexural strength, and impact resistance, indicating that increased fiber content typically correlates with enhanced mechanical properties. Sekaran et al. observed that this enhancement may reach a plateau, occasionally resulting in an adverse hybrid effect due to fiber agglomeration at elevated loadings (Sekaran, Kumar, and Pitchandi 2015). Many authors, such as Sathish Gandhi et al. (2025), N. Ayrilmis et al. (2010), and Francesc X. Espinach et al. (2020), have studied natural waste reinforced composite materials and found that these reinforcements have a performance-improving effect on the polymer matrix (Ayrilmis, Buyuksari, and Dundar 2010; Espinach et al. 2020; Gandhi et al. 2025).

Studies have shown that green reinforcements contribute to improving the performance of composite materials. However, incompatibility issues that occur at the interface between natural reinforcements and the matrix should not be ignored. The interfacial bonds between the reinforcement and the matrix are critical to the overall performance of the final product. This incompatibility between the reinforcement phase and the matrix is due to the hydrophilic properties of the reinforcements and the hydrophobic properties of the polymer matrices. Natural waste materials tend to absorb water due to their hydrophilic nature, which is negative for the stability of the material. This leads to poor fiber-matrix adhesion and insufficient stress transfer. To solve these problems, surface modification processes should be applied to natural reinforcements. Surface modification processes improve natural reinforcements for better bonding by changing the matrix surface structures (Şişmanoğlu 2020; Tayfun, Dogan, and Bayramli 2014).

Surface modification involves various chemical or physical processes that increase surface energy, introduce chemical functional groups, and increase the microroughness of natural reinforcements. As a result of these factors, the bonds at the reinforcement-matrix interfaces become stronger and more developed. As a result of these processes, the reinforcement material achieves microstructural stability and shows a uniform and homogeneous distribution within the matrix. This process makes the composite material more stable, improving mechanical and tribological performance (Shuai et al. 2020; Şişmanoğlu 2020). Surface modification treatments of lignocellulosic reinforcements can be carried out by alkalization, which is an effective and widespread method. The utilization of sodium hydroxide (NaOH) solution facilitates the elimination of lignin and hemicellulose constituents from the surface of natural reinforcements. (Jamilah and Sujito 2021; Rajeshkumar et al. 2021). The micro-roughness of the reinforcement components increases as the quantity of surface hydroxyl groups rises; this treatment allows the hydroxyl groups to form stronger physical or chemical bonds with the matrix. The alkalization process facilitates the uniform distribution of reinforcements within the matrix, thus increasing the stability of the material. Accordingly, the thermal, mechanical and tribological performance of the material also improves considerably.

In this study, the mechanical and tribological performance of composite materials reinforced with hazelnut and walnut shells, which are lignocellulosic agricultural wastes, were investigated. Walnut and hazelnut shells were first ground and sieved before surface modification processes. Then, the surface modification process was carried out by alkalizing process. Test samples were produced by adding surface modified and unmodified shell particles to the epoxy matrix at 10% concentration. The hardness of these samples was measured repeatedly by Shore D method. In order to evaluate the tribological performance of the composite materials, tests were carried out using ball-on-flat wear device. Wear zone was analyzed using SEM and EDX analysis. Wear mechanisms in the wear zone were analyzed. The results show that modified hazelnut shells can function as a more stable and effective reinforcement phase in the composite structure. This study advances the development of green composite materials based on recycling and reveals the potential for performance increase with surface modification applications.

2. Materials and Methods

2.1. Preparation of Hazelnut and Walnut Shell Powder

The goal of this step was to enlarge the particle surface area because it improves their contact with the polymer network. Firstly, raw hazelnuts and walnuts were sourced from a local market, and the nuts were manually cracked to separate the shells from the edible kernel. The shells received manual crushing using a hammer to make them suitable for additional processing operations. The initial reduction of shells is required to facilitate the uniform grinding process. The pre-crushed shell fragments proceeded with mechanical grinding. The laboratory grinding machine was used to produce powder from shell fragments. A 125 µm mesh sieve was used to separate particles of the ground powder with uniform dimensions and remove any large-sized residues. The sieving activity allowed researchers to collect only uniform minute particles suitable for composite reinforcement applications. After the filtration process, the collected powder was stored in airtight pouches for further treatment purposes (Figure 1a, b, c and d).

2.2. Heat Treatment of Hazelnut and Walnut Shell Powder

This protocol worked to eliminate water content while eliminating volatile organic compounds and promoting stability of the shell component structure. Natural fillers become more compatible with thermosetting matrices through heat treatment due to their ability to reduce surface polarity (Frackowiak, Ludwiczak, and Leluk 2018; Rogovina 2016). A controlled heat treatment process was carried out on the finely ground shell powder to improve its thermal and structural properties. Moreover, in high-temperature-resistant ceramic cups, the samples of the powder were placed into a laboratory oven at a constant temperature of 100 °C for a duration of 175 minutes. The heat-treated powders were then collected in the sample pouches (Figure 1e and f).

2.3. Surface Modification via Alkaline Treatment

The alkali treatment enables particle surface cleaning by reducing hemicellulose, lignin and surface impurities, then enhances surface roughness while boosting the composite adhesion capacity (Varma and Chandran 2025). To enhance the bonding between the shell particles and the polymer matrix, surface modification of the heat-treated powder was performed using NaOH alkali treatment. The procedure involved using 2 grams of NaOH pellets to dissolve in 100 ml of distilled water for creating a 2 wt.% NaOH solution. The combination of 30 milliliters NaOH solution with 2 grams shell powder allowed for the mixture. The magnetic stirrer functioned at 400–500 rpm to mix the solution for 2 hours. 0.5 ml of acetic acid was added to the mixture at the end of the process to remove excess NaOH in the mixture. After the mixing process, filtering, drying in the oven, and grinding again in the mortar took place. After the alkali treatment, the modified powders were stored in labelled sample pouches. Three variations of the powder were stored for composite fabrication: untreated powder, heat-treated powder, and heat-treated plus surface-modified powder (Figure 1g and h).

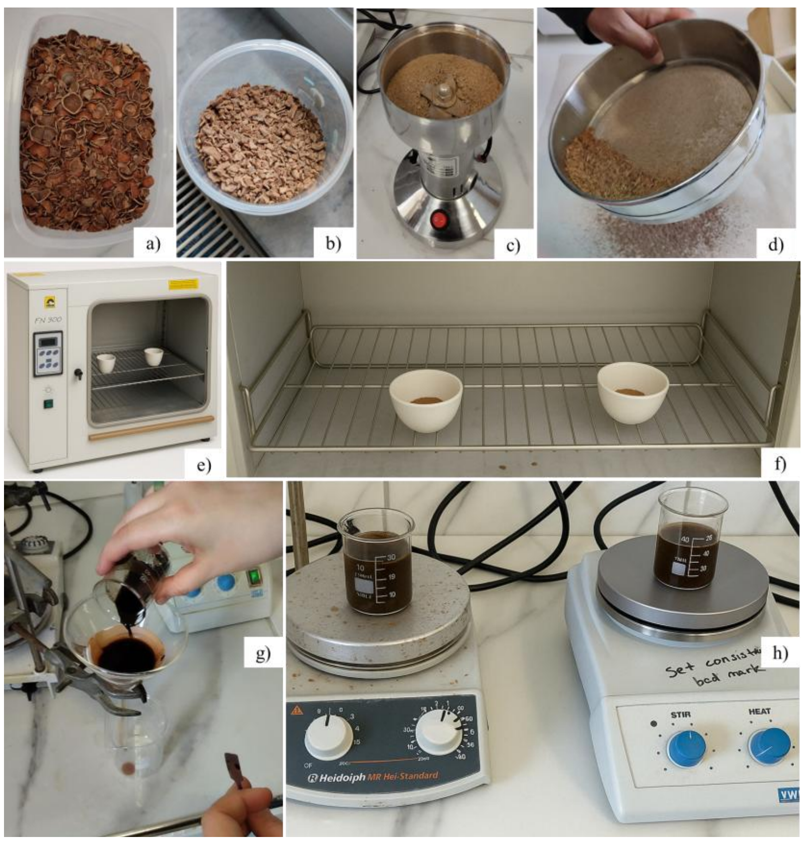


Figure 1. Preparation of shell powders: (a) hazelnut, (b) walnut, (c) grinding, (d) sieving, (e – f) heat treatment, (g – h) surface modification.

2.4. Composite Production

Commercially available epoxy was selected as the matrix material. The epoxy and hardener ratio used was 2:1. Three different composite material combinations were prepared by mixing untreated, heat-treated and surface-modified hazelnut powders with epoxy at a ratio of 10%. The mixing was carried out manually for about five minutes to obtain homogenous mixture, so the filler spread evenly through the resin. The mixture was then transferred into molds made of silicon. An external flame source was applied to the fluid resin poured into the mold. The heating activity of the flame source helped to remove air bubbles formed during casting. The molds were then left to cure at room temperature, where the molds remained stationary for a period of 48 hours until the epoxy resin was fully cured (Figure 2).

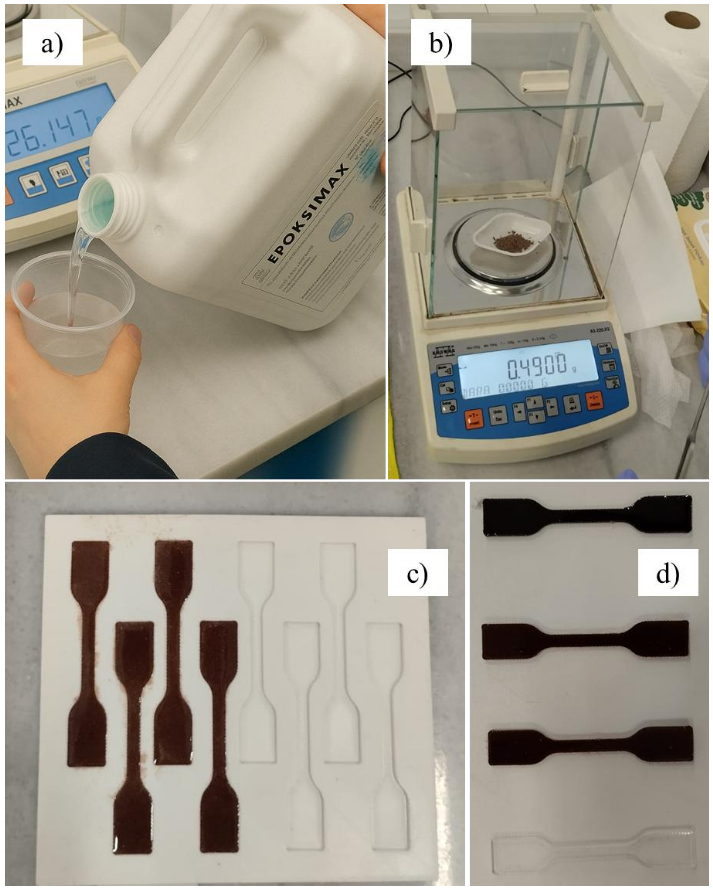


Figure 2. Composite production: (a) epoxy matrix, (b) weighing the reinforcement ratio, (c) mixing with epoxy matrix and pouring into the mold, and (d) samples.

Following the production of the composite materials, the samples were labelled using abbreviations to indicate their composition. According to the abbreviations epoxy sample was denoted as "EP", epoxy + raw hazelnut sample was denoted as "EP + H", epoxy + heat treated hazelnut sample was denoted as "EP + H. H", and epoxy + alkalized hazelnut sample was denoted as "EP + A. H". Similarly, samples containing additive "walnut" were denoted as "EP + W", "EP + H. W", and "EP + A. W". This abbreviation was applied consistently throughout the manuscript for clarity and ease of interpretation, and the abbreviations used for all samples are presented in Table 1.

Table 1. Abbreviations and compositions of the prepared composite samples.

Abbreviation	Materials
EP	Epoxy
EP + H	Epoxy + Raw Hazelnut
EP + H. H	Epoxy + Heat Treated Hazelnut
EP + A. H	Epoxy + Heat Treated and Alkalized Hazelnut
EP + W	Epoxy + Raw Walnut
EP + H. W	Epoxy + Heat Treated Walnut
EP + A. W	Epoxy + Heat Treated and Alkalized Walnut

2.5. Mechanical Characterization

Hardness measurements were performed using the Shore D method to investigate the mechanical behavior of the composites. The measurements were recorded by taking the average of 5 repetitions. Wear tests were performed on the ball-on-flat device to investigate the tribological performance of the samples. Wear parameters were determined as 20 N load, 50 mm/s speed, 5 mm stroke distance, and 100 m wear path. As a result of the wear tests, friction coefficient and weight loss data were obtained.

2.6. Morphological Characterization

SEM and EDX analyses were performed with Carl Zeiss Ultra Plus Gemini scanning electron microscope to examine the wear mechanisms occurring in the wear marks and to perform elemental analysis. SEM images were obtained at 250x zoom ratio and 100 µm scale.

3. Results and Discussion

3.1. Mechanical Results of Composite Materials

3.1.1. Hardness Results of Hazelnut Filled Composites

The hardness measurement results are presented in Table 2. According to Table 2, the Shore D hardness value of the EP sample was determined as 82, the EP + H sample as 87, the EP + H. H sample as 88, and the EP + A. H sample as 90. The hardness measurement results are also illustrated in Figure 3. According to the hardness test results, the lowest hardness value was observed in the EP sample. This indicates that the material is less resistant to external loads (Kiryushina and Semeykin 2020). The hardness value in the EP + H sample, which contains raw hazelnut shell reinforcement, increased significantly compared to the EP sample. The positive mechanical effect of the reinforcement on the matrix can explain this (Kiryushina and Semeykin 2020). In the EP + H. H sample, the heat-treated hazelnut shell particles appear to have partially improved the reinforcement–matrix bonding, which positively impacted the hardness value. In the EP + A. H sample, it can be claimed that the surface modification process enhanced the reinforcement–matrix interaction, thereby allowing for more efficient load transfer (Nemani et al. 2018). The surface modification process maximized the mechanical performance of the composite materials in this study.

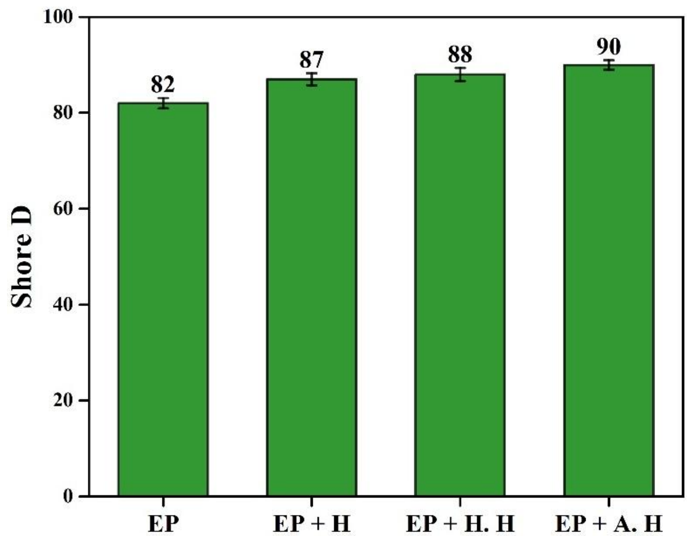


Figure 3. Hardness measurement results of hazelnut filled composite materials.

Table 2. Shore D hardness values composite materials.

Abbreviation	Shore D	Standard Deviation (±)
EP	82	1.08
EP + H	87	1.26
EP + H. H	88	1.4
EP + A. H	90	0.99

3.1.2. Hardness Results of Walnut Filled Composites

The hardness measurement results are presented in Table 3. According to Table 3, the Shore D hardness value of the EP sample was determined as 82, the EP + W sample as 82, the EP + H. W sample as 84, and the EP + A. W sample as 89. The hardness measurement results are also illustrated in Figure 4. Based on the results, the fact that EP and EP + W samples exhibited the same hardness value indicates that adding raw walnut shells to the material did not cause a significant change in hardness. Adding heat-treated walnut shells to the EP matrix increased the hardness value, resulting in a composite material with improved mechanical properties. Including surface-modified walnut shell into the EP matrix is thought to have strengthened the reinforcement–matrix interfacial bonding, leading to a superior hardness value compared to the other composite materials.

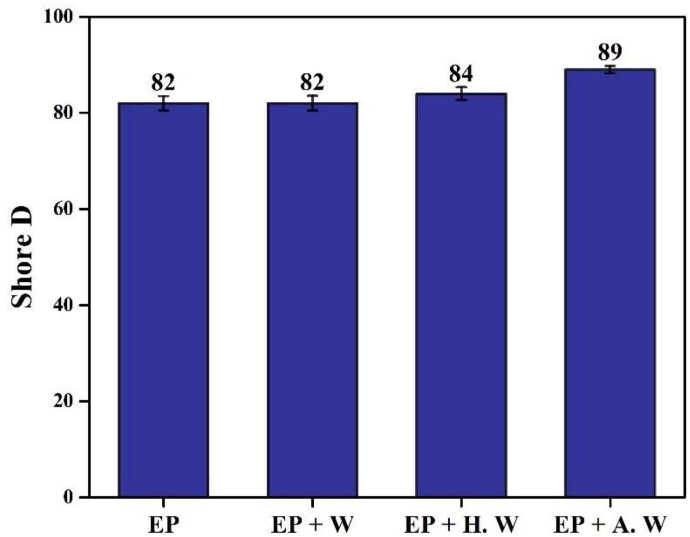


Figure 4. Hardness measurement results of walnut filled composite materials.

Table 3. Shore D hardness values composite materials.

Abbreviation	Shore D	Standard Deviation (±)
EP	82	1.49
EP + W	82	1.55
EP + H. W	84	1.31
EP + A. W	89	0.76

3.1.3. Tensile Test Result of Hazelnut Filled Composites

Stress values observed as a result of tensile tests of composites were found as 33.984 MPa, 32.021 MPa, 34.570 MPa, and 52.536 MPa for EP + H, EP + H. H, EP + A. H, and EP, respectively. Strain values were found to be 30.74, 5.40, 5.5, and 6.81 in the same order (Table 4). According to these values, the maximum tensile strength was found in EP material. This is an expected situation in particle-reinforced composite materials. Since the reinforced polymers are completely homogeneous and uniform during tensile testing, they exhibit higher tensile strength. However, the particle reinforcements in the content of composites cause discontinuity in the material. This causes the material to break at an unexpected point (Göde 2011). When composite materials were evaluated in this study, it was seen that higher tensile strength occurred in the hazelnut shell filled composite material where the alkalization process was performed. This proves that the surface modification process has an effect on increasing the mechanical performance of the material. When the strain values are examined, it is seen that the highest elongation value is obtained in the E + H composite. It is understood that the elongation values at break of the EP+H.H, EP+A.H and EP composites are close to each other, but the heat treatment and alkalization process cause brittleness in the material (Figure 5).

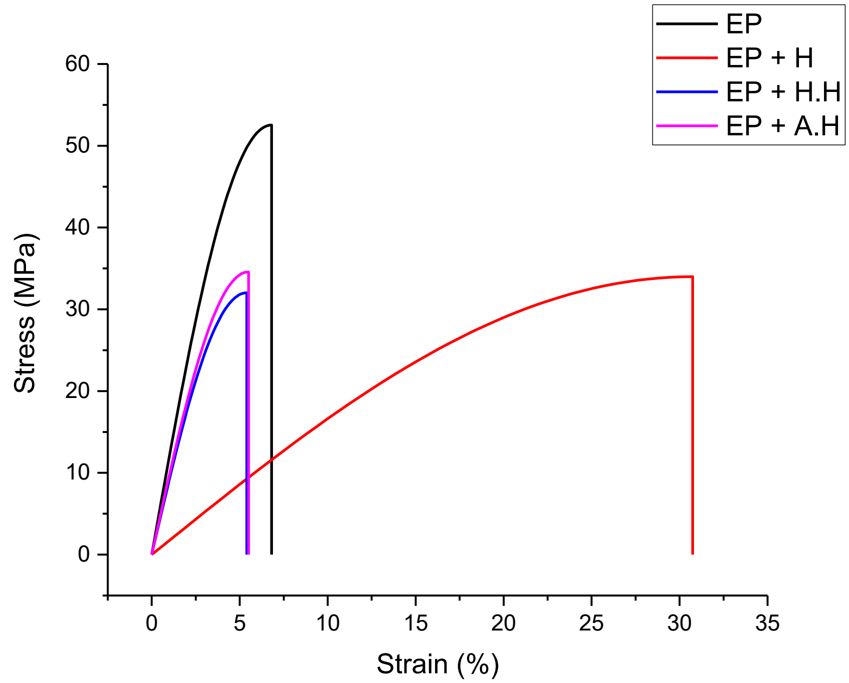


Figure 5. Tensile test results for hazelnut filled composites.

Table 4. Tensile test results for hazelnut filled composites.

Composite	Tensile Force (N)	Displacement (mm)	Stress (MPa)	Strain (%)
EP + H	271.87	7.68	33.984	30.74
EP + H. H	256.25	1.35	32.021	5.40
EP + A. H	276.56	1.38	34.570	5.5
EP	420.31	1.70	52.536	6.81

3.1.4. Tensile Test Results of Walnut Filled Composites

Stress values obtained as a result of tensile tests of composites were found to be 39.648 MPa, 35.743 MPa, 42.187 MPa, and 52.536 MPa for EP + W, EP + H. W, EP + A. W, and EP, respectively. Strain values were found to be 7.6, 5.03, 9.1, and 6.81 in the same order (Table 5). According to walnut-filled composite material experiments, the maximum tensile strength was found in the EP material. Particles in the material caused discontinuity in the material, causing a decrease in the maximum tensile strength. When walnut shell-filled composite materials were evaluated in this study, it was seen that higher tensile strength occurred in the composite material where the alkalization process was performed. This proves that the surface modification process has an effect on increasing the mechanical performance of the material. When the strain values were examined, it was seen that the elongation values at break were quite close to each other for all composites. However, the highest elongation at break was obtained in the EP + A. W composite (Figure 6). In hazelnut reinforced composites, the highest tensile stress was obtained in the untreated sample (EP + H), while in the walnut reinforced series, it was obtained in the alkalized sample (EP + A. W). This discrepancy can be attributed to the microstructural and compositional differences between hazelnut and walnut shells. However, particle dispersion and interfacial bonding quality may have changed between the two systems depending on the treatment. This may have affected the elongation capabilities.

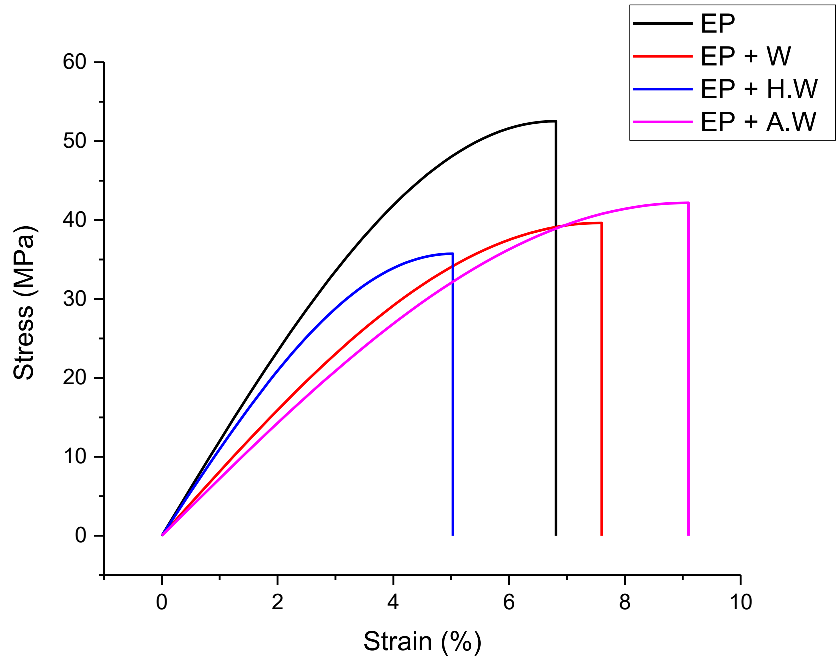


Figure 6. Tensile test results for walnut filled composites.

Table 5. Tensile test results for walnut filled composites.

Composite	Tensile Force (N)	Displacement (mm)	Stress (MPa)	Strain (%)
EP + W	317.87	1.90	39.648	7.6
EP + H. W	285.93	1.25	35.743	5.03
EP + A. W	337.50	2.27	42.187	9.1
EP	420.31	1.70	52.536	6.81

3.2. Wear Test Results of Composite Materials

3.2.1. Wear Test Results of Hazelnut Filled Composites

The weights of composite materials measured before and after the wear tests are presented in Table 6. According to the results in Table 6, the average weight loss measured after wear tests was found to be 0.0013 g from the EP sample, 0.0011 g for the EP + H sample, 0.011 g for the EP + H. H sample, and 0.001 g for the EP + A. H sample. According to the weight loss results measured after the wear tests, the highest weight loss was observed in the EP sample. The EP + H and EP + H. H samples showed lower wear rates with similar values of 0.0011 g. This indicates that adding raw and heat-treated hazelnut shells to EP improved the wear resistance somewhat, although the effect was limited. Among these, the sample with the highest wear resistance was EP + A. H. This result suggests that the surface modification enhanced the bonding between the hazelnut shells and the matrix, further increasing the wear resistance (Tayfun et al. 2014).

Table 6. Weight measurement of composite materials before and after wear tests.

Materials	Pre-Test Weight (gr)	Post-Test Weight (gr)
EP	0.7750	0.7737
EP + H	0.7009	0.6998
EP + H. H	0.6465	0.6454
EP + A. H	0.6825	0.6815

The wear tests were also evaluated by calculating the average friction coefficients measured during the experiments (Table 7). According to the results presented in Table 7, the lowest average friction coefficient was observed for the EP sample, with a value of 0.332. However, the low friction coefficient of the EP sample does not, by itself, indicate high wear resistance. The friction coefficient is influenced by surface roughness, the homogeneity and smoothness of the surface, and, especially in composite materials, the quality of the reinforcement–matrix bonding (El-Sayed et al. 1995). Therefore, the EP sample exhibited the lowest average friction coefficient due to its homogeneous and uniform structure. The EP + H sample has the highest average friction coefficient (0.394). This result is attributed to the inadequate compatibility between the raw hazelnut shells and the matrix, leading to increased friction. The average friction coefficient of the EP + H. H sample is lower than that of the EP + H sample (0.381). This result shows that the heat treatment applied to the hazelnut shells somewhat improved the reinforcement–matrix compatibility. Among the reinforced samples, the EP + A. H sample has the lowest average friction coefficient (0.366). This result indicates that the surface modification process improved the reinforcement–matrix compatibility and thus led to the formation of a more homogeneous and low-friction surface structure. When the tribological data are generally evaluated, it is seen that the surface modification process has a significantly improving effect on both the wear resistance and the average friction coefficient (Figure 7).

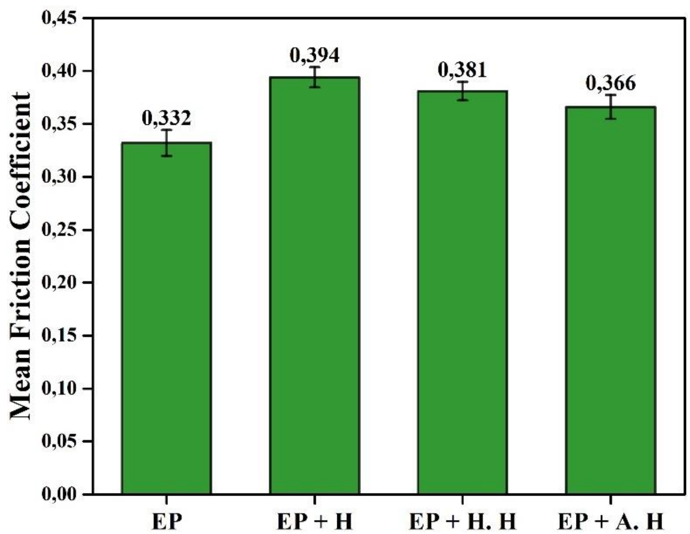


Figure 7. Mean friction coefficient values of hazelnut filled composite materials.

Table 7. Friction coefficient values of composite materials.

Materials	Friction Coefficient	Standard Deviation (±)
EP	0.332	0.0122
EP + H	0.394	0.0096
EP + H. H	0.381	0.0087
EP + A. H	0.366	0.0113

3.2.2. Wear Test Results of Walnut Filled Composites

The weights of the composite materials measured before and after the wear tests are presented in Table 8. According to the results in Table 8, the weight losses after wear tests were found to be 0.0013 g for the EP sample, 0.0009 g for the EP + W sample, 0.0010 g for the EP + H.W sample, and 0.0007 g for the EP + A.W sample. Based on these results, the highest material loss occurred in the EP sample, while the lowest material loss was observed in the EP + A. W sample. It is considered that this result is due to the surface modification applied during composite manufacturing, which strengthened the reinforcement–matrix interface and thus improved the wear resistance of the produced composite material. Although the EP + W and EP + H. W composites showed lower weight loss than the EP sample, they were less effective in wear resistance than the EP + A. W composite.

Table 8. Weight measurements of composite materials before and after wear tests.

Materials	Pre-Test Weight (gr)	Post-Test Weight (gr)
EP	0.7750	0.7737
EP + W	0.6372	0.6363
EP + H. W	0.7261	0.7251
EP + A. W	0.7259	0.7252

Additionally, the average friction coefficient values obtained after the wear tests are presented in Table 9. According to the results in Table 9, the sample with the lowest average friction coefficient is the EP sample, with a value of 0.332. However, the higher amount of wear observed in the EP sample than in the other samples indicates that a low friction coefficient alone is insufficient to evaluate the wear performance comprehensively. The highest friction coefficient value was recorded for the EP + W sample, at 0.439, indicating poor surface compatibility between the raw walnut shells and epoxy matrix, leading to increased friction. The EP + A. W (0.357) and EP + H. W (0.398) samples exhibited lower friction coefficients compared to the raw walnut shell (EP + W) sample (Figure 8). These results indicate that treatments applied to walnut shells positively influence the tribological performance of the composite materials. The applied surface modification significantly strengthens the reinforcement-matrix interfacial bonding, enhancing the tribological performance (Tyona and Itodo 2023).

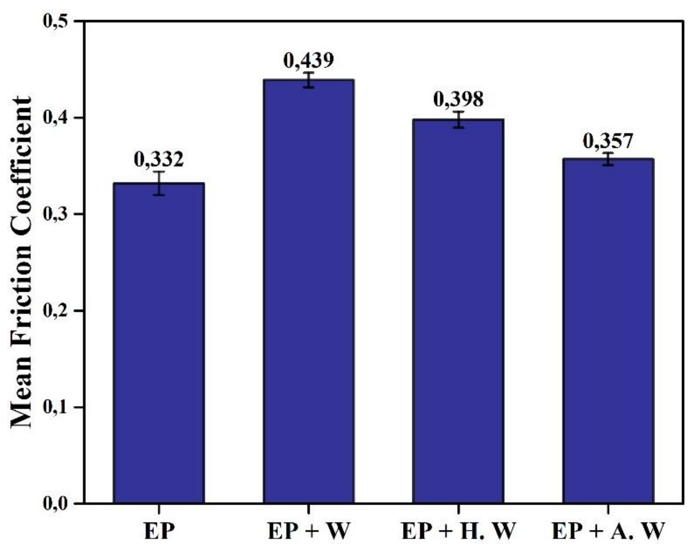


Figure 8. Mean friction coefficient values of walnut filled composite materials.

Table 9. Friction coefficient values of composite materials.

Materials	Friction Coefficient	Standard Deviation (±)
EP	0.332	0.0122
EP + W	0.439	0.0075
EP + H. W	0.398	0.0084
EP + A. W	0.357	0.0062

3.3. Morphological Results of Composite Materials

3.3.1. Morphological Results of Hazelnut Filled Composites

The wear regions observed on the composite materials after the wear tests are presented in Figure 9. When the wear region of the EP sample is examined, it is seen that deep cracks have formed on the surface (Figure 9.a). This indicates that the EP sample has low resistance to impact and friction. In addition, the absence of any reinforcing element in the material likely prevented the uniform distribution of the applied load on the surface, which in turn caused crack propagation and more severe surface damage. When the SEM images of the EP + H sample are examined, large voids and wear debris are observed on the surface. These structures indicate that the raw hazelnut shells could not form a good bond with the epoxy matrix and that a homogeneous distribution was not achieved (Figure 9.b). In the SEM images of the EP + H. H sample, stacked and layered surface structures are observed. These structures show that the heat treatment applied to the hazelnut shells partially improved the reinforcement–matrix bonding, but the surface homogeneity and integrity remained weak (Figure 9.c). EP + A. H sample shows that the smoothest surface was obtained after wear testing compared to the other samples (Figure 9.d). This result is believed to be related to the surface modification process applied during composite production, which supported the formation of a strong bond between the reinforcement and the matrix, thereby minimizing wear damage (Behera et al. 2021).

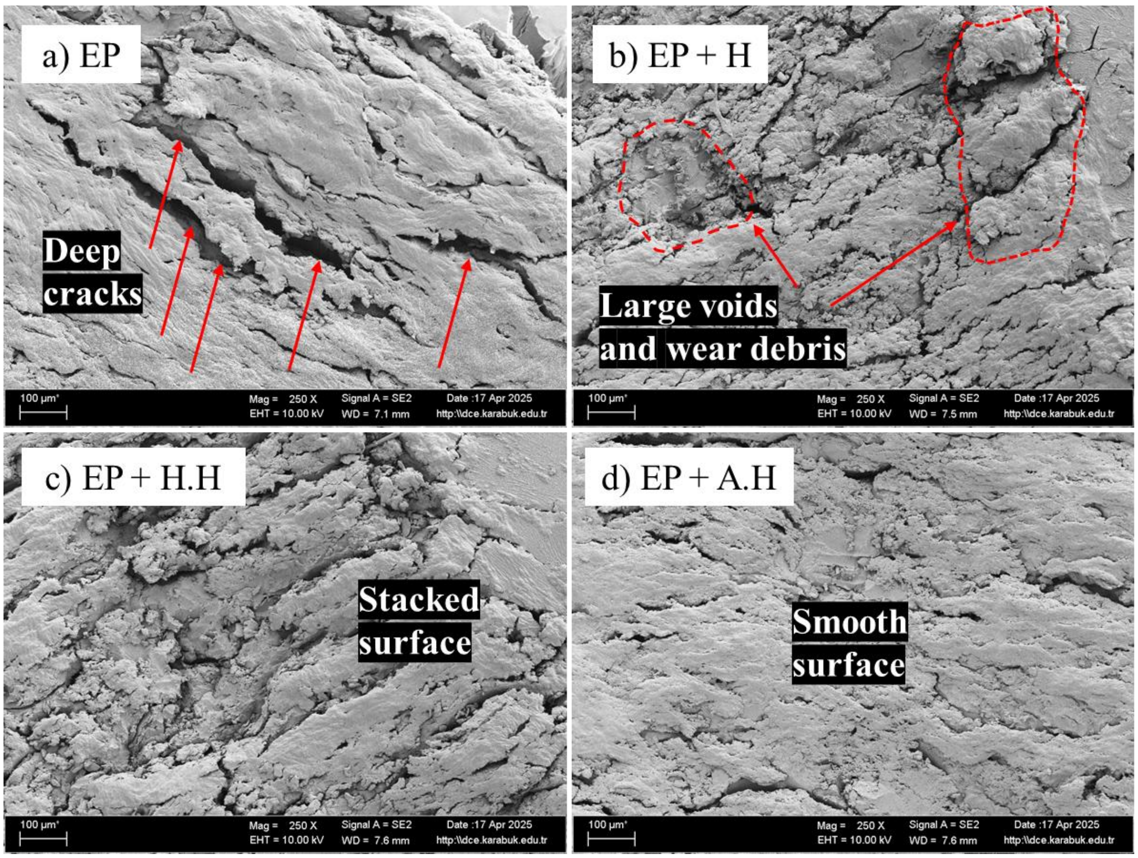
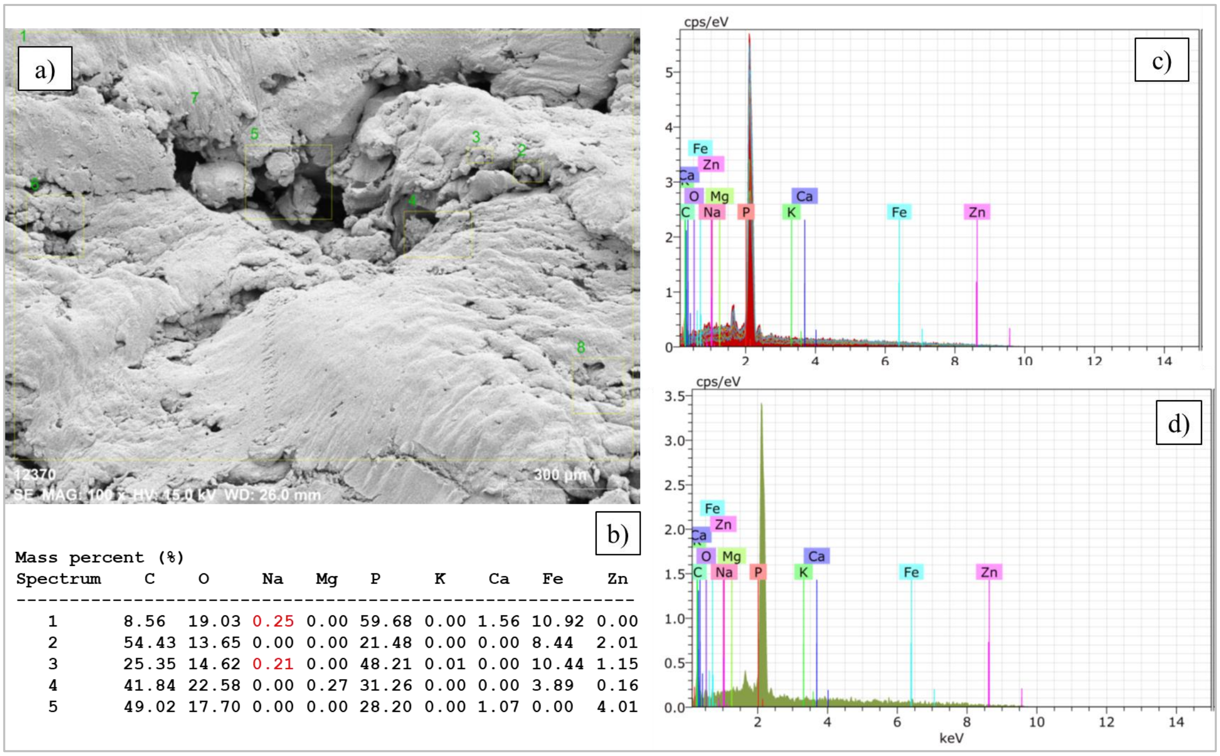


Figure 9. SEM images of the wear regions of composite materials, (a) EP, (b) EP + H, (c) EP + H. H, and (d) EP + A. H.

To observe the reinforcements in the composite material subjected to surface modification, an EDX analysis was performed on the worn region (Figure 10). According to the EDX results, sodium (Na) used in the surface modification process was detected in the EP + A. W sample (Figure 10.b). The detection of the Na element indicates that the NaOH chemical used in the surface modification process was successfully integrated into the composite. This result confirms that the surface modification treatments were successfully carried out and affected the sample's structure. As it is well-established in the literature, the presence of Na is considered a direct indicator of successful surface modification via alkaline treatment (Adi et al. 2023). Therefore, the detection and presentation of Na was deemed sufficient for verifying the effectiveness of the surface modification.



Mass percent (%)

Spectrum	C	O	Na	Mg	P	K	Ca	Fe	Zn
1	8.56	19.03	0.25	0.00	59.68	0.00	1.56	10.92	0.00
2	54.43	13.65	0.00	0.00	21.48	0.00	0.00	8.44	2.01
3	25.35	14.62	0.21	0.00	48.21	0.01	0.00	10.44	1.15
4	41.84	22.58	0.00	0.27	31.26	0.00	0.00	3.89	0.16
5	49.02	17.70	0.00	0.00	28.20	0.00	1.07	0.00	4.01

Figure 10. EDX analysis of wear marks.

3.3.2. Morphological Results of Walnut Filled Composites

The wear regions observed on the composite materials after the wear tests are presented in Figure 11. Upon examining the wear damage, it is seen that deep cracks have formed on the surface of the EP sample (Figure 11.a). These cracks are thought to have occurred due to the low resistance of the EP sample against impact and friction during wear. In addition, the absence of any reinforcing element in the material likely prevented the uniform distribution of the applied load on the surface, which in turn caused crack propagation and more severe surface damage. The SEM images of the EP + W sample reveal the presence of large voids and agglomerations on the surface (Figure 11.b). This is related to the weak interfacial bonding between the raw walnut shells and the epoxy matrix and the inadequate dispersion of the filler within the matrix. The SEM images in the EP + H. W sample show a smoother surface and medium-sized cracks (Figure 11.c). The thermal treatment applied to the walnut shells is thought to have contributed to the formation of better bonding with the epoxy matrix, thus allowing a more uniform distribution of the applied load on the surface (Oladele et al. 2025). Consequently, the wear zone exhibits more limited crack propagation. SEM images in the EP + A. W sample show that the smoothest surface was obtained after wear testing compared to the other samples (Figure 11.d). This result is believed to be related to the surface modification process applied during composite production, which supported the formation of a strong bond between the reinforcement and the matrix, thereby minimizing wear damage (Behera et al. 2021).

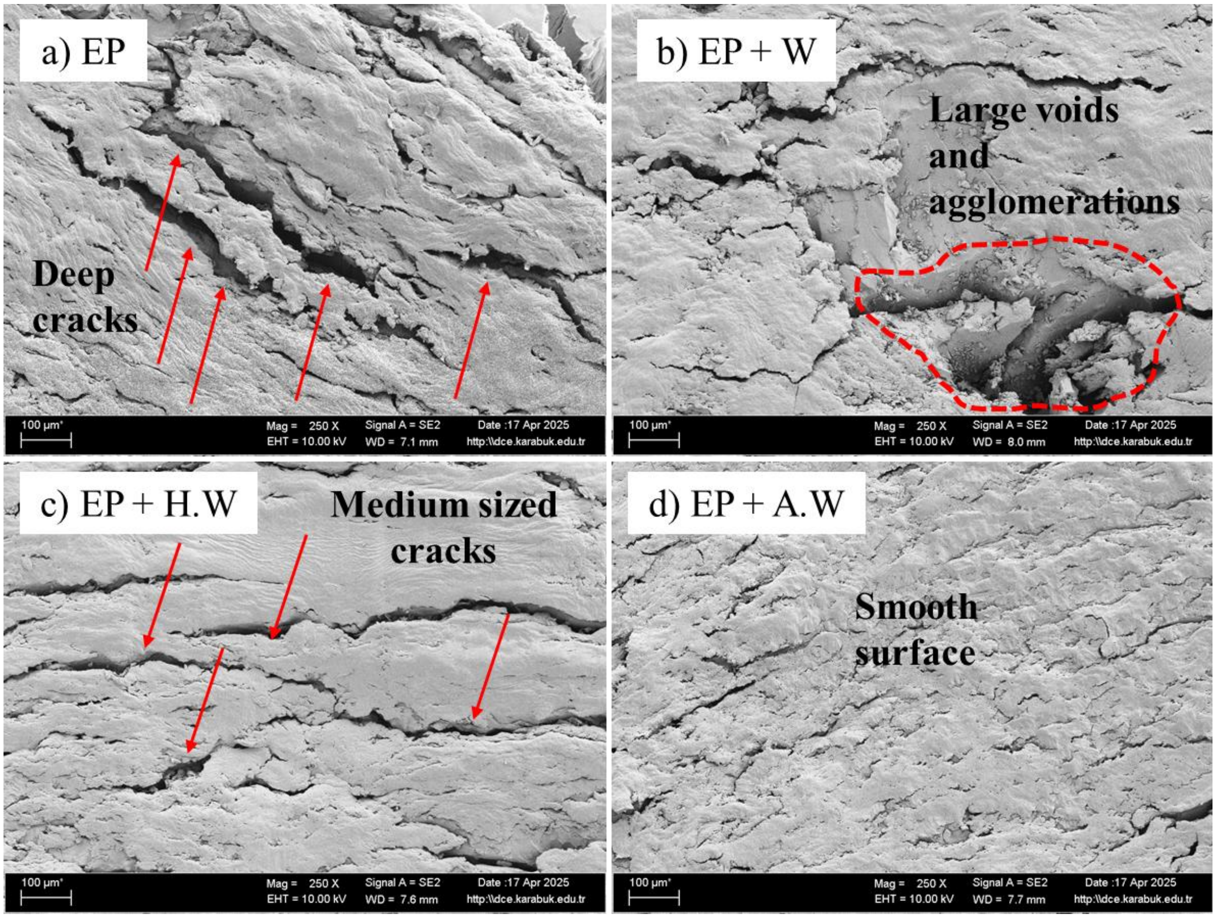


Figure 11. SEM images of the wear regions of composite materials, (a) EP, (b) EP + W, (c) EP + H. W, and (d) EP + A. W.

To observe the reinforcements in the composite material subjected to surface modification, an EDX analysis was performed on the worn region (Figure 12). According to the EDX results, sodium (Na) used in the surface modification process was detected in the EP + A. W sample (Figure 12.b). This indicates that the surface modification process was successful, and the modifying agent was effectively distributed within the sample.

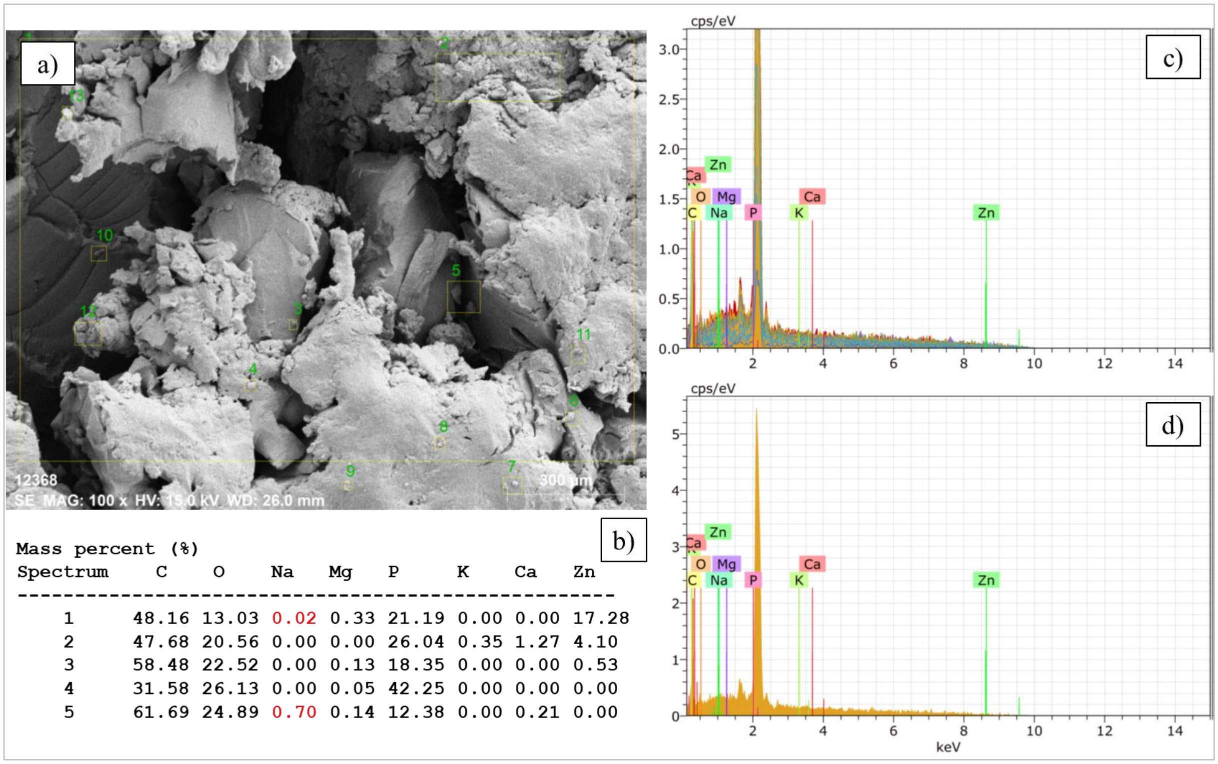


Figure 12. EDX analysis of wear marks.

4. Comparison with Literature Studies

The findings of this study clearly demonstrate that the surface modification of lignocellulosic particles via alkalization significantly contributed to the overall performance of the composite materials. Firstly, the hardness values of the surface-modified composites increased compared to those of the untreated and heat-treated counterparts, indicating an enhancement in the matrix–filler interfacial bonding. Additionally, the tensile strength of the surface-modified samples was found to be higher than that of the unmodified composites, although the neat epoxy (EP) sample still exhibited the highest value as expected. This improvement in tensile strength reflects a more efficient load transfer mechanism due to better interfacial adhesion. From a tribological standpoint, surface-modified composites exhibited lower friction coefficients and reduced weight loss in wear tests, confirming improved wear resistance. These enhancements can be attributed to the more uniform filler dispersion and better interlocking between the polymer matrix and the modified particle surfaces. SEM images further supported these findings, revealing a denser and more homogeneous microstructure with fewer voids in the surface-modified samples. Taken together, the mechanical, morphological, and tribological data coherently support the conclusion that surface modification via alkalization is a beneficial pretreatment step that enhances the structural integrity and functional performance of lignocellulosic waste-reinforced composites. Literature studies conducted parallel to this study are given in Table 10. As a result of the literature review, it is seen that the mechanical and tribological results obtained within the scope of this study coincide with the literature.

Table 10. Results of literature studies.

References	Matrix Material	Reinforcement Materials	Results
(Cherkashina et al. 2023)	Polystyrene	Hazelnut shell powder	The results of modifying hazelnut powder particles to form polystyrene shells on their surfaces were investigated. Modification of the filler increased the contact angle from 60.16° to 87.02° when wetted with water, thus increasing the hydrophobicity and compatibility of the material.

(Sismanoglu, Tayfun, and Kanbur 2019)	Thermoplastic polyurethane (TPU)	Date palm seed	This study applied surface treatments to date palm seed, an agricultural waste, to enhance its compatibility with an eco-grade TPU matrix. Surface modification results indicated that the hardness, hydrophobicity, storage modulus, and thermal stability of the material increased. SEM micrographs confirmed better interfacial adhesion between surface-modified reinforcement particles and TPU.
(Shejkar et al. 2022)	Epoxy	Walnut shell particulates	The addition of surface modified walnut shells treated with NaOH solution to epoxy improved the mechanical performance of tensile strength and flexural strength. However, compressive strength and hardness increased as the filler content increased. SEM images showed that the contact between the matrix and the filler improved.
(Kocaman and Ahmetli 2020)	Epoxy	Hazelnut	The use of NaOH, acrylic acid and acetic anhydride to modify hazelnut shell waste allowed the production of stronger and less water-absorbing biobased epoxy composites. It was shown that the application of Acetic anhydride treatment to hazelnut shell waste led to increased tensile strength, elongation at break and better hydrophobicity. In addition, good bonding between layers and improved mechanical properties were obtained.
(Şahin et al. 2024)	Polypropylene (PP)	Pistachio and walnut shells waste	Mixing pistachio, walnut and hazelnut shells made polypropylene more durable and stable. These reinforcements contributed to the increase in the tribological performance of the material's strength. However, the increase in the reinforcement ratio reduced ductility and made the material more brittle.
(Moustafa, N. M. et al. 2020)	Polypropylene (PP)	Walnut shell powder	Increasing the walnut shell powder content in polypropylene decreased tensile strength, bending stress and elasticity, but enhanced in hardness, impact resistance and wear resistance.
(Islam and Islam 2015)	Recycled polyethylene	Sawdust	Chemical treatment of sawdust was used to produce composites. This surface modification resulted in strong fiber-matrix adhesion, improved strength and less water absorption.

5. Conclusion

In this study, hazelnut and walnut shell-reinforced epoxy composite materials were produced, and their mechanical and tribological properties were investigated. For this purpose, four composite materials were prepared: unreinforced, raw shell-reinforced, heat-treated shell-reinforced, and surface-modification shell-reinforced composites. The hardness values of the produced samples were measured using the Shore D hardness test. Their tribological behavior was evaluated based on weight loss and average friction coefficient values. To support the results, morphological analyses were performed using SEM and EDX.

- As a result of the hardness tests for hazelnut filled composites, the highest hardness value was observed in the EP + A. H sample. This indicates that the surface modification process positively affected the mechanical properties of the composite materials.
- According to the hardness test results for walnut filled composites, the EP + A. W sample showed an 8.5% increase in hardness value compared to the EP sample.
- As a result of the tensile test for reinforced with hazelnut shell composites, the highest tensile strength was obtained in the EP sample, followed by EP + A. H, EP + H, and EP + H. H, respectively. The highest strain values were found in the EP + H sample, followed by EP, EP + A. H, and EP + H. H, respectively.
- As a result of the tensile test for reinforced with walnut shell composites, the highest tensile strength was obtained in the EP sample, followed by EP + A. W, EP + W, and EP + H. W, respectively. The highest strain values were found in the EP + A. W sample, followed by EP + W, EP, and EP + H. W, respectively.

- According to the wear test results for reinforced with hazelnut shell composites, the highest weight loss was observed in the EP sample, while the lowest weight loss was recorded in the EP + A. H sample. When the average friction coefficient values were examined, it was found that the EP + A. H sample had the lowest friction coefficient among the reinforced samples.
- Based on the wear test results for reinforced with walnut shell composites, the lowest friction coefficient was observed in the EP sample. The friction coefficient (COF) of the EP + W sample increased by 32.2%, the EP + H. W sample by 19.8%, and the EP + A. W sample by 7.5%, all relative to the EP sample. The lowest wear rate was observed in the EP + A. W sample, supported by both weight loss and mean friction coefficient data.
- Morphological analysis showed that the smoothest surface after wear was obtained in the EP + A. H, and EP + A. W sample.
- When all results are evaluated collectively, it was observed that the mechanical and tribological properties of the EP material improved with all reinforcements except for raw shell. The surface modification enhanced the interaction between the matrix and the reinforcement particles, resulting in the optimum composite material production.

Conflict of Interest Statement

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 article.

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