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UV Weathering of Green Composites Based on Polyamide 6 (PA6) and Sunflower Seed (*Helianthus Annuus* L.) Husk, Pistachio (*Pistacia Vera* L.) Shell and Walnut (*Juglans Regia* L.) Shell Flour

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Anahtar Kelimeler

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Mekanik Özellikler
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Graphical/Tabular Abstract (Grafik Özet)

This research used powdered pistachio shell, sunflower seed husk, and walnut shell as natural fillers in PA6 to produce green composites. The study evaluated tensile strain, tensile strength, flexural strain, and flexural strength of PA6 and the green composites. Additionally, UV ageing effects on PA6 and the composites were investigated. / Bu araştırma, yeşil kompozitler üretmek için PA6'da doğal dolgu malzemesi olarak toz haline getirilmiş Antep fıstığı kabuğu, ayçiçeği çekirdeği kabuğu ve ceviz kabuğunu kullanmıştır. Çalışmada, PA6 ve yeşil kompozitlerin çekme gerinimi, çekme dayanımı, eğme gerinimi ve eğme dayanımı değerlendirilmiştir. Ayrıca, UV yaşlanma etkileri PA6 ve kompozitler üzerinde incelenmiştir.

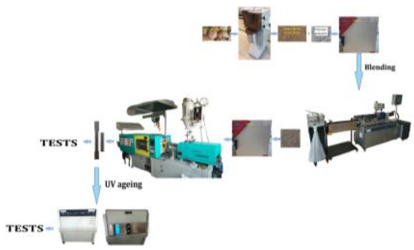

***Figure A**: Experimental setup /**Şekil A:** Deney düzeneği*

Highlights (Önemli noktalar)

- *Agricultural shells (sunflower seed husk, walnut shell, pistachio shell) were used as natural fillers in PA6-based composites for outdoor applications. / Tarımsal kabuklar (ayçiçeği çekirdeği kabuğu, ceviz kabuğu, Antep fıstığı kabuğu) dış mekan uygulamaları için PA6 bazlı kompozitlerde doğal dolgu malzemesi olarak kullanılmıştır.*
- *Despite decreased tensile strength, agricultural shell flour-filled PA6 composites remain feasible for certain applications due to their low cost. / Çekme dayanımındaki azalmaya rağmen, tarımsal kabuk unu dolgulu PA6 kompozitleri düşük maliyetleri nedeniyle bazı uygulamalar için uygun kalmaktadır.*
- *UV ageing slightly increased the tensile and flexural strength of agricultural shell flour-filled PA6 composites.* / UV yaşlanma, tarımsal kabuk unu dolgulu PA6 kompozitlerinin çekme ve eğme dayanımını hafifçe artırmıştır.

Aim (Amaç): *Current research aims to evaluate agricultural shells' potential for use at outdoor applications by determining the UV ageing of agricultural shell filled composites. / Mevcut araştırma, tarımsal kabuk dolgulu kompozitlerin UV yaşlanmasını belirleyerek, tarımsal kabukların dış mekan uygulamalarında kullanılma potansiyelini değerlendirmeyi amaçlamaktadır.*

Originality (Özgünlük): *Ageing behavior for pistachio shell, sunflower seed husk and walnut shell flour filled PA6 composites has not been investigated. The aim of current research was the emphasize relationships between mechanical properties as a function of agricultural shell kind and UV ageing time. / Antep fıstığı kabuğu, ayçiçeği çekirdeği kabuğu ve ceviz kabuğu unu dolgulu PA6 kompozitlerinin yaşlanma davranışı daha önce incelenmemiştir. Mevcut araştırmanın amacı, tarımsal kabuk türü ve UV yaşlanma süresine bağlı olarak mekanik özellikler arasındaki ilişkileri vurgulamaktır.*

Results (Bulgular): *UV ageing increased the tensile and flexural strength of agricultural shell flour filled PA6 composites. / UV yaşlanma, tarımsal kabuk unu dolgulu PA6 kompozitlerinin çekme ve eğme dayanımını artırmıştır.*

Conclusion (Sonuç): *The research suggests that agricultural shell-filled composites can be used in outdoor conditions due to their improved performance after UV ageing. / Araştırma, tarımsal kabuki dolgulu kompozitlerin, UV yaşlanma sonrasında iyileşen performansları nedeniyle dış mekan koşullarında kullanılabileceğini önermektedir.*

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Abstract

Current research aims to evaluate agricultural shells' potential for use at outdoor applications by determining the ultraviolet (UV) ageing of agricultural shell filled composites. Therefore, in current work, three different agricultural shells were utilized as natural fillers in the production of polyamide 6 (PA6) based composites. Dakota type sunflower seed husk, walnut shell and pistachio shell were employed as natural fillers. It was concluded that the tensile behavior of PA6 altered from ductile to brittle after the loading of pistachio shell, sunflower seed husk and walnut shell flour. Although the agricultural shell flour decreased tensile strength of pure PA6 polymer, the strength values were still acceptable in some applications and low price of agricultural shell flour filled PA6 composites made them feasible. In general, tensile strength increased slightly after UV ageing in agricultural shell flour filled PA6 composites. The highest increase was found with the 24-hour UV aged walnut shell flour filled PA6 composite. Although agricultural shell loading led to decrement in tensile strength of PA6 polymer, fact that these composites cause little change or even an increment in the tensile strength after exposure to UV ageing indicated that agricultural shell filled composites can be utilized in outdoor conditions. UV ageing increased the flexural strength of all agricultural shell flour filled PA6 composites and this result indicated that agricultural shell filled composites can be used in outdoor conditions. Among green composites, the greatest flexural strength was achieved by the 24-hour UV aged walnut shell flour filled PA6 composite.

Poliamit 6 (PA6) ve Ayçiçeği Çekirdeği (*Helianthus Annuus* L.) Kabuğu, Antep Fıstığı (*Pistacia Vera* L.) Kabuğu ve Ceviz (*Juglans Regia* L.) Kabuğu Unu Bazlı Yeşil Kompozitlerin UV Yaşlanması

Makale Bilgisi

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Öz

Mevcut araştırma, tarımsal kabuk dolgulu kompozitlerin ultraviyole (UV) yaşlanmasını belirleyerek tarımsal kabukların dış mekan uygulamalarında kullanım potansiyelini değerlendirmeyi amaçlamaktadır. Bu nedenle mevcut çalışmada poliamit 6 (PA6) bazlı kompozitlerin üretiminde doğal dolgu maddesi olarak üç farklı tarımsal kabuk kullanılmıştır. Doğal dolgu maddesi olarak Dakota tipi ayçiçeği çekirdeği kabuğu, ceviz kabuğu ve Antep fıstığı kabuğu kullanılmıştır. Antep fıstığı kabuğu, ayçiçeği çekirdeği kabuğu ve ceviz kabuğu ununun eklenmesinden sonra PA6'nın çekme davranışının sünek durumdan gevrek duruma doğru değiştiği sonucuna varılmıştır. Tarımsal kabuk unu, saf PA6 polimerinin çekme mukavemetini azaltmasına rağmen, bazı uygulamalarda mukavemet değerleri hala kabul edilebilir düzeydeydi ve tarımsal kabuklu un dolgulu PA6 kompozitlerinin düşük fiyatı bunları uygulanabilir kılmaktadır. Genel olarak tarımsal kabuk unu dolgulu PA6 kompozitlerinde UV yaşlandırma sonrasında çekme mukavemeti bir miktar artmıştır. En yüksek artış 24 saat UV ile yaşlandırılmış ceviz kabuğu unu dolgulu PA6 kompozitte görülmüştür. Tarımsal kabuk eklenmesi PA6 polimerinin çekme mukavemetinde azalmaya yol açsa da, bu kompozitlerin UV yaşlandırmaya maruz kaldıktan sonra çekme mukavemetinde çok az değişikliğe veya hatta artışa neden olması, tarımsal kabuk dolgulu kompozitlerin dış mekan koşullarında kullanılabileceğini göstermiştir. UV yaşlandırma, tarımsal kabuk unu dolgulu tüm PA6 kompozitlerin eğme mukavemetini arttırmıştır ve bu sonuç, tarımsal kabuk dolgulu kompozitlerin dış mekan koşullarında kullanılabileceğini göstermiştir. Yeşil kompozitler arasında en büyük eğme mukavemeti, 24 saat UV ile yaşlandırılmış ceviz kabuğu unu dolgulu PA6 kompozit ile elde edilmiştir.

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1. INTRODUCTION (GİRİŞ)

Inorganic fibers (aramid, carbon and glass fibers, etc.) are replaced by natural fillers in polymeric composites in recent years because of environmental awareness [1]. Addition of natural fillers to thermoplastics induce to develop renewable green composites [2]. Natural fiber filled polymeric composites are known as "green composites" [3]. They are eco-friendly materials and reduce pollution and cost. With the increment in environmental awareness, ecological concerns and novel regulations force composite sector to produce more environmentally friendly materials. With partially changing polymers by natural filler, low price materials were developed by diminishing amount of polymeric materials [4]. Usage of low-value agricultural residue to produce polymeric composites has high economic and environmental pros [5]. Incorporation of agricultural waste in polymeric material to produce composites is viable method to be gained additional value to agricultural waste. That endeavor also causes the decrement for usage of more expensive polymers [1]. Therefore, there is several attempts to produce composites filled with natural fillers such as agricultural waste flour [6].

Pistachio (*Pistacia Vera* L.), sunflower seed (*Helianthus Annuus* L.) and walnut (*Juglans Regia* L.) are important resources for nutrient food and vegetable oil. But after consuming pistachio, sunflower seed and walnut, the husks and shells of them are regarded as an agricultural waste. Generally, agricultural shells are disposed of by leaving them in the environment or by burning them. Both solutions lead to environment pollution. Another feasible solution could be to add additional value to agricultural waste by adding agricultural shells as fillers to the polymeric matrix to produce composites [7]. Loading of agricultural wastes in polymeric materials prevents environment from pollution and may provide additional income to farmers. These agricultural waste shell flours could provide wood like appearance to polymer composites thus could contribute to preserve forest sources [1].

Pistachio, sunflower seed and walnut productions in worldwide were 1026802.86, 54285948.66 and 3874024.7 tons from total harvested region of 1217974, 29257983 and 1247938 ha in 2022 in accordance with Food and Agricultural Organization of the United Nations (FAO), respectively. Turkey is the world's third greatest producer of pistachio after the USA and Iran, with production of 239289 tons. With a production of 2550000 tons, Turkey is the fifth largest sunflower seed producer in the world after Russian Federation, Ukraine, Argentina and China. Turkey is the world's fourth biggest walnut producer after China, the USA and Iran, with a production of 335000 tons [8]. The shells of pistachio constitute almost 47% of its total weight [9], accounting for approximately 483000 tons of pistachio shells worldwide each year. Major constituent of this agricultural waste is lignocellulosic material. Pistachio shells contain approximately 47.08% cellulose, 26.56% hemicellulose and 13.74% lignin [10]. Approximately 30% of sunflower seeds are husks [11]. This leads to approximately 16.3 million tons sunflower seed husk wastes worldwide each year. Sunflower seed husks contain about 37.3% cellulose, 35.0% hemicellulose and 22.9% lignin [12]. It is declared that walnut shells constitute 67% of total walnut crop weight [13]. Therefore, about 2.6 million tons of walnut shells are left behind every year, and the amount is rising every year. Walnut shell is lignocellulosic material composing of the thin husk or endocarp of walnut tree fruit and has no significant industrial use since it is an agricultural residue [14]. Chemical composition of walnut shells varies depending on area harvested and is found to contain about 36.90% lignin, 36.06% hemicellulose and 17.74% cellulose [15].

Due to cellulose and lignin content of these agricultural shells, they could be utilized as filler material in polymeric materials. For this reason, some works regarding the loading of pistachio shell [16-18], sunflower seed husk [12, 19, 20] and walnut shell [18, 21-23] flour to various polymers such as polyethylene (PE) [12, 19], epoxy [20-23], polypropylene (PP) [16, 18, 21-23] and poly(lactic acid) (PLA) [17] were seen in the literature. However, there is very rare attempt to combine PA6 with agricultural shell flour. Peanut shell [24] was employed to develop PA6 based green composites. Besides, to the best of authors' knowledge, no research regarding addition of pistachio shell, sunflower seed husk and walnut shell flour to PA6 polymer to develop green composites has available.

Mechanical properties of agricultural shell flour filled polymeric composites should be evaluated at various weathering environments to understand their potential employing at indoor or outdoor applications. However, ageing behavior for pistachio shell, sunflower seed husk and walnut shell flour filled PA6 composites has not been investigated. The aim of current research was the emphasize relationships between mechanical properties as a function of agricultural shell kind and UV ageing time.

2. MATERIALS AND METHODS (MATERYAL VE METOD)

2.1. Materials (Materyal)

Polyamide 6 (PA6, Rugopa M60 100 NC00) with 1.13 g/cm^3 density purchased from Politem (Turkey) was employed as polymeric matrix. PA 6 was chosen as the matrix material due to its high mechanical strength, thermal stability, chemical resistance, and ease of processing, making it ideal for composite applications. Its wide usage in automotive, aerospace, textiles, electronics, and industrial sectors further supports its suitability for high-performance materials [25-29]. Pistachio shells were obtained from food industry in Sanliurfa, Turkey. Dakota type sunflower seed husks and walnut shells were purchased from market in Kocaeli, Turkey. Husks and shells were subjected to grinding process via knife mill with sieve size of 400 µm (Figure 1). Only particles passing the 400 µm sieve were used in the current study, so maximal particle size was smaller than 400 µm.

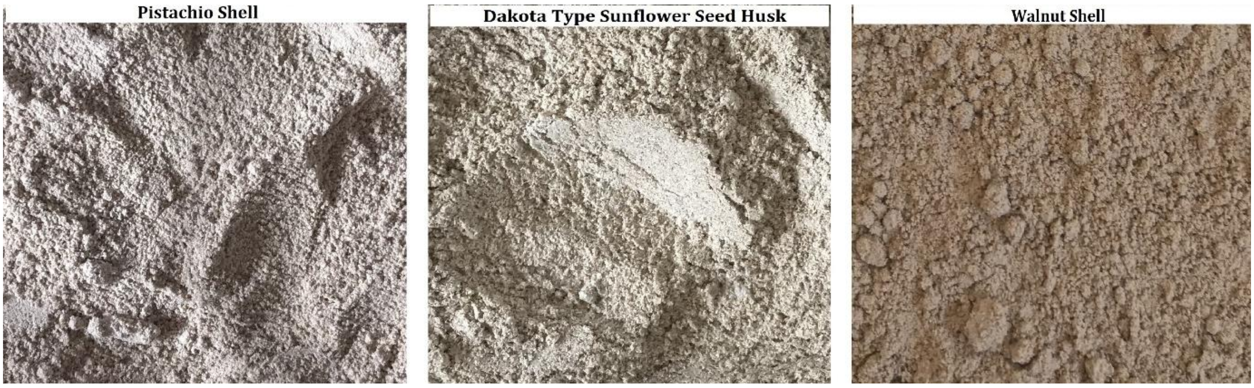

Figure 1. Photos for ground agricultural waste flour (Öğütülmüş tarımsal atık unlarının fotoğrafları)

2.2. Compounding (Karıştırma)

Agricultural waste flour based PA6 composites development procedure, manufacturing of samples and UV ageing are demonstrated in Figure 2. Initially, husks and shells were subjected to grinding process via knife mill with sieve size of 400 µm. Then PA6 pellets, shell and husk flours were mixed manually at fixed weight ratios (5 wt%), and the nomenclature of the produced composites are presented in Table 1. The choice of a 5 wt% reinforcement rate in a composite material is often based on a balance between mechanical performance, processability, and material properties. After drying into oven (Binder FD 56) at 80 °C for 3 hours, PA6 pellets were blended with natural fillers using co-rotating twin-screw extruder (length/diameter (L/D) = 40) at temperature ranging from 129, 195, 195, 210, 215, 215, 220, 225, 225, 225 °C (from feed to die) and 12 rpm screw speed. The extruded rods were cooled at a water bath and granulated to 2-3 mm long pieces. The resulting pellets were dried again in oven at 80 °C for 3 hours prior to the injection molding stage.

Table 1. Nomenclature of PA6 and developed PA6 composites (PA6 ve geliştirilen PA6 kompozitlerinin isimlendirilmesi)

Name	PA6 (Weight %)	Pistachio Shell Flour (Weight %)	Sunflower (Dakota) Seed Husk Flour (Weight %)	Walnut Shell Flour (Weight %)
PA6	100	0	0	0
PA6+P	95	5	0	0
PA6+S	95	0	5	0
PA6+W	95	0	0	5

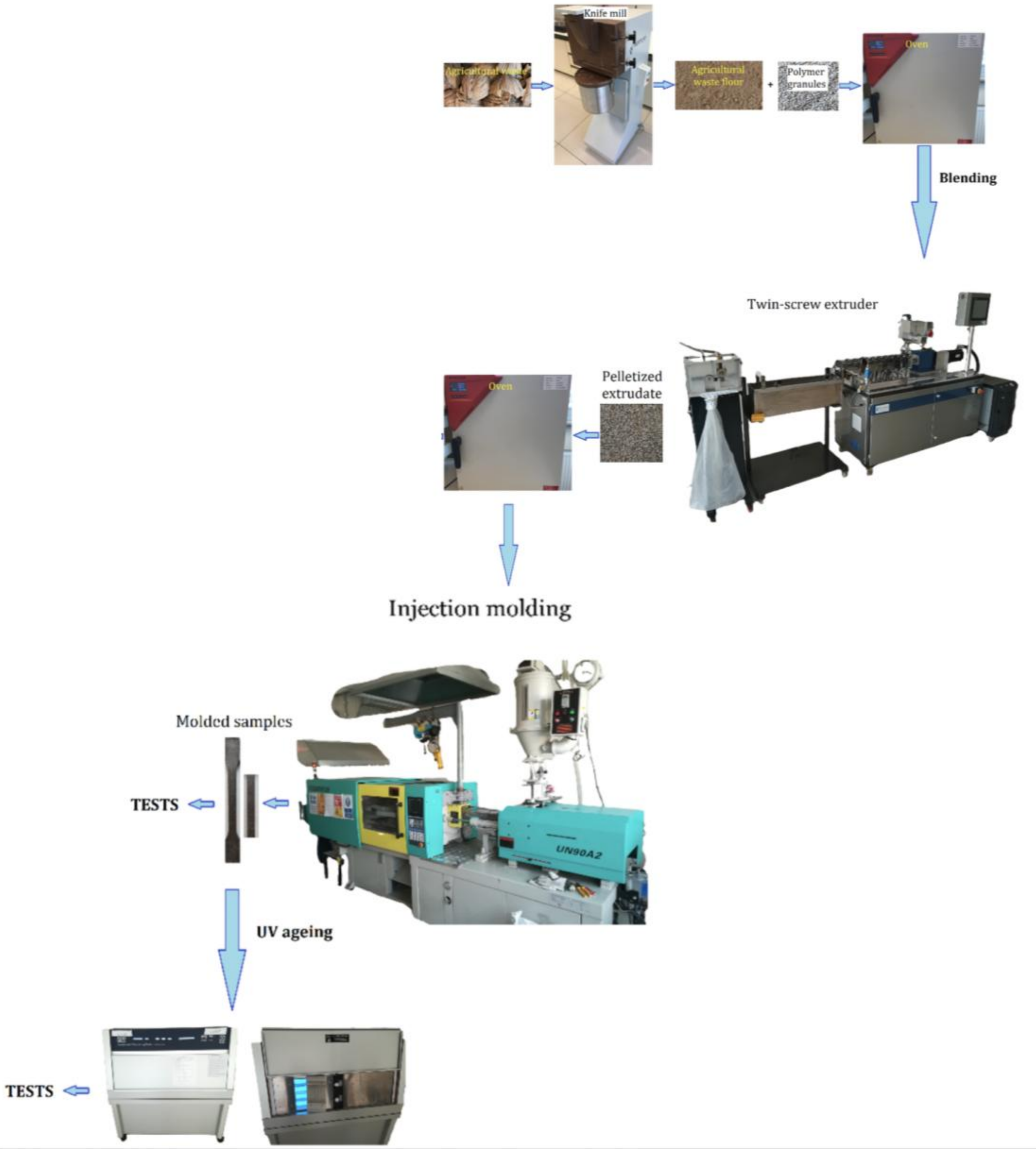

Figure 2. Procedure of developing agricultural waste flour filled PA6 composites, manufacturing test specimens and UV weathering (Tarımsal atık un dolgulu PA6 kompozitlerinin geliştirilmesi, test numunelerinin üretilmesi ve UV yaşlanmaya tabi tutulması prosedürü)

2.3. Manufacturing of Samples (Numunelerin İmalatı)

After drying, all produced PA6 composite pellets were molded in shape of dumbbell (Figure 3) in accordance with ISO 527 [30] and prismatic (Figure 3) according to ISO 178 [31] standards via YIZUMI-UN90A2 plastic injection molding machine worked at constant injection conditions presented in Table 2. To fabricate the test samples, the four-cavity mold having a capability of producing double tensile specimens and double flexural samples was utilized.

Table 2. Values of injection parameters (Enjeksiyon parametrelerinin değerleri)

Parameters	Unit	Values
Melt temperature	°C	235
Mold temperature	°C	60
Injection pressure	bar	47
Holding pressure	bar	57
Holding time	s	5
Cooling time	s	15

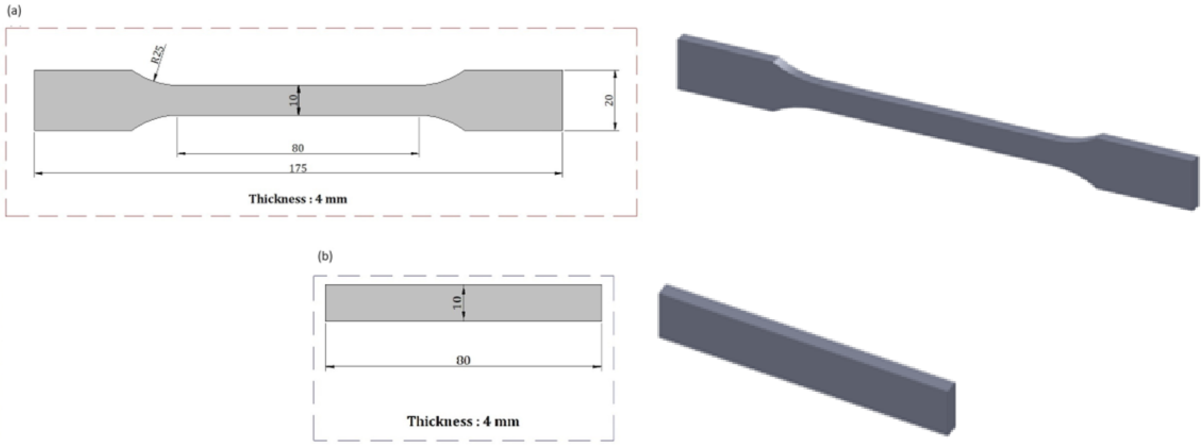

Figure 3. Dimensions for (a) tensile and (b) three-point flexural specimens (units are in mm) ((a) çekme ve (b) üç noktalı eğme numunelerinin boyutları (birimler mm cinsindendir))

2.4. Artificial (UV) Weathering Conditions
(Yapay (UV) Yaşlanma Koşulları)

UV weathering was performed using accelerated ageing device (QUV/se model). Fluorescent UV-A lamps providing 340 nm UV solar spectrum were used for UV weathering. Each 8-hour ageing cycle consists of 4 hours of dry UV exposure at 50 °C (irradiation level = 0.68 W/m^2) followed by a 4-hour water spray phase (condensation exposure at 50 °C without UV exposure). The cycles were repeated 3, 9, 15 and 21 times for a total exposure time of 24, 72, 120 and 168 hours, respectively. After UV ageing, the specimens were discarded from tester. After specimens were dried with paper towels, they were kept at room temperature for at least 10 minutes prior to testing. All tests were then conducted on these specimens.

2.5. Tests (Testler)

Tensile behaviour of PA6 and developed composites was determined via universal testing device (Instron 5569) at laboratory condition. Fixed crosshead speed of 50 mm/min was utilized at tensile testing. Tensile strength and strain values were derived from tests.

Flexural properties were evaluated with three-point bending test at room temperature with Instron 5569 universal testing device. Flexural strain and strength were obtained at fixed crosshead speed of 10 mm/min and with supporting span of 60 mm.

After the tensile tests, scanning electron microscopy (SEM) examination was done with Philips XL 30 SFEG device with acceleration voltage of 15 kV to understand fracture surface of tensile specimens. Before examinations, surface of specimens was coated by thin layer of gold (approximately 30 nm thick) with Quorum SC7620 sputter coater to prevent electrical charging at examination and to make them more conductive and visible. Samples kept fixed and placed rigidly in the circular metal specimen holder via adhesive carbon tape. SEM micrographs were derived at 65× magnifications in high vacuum for secondary electrons.

3. EXPERIMENTAL RESULTS AND DISCUSSION (DENEY SONUÇLARI VE TARTIŞMA)

3.1. Tensile Test (Çekme Testi)

Figure 4 depicts typical tensile stress-strain curves for pure PA6 and PA6 filled by pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites. Figures were given for unaged samples and samples of UV aged at various ageing time. Pure PA6 showed necking and cold drawing. The value of stress diminished after necking. After this, neck continued at approximately constant stress, but the stress value increased again until failure. UV ageing process and duration did not affect this typical tensile stress-strain behavior of pure PA6 much, but only changed the tensile strength and strain values, as explained later. Tensile stress-strain behavior of agricultural waste flour filled PA6 composites was different in comparison to pure PA6 polymer, showing brittle behavior. It was concluded that the tensile behavior of PA6 evolved from ductile to brittle after the loading of pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour. As found in pure PA6 polymer, UV ageing process and duration did not affect typical tensile stress-strain behavior of agricultural waste flour filled PA6 composites much, but only changed the tensile strength and strain values.

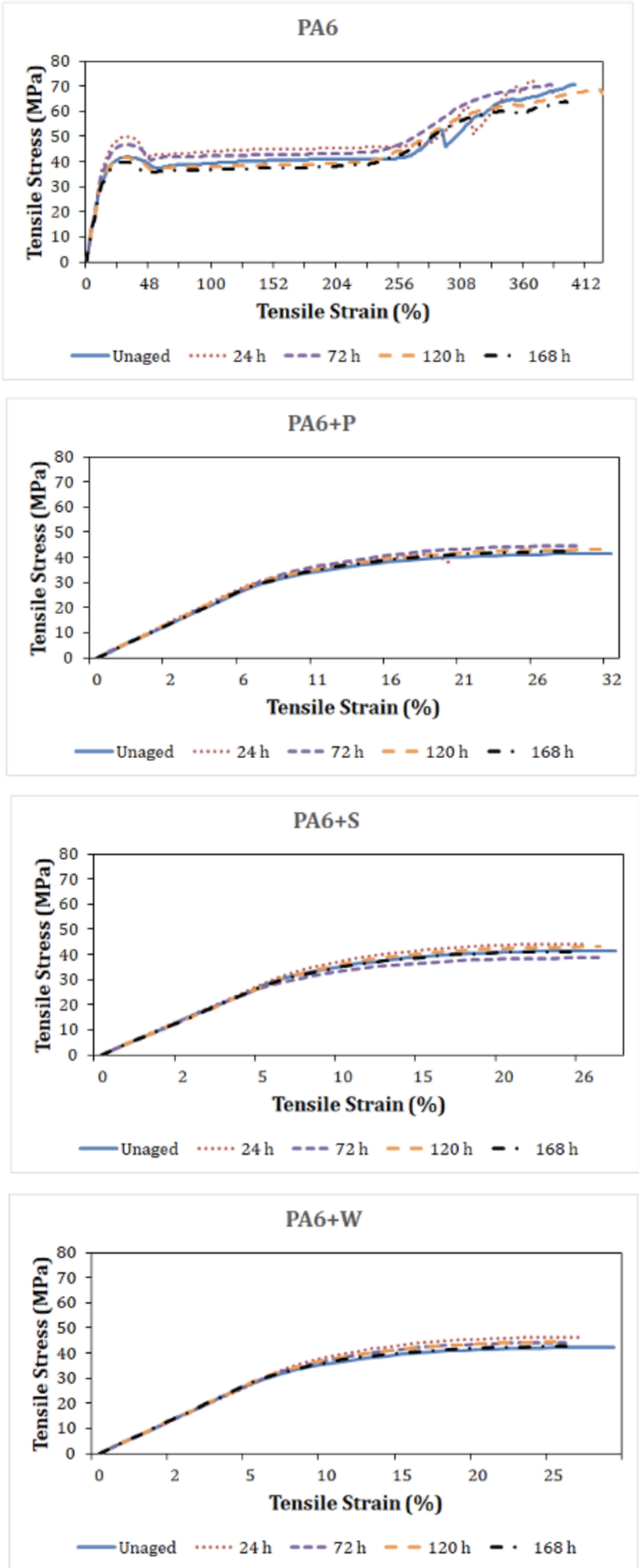

Figure 4. Typical tensile stress-strain graphs of agricultural waste flour based PA6 composites as a function of UV ageing time (UV yaşlanma süresinin bir fonksiyonu olarak tarımsal atık un bazlı PA6 kompozitlerinin tipik çekme gerilmesi-gerinimi grafikleri)

Tensile strength results of pure PA6 and PA6 filled by pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites are given in Figure 5a. Results were given for unaged and aged samples. Tensile strength values of PA6 polymer were found to be between 68.02-69.87 MPa for unaged, 24 h, 72 h and 120 h aged specimens. After 168 h ageing, this value dropped to 64.08 MPa, giving a decrease of 5.79%. For unaged and aged samples, blending PA6 polymer with agricultural waste flour led to decrement in tensile strength compared to pure PA6 and drop in tensile strength by loading of pistachio shell flour in PP was declared in other study [32]. The capability to support stress transmitted from polymeric matrix was rather weak for natural filler and this was reason of smaller tensile strength by addition of natural filler into polymer [33]. It is assumed that because these agricultural shells, which are lignocellulosic filler, have highly polar groups, interphase adhesion of composite is negatively influenced. Difference between polarities of polymeric matrix and filler prevented proper load transfer and caused the tensile strength values to decrease [32]. Tensile strength of unaged PA6+P, PA6+S and PA6+W composites diminished by 39.41, 39.70 and 37.11%, respectively in comparison to unaged PA6. After UV weathering, changing at tensile strength of agricultural waste filled PA6 composites was smaller. Tensile strength values of PA6+P, PA6+S and PA6+W composites were between 40.54-43.57 MPa, 38.85-43.42 MPa and 42.28-46.18 MPa, respectively for unaged and aged samples. Generally, tensile strength increased slightly after UV ageing in PA6 composites with agricultural waste flour. The highest increase was obtained with the 24-hour UV aged walnut shell flour filled PA6 composite (PA6+W), which increased the tensile strength by 7.94% compared to the unaged version. Although the agricultural shell addition caused decrement in tensile strength of PA6 polymer, fact that these composites cause little change or even an increment in tensile strength after exposure to UV ageing showed that agricultural shell filled composites can be used in outdoor conditions. Before and after UV weathering the greatest tensile strength was obtained by walnut shell flour filled PA6 (PA6+W) composites among all green composites. Similar to our study, it was found in the literature that walnut shell filled PP composite gave higher tensile strength than pistachio shell filled PP composite [18]. After UV weathering, the greatest tensile strength values were achieved by PA6+W composite among all green composites. It was stated that greater lignin amount in green composites behaved as heat insulation agent and photostabilizer at the composites hence providing the best UV and thermal stability [34]. Lignin amount of walnut shell (36.90%) was the greatest [15] among agricultural shell flour employed at present work.

Figure 5b demonstrates tensile strain results for pure PA6 and PA6 filled with pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites as function of UV ageing time. Tensile strain values for PA6 polymer were obtained between 364.62-426.30% for unaged and aged samples. After 120 h ageing, tensile strain increased to 426.30%, giving an increase of 12.68%. Compounding PA6 polymer with agricultural shell flour caused an enormous decrement in tensile strain relative to pure PA6 and decrease was also found for sunflower seed husk flour filled PP composite [35]. Conclusion may be attributed to discontinuities (increase in material heterogeneity) with the addition of lignocellulosic fillers to polymer matrix [36], restricting deformability and mobility of PA6 matrix, leading to smaller tensile strain as compared to pure PA6. It was stated that higher lignin content led to the increase in brittleness of lignocellulosic material while higher cellulose content reduced brittleness [37]. The lowest lignin content of pistachio shell [10] was reason why pistachio shell flour filled PA6 presented the greatest tensile strain among all green composites. Tensile strain of unaged PA6+P, PA6+S and PA6+W composites decreased by 91.93, 92.69 and 92.59%, respectively with respect to unaged PA6. After UV weathering, changing at tensile strain of agricultural shell flour filled PA6 composites was found to be smaller. Tensile strain values of PA6+P, PA6+S and PA6+W composites were between 22.71-30.53%, 25.80-27.64% and 25.70-28.02%, respectively for unaged and aged samples.

3.2. Flexural Test (Eğme Testi)

Figure 6 demonstrates typical flexural stress-strain graphs for pure PA6 and PA6 filled by pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites. The flexural behavior of pure PA6 and green composites was found to be similar, showing brittle failure. UV ageing process and duration did not affect typical flexural stress-strain behavior of pure PA6 polymer and agricultural waste flour filled PA6 composites much, but only changed the flexural strength and strain values.

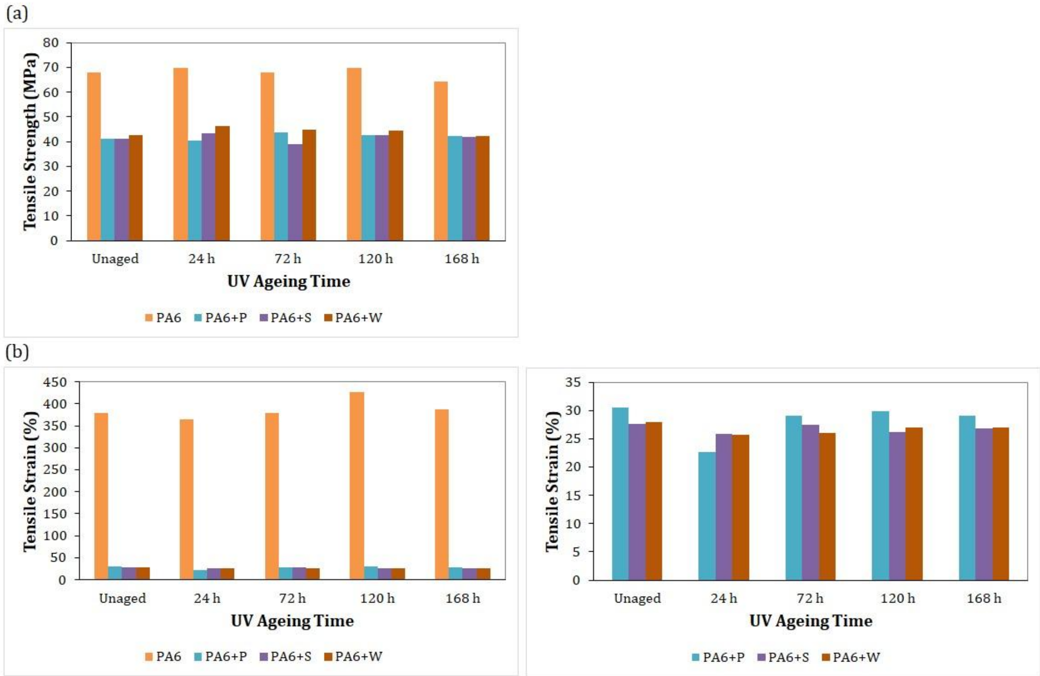

Figure 5. (a) Tensile strength and (b) tensile strain values of agricultural waste flour based PA6 composites as a function of UV ageing time ((a) Tarımsal atık un bazlı PA6 kompozitlerinin UV yaşlanma süresinin bir fonksiyonu olarak çekme mukavemeti ve (b) çekme gerinimi değerleri)

Flexural strength results of unaged and aged pure PA6 and PA6 filled by pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites are demonstrated in Figure 7a. Flexural strength values of PA6 polymer were found to be between 47.28-62.45 MPa for unaged and aged samples. UV ageing increased flexural strength of pure PA6 polymer. Flexural strength increased by 32.09% after 24 hours of UV ageing, 24.21% after 72 hours of UV ageing, 20.44% after 120 hours of UV ageing and 18.31% after 168 hours of UV ageing. That is, for pure PA6 polymer, the increase in flexural strength with UV ageing was less with the increase in UV ageing time. For unaged samples, blending PA6 polymer with sunflower seed husk and walnut shell flour led to decrement in flexural strength with respect to pure PA6. Flexural strength of unaged PA6+S and PA6+W composites reduced by 11.39 and 1.61%, respectively in comparison to unaged PA6. However, blending PA6 polymer with pistachio shell flour increased flexural strength in comparison to pure PA6. Flexural strength for unaged PA6+P composite increased by 10.64% with respect to unaged PA6 polymer. Lignocellulosic fiber strength determines the mechanical strength of the composite under the same matrix and production process. Cellulose has significant effects on the properties of agricultural shell flour filled polymer composites, and high cellulose content enhanced their mechanical properties [38]. Therefore, the greatest flexural strength was achieved by PA6+P composite because of the greatest cellulose amount of pistachio shell (47.08%) [10]. UV ageing increased the flexural strength of all agricultural shell flour filled PA6 composites. For PA6+P composite, flexural strength increased by 7.55% after 24 hours of UV ageing, 3.85% after 72 hours of UV ageing, 7.60% after 120 hours of UV ageing and 0.72% after 168 hours of UV ageing. For PA6+S composite, increment in flexural strength with UV ageing was higher. After 24, 72, 120 and 168 hours of UV ageing, flexural strength increased by 38.11%, 30.40%, 31.07% and 26.76%, respectively. For PA6+W composite, flexural strength increased by 27.26% after 24 hours of UV ageing, 20.34% after 72 hours of UV ageing, 19.54% after 120 hours of UV ageing and 12.87% after 168 hours of UV ageing. An increase in the flexural strength after exposure to UV ageing indicated that agricultural shell filled composites can be used in outdoor conditions. Among green composites, the greatest flexural strength was achieved by the 24-hour UV aged walnut shell flour filled PA6 composite (PA6+W). Generally, it was concluded that pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour filled PA6 composites can compete with pure PA6 when flexural strength was taken into consideration. Hence, more environmentally friendly composites having moderate flexural strength were prepared.

Figure 7b depicts flexural strain values for pure PA6 and PA6 filled by pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour composites as a function of UV ageing time. Flexural strain values of PA6 polymer were between 11.34-13.44% for unaged and aged samples. UV ageing caused a decrease in flexural strain for pure PA6. Flexural strain for unaged PA6+S and PA6+W composites reduced by 5.66 and 3.57%, respectively with respect to unaged PA6 polymer. Flexural strain values for PA6+P, PA6+S and PA6+W composites were between 11.77-13.92%, 11.87-12.68% and 11.74-12.96%, respectively for unaged and aged samples.

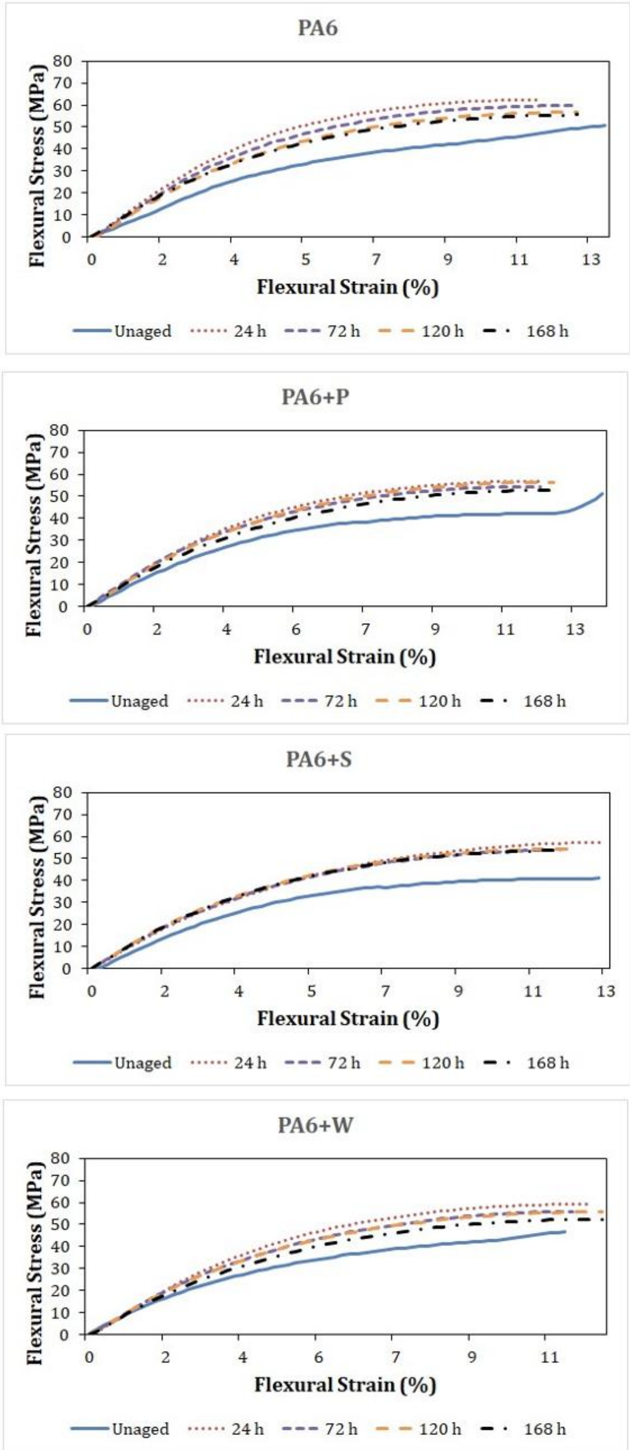

Figure 6. Typical flexural stress-strain graphs of agricultural waste flour based PA6 composites as a function of UV ageing time (UV yaşlanma süresinin bir fonksiyonu olarak tarımsal atık un bazlı PA6 kompozitlerinin tipik eğme gerilmesi-gerinimi grafikleri)

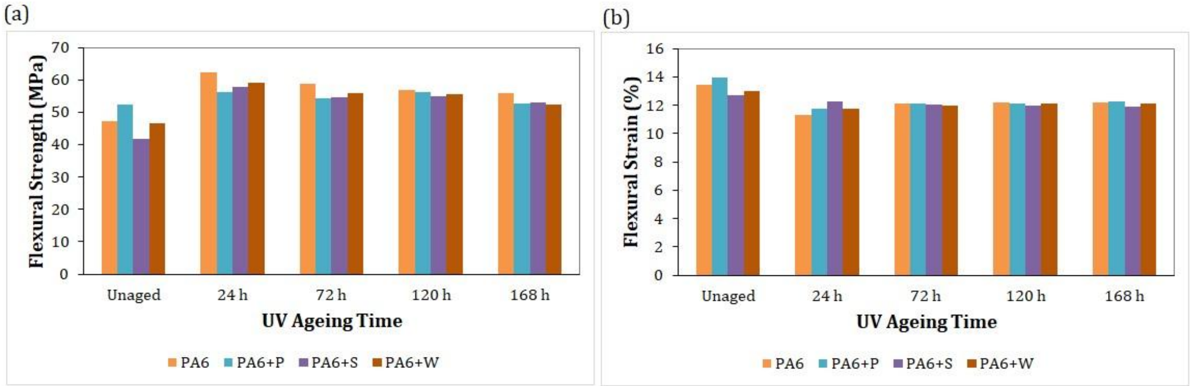

Figure 7. (a) Flexural strength and (b) flexural strain values of agricultural waste flour based PA6 composites as a function of UV ageing time ((a) UV yaşlanma süresinin bir fonksiyonu olarak tarımsal atık un bazlı PA6 kompozitlerinin eğme mukavemeti ve (b) eğme gerinimi değerleri)

3.3. Morphological Examination (Morfolojik İnceleme)

Tensile fractured surface morphology for pure PA6, PA6+P, PA6+S and PA6+W composites after tensile tests are given in Figure 8 as a function of UV ageing time. Pull-out of pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour were seen onto fractured surface of green composites. Also, voids between matrix and agricultural shell flour were seen onto fractured surface of agricultural waste flour filled PA6 composites. It is thought that such situations would negatively affect mechanical properties of green composites [39]. No significant change was found on the fractured surface with UV ageing for pure PA6 polymer and agricultural shell flour filled PA6 composites.

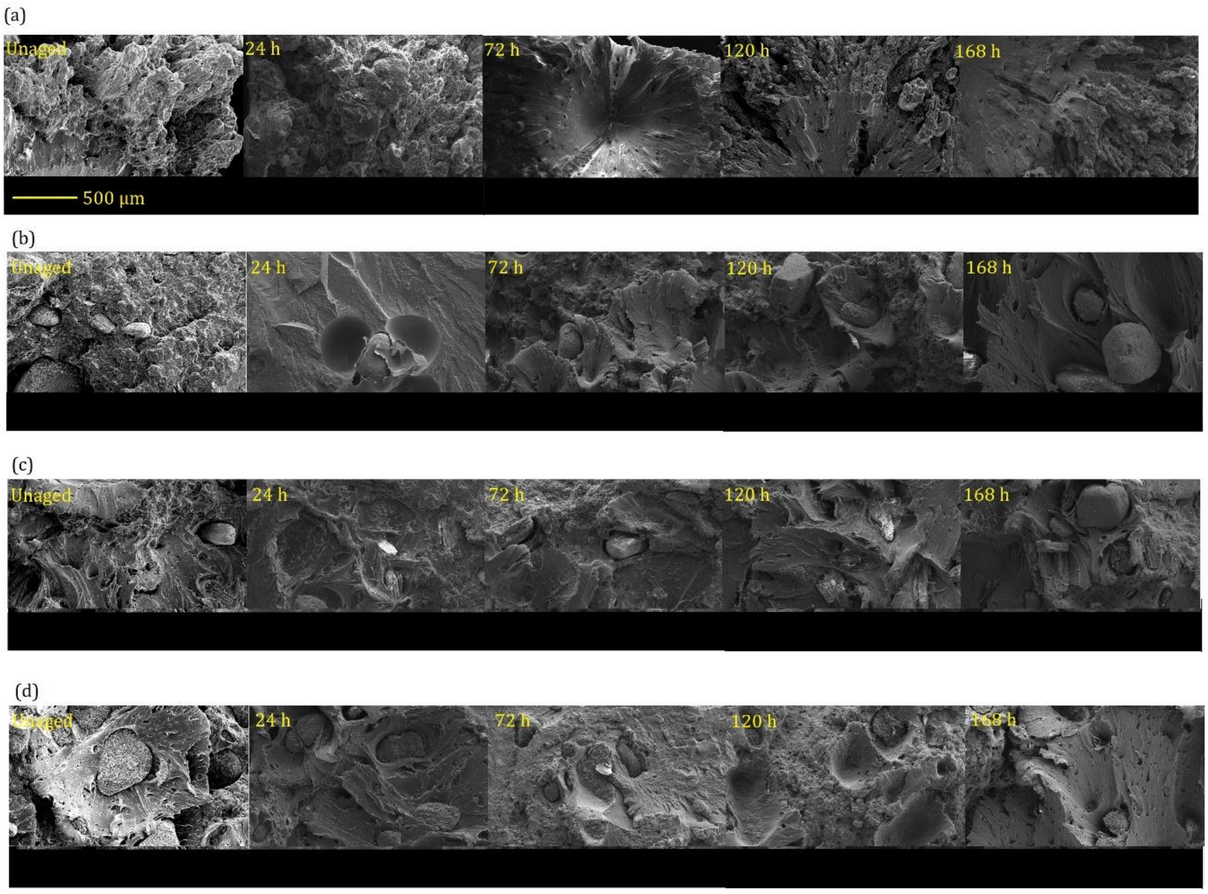

Figure 8. SEM results for (a) PA6, (b) PA6+P, (c) PA6+S and (d) PA6+W as a function of UV ageing time (UV yaşlanma süresinin bir fonksiyonu olarak (a) PA6, (b) PA6+P, (c) PA6+S ve (d) PA6+W için SEM sonuçları)

4. CONCLUSIONS (SONUÇLAR)

Pistachio shell, sunflower seed husk and walnut shell flour are cheap, readily available, and tends to be processed into several kinds of polymeric matrices as agricultural waste. Therefore, in this research, the powdered pistachio shell, sunflower seed husk (Dakota type) and walnut shell were employed as natural fillers with PA6 in order to produce green composites. Tensile strain, tensile strength, flexural strain and flexural strength were determined for pure PA6 and green composites. Besides, UV ageing for pure PA6 and produced green composites were investigated. It was concluded that the tensile behavior of PA6 changed from ductile to brittle after the loading of pistachio shell, sunflower seed (Dakota type) husk and walnut shell flour. UV ageing process and duration did not affect this typical tensile stress-strain behavior of pure PA6 and agricultural waste flour filled PA6 composites much, but only changed the tensile strength and strain values. For unaged and aged samples, blending PA6 polymer with agricultural waste flour caused decrease in tensile strength as compared to pure PA6. Tensile strength for unaged PA6+P, PA6+S and PA6+W composites decreased by 39.41, 39.70 and 37.11%, respectively in comparison to unaged PA6. After UV weathering, changing at tensile strength of agricultural flour filled PA6 composites was smaller. In general, tensile strength increased slightly after UV ageing in agricultural shell flour filled PA6 composites. The highest increase was found with the 24-hour UV aged walnut shell flour filled PA6 composite, which increased tensile strength by 7.94% in comparison to the unaged one. Although the agricultural shell loading led to decrement at tensile strength of PA6 polymer, fact that these composites cause little change or even an increment in the tensile strength after exposure to UV ageing indicated that agricultural shell filled composites can be utilized in outdoor conditions. Compounding PA6 polymer with agricultural shell flour resulted in an enormous decrease in tensile strain. Pistachio shell flour filled PA6 presented the greatest tensile strain among green composites. Tensile strain of unaged PA6+P, PA6+S and PA6+W composites reduced by 91.93, 92.69 and 92.59%, respectively as compared to unaged PA6. After UV weathering, changing in tensile strain of agricultural shell flour filled PA6 composites was found to be smaller. The flexural behavior of pure PA6 and green composites showed brittle failure. UV ageing process and duration did not affect typical flexural stress-strain behavior of pure PA6 and agricultural waste flour filled PA6 composites much, but only changed the flexural strength and strain values. UV ageing increased the flexural strength by 32.09% after 24 hours of UV ageing, 24.21% after 72 hours of UV ageing, 20.44% after 120 hours of UV ageing and 18.31% after 168 hours of UV ageing for pure PA6 polymer. For unaged samples, blending PA6 polymer with sunflower seed husk and walnut shell flour caused decrement in flexural strength with respect to pure PA6, while blending PA6 polymer with pistachio shell flour increased flexural strength as compared to pure PA6. UV ageing increased the flexural strength of all agricultural shell flour filled PA6 composites and this result indicated that agricultural shell filled composites can be used in outdoor conditions. Among green composites, the greatest flexural strength was achieved by the 24-hour UV aged walnut shell flour filled PA6 composite. UV weathering resulted in decrease in flexural strain for pure PA6 polymer.

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DECLARATION OF ETHICAL STANDARDS (ETİK STANDARTLARIN BEYANI)

The author of this article declares that the materials and methods they use in their work do not require ethical committee approval and/or legal-specific permission.

Bu makalenin yazarı çalışmalarında kullandıkları materyal ve yöntemlerin etik kurul izni ve/veya yasal-özel bir izin gerektirmediğini beyan ederler.

AUTHORS' CONTRIBUTIONS (YAZARLARIN KATKILARI)

***Emel KURAM*:** She conducted the experiments, analyzed the results and performed the writing process.

Deneyleri yapmış, sonuçlarını analiz etmiş ve makalenin yazım işlemini gerçekleştirmiştir.

***Fatih AYDINLI*:** He conducted the experiments and analyzed the results.

Deneyleri yapmış ve sonuçlarını analiz etmiştir.

***Omer Faruk AKKUZU*:** He conducted the experiments and analyzed the results.

Deneyleri yapmış ve sonuçlarını analiz etmiştir.

***Babur OZCELIK*:** He analyzed the results.

Sonuçları analiz etmiştir.

CONFLICT OF INTEREST (ÇIKAR ÇATIŞMASI)

There is no conflict of interest in this study.

Bu çalışmada herhangi bir çıkar çatışması yoktur.

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