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# POLYMER BIOCOMPOSITES BASED ON AGRO WASTE: PART III. SHELLS OF VARIOUS NUTS AS NATURAL FILLER FOR POLYMER COMPOSITES

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**Abstract.** Today, there is a rapidly growing demand for composites from the windpower engineering, aerospace, transport engineering, and defence sphere. The main factor holding back the further production and consumption of goods made of polymer composites in the world market is their high cost. One of the ways to reduce the cost of polymer composites is to replace expensive filler with a cheaper one. Great hopes in this direction are associated with the waste of the agricultural sector (agro waste). Agro waste of plant origin is considered an excellent lignocellulosic reinforcing filler for polymer composites. Polymer-based composites made using lignocellulosic materials have been increasing recently. In this regard, in this review, lignocellulosic nutshells are considered aspotential filler or reinforcing material for polymer composites with various matrices. Summarizing the literature data, we can say that the nutshell particles have good structural and thermal properties, and they can be used as an alternative to synthetic and artificial fillers. And also the use of nutshells in the production of composite materials can not only partially reduce the wood deficit in some nut-rich countries, but can also lead to several benefits, such as environmental and socio-economic. Waste raw materials and low operating costs make these biocomposites promising for technological applications.

***Keywords:*** *biocomposites, agro waste, nut shell, reinforcing agent, eco friendly.*

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## 1. Introduction

Increased demand for environmentally friendly materials resulted in worldwide interest in manufacturing composite materials from agricultural waste materials. Agricultural residues are excellent alternative materials to lignocellulosic materials because they are inexpensive, easily processed, plentiful, and renewable (Singh *et al.*, 2018a; Ashori & Bahreini, 2009; Arzumanova & Kakhramanov, 2020). The plastic industry is one of the areas where agricultural wastes can be used most effectively. Some advantages, such as low density, high specific properties, low hygroscopicity and high dimensional stability of polymer composites filled with organic materials make it possible to use some agro-waste in polymer composites as fillers and reinforcing elements (Nitin & Singh, 2013).

Nutshells are one of the sources of renewable lignocellulosic materials that can be obtained as by-products of agriculture. They are often used in relatively inexpensive applications, such as composts, mulch, fertilizer, and animal feed (Sutivisedsak *et al.*, 2012). Recently, their possible application as fillers for polymer composites has been studied (Mrowka *et al.*, 2021). The use of these materials as fillers is associated with their lower-specific density relative to mineral fillers, stability (being natural renewable materials), biodegradability and lack of toxicity, which makes them more environmentally friendly in terms of utilization.

Usually in everyday life, nuts are called any edible fruit, consisting of a shell (hard or soft) and an edible kernel. A more precise definition and range of plants, the fruits of which are called nuts, depends on the point of view from which the issue is considered. In botany, a nut is a dry, non-opening syncarpous lower fruit with a woody pericarp, inside which one (rarely two) free-lying seed is placed. In a culinary sense, a wide variety of dried seeds are called nuts and these "nuts" from the point of view of botany are fake nuts or incorrectly called nuts. Fig. 1 illustrates some of the common types of botanical and culinary nuts.


**Figure 1.** Some types of botanical and culinary nuts

In the marketing year of 2019/2020, the worldwide production of various types of nuts (kernel basis) is presented in Fig.2 (all kernel basis except pistachios are in-shell). Production data relate to the weight of nuts in the shell or husk, as the shell or husk content of the nut ranges from 20% for chestnuts to 30% for cashews, which means that the amount of agricultural waste in the form of shell or husk is very high.

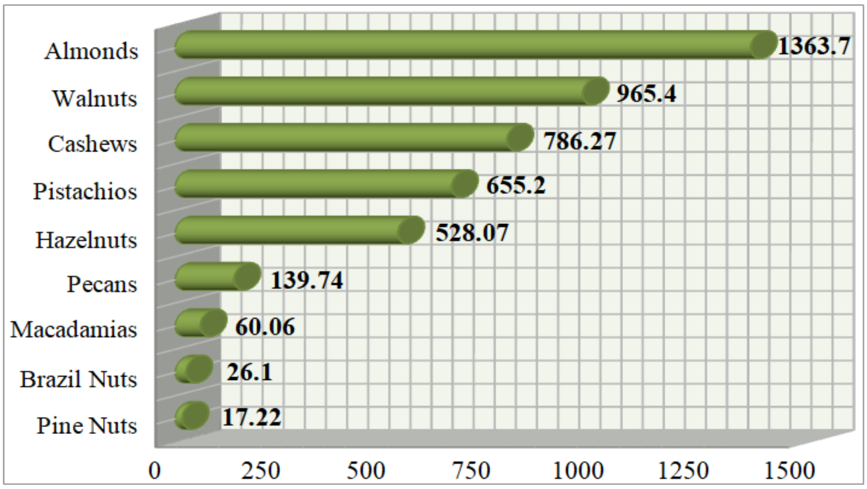


**Figure 2.** Production of tree nuts worldwide in 2019/2020, by type (Statista. Production of Tree Nuts Worldwide in 2019/2020, by Type (in 1,000 Metric Tons). Retrieved from https://www.statista.com/statistics/1030790/tree-nut-global-production-by-type/

The use of shells or husks of various nuts as reinforcing filler for polymers is reported in the literature. Some examples of nutshells as fillers in various thermoplastic polymer matrices given in the literature are summarized in Table 1.

**Table 1.** Prior reports of nutshells as natural filler in various polymer matrices

| Filler(s) | Polymer | Treatment method | References |
|---|---|---|---|
| ***Walnut*** | PP | PP-g-MA | (Dobrzyńska-Mizera *et al.*, 2019) |
| | | - | (Obidiegwu *et al.*, 2014) |
| | | PP-g-MA | (Ayrilmis *et al.*, 2013) |
| | | PP-g-MA | (Zahedi *et al.*, 2013) |
| | | PP-g-MA | (Akbaş *et al.*, 2013) |
| | HDPE | - | (Ogah & Afiukwa, 2014) |
| | | lubricant | (Ogah *et al.*, 2014) |
| | | lubricant | (Ogah & Chukwujike, 2017) |
| | | PE-g-MA | (Akbaş *et al.*, 2013) |
| | LDPE | - | (Mohammed, 2014) |
| ***Hazelnut*** | PP | lubricant | (Karakuş *et al.*, 2017) |
| | | lubricant | (Demirer *et al.*, 2018) |
| | | - | (Gurbanov *et al.*, 2018) |
| | | PP-g-MA | (Avci *et al.*, 2013) |
| | | NaOH, PP-g-MA | (Kufel & Kuciel, 2020) |
| | HDPE | PE-g-MA | (Boran, 2016) |
| | | - | (Salasinska & Ryszkowska, 2012) |
| | | PE-g-MA | (Tufan & Ayrilmis, 2016) |
| | LDPE | lubricant | (Karakuş *et al.*, 2017) |
| ***Peanut*** | PP | PP-g-MA | (Chatterjee & Singh 2019) |
| | rPP | polyvinyl alcohol | (Zaaba *et al.*, 2014) |
| | rPP | ethylene/acrylic acid | (Zaaba *et al.*, 2013; 2016) |
| | rPP | ionizing radiation | (Zaaba *et al.*, 2018; Zaaba & Ismail, 2018) |
| | LDPE | PE-g-MA | (Obasi, 2015) |
| ***Pistachio*** | HDPE | PE-g-MA | (Najafabadi *et al.*, 2014) |
| | | PE-g-MA | (Najafabadi *et al.*, 2017) |
| | | - | (Salasinska & Ryszkowska, 2015) |
| | LDPE | - | (Sutivisedsak *et al.*, 2012) |
| ***Almond*** | PP | SEBS-g-MA | (Essabir *et al.*, 2013) |
| | | PP-g-MA | (Lashgari *et al.*, 2013) |
| | | PP-g-MA | (Zahedi *et al.*, 2015) |
| | | PP-g-MA | (Hosseinihashemi *et al.*, 2016a) |
| | | PP-g-MA | (Hosseinihashemi *et al.*, 2016b) |
| | LLDPE | PP-g-MA | (Altay *et al.*, 2019) |

## 2. Use of nutshells as filler in various polymer matrices

***2.1. Walnut*** (*Júglans régia* L.) is an important crop grown in all temperate regions of the world as edible nuts (Shailja, 2018; Khantwal *et al.*, 2016). Worldwide walnut production in 2019/2020 was approximately 965,400 tons (Barbu *et al.*, 2020). Since walnut shells make up 67% of the total weight of the fruit (Han *et al.*, 2018), about 646,818 tons of walnut shells remain as agricultural waste each year (Fig. 3). This annual agricultural waste is the lignocellulosic material forming the shell of the walnut fruit.Walnut shells, as biowaste, have no economic value or industrial use and are usually thrown away or incinerated in a burner or otherwise disposed of, although the incineration of agricultural waste causes serious environmental problems (Bhuvaneshwari *et al.*, 2019). Walnut shells have many advantages, such as sufficient reactive functional groups, high carbon content, compatibility with diverse industrial chemicals, good stability, mechanical properties due to the presence of aromatic rings, good rheological and viscoelastic properties making it a potential candidate to be used as a reinforcing material in polymer composites (Członka *et al.*, 2020). Over the past several decades, research has been carried out on the use of walnut shells as a reinforcing material for the manufacture of composite boards (Rao & Gope, 2015; Gope & Rao, 2016). This lignocellulosic material provides sufficient strength at low cost, low density, environmental friendliness and non-toxicity. The chemical composition of walnut shells consists of 23.9% cellulose, 22.4% hemicellulose, 50.3% lignin and 3.4% ash (Jahanban-Esfahlan *et al.*, 2019).


**Figure 3.** Walnut: a – plant, b – fruit, c – shell, d – shell powder

Walnut shells as reinforcing filler have significant competitive advantages for thermoplastic composites in outdoor applications requiring high dimensional stability. These advantages are lower amounts of hygroscopic materials (cellulose and hemicellulose) and higher amounts of hydrophobic materials (lignin and extractives) in the cell walls of the walnut shell (Pirayesh *et al.*, 2013).

In addition to the main components, walnut shells also contain extractives, such as tannins, pectins, fats, waxes, resins, essential oils, volatiles and ash (Pirayesh *et al.*, 2012). The high content of extractives, combined with the poor wettability of the walnut shell, can lead to weak bonding between particles and low internal bond strength in the final product. Therefore, the introduction of a compatibilizer is often necessary to improve the interfacial adhesion between components. A study of the effect of walnut shells and PP-g-MA (polypropylene-graft-maleic anhydride) coupling agent on the crystallization characteristics, heat resistance and thermomechanical properties of composites based on polypropylene (PP) showed that the introduction of a bio-filler into a polymer matrix increased its rigidity without changing the kinetics of PP crystallization (Dobrzyńska-Mizera *et al.,* 2019). The PP/walnut shell composite generally shows characteristic changes in properties (Obidiegwu *et al.*, 2014). Density and water absorption showed a gradual increase, while tensile properties showed no noticeable improvement. The decrease in tensile strength by 20-50% indicates poor adhesion between the walnut shell and the PP matrix. It is assumed that the tensile strength of the composite can be increased by using a coupling agent. In a study of the dimensional stability and mechanical properties of composites prepared from walnut shells and PP with and without PP-g-MA, the compatibilizer was found to be effective in improving the dimensional stability and mechanical properties of composites (Ayrilmis *et al.,* 2013). PP-g-MA had a more pronounced effect on strength properties. For example, the introduction of 3 wt% PP-g-MA showed an increase in the tensile strength and modulus by 12 and 5%, respectively. Based on the research results, it can be said that the formulation of walnut shells/PP/PP-g-MA at a ratio of 40/57/3 can be used in external applications requiring dimensional stability.

Studies have shown that walnut shells can be successfully used for the manufacture of composites based on PP with useful physicomechanical properties. An improvement in the elastic and strength properties of PP/walnut shell composites was observed with the addition of 3 wt% organoclay (Zahedi *et al.*, 2013). The water absorption and swelling thickness of the composites decreased (from 0.84% to 0.53% and from 1.5% to 0.99 %, respectively) with an increase in the content of the organoclay. Besides, the addition of 6 wt% PP-g-MA improved the mechanical and physical properties of the composites. The maximum flexural strength and modulus value were found to be 22.67 MPa and 2.08 GPa respectively for composites made with 3% organo-clay and 6% MAPP, while these quantities were 15.01 MPa and 1.41 GPa for composites made without organo-clay and 4% MAPP respectively. The SEM study showed that samples containing 3 wt% organoclay had a higher intercalation order and better dispersion of clay layers in polymer-matrix composites.

Tests of the flexural strength of highly filled composites based on high-density polyethylene (HDPE) and walnut shells showed that at 65 wt% filler concentration the flexural strength decreases (Ogah *&* Afiukwa, 2014). HDPE/walnut shell composites showed low flexural strength below 15 MPa compared to pure HDPE. With the addition of 3 wt% lubricants, the rheological properties of these composites were studied (Ogah *et al.,* 2014).The walnut shell composite showed an unusual decrease in storage modulus with an increasing shear rate. Damping factor (tanδ) decreased with increasing shear rate at 65 vol.% filler concentration. Walnut shell composites gave higher torque and steady-state torque values.

And when determining the elastic and impact, water-absorbing and swelling properties of polyethylene composites filled with 65 wt% walnut shells, it was found that the composites have better unnotched Izod impact strength and demonstrate higher water absorption values and higher values of swelling in thickness by 6.45% for HDPE/walnut shell composites (Ogah *&* Chukwujike, 2017).

When studying the mechanical properties of composites based on walnut shell and low-density polyethylene (LDPE), an obvious improvement in mechanical parameters was recorded with the addition of 10 wt% walnut shells (Mohammed, 2014). The maximum ultimate strength and modulus of elasticity value were found to be 41.818

MPa and 932.34 MPa, respectively. Walnut shell is characterized by rigidity, which in turn increases the stiffness of the polymer and reduces elongation from 109% to 7.8%.

A comparative analysis of the possibility of using walnut shells in PP and HDPE matrix composites due to its relative hardness and availability showed that the best results were obtained in composites containing, respectively, 47% walnut shell, 3% PP-g-MA and 50% PP, which can be used in applications requiring mechanical properties (Akbaş *et al.*, 2013). The use of a coupling agent markedly improved tensile strengthand flexural modulus from 8.24 MPa to 11.30 MPa and from 1280 to 1514 MPa respectively but did not significantly affect the impact strength of HDPE composites filled with walnut shells. The impact strength decreased from 41.9 to 30.73 J/M both PP and HDPE. Based on TGA and DSC studies, the thermal stability of polymers increased with the participation of PP-g-MA and PE-g-MA (polyethylene-graft-maleic anhydride).

New green composites were prepared by melt mixing of a binary mixture of polylactide and poly(ε-caprolactone) with walnut shell particles, which was obtained as a waste of the agricultural food processing industry (Montava-Jordà *et al.*, 2019). Maleinized linseed oil was added to remove the inherently poor compatibility between the biopolymer blend and lignocellulosic fillers. Although the introduction of walnut shells tended to reduce the mechanical strength and thermal stability of the binary mixture of polylactide and poly (ε-caprolactone), maleated linseed oil-containing composites filled up to 20 wt% walnut shells showed superior plasticity and more balanced thermomechanical change. In particular, the elongation at break increased up to approximately 55%.

Walnut shell can also be used successfully with thermoplastic starch in walnut shell/thermoplastic starch composites (Sarsari *et al.*, 2016). The introduction of 40 wt% and 50 wt% walnut shells improved the mechanical properties of the composites in comparison with pure thermoplastic starch. Tensile strength (1.9 times), flexural strength (1.7 times), modulus of elasticity (2.79 times) and impact strength (2.81 times) increased with increasing concentration of walnut shells and adding nanoclay. Although walnut shells are biodegradable, the biodegradation of the composite was accelerated by increasing the concentration of starch in their mixture.

Studies have been conducted on the suitability of walnut shells for the production of composites based on thermosetting polymers. The results of the study of determining the parameters (the ratio of urea and formaldehyde, the reaction temperature and the reaction period) affecting the polymer composite particleboards made of walnut shell and urea-formaldehyde and the influence of these parameters on the hardness showed that the maximum bending strength is 3.8 $N/mm^2$, at a ratio of urea-formaldehyde 1:1, a reaction temperature of 70°C, a reaction time of 25 min (Gürü *et al.*, 2008).

The concentration of walnut shell plays an important role in the formation of the physicomechanical properties of composites. An increase in the concentration of walnut shells from 10 wt% to 20 wt% plays an important role in reducing the tensile strength and increasing the relative elongation of the composite based on the epoxy matrix, for example, the highest tensile strength value – 42.95 MPa is observed at 10 wt % concentration of walnut shell particles, and then sharply drops first to 20 wt% fillings, and then slowly decreases to 34.0 MPa (Nitin & Singh, 2013). This decrease in tensile strength is due to porosity, poor adhesion and poor interfacial interaction between the epoxy resin and the walnut shell particles. It was also found that the density of the composition decreases with an increase in the percentage of walnut shell particles. It can be seen that a slow decrease in density is observed at the concentration range of walnut shell particles from 10-30 wt%, but at the range of 30-40 wt%, there is a sharp decrease in density. It can be said that the tensile strength of 33-41 MPa achieved due to the reinforcement of the walnut shell with particles is sufficient for materials replacing wood.

The results of studying the particles of walnut and coconut fiber as a biocomposite reinforcing material for epoxy resinshowed that the tensile strength, modulus of elasticity and yield strength of the obtained hybrid biocomposite are about 54.3%, 86.4% and 88.3% of pure epoxy resin, respectively (Rao *et al.*, 2015). Fracture of coconut fiber and pull out of walnut shell particles is the main failure mechanism observed in this hybrid biocomposite. The variance and coefficient of variance of biocomposite exceed 10%. This indicates that the failure of the biocomposite depends on several factors, such as good dispersion, quality bonding, and uniform distribution of particles or fibers in the matrix.

Walnut shell particles have also been used to reinforce high-performance thermosetting materials based on the epoxy/diaminodiphenylmethane system and epoxy resin/benzoxazine based on diaminodiphenylmethane (Shah *et al.*, 2018). Alkaline treatment of the walnut shell particles confirms the removal of hemicellulose and some of the lignin from the shell particles. It has been noted that walnut shells improve thermal stability after 1% alkaline treatment. Alkaline treatment of walnut shell also increases the crystallinity index of the particles to 67%, it should be noted that the crystallinity index for the particles of untreated walnut shells is 58%. In short, a new composite system based on the treated walnut shell can be designed with improved thermal and thermomechanical properties with significant weight savings.

Walnut shell has also been used as an alternative filler for ethylene propylene diene monomer rubber (Güngör *et al.*, 2019). The walnut shell surface was modified with bis[3-(triethoxysilyl)propyl]tetrasulfide to achieve better interfacial interaction with the matrix. A study of the effect of walnut shell particle size, filler concentration, modification with silane and curing temperature showed that rubber samples based on a copolymer of ethylene, propylene and diene monomer, reinforced with 30 wt% silane-modified walnut shell, particles of which are less than 250 μm and which cure at 170°C for 5 minutes showed the best results.

An increase in void content indicates poor quality composites and changes in mechanical properties. Based on the carried out experimentsit can be concluded that the void content percentage increases with an increase in the concentration of walnut shell particles up to 30 wt% and decreases from 30 to 40 wt% (Singh *et al.*, 2018b). An increase in the concentration of walnut shell particles decreases the tensile strength of polyester composites. It was found that the tensile modulus of the composite specimen at 40 wt% walnut shells is 2.14 times higher than that of pure polyester.

Thus, summing up the literature data we can say that the use of the walnut shell in the production of composite materials can not only partially reduce the wood deficit in some walnut-rich countries, but can also lead to several benefits, such as environmental and socio-economic.

***2.2. Hazelnut*** (*Corylus avellana* L.) is the most popular and most commonly grown nut after almonds all over the world. Hazelnut shell is a renewable lignocellulosic material that is obtained as a by-product of agriculture (Fig. 4). In the marketing year of 2019/2020 world production of in-shell hazelnut amounted to roughly 646,818 tons (Barbu *et al.*, 2020). Consequently, this high production volume comes at a price, causing a large amount (approximately 353,807 tons) of hazelnut shells as waste. This hazelnut shell waste is mainly used as fuel and biomass (Demirkaya *et al.*, 2019). Apart from the high phenol content in the shell, there is limited research on its industrial application, especially in the preparation of composites.


**Figure 4.** Hazelnut: a – plant, b – fruit, c – shell, d – shell powder

Hazelnut shell is characterized by low density; as reported (Çöpür *et al.*, 2007), the density of the hazelnut shell is 0.23 g/cm$^3$ (±0.21), which appears to be a lower value compared to untreated wood material (0.40-0.75 g/cm$^3$). Hazelnut shell powder can be used as reinforcement/filler with a wide variety of polymeric matrices. It can provide a wood-like appearance to polymer composites that contribute to preserving forestry resources (Balart *et al.*, 2016). The most preferred biomatrix in these composites is polylactic acid (Battegazzore *et al.*, 2014; Mitra, 2014). The obtained research results show that hazelnut shell can be optimally used as a reinforcing filler in fully biodegradable composites with a polylactic acid matrix (Balart *et al.*, 2018).

Also, several studies have been published in the literature on other thermoplastic and thermosetting polymers, such as polyethylene, polypropylene, epoxy resin, urea-formaldehyde, as a polymer matrix in composites filled with hazelnut shell.

Investigation of polymer composites based on LDPE and PP, including various ratios of hazelnut shell and made by injection, showed that composites based on PP provide better mechanical properties compared to composites based on LDPE (Karakuş *et al.*, 2017). The addition of hazelnut shell to polymer matrices improved the flexural modulus values for LDPE from 133.82 MPa to 786.03 MPa and for PP from 1077.18 MPa to 1917.68 MPa while reducing tensile strength for LDPE from 9.04 MPa to 3.68 MPa and for PP from 29.01 MPa to 11.52 MPa, elongation for LDPE from 103.75% to 4.68% and for PP from 465% to 3.25%. The results showed that flexural strength is highly dependent on filler concentration.

The results of the study showed that when microcrystalline cellulose and hazelnut shells are used together in composites based on HDPE, higher flexural modulus (1600

MPa) and higher tensile modulus (682 MPa) are observed (Boran, 2016). Based on SEM images, it can be said that the use of hazelnut shell and microcrystalline cellulose resulted in better-dispersed structures in the polymer matrix. Thus, the presence of hazelnut shell in HDPE reinforced with microcrystalline cellulose provided significant improvements in the mechanical properties of the composites.

Physical, mechanical and flammable properties of physically modified secondary HDPE film with finely ground hazelnut shells showed that the resulting composite can be used inside and outside buildings (Salasinska & Ryszkowska, 2012). The addition of a hazelnut shell negatively affected water absorption (25.03%) and swelling thickness (8.43%) of composites based on secondary HDPE fllled with 60 wt% hazelnut shell (Tufan & Ayrilmis, 2016). The loading of PE-g-MA into polymer composites had a positive effect on the value of water absorption (22.12%) and swelling thickness (7.33%).

The suitability of ground hazelnut shells in matrix PP composites has been investigated due to their relative hardness, characteristic colour, and availability (Demirer *et al.*, 2018). The modulus of elasticity (from 869.05 MPa to 1925.48 MPa), hardness (from 74Shore D to 77.7Shore D), heat reflection (from 57.2°C to 66.3°C) and Vicat heat resistance (from 155.6°C to 159°C) values increase with an increase in the amount of crushed hazelnut shells flour in the PP matrix. However, tensile strength (from 30.84 MPa to 27.21 MPa), force at break, elongation at break (from 47.84% to 5.33%), the Izod impact (from 3.37 $kJ/m^2$ to 2.28 $kJ/m^2$) and melt flow index (from 6.015 g/10min to 4.347 g/10min) values decreased.

In the work (Gurbanov *et al.*, 2018) it was found that the impact resistance values of all composites filled with hazelnut shells (43.55-72.90 J/m) are higher than the impact resistance value of pure PP (26.74 J/m). It became clear that increasing the concentration of hazelnut shell, used in different quantities, reduces mechanical properties and increases the rate of swelling and water absorption. It was found that the best result is achieved in composites using 30 wt% hazelnut shells.

The results obtained in the study of Avci and co-authors (2013) showed that reinforcement with biological waste affects the mechanical properties of biocomposites under tension. The tensile strength of the composites varied from 25.43 $N/mm^2$ to 30.47 $N/mm^2$. Statistical analysis showed that there was no significant difference between the tensile strengths of the original PP and the biocomposite filled with 10 wt% hazelnut shell, although there were significant differences between biocomposites with different concentrations (10-30 wt%) of hazelnut shell. The tensile strength values decreased with the increasing concentration of hazelnut shell from 10 wt% to 50 wt%. The maximum rate of decrease in tensile strength is about 14.6% in a composite filled with 50 wt% hazelnut shell. The highest tensile strength values were obtained for the composite filled with 10 wt% hazelnut shell.

Hazelnut shell can be used asa filler in PP hybrid composites (Kufel & Kuciel, 2020). Composites reinforced with hazelnut shell are characterized by low strength properties. However, the addition of both basalt fibers and hazelnut shells resulted in increased tensile strength and tensile modulus. The tensile strength increased by 56% and the elastic modulus increased by 74% for composites already reinforced with 10 wt% filler. The results showed that the addition of fillers successfully improved thermal and creep stability. The effect of water absorption on the mechanical properties of composites was not significant. After thermal aging tensile strength andtensile modulus significantly decreased.

The results of the study by Müller et al (2018) proved the possibility of the utilization of this waste in the field of polymer-particle composites. It can be concluded that a low concentration of filler based on hazelnut shell microparticles (5 wt%) increases the tensile strength of epoxy composites. The strength is increased by approximately 11% compared to the matrix. Higher filler concentrations (18 wt%) reduce tensile strength. Besides, an increase in themicroparticle filler concentration based on a hazelnut shell did not have a significant effect on the hardness of the studied material. It has been shown that hazelnut shell microparticles are effective filler in the field of adhesive joints.

Untreated, alkali-treated, acrylic acid and acetic anhydride modified hazelnut shell wastes were used as inexpensive reinforcement materials in an epoxy matrix system (Kocaman & Ahmetli, 2020). The effect of chemical modification and concentration of the reinforcing agent on the properties of composites has been investigated. Morphological results show improved adhesion between hazelnut shell and matrix upon chemical treatment. Composites reinforced with modified hazelnut shell showed an increase of 7.7-46.2% in elongation at break when compared to composite reinforced with untreated hazelnut shell at more appropriate 20 wt% of filler. Also, the tensile strengths of all chemically modified hazelnut shell composites are higher than that obtained with pure epoxy and untreated hazelnut shell composites. It was observed that composite reinforced with 20 wt% acetic anhydride-modified hazelnut shell exhibited higher tensile strength (66 MPa) and elastic modulus (6.72 GPa). TGA analysis showed that hazelnut shells can significantly improve the thermal stability of pure epoxy. The Vicat softening point of the composites was higher than that of the epoxy matrix. Besides, all composites have hydrophobic surfaces. The loading of a hazelnut shell reduces the wetting and hydrophilicity of synthesized epoxy resin.

The loading of agricultural waste into the epoxy resin matrix led to a change in the combustibility and smoke emission of the polymer matrix (Salasinska *et al.*, 2019). Materials containing hazelnut shells showed a reduction in heat and vapor emission compared to unmodified epoxy. The formation of aless combustible char layer inhibited the decomposition process of composites and limited the smoke emission. It was noted that composites containing ground hazelnut shell showed a residue as swollen char formed in the multicellular layers. It was found that the addition of agricultural waste reduces the amount and the number of emitted products, and also determines their type. Based on the thermogravimetric analysis, it was found that composites have higher thermal stability in the temperature range up to 300°C compared to epoxy resin. The decomposition rate decreased depending on the increase in the filler content, and the residue yield corresponded to the amount of lignin contained in the plants.

Hazelnut shell combined with jute fiber has found application as natural and biodegradable filler in non-asbestos organic non-metallic friction composites in which phenolic resin was used as a binder (Matějka *et al.*, 2013).

Flexible polyurethane foams have been synthesized with the addition of environmentally friendly fillers, such as walnut shell and hazelnut shell to increase the environmental potential and improve thermal stability and desired physical and mechanical properties (Bryśkiewicz *et al.*, 2016).

Gürü et al (2009a) prepared a urea-formaldehyde based hazelnut shell particleboard and eliminated its disadvantages, such as flammability, water absorption, swelling thickness, using fly ash and phenol-formaldehyde. The results of the study showed that the maximum bending strength is 4.1 N/mm$^2$, at the urea-formaldehyde ratio of 1.0, the reaction temperature of 70°C, reaction time of 25 min, hazelnut shell/urea-formaldehyde resin of 2.4 and a mean particle size of 0.1 mm. Fly ash, which creates air pollution, can be used as a fire retardant instead of chemicals or mineral agents in the composite. Thus, it prevents environmental pollution. Also, phenol-formaldehyde can be used as a waterproof material. Water absorption and increase in swelling thickness exponentially decreased with increasingphenol-formaldehyde concentration.Waste raw materials and low operating costs make this research promising for technological applications.

***2.3. Peanut*** (*Arachis hypogaea* L.) is one of the major food crops in the world. Peanuts are capable of producing high-volume shells (Fig. 5). Efforts to find the utilization of these waste materials have led to low-value or limited applications (Zaaba & Ismail, 2019). In this regard, the peanut is an interesting candidate due to its chemical composition. Peanut shells are mainly composed of cellulose, hemicellulose and lignin microfibrils. The chemical composition of peanut shell: cellulose – 35.7%, hemicellulose – 18.7%, lignin – 30.2%, protein – 8.2%, carbohydrates – 2.5% and ash content - 4.7% (Raju & Kumarappa, 2011). Therefore, the consumption of peanut shells as natural fillers in thermoplastic/natural filler composites tends to open up a new avenue of use in converting agricultural waste into useful resources in the plastics industry.


**Figure 5.** Peanut: a – plant, b – fruit, c – shell, d – shell powder

The presence of PE-g-MA in composites and its compatibility with the agro-filler contributes to better dispersion and uniformity of the agro-filler in the matrix and, consequently, to the improvement of properties (Obasi, 2015). The higher content of peanut shells in the LDPE reduces tensile strength and elongation due to the weak interfacial bond between the peanut shell and the LDPE matrix. Young's modulus, flexural strength and elastic modulus, toughness and hardness increase with increasing filler content. Modification of the peanut shell/LDPE composites through compatibilization enhanced interfacial adhesion at the filler/matrix interface, as indicated by a decrease in water absorption and swelling of the composite thickness. Besides, the weight loss of the composites through enzymatic degradation indicated that both composites were biodegradable even at high filler loading levels. However, composites with PE-g-MA showed less weight loss.

A study aimed at investigating the possibility of using untreated and alkali-treated peanut shells, with two different particle sizes (0-300 μm and 300-600 μm) with a particle concentration in the range from 0% to 30% as a filler in a matrix of recycled PE and evaluation their mechanical properties and biodegradability showed that a composite based on recycled PE reinforced with 20 wt.% of alkali-treated peanut shells with particle sizes ranging from 0 to 300 μm has a higher strength of 7.7 $MN/m^2$ (Usman *et al.*, 2016). This sample also has a lower water absorption rate. The data on the growth of *Aspergillus niger* (fungi) in the samples suggests that the PE/peanut shell composite is biodegradable. Thus, peanut shells are suitable reinforcing filler for recycled polyethylene.

Peanut shells have the potential to act as a filler to improve the mechanical properties of PP composites when combined with PP-g-MA (Chatterjee & Singh2019). An increase in the concentration of PP-g-MA in composites leads to an improvement in mechanical properties, which emphasizes the effectiveness of the coupling agent. Composites prepared by loading 4 wt% PP-g-MA show the best results in all cases. Flexural modulus increases by 243% (1154 MPa) at 50 wt% filler concentration and 4 wt% PP-g-MA relative to pure PP (474 MPa). SEM images and dynamomechanical analysis indicate the best interfacial bonding between filler and matrix with the addition of a coupling agent. The maximum moisture absorption of composites is about 0.3% with the loading of 50 wt% peanut shells with 4 wt% PP-g-MA, which indicates that the composites can be used for external use.

The results of studying the effect of chemical modification of peanut shell powder using polyvinyl alcohol showed that composites of recycled PP (rPP) with peanut shell modified with polyvinyl alcohol had higher values of tensile strength, elongation and modulus of elasticity in tension, but lower water resistance than composites recycled PP with unmodified peanut shell (Zaaba *et al.*, 2014). FTIR analysis revealed small changes in the positions and intensities of the bands, indicating a clear interaction between the hydroxyl groups of the peanut shell and the polyvinyl alcohol. Composites of rPP/peanut shell modified with polyvinyl alcohol had better interfacial adhesion between the matrix and filler than composites of rPP/unmodified peanut shell, as shown in photomicrographs of a scanning electron microscope.

Zaaba et al (2013; 2016) used an ethylene/acrylic acid copolymer to chemically modify the surface of the peanut shell, and this led to an increase in tensile strength of the rPP/peanut shell composites. The results can be explained in terms of better adhesion at the filler-matrix interface due to the presence of the compatibilizer. Interfacial adhesion can develop through the formation of ester groups between acrylic acid from an ethylene-acrylic acid copolymer and hydroxyl groups on the surface of the peanut shell. Good interfacial bonding can reduce the concentration of interfacial stress and can prevent filler-to-filler contact.

Among all methods for modifying the surface of natural filler, ionizing radiation can be used as an alternative in the development of new polymer materials by enhancing interfacial adhesion between natural fillers and a polymer matrix. The results of a study of the effect of electron beam irradiation on the properties of composite materials made of rPP and peanut shells showed that there is an improvement in tensile strength and elastic modulus during stretching of irradiated composites of rPP/peanut shell with a simultaneous decrease in the elongation by 3 times (Zaaba *et al.*, 2018; Zaaba & Ismail, 2018). An increase in gel content upon irradiation indicates that the irradiation is causing crosslinking between the components. The thermal stability of the irradiated composites has also been improved over the non-irradiated composites. SEM analysis indicates improved interfacial adhesion and crosslinking between components of irradiated composites. The decrease in water absorption in the irradiated composite also indicates a strong adhesion between the peanut shell and the recycled PP under electron beam irradiation.

The results of the study of the effect of the concentration of peanut shells on the thermal properties of composites based on polylactic acid showed that the addition of peanut shells caused a decrease in the melting point from 152.5°C to 143.4°C and decomposition temperature from 357.5°Cto 302.5°C (Yamoum & Magaraphan, 2017). Besides, the crystallinity of biocomposites slightly increased with an increase in the concentration of peanut shells up to 30 wt%. A morphological study showed poor interfacial adhesion between the peanut shell and thepolylactic acid matrix. However, the study of mechanical properties showed that the maximum value of tensile strength and Young's modulus is achieved with the introduction of 30 wt% peanut shells and decreases when more peanut shells are introduced into the matrix. The toughness decreased with increasing peanut shell content. Also, the presence of peanut shells enhanced the biodegradability of biocomposites. And in another study (Adeosun *et al.*, 2016), the mechanical and morphological characteristics of polylactic acid composites reinforced with peanut shells were examined. Tensile test results showed that at 6 wt% concentration of untreated peanut shells, the composite had the best tensile stiffness of 24.62 MPa. This corresponds to an increase in the modulus of elasticity by 2.201% compared to unreinforced polylactic acid (1.07 MPa). The composite based on polylactic acid, reinforced with 5 wt% untreated peanut shells, showed a better combination of properties compared to pure polylactic acid with an increase of 286% (4.43x10-4 HB), 1.502% (1.07 MPa), 286% (0.22 MPa), 6.8% (0.05 J) and 1.081% (~ 0.15 MPa) in hardness, stiffness, tensile strength, energy at break and stress at break, respectively. However, the ductility decreased by ~ 33.3% compared to the pure polylactic acid (18.27). The polylactic acid composite reinforced with 5 wt% untreated peanut shells showed the highest tensile strength (0.855 MPa).

Also in the literature, there are many studies of lignocellulosic plant residue – peanut shells as filler for thermosetting polymers. Vinyl ester resin has excellent physical and mechanical properties and is known for its versatility as a composite matrix. The results of the study (Raju *et al.*, 2012a) showed that it is possible to prepare composite panels using peanut shell particles and vinyl ester resin as an adhesive. Particle addition improved mechanical properties and then decreased with increasing filler concentration in samples. A sample reinforced with 40 wt% peanut shell particles has a maximum tensile strength (28.09 MPa) and tensile modulus (1872.65 MPa). But sample reinforced with 50 wt% peanut shell particles has maximum impact strength (42.91 KJ/m$^2$). The latter is the optimal composite material for use as particleboard or roofing material.

Among thermosetting polymers, polyester resin is durable, relatively inexpensive, has excellent corrosion resistance and is light in weight. Polyester resin composites reinforced with untreated and treated peanut shells have been investigated for their thermal stability, mechanical properties and water resistance (Ikladious *et al.*, 2017). The loading of peanut shells into the thermosetting matrix resulted in higher thermal stability of all composites, and greater improvement was achieved by increasing the filler concentration. The results of mechanical strength showed that increasing the concentration of the treated filler in the composites resulted in significant improvements. The maximum values of the mechanical properties were reached at 35 wt% filler due to sufficient wetting and good interfacial adhesion. Moreover, with a further increase in the amount of treated filler to 55 wt%, the strength values were still satisfactory. All composite samples showed similar water absorption behavior. The decrease in the hydrophilicity of the filler due to alkaline and silane treatment of the filler surface made the composites more resistant to water absorption.

Evaluation of the mechanical and thermal properties of polyester resin/peanut shell composites by varying the amount of peanut shell (5, 10, 15 and 20 wt%) showed that a polyester composite reinforced with 15 wt% peanut shell has the highest tensile strength 79.91 MPa (Prabhakar *et al.*, 2015a). However, the tensile strength decreased (75.3 MPa) as the peanut shell content was further increased. In contrast, the tensile modulus increases uniformly with increasing peanut shell reinforcement. Flexural strength increased linearly until the concentration of peanut shells reached about 15 wt%, and then suddenly decreased with a further increase in the content of reinforcing material. At the composite of 5%, 10%, 15% and 20% of the peanut shell, the flexural strength of the composites was found to be 1850, 2800, 3200, 2900 MPa respectively. In contrast to flexural strength, the flexural modulus demonstrated a rising trend with an increase in the peanut shell reinforcement content. However, after 15 wt%, the increase in flexural strength was negligible. Thermogravimetric analysis of composites based on polyester reinforced with peanut shells confirmed the thermal stability of the developed composites.

The cured epoxy systems generally exhibit good dimensional stability, thermal stability, and resistance to most fungi. Epoxy resin composites, reinforced with chemically modified peanut shell particles, were prepared with different weight percentages of peanut shell particles and epoxy resin (Raju & Kumarappa, 2012). The maximum strength was observed for a sample with a filler content of 50 wt% and a particle size of 0.5 mm. However, a sample with a filler content of 85 wt% and a particle size of 1 mm has a maximum modulus of elasticity. It was noted that the thermal conductivity of composite samples is in the range from 0.07638 to 0.3487 W/(m·K), and the linear thermal expansion varies from $0.725\times10^{-6}$to $1.296\times10^{-6}$/°C. The results of this study showed that peanut shell particles can be successfully used to create a useful composite that could replace wood-based panels in many applications. The authors also applied Taguchi methodology to determine the best combination of process parameters to optimize thermal properties, such as thermal conductivity, linear thermal expansion, and specific heat of peanut particles reinforced with polymer composites (Raju *et al.*, 2012b). The size of the filler particles, the filler concentration, and the type of matrix was selected as process parameters. Three different polymer resins were used as matrix materials, namely epoxy, vinyl ester and polyester. The best combination of process parameter settings for minimum thermal expansion is a 1.5 mm particle size with 60 wt% peanut shell particles using polyester resin as a matrix. On the other hand, the optimum combination of process parameter settings to maximize the specific heat of the polymer composite reinforced with peanut shell particles is 1 mm particle size with 60 wt% filler particles using a polyester resin as a matrix. Thermal stability is valuable information needed to produce more thermally stable composites, possibly with good fire resistance. A composite sample with a particle size of 1.5 mm, 60 wt% filler using a vinyl ester resin as a matrix has higher heat resistance.

A study of composites prepared by introducing a treated peanut shell powder as a natural filler into an epoxy resin matrix showed that tensile strength (from 24 MPa to35.56 MPa) and tensile modulus (from 1200 MPa to 1960 MPa) increase with an increase in the content of bio-filler (Prabhakar *et al.*, 2015b). The highest mechanical properties of the epoxy composite filled with peanut shells treated with 7% alkali were achieved with 15 wt% bio-filler. The morphology of the composites shows a better bond between filler and resin, resulting in improved mechanical properties. The TGA results showed that polymer composites exhibited thermal stability with increasing NaOH concentration and filler content.

A comparative study of the mechanical properties of peanut shell/epoxy resin composites with rice husk/epoxy resin composites showed that peanut shell epoxy composites exhibit higher mechanical properties compared to rice husk epoxy composites (Akindapo *et al.*, 2017). The highest mechanical properties of the peanut shell reinforced epoxy composites were: impact strength (7.91 J/mm$^2$ at 12.5%), hardness (7.8 HRF at 5%), flexural strength (43.43 N/mm$^2$ at 12.5% ) and tensile strength (41.60 N/mm$^2$ at 2.5%) while the highest mechanical properties for the rice husk reinforced epoxy composites were: impact strength (4.91 J/mm$^2$ at 7.5%), hardness (8.7 HRF at 2.5%), flexural strength (28.21 N/mm$^2$ at 5%) and tensile strength (16.67 N/mm$^2$ at 5%). This behavior is to be expected because dispersed peanut shell fibers are relatively hard and more brittle than corresponding rice husk fibers.

When studying the thermal properties of composites based on epoxy resin, reinforced with peanut shells, treated with 5% alkali, it was observed that the thermal conductivity of the peanut shell / epoxy resin composite decreased (0.355-0.221 W/mK) with an increase in the percentage of peanut shell; while the thermal resistance increases (Jubu *et al.*, 2018). Thermal diffusion decreases with increasing peanut shell particle content.

Peanut shells can be used as semi-reinforcing filler in the rubber industry (Sareena *et al.*, 2011). Curing characteristics, such as anneal time and curing time of natural rubber compounds decrease with increasing filler content, but show an increase in minimum torque and maximum torque. Swelling resistance and crosslinking density increase with the increasing concentration of peanut shells in natural rubber compounds. Mechanical properties, such as tensile strength and elongation tend to decrease with increasing filler content and the higher the concentration of the peanut shell, the poorer the mechanical properties. The best rubber-filler interactions were observed in natural rubber/alkali-treated peanut shells, and rubber-filler interactions decreased with increasing filler content. However, composites containing 40 phr filler in peanut shells showed better hardness. Among the investigated fillers, peanut shell particles (0-45 microns) treated with alkali provide the highest degree of hardening and better physical and mechanical properties due to their higher specific surface area.

Together with other agricultural waste, peanut shells are used as reinforcing filler in hybrid composites to achieve the desired properties. The introduction of coconut shell and peanut shell into thermosetting materials is used to reduce the cost of manufacturing molded products (Muthukumar & Lingadurai, 2014). An experimental study of the mechanical behavior of the epoxy/coconut shell/peanut shell composite has shown that mechanical behavior is highly dependent on the volume fraction of the filler. Maximum tensile strength is obtained for a composite filled with 40 vol.% coconut/peanut shell. Maximum flexural strength is obtained for a composite filled with 50% coconut/peanut shell. Therefore, the composite filled with 40% to 50% coconut shell/peanut shell is suitable for use in the interior part of an aircraft, motor car and automobile where materials with good tensile strength characteristics are required.

The paper (Prithivirajan, 2016) investigates the effect of particle hybridization on the mechanical behavior and swelling of epoxy composites. The hybridization of particles in an epoxy matrix has a large impact on the tensile properties and elastic properties of composites. The hybridization of peanut shell particles with rice husks improved the mechanical properties to a greater extent. The hybridization of particles also had a strong influence on the swelling of the composites. It was found that the swelling was minimal for composites made from 22.5% rice husks and 7.5% peanut shells.

The results of the analysis of literature data showed that peanut shell reinforced composites are light in weight, economical and have good thermal stability and mechanical properties. Hence, they can be used for applications, such as car interior parts, electronic packages, structures, sporting goods, etc.

***2.4. Pistachio*** (*Pistacia vera* L.) is one of the most ancient nuts known in human history. The pistachio nut processing industry produces large quantities of pistachio shells as waste (Fig. 6). Millions of tons of pistachio shells are thrown away and either burned or left in the field every year. Therefore, the use of pistachio shells as filler in polymer composites is very important from an economic and environmental point of view. Pistachio shells were mainly used as a medium for orchids, animal feed, woodwork additives, etc. (Maghsoudi *et al.*, 2010; Marhoon, 2016).

Pistachio shell particles are composed of 47.08% cellulose, 26.56% hemicellulose, 13.74% lignin, 7.52% moisture, 0.92% waxes and 4.18% ash (Balasundar *et al.*, 2019). The cellulose content of pistachio shell particles is 47.08%, which is lower than that of some natural fibers (Senthamaraikannan & Kathiresan, 2018), but higher than that of other nutshell particles, such as hazelnut, almond, walnut, peanut and chestnut (Queirós *et al.*, 2020). This indicates that the mechanical and thermal properties of the polymer composite filled with pistachio shell particles may be higher than that of other nutshells.

Pistachio shell particles have high strength and elastic properties. The preparation of polymer composites with this filler is suitable for many technical applications. Gürü et al (2009b) investigated the thermal properties and burning characteristics of pistachio shell-filled polymer composite particle board using fly ash as a flame retardant. It was concluded that pistachio shell particles can be securely and economically used in construction applications due to their improved surface, hardness and fire-retardant properties.

Karaağaç (2014) investigated the mechanical, thermal and morphological properties of rubber matrix filled with microparticles of pistachio shells. The results showed that the elongation at break was increased up to 25%, besides, agglomeration of particles with different particle sizes was observed in the SEM images, wherein the larger particles cause weak points for breaking the sample.

The study (Alsaadi *et al.*, 2018) investigated the possibility of using pistachio shell particles as a filler for polyester resins by evaluating the tensile, bending and Charpy impact behavior of polyester composites filled with pistachio shells. Tests on tensile impact strength, flexural impact strength and Charpy impact strength show that the addition of pistachio shell powder significantly affects the mechanical properties of composites based on the polyester matrix. Tests have shown an improvement as well as deterioration in the mechanical properties depending on the concentration of pistachio shell particles. SEM images show that good pistachio particle distribution was obtained at 5 and 10 wt% pistachio shell particle concentrations. Moreover, particle aggregation occurs at concentrations above 10 wt%. Even though significant losses of mechanical properties can be found at high concentrations of pistachio shells, the manufacture of an environmentally friendly, low-cost polymer composite can be considered an advantage of using pistachio shells as particulate filler.


**Figure 6.** Pistachio: a – plant, b – fruit, c – shell, d – shell powder

In other research potential pistachio shells as natural filler is investigated using the epoxy matrix (Gairola *et al.*, 2020). With the loading of the filler, an increase in moisture absorption was observed. The impact of various environmental conditions, i.e. water, petrol and kerosene, on impact strength was also studied, and the sample test results were compared with the pure epoxy composite. With the loading of 10% filler, an increase in impact strength of 36.56% was observed under ambient conditions. A further decrease in toughness was observed for the sample exposed to various environmental conditions. Similar studies were carried out in a hybrid composite pistachio shell/pine needle/epoxy resin (Gairola *et al.*, 2019). The developed epoxy composites were exposed to a variety of environmental conditions, i.e. water, petrol and kerosene. It was concluded that the samples tested under ambient conditions showed better impact strength compared to samples immersed in water, petrol and kerosene. The hybrid composite exhibited a strength of 23.33 kJ/m$^2$ with 40.54% increase over pure epoxy matrix. Decreases in the strength of 27.60%, 28.84% and 30.56% were observed when this composite was exposed to water, petrol and kerosene, respectively.

Analysis of results of studies carried out indicate that pistachio shell particles have good structural and thermal properties, and surface energy can replace the best alternative to synthetic and artificial filler particles with potential use as a bio-filler.

***2.5. Almond*** (lat. *Prunus amygdalus*) is one of the most important and largest nut industries in the world (Simsek & Kizmaz, 2017; Pirayesh & Khazaeian, 2012). Besides, almond is one of the oldest crops used by humans, but their climatic requirements limit their commercial production to specific areas of the world. (Simsek, 2017). The processing of almonds to produce edible seeds separates the shell – agricultural residue, which is a lignocellulosic material that forms the thick endocarp or husk of the almond treefruits (Fig. 7) and, since it has no important industrial applications, is usually burned or discarded. The shell is more than 50% by dry weight of the almond fruits (Esfahlan *et al.*, 2010). This is huge number of shells has enormous economic and practical potential, and the best way to use it can attract increasing attention. For this reason, almond shell flour, produced in large quantities, can play an important role in the production of filled thermoplastic composites, reducing the wood deficit.


**Figure 7.** Almond: a – plant, b – fruit, c – shell, d – shell powder

The main chemical constituents of cellulose, hemicellulose and lignin in almond shells account for 38.48%, 28.82% and 29.54%, respectively. The cellulose content in the almond shell is higher than in other nut shells except for the pistachio shell. This indicates that the mechanical properties of the almond shell composite may be higher than that of most nutshells. Lignin can be useful to improve compatibility with thermoplastic, and it has a certain flame retardant effect, which is important for composites used as building materials. The special ring structure and hydroxide structure of hemicellulose give a reactive activity that is generally higher than that of cellulose. The content of hemicellulose in almond shells is higher than that of other nutshells. This indicates that almond shells may have more prospects for modification (Li *et al.*, 2018).

Almond shells were used to reinforce PP in the extrusion process (Essabir *et al.*, 2013). The mechanical, thermal, and rheological properties of PP/almond shell composites with a compatibilizer (PP-g-MA; SEBS-g-MA (styrene-ethylene/butylene-styrene-maleic anhydride-graft)) and without compatibilizer with various particle contents (5, 10, 15, 20, 25, 30 wt%) were studied. The results show a clear improvement in mechanical and rheological properties when using almond shell particles in the matrix without and with compatibilizer, which corresponds to an increase in Young's modulus of 56.2% and 35%, respectively, at 30 wt% almond shell loading. Thermal analysis showed that the loading of almond shell particles into composites leads to an increase in the initial thermal decomposition temperatures.

Natural fiber-reinforced polymers containing nanoclay could be a promising new approach to better quality products. Lashgari et al (2013) investigated the effect of montmorillonite (0, 2.5 and 5 phr) and almond shell (30, 35 and 40% phr) on the flexural and tensile properties, and impact strength of injection-molded PP composites. PP-g-MA content was kept constant at 2 phr for all composites. The tensile and flexural modulus of PP composites containing 5 phr nanoclay increased marginally as compared with composites made up of 2.5 phr nanoclay. However, the tensile and flexural strength of composites obtained using nanoclay and almond shells decreased by about 37.7% and 25.8%, respectively, with the addition of 2.5 phr nanoclay. Besides, the impact strength of the composites significantly decreased with both fillers. Similar studies were carried out by Zahedi et al (2015).The experimental results of the study showed that the elastic and mechanical tensile properties of PP/almond shell composites improved with the loading of 3 wt% organo-modified montmorillonite. The water absorption and swelling thickness of composites decreased with an increase in the content of organo-modified montmorillonite. Furthermore, the loading of 40 wt% almond shells improved the mechanical and physical properties of the composites better than 60 wt%. SEM analysis showed that the addition of organo-modified montmorillonite (up to 3 wt%) can improve interfacial adhesion, which leads to a decrease in the number of voids and the stretching of fibers.

And also the combined influence of montmorillonite and almond shell on the hardness, decay and water resistance of PP composites was investigated (Hosseinihashemi *et al.*, 2016a). The study results of montmorillonite concentration influence on the hardness of composites PP/montmorillonite/almond shells, exposed white-rot fungus, showed that the hardness of the composites increased with increasing of montmorillonite contentfrom 61.3 Shore D to 66 Shore D. This is because montmorillonite protects composites from fungal attack by reducing oxygen content, moisture absorption and lack of nutrients that are necessary for the functioning of the fungus. The hardness of decayed composites (61.3 Shore D) was lower than that of undecayed composites (66 Shore D). The weight loss of the composites decreased with increasing montmorillonite content. This revealed the thermal stability of composites improved with the loading of montmorillonite. The water absorption of undecayed and decayed composites decreased with an increase in the amount of montmorillonite at a content of 30-40 wt% almond shell. SEM analysis confirmed that montmorillonite reduces voids and defects at the filler/matrix interface. The water absorption of decayed composites was higher than that of undecayed ones, but their swelling thickness was lower.

Also, the combined effect of montmorillonite and almond shell on thermal stability, X-ray diffraction, and morphological characterization of PP-based composites was studied (Hosseinihashemi *et al.*, 2016b). Similar results were obtained, for example, the total weight loss of PP/montmorillonite/almond shell composites decreased with increasing filler concentration, and thermal stability increased with increasing montmorillonite concentration. By X-ray diffraction analysis, composites with 2.5 wt% and 5.0 wt% montmorillonite exhibited peak shifts to lower diffraction angles (2θ) than pure montmorillonite, and the relative intercalation of composites with 2.5 wt% montmorillonite was higher than that of composites with 5.0 wt% montmorillonite. The thermal stability of PP/montmorillonite/shell nanocomposites was improved by loading montmorillonite.

Sabbatini et al (2017) evaluated the introduction of almond shells to compare their effectiveness with the partial replacement of aluminium trihydrate in polymethyl methacrylate (PMMA) matrix. This is of particular importance since the loading of almond shells leads to some weight loss (the density of aluminium trihydrate is about 2.4, and for almond shells 0.6 $g/cm^3$). The aim was also to reduce costs somewhat, given that aluminium trihydrate, when ordered on a large scale, has a market price of around € 1,000 per tonne, while almond shells come from the food processing system at virtually no cost. The study results showed that the replacement of aluminium trihydrate in composite materials based on PMMA with organic bio-waste filler, in particular, almond shells, is possible up to 15 wt%. However, achieving effective results will depend on the morphology and distribution of the filler itself.

The study Pirayesh & Khazaeian (2012) investigated the suitability of almond shell particles as an additive in the production of three-layer particleboard, reducing the shortage of raw materials in the forest industry. The loading of almond shell particles to the particleboard significantly improved the water-resistance of the panels. However, the amount of almond shell particles should be 30% in the mixture to meet the standard required for mechanical properties. A valuable annual crop residue, almond shells, can be used with a mixture of wood particles in the production of particleboards. The use of almond shells in particleboard production not only reduces wood shortages in some almond-rich countries but can also lead to many benefits, such as environmental and socio-economic impacts.

## 3. Conclusion

The growing concern towards environmental issues and, on the other hand, the need for more universal polymer-based materials has led to increasing interest in polymer composites filled with natural fillers, i.e. fillers coming from renewable sources. And this review is intended to stimulate the interest of researchers to consider the potential of nutshells as another approach to replacing synthetic fillers as reinforcements in different types of polymer composites. Research on nutshells powder reinforced polymer composites is creating increased consideration, owing to their attractive characteristics, such as lower specific gravity relative to mineral fillers, sustainability (being natural renewable materials), biodegradability, and lack of toxicity, thereby more environmentally friendly in terms of disposal.

Summarizing the literature data, we can say that:

- the nutshell particles have good structural and thermal properties, and they can be used as an alternative to synthetic and artificial fillers;

- and also the use of nutshells in the production of composite materials can not only partially reduce the wood deficit in some nut-rich countries, but can also lead to several benefits, such as environmental and socio-economic;
- waste raw materials and low operating costs make these biocomposites promising for technological applications;
- many studies have shown that construction materials produced from different nutshells are relatively inexpensive, have lower cost, and are lightweight, and environmentally friendly than traditional.

Nutshell reinforced polymer composites prove to have an optimistic prospect amongst other natural filler reinforced composites for numerous applications.

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