# Natural fiber composites: the effect of the kind and content of filler on the dimensional and fire stability of polyolefin-based composites

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**Abstract:** Composites of polyethylene matrices and fillers consisting of finely ground pistachio shells and sunflower husks were manufactured. These materials were subjected to a series of tests for the purpose of examining their processing qualities, physical, mechanical and thermal characteristics, flammability and resistance to environmental factors, determining their feasibility and application paths. The relationship between the natural fiber composites' morphology and stability was described. Based on the obtained test results, the influence of the lignin content and secondary components in the fillers' structure on the thermal stability of the composites was confirmed. It was also proven that the porosity of the composites and the hemicellulose content in the filler influenced the composites' capacity to take up considerable amounts of water.

**Keywords**: polymer-matrix composite, scanning electron microscopy, computer tomography, thermogravimetric analysis, differential scanning calorimetry, durability, fire stability.

## Kompozyty polimerowe z napełniaczami roślinnymi: wpływ rodzaju i zawartości napełniaczy na stabilność wymiarową oraz palność kompozytów na osnowie poliolefin

**Streszczenie**: W ramach pracy wytworzono kompozyty na osnowie polietylenu napełnione drobno mielonymi łupinami pistacji oraz łuskami słonecznika. Materiały te poddano serii badań mających na celu poznanie ich właściwości przetwórczych, fizycznych, mechanicznych i termicznych, palności oraz odporności na działanie czynników środowiskowych, warunkujących możliwości i kierunki ich zastosowania. Określono związek między morfologią a stabilnością badanych kompozytów polimerowych z napełniaczami roślinnymi (NFC, z ang. *natural fibre composites*). Zbadano wpływ zawartości ligniny i pozostałych składników napełniaczy na stabilność termiczną NFC. Dowiedziono również, że na zdolność NFC do pochłaniania znacznych ilości wody zasadniczy wpływ ma porowatość kompozytów oraz zawartość hemicelulozy w napełniaczu.

**Słowa kluczowe**: kompozyt z osnową polimerową, skaningowa mikroskopia elektronowa, tomografia komputerowa, analiza termograwimetryczna, różnicowa kalorymetria skaningowa, trwałość, stabilność wymiarowa, palność.

Natural fiber composites (NFCs) constitute a group of polymers that are filled with particles or lignocellulose fibers other than wood. These types of fillers can be obtained from any part of the plant and one unquestionable advantage of their use is the possibility of using locally available resources. Their renewability and relatively low acquisition costs satisfy the present needs of producers by lowering production costs and making products ecologically sustainable. In addition to their superior mechanical properties, *i.e.* stiffness or hardness, that are possible while maintaining a relatively low specific weight of the product, NFCs are characterized by good insulation properties and they ensure good acoustics inside closed spaces or vehicles [1]. Component mixing, which is performed using methods applied in polymer processing, makes it possible to manufacture an end product that possesses the intended shape and color. Among the technologies used for this purpose, the following are of particular interest: extrusion (used to obtain construction products such as floor panels, jetty objects, fences, window profiles and doors), extrusion in combination with pressing and rotation molding (used to produce large-dimension products) and injection molding (used for furniture, utility goods and car fittings, among others) [2]. NFCs look like wood, but they are more durable and need no extra treatment, such as impregnation or painting, during their many years of use, and, therefore, they

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can replace wood in numerous applications. To ensure high resistance to environmental factors (radiation, atmospheric precipitation, microorganisms and pests or fire) it is necessary to apply physical modifications of plant fibers (corona treatment or plasma treatment) or chemical modifications (silane treatment, alkaline treatment, acetylation, maleated coupling or enzyme treatment) [3] and to introduce a significant amount of additives into the mixture to improve the durability of the material. The application of such procedures negatively affects the price and ecological aspects of the product and limits its possible applications. At present, no methods other than those mentioned above are used to improve the dimensional and thermal stability of NFCs.

The processing temperature is the factor that determines the possibility of using a polymer as an NFC matrix. This temperature should not exceed 190 °C because of the thermal degradation of lignin, which is the basic element of plant fibers. Numerous examples of thermoplastic polymer-based NFCs can be found in the literature [4–6]. They satisfy highly stringent market criteria, and they are used in industry. Among the polymers used in NFC matrices, the following are of note:

– biopolymers formed by microorganisms, *i.e.* polyhydroxybutyrate [7];

– polymers synthesized from renewable resources such as polylactic acid [8];

– polyethylene (PE) from renewable resources [9];

– natural polymers, *e.g.* thermoplastic starches [10];

– oxo-biodegradable PE [11].

However, PE, polypropylene (PP) and poly(vinyl chloride) (PVC) of petrochemical origin are the polymers that are most often used in NFC matrices. In the case of thermoplastics, it is possible to lower the price of the product with recyclates, which is especially common in the USA. Taking into consideration the demand of industrial sectors for polymer raw materials and the amount of produced waste, as estimated by PlasticEurope organizations [12], the availability of thermoplastic waste for NFC matrices has been analyzed in UE countries. The consumption of polyolefin and PVC in twenty seven UE countries and in Norway together with Switzerland constituted 48 % and 12 %, respectively, of the total volume of plastics consumed in 2011. Most PE and PP are used in the packaging industry for short-duration use and in branches referred to as "other" (*e.g.*, consumer goods, furniture, agriculture, sport, health care and protective cloths) [12]. The said industries constitute a prospective source of thermoplastic waste that may be possible for use in NFC matrices. For instance, in Poland, the share of used packaging in the stream of polymer waste in 2011 was 55.1 %, while that of the "other" industries amounted to 26.5 % [13]. Because PVC is intended mostly for long-term applications, its availability in the waste stream is presently limited. However, there is hope that in the near future, following the example of West European countries, new regulations will be introduced in Poland to ban the dumping of high energetic resources at landfills, thereby causing the available amount of cheap thermoplastic recyclates to gradually grow.

Lignocellulose products are obtained from various parts of the plant, *i.e.* the stem (flax, jute, hemp and ramie), leaf (pineapple, sisal and abaca), seed (coconut, cotton and kapok) and fruit (coconut), and also from grasses and reeds (bamboo and rice). For dozens of years, wood has been the most common source of plant fillers, and composites that are filled with wood particles or fibers are referred to as wood polymer composites (WPC). Europe's consumption of WPC and NFC in 2010 in the building and automotive industries, to which more than 50 % of plant-filled composites are sent, was 315 and 145 kt, respectively [14]. However, the growing prices of wood and the increasing struggle to protect forest resources in some countries have resulted in greater interest from researchers in other plant resources. Among the sources under consideration, apart from useless biomass [15], are farm and food-industry waste. The use of the inedible parts of plants is justified, first of all, from the ecological point of view, as it helps to utilize waste, the amount of which has been growing in tandem with the considerable growth in food production in the past several decades. Such waste is burnt or composted but, unfortunately, it is quite often sent to a landfill. The use of waste resources that are not used in the food industry or other areas such as the power industry (straw and energy willow) or in the production of polymers (corn and sugar cane) will positively influence the price of NFC products. This waste may include pistachio shells or sunflower husks. Pistachios are primarily used in the food and sweets industries. Oil is extracted from the seeds, the leaves are used to obtain dyes for the textile industry, and the wood itself is used to make furniture and to obtain resin for the production of varnish. According to the Foundation of Programmes for Agriculture (FAPA/FAMMU), the world's annual pistachio crops constitute approximately 600 kt, and Iran and the USA are the leading producers. In Europe, pistachios are grown primarily in Italy and Greece. As for Poland, pistachio crops can be found on amateur plantations only, yet pistachio nuts constitute an important raw material for the food and confectionery industries. Investigations have shown that a pistachio shell accounts for as much as 56 wt % of the entire fruit. In the case of sunflowers, the contribution of the husk constitutes over 44 wt % of seed [16]. The sunflower acreage in Poland amounts to 3000 ha, and the annual crops reach nearly 4.5 kt [17]. Sunflower is one of the most common oil plants. It is used in the food industry but its use is most widespread in the pharmaceutical and cosmetic industries. According to the data from FAPA/FAMMU concerning the 2011/2012 season, the world's sunflower crops reached some 40 Mt, and Russia, and Ukraine were the main producers.

The purpose of this study was the selection of the type and participation of given waste components allowing

the manufacture of NFC without additives, possessing functional properties characteristic of known composites with plant fillers (NFC and WPC). Additionally, attempts were made to determine to what degree the chemical constitution and geometry of the plant fillers affect the thermal and dimensional stability of the produced NFCs. No modifiers were used so that the relations among the composites' properties and the features of the used components could be better investigated, undisturbed by the presence of other chemical agents.

## EXPERIMENTAL PART

### Materials

A full characterization of the components used along with the NFC preparation technology and the methodology of the investigations are described here in detail or they are identical to descriptions presented in previous articles [18–20].

Pistachio (*Pistacia vera* L., Specimen) and sunflower seeds (*Helianthus* L., Specimen) were purchased from retailers and commercial farms in Poland in the summers of 2009 and 2008, respectively. The preparatory work included breaking the outer layer and removal of the fruit. Using the EN 933-10:2009 standard, an analysis of the grain-size distribution was performed, and on the basis of this analysis, it was determined that:

– 88 % of the pistachio-shell particles were below 63 μm in size,

– 66 % of the sunflower-husk particles ranged between 180 and 850 μm in size.

The density of the raw plant materials, which was determined using a helium pycnometer (Thermo Scientific), was 1.4387 g/cm$^3$ for the pistachio shells and 1.4219 g/cm$^3$ for the sunflower husks.

White transparent high-density polyethylene (PE-HD) foil (Marvink Pack System) was used as a matrix. The melt mass-flow rate of the polymer, which was determined at 190 °C and at a load of 2.16 kg, was equal to 0.88 g/10 min.

### Preparation of samples

Two-stage processing was applied to manufacture samples of normalized shapes. Stage one included mixing of the components using a Farrel Bridge mixer (David Bridge & Co.) and a LWII roller (Veb Erste Maschinenfabrik). The obtained mixtures, in the form of larger flakes, were ground using a Rapid 150-21 mill (Rapid Granulier-Systeme GmbH & Co.) and the obtained powder was subjected to an injection process using a BOY 22 A (Dr. BOY GmbH & Co. KG). Two composite series were manufactured using various contents of both fillers and the symbols of these samples are specified in Table 1. Such contents were selected based on data from the literature and the experience gained during work regarding these types of materials. For comparison, samples of unfilled polymer were also prepared.

**T a b l e 1. The content of fillers in prepared compositions**

| Symbol of sample | Filler type | content, wt % |
|---|---|---|
| PE-P15 | Pistachio shells | 15 |
| PE-P35 | | 35 |
| PE-P55 | | 55 |
| PE-S5 | Sunflower husks | 5 |
| PE-S15 | | 15 |
| PE-S30 | | 30 |

### The method of filler characterization

The cellulose content in the filler was determined using the Seifert method according to the PN-P-50092:1992 standard. The filler was extracted with a mix of chloroform and ethanol [21].

The hemicellulose content was calculated from the difference between holocellulose and cellulose. The holocellulose percentage content was determined by the gravimetric method using sodium chlorite in accordance with the PN-P-50092:1992 standard.

The determination of lignin in the fillers was conducted in accordance with the PN-P-50092:1992 standard and its total content was defined based on the sum of the lignin that was soluble in sulfuric acid and the lignin that was insoluble in sulfuric acid.

For each of the fillers, triple independent determination of the cellulose, hemicellulose and lignin contents were made and standard deviations were estimated.

The protein content was determined by acid hydrolysis to ammonium ions [22], which were then detected using a spectrophotometric method [23].

The determination of the crude-fat content was performed using an extraction in a Soxhlet apparatus with chloroform. The milled and dried fillers were weighed in a dry and porous cellulose thimble. The total extraction time was 10 h. Next, the solvent was removed by distillation. The flask's contents were dried at 105 °C to a constant mass and weighed. At least two determinations were performed for each filler.

### The methods of composite characterization

A thermogravimetric analysis (TGA) was carried out using Q500 apparatus (TA Instruments). Each of the materials was tested in an atmosphere of nitrogen and air. During the analyses, gas flow rates of 30 cm$^3$/min in the chamber and 70 cm$^3$/min in the oven were used. The samples were heated to 600 °C at a rate of 10 deg/min.

Differential scanning calorimetry (DSC) was performed using Q1000 apparatus (TA Instruments). Each of the previously prepared samples, which weighed 9–10 mg, was placed in a closed aluminum crucible. The analysis included 3 cycles:

– heating from room temperature to 220 °C and then maintaining this temperature for 5 min to remove the thermal history of the polymer,

– cooling to a temperature of -100 °C to obtain crystallization information,

– reheating to 220 °C to record the melting behavior.

The heating and cooling was performed at a rate of 10 deg/min, and the helium flow rate in the measuring cell was 30 $cm^3$/min.

The oxygen index (*OI*) was determined using apparatus that was designed for inflammability testing (Fire Instrumentation Research Equipment Ltd.). Investigations were performed in accordance with the PN-EN ISO 4589--2:2006 standard. The profile size was 10 × 4 × 80 mm. The error of *OI* determinations was below 0.2 %.

A crucible method was used to determine the heat of combustion ($Q_{PCS}$) of the composites in accordance with the PN-EN ISO 1716:2013 standard. The determination consisted of the complete burning of a sample in an oxygen atmosphere under a pressure of 2 MPa. The test was conducted using a bomb calorimeter. The bomb was submerged in water, and the increase of temperature in the calorimetric pot was measured. The results were calculated as the arithmetic means of at least three tests, with a difference between the maximum and minimum values of less than 0.2 MJ/kg.

The density was measured according to the PN-EN ISO 1183-1 standard using a Radwag 180/W scale that was equipped with a density measurement kit for solid bodies.

The morphology of the composites, which had been previously sputtered with gold and fixed to a table using carbon conducting tape, were investigated using a TM 3000 scanning electron microscope (SEM), Hitachi. The observations were carried out at 80x magnification and an accelerating voltage of 5 kV.

The morphology of the composites was also investigated using computer tomography (μCT). The device used in this study was an Xradia 410CT equipped with software that provided a tomographic slice-reconstruction algorithm. During scanning, the source voltage was 60 kV, the source current was 100 mA, the power was 10 W, and the exposure time was 1.5 s. The rotation step was 180°. The total number of frames was 1260, and a frame-averaging number of 15 was applied. The lens magnification selected for this investigation was 4×, and the source filter marked #LE3 was used. The pixel size of the resulting image was 5.02 μm. Afterwards, the CT-vol software package was applied to obtain the average equivalent diameter of the extender and the porosity of the investigated samples.

Tests of the swelling in length, width and thickness, as well as absorption after soaking in water, were conducted according to EN 317:1999 standard. The water-absorption capacities of the NFC were determined. The method was based on the measurements of differences in sample size and their growth in volume after 1, 2, 4, 7, 17 and 28 days.

The moisture resistance under cyclic test conditions was performed according to the EN 321:2001 standard. The cycles were as follows:

– Cycle I – soaking for 28 days, freezing for 24 h, drying for 72 h and cooling for 4 h;

– Cycle II – soaking for 72 h, freezing for 24 h, drying for 72 h and cooling for 4 h;

– Cycle III – soaking for 72 h, freezing for 24 h and drying for 72 h.

The final stage lasted for 72 h and consisted of conditioning the samples at room temperature. After cyclic testing the swelling in thickness was determined, and the materials were tested for static stretching.

The mechanical properties at static stretching were determined using a Zwick Z005 testing machine in accordance with EN ISO 527-1:1998 and EN ISO 527-2:1998 standards. Measurements were performed using an extensometer. The assumed length of the measured distance was 50 mm, and the stretching speed was 10 mm/min.

## RESULTS AND DISCUSSION

As part of this study, an analysis of the influence of the chemical composition of the fillers on the properties of the obtained NFC was planned. The composition of pistachios shell and sunflower husk used as fillers are collected in Table 2.

In the examined fillers, there is more cellulose than in almond shells [24], rye husks [4] or coconut shells [25], similar to softwood [6], peanut hulls [24] and barley husks [25] and lower than in jute, flax and hemp [2, 26]. This knowledge will facilitate the selection of the correct type of filler for an NFC, as cellulose, along with hemicellulose, participates in the so-called plant irrigation process [1]. The hemicellulose content in sunflower husks is slightly higher than in pistachio shells and ranks highly overall in comparison with the literature data. Indeed, similar cellulose contents can be found only in selected types of hardwood [6], almond shells [24], bamboo [2], cereal [24] and rye straw [6, 2]. The levels of the other determined components differ considerably in the two fillers used in this study. The lignin content in pistachio shells is similar to that of such raw plant materials as cereal straw [24], rye husks [4] or jute [6, 2], while in sunflower husks, it is comparable to hardwood [6], bagasse and bamboo [2], as well as barley husks [25]. Lignin protects plants from the harmful influence of fungi but, unfortunately, it can also contribute to a local decolorization of NFC as a result of photochemical degradation processes. In addition, a high content of lignin and secondary components can weaken the thermal stability of an NFC. The protein content in pistachio shells is over six times lower than in sunflower husks and is comparable to the level found in softwood [4], while in the case of sunflower husks, it is similar to that of coconut shells [2]. The fat content in sunflower husks is nearly twice as high as that in pistachio shells but similar to that of rye husks [4], while in pistachio shells, the fat level is similar to those of barley husks and coconut shells [25].

**T a b l e 2. Chemical compositions of pistachio shells and sunflower husks (the values in parentheses are the standard deviations)**

| Filler | Cellulose wt % | Hemicellulose wt % | Lignin wt % | Protein wt % | Fat wt % |
|---|---|---|---|---|---|
| Pistachio shells | 42.7 (0.28) | 29.9 (0.39) | 13.5 (0.18) | 0.26 (0.02) | 4.1 (0.04) |
| Sunflower husks | 37.3 (0.23) | 35.0 (0.41) | 22.9 (0.25) | 1.72 (0.05) | 7.2 (0.17) |

An additional tool, which was used for confirmation of the chemical composition of the fillers, was thermogravimetric analysis. This analysis was performed for the two fillers, the composites and the unfilled polyethylene. The mass-loss curves (TG) and derivative thermogravimetry results (DTG) for the composites, sunflower husks and polymer used for the manufactured NFC are shown in Fig. 1. Based on the change in mass presented in the TG curves, it was found that the water content was 5 wt % in the finely ground pistachio shells and 4 wt % in the sunflower husks. The same analysis was performed for fillers that were subjected to several days of drying under vacuum in a lab dryer at approximately 60 °C, which resulted in the reduction of the moisture content to 1.6 wt % for the pistachio shells and only 3.4 wt % for the sunflower husks. The introduction of small amounts of moisture along with a hydrophilic plant component seems unavoidable. However, it is important that the amount of water contained in the plant raw material be as low as possible to prevent excessive porosity in the composite and to improve the adhesion of the components. The moisture content in NFC samples produced using pistachio shells ranged between 0.66 and 2.45 wt %, while in the case of the samples produced with sunflower husks, it ranged from 0.25 to 0.58 wt %. The assessment of the moisture content was also performed for hydrophobic PE. The water content in the polymer amounted to 0.09 wt %.

Analyses conducted in an oxygen atmosphere were used to determine the amounts of all components that remained at a temperature of 600 °C, below which the complete decomposition of the two components occurs. The contribution of organic elements in the pistachio shells was 91.1 wt % and that of inorganic materials and dust was 3.9 wt %, whereas the composites with sunflower husks contained 90.8 wt % organic elements and 5.2 wt % inorganic materials and dust. The first peak in the fillers' DTG curves occurs at 67 °C, and in the case of the NFC, the first peak is located in the region of 135 °C. These peaks are related to water evaporation. The other two peaks that are present in the DTG curves of the pistachio shells and the composites made from them occur near 270 and 330 °C and correspond to hemicellulose decomposition and the glycosidic linkage of cellulose and α-cellulose [26–30]. No peaks originating from lignin degradation were observed in the case of the sunflower husks or the NFC prepared from them because the transformation coincided with the peak that resulted from the decomposition of the remaining components. In other natural materials, the peak associated with the maximum rate of lignin degradation usually occurs in the range 190 and 500 °C [4, 28]. In the DTG curves of all manufactured NFC samples and the unfilled PE, the occurrence of a peak resulting from polymer degradation was observed at temperature about 480 °C.

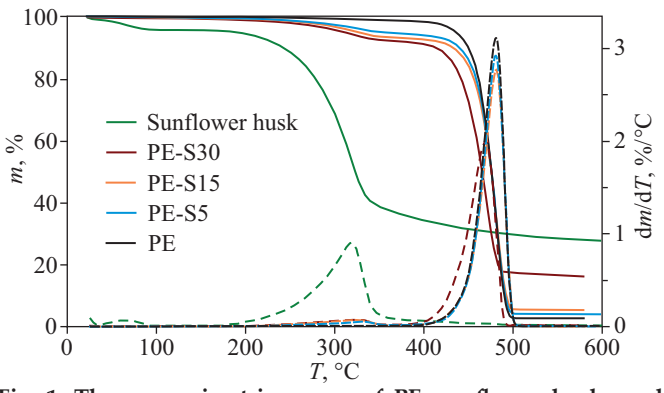


**Fig. 1. Thermogravimetric curves of PE, sunflower husks and their composites (*m* – mass of sample, *T* – temperature)**

The temperatures corresponding to 5 % of mass-loss ($T_{5\,\%}$), which were obtained from the TG curves, made it possible to determine the thermal stability of the materials. It is assumed that $T_{5\,\%}$ is related to the onset of degradation of the polymers. The temperature drops with increasing filler content in the composites, so for the NFC with pistachio shells, it ranged between 305 and 247 °C, while in the case of the composites with sunflower husks, it ranged from 360 to 214 °C. A comparison of these values permits us to state that the composites with finely ground sunflower husks exhibited lower performance with respect to thermal characteristics, which can be attributed to the larger amount of secondary-component and lignin in the filler.

The influence of the type and content of plant filler on the temperature of melting and the change in the degree of crystallinity of polymers, conditioning of the physical and mechanical properties of the composites was investigated by DSC. The values of melting ($T_m$) and crystallization ($T_c$) temperatures, melting enthalpy ($\Delta H_m$), and degree of crystallinity ($\chi_c$) of the manufactured NFC samples and unmodified PE are listed in Table 3. The degree of crystallinity of the polymer matrix of each NFC was determined using equation:

$$\chi_c = \frac{\Delta H_m}{(1-\varphi)\Delta H_m^0} \tag{1}$$

where: $\Delta H_m$ – the melting enthalpy obtained from the DSC curve of the analyzed sample, φ – share of the filler in the composite, $\Delta H_m^0 = 290$ J/g – the melting enthalpy of a standard sample that contains 100 % of crystal phase [29].

**T a b l e 3. Characteristic temperatures and degrees of crystallinity of PE-based composites obtained from the DSC curves**

| Sample name | $T_m$, °C | $\Delta H_m$, J/g | $T_c$, °C | $\chi_c$, % |
|---|---|---|---|---|
| PE | 130 | 163 | 120 | 56 |
| PE-P15 | 130 | 143 | 120 | 58 |
| PE-P35 | 129 | 116 | 119 | 70 |
| PE-P55 | 127 | 74 | 118 | 75 |
| PE-S5 | 130 | 161 | 120 | 56 |
| PE-S15 | 130 | 147 | 120 | 59 |
| PE-S30 | 130 | 116 | 120 | 59 |

The exemplary course of the DSC curves for PE-S% composite are shown in Fig. 2. The addition of a plant filler in the form of finely ground husks did not affect the melting temperature ($T_m$) of the polymer matrix. Similar observations can be found in the literature [30]. This means that no chemical bonding took place between the matrix and the filler. In the case of the composites that contained over 30 wt % of pistachio shells, the melting temperature decreased by 1–3 deg. The changes in this value were correlated with the changes that were observed for the same composites in the temperature corresponding to the crystallization process ($T_c$). The introduction of the filler has an initiating effect on the nucleation process, causing an increase of $\chi_c$ of the polymer matrix. $\chi_c$ increases with increasing of the filler content in composites. A considerable growth $\chi_c$ was observed when the filler content exceeded 30 wt %.

NFC products can be used, for example, in the manufacture of furniture, interior furnishings or elements of track vehicles, so it is critical to understand how the manufactured composites may behave in the case of fire. The analysis of the literature data conducted by Jurkowski and Jurkowska [31] confirms that *OI* values for cellulose and polyethylene, which are equal to 16–19 % and 17–18 %, respectively, satisfy the conditions for flammable materials (*OI* ≤ 28 %). The effect of natural filler content on *OI* and $Q_{PCS}$ values of the studied composites are shown in Fig. 3. The introduction of both natural fillers considered in this study into PE caused a slight decrease in the *OI* value compared to the unfilled polymer, thus making them more susceptible to catching fire from a small flame. The *OI* values that were obtained for both composite series were alike, differing by merely a few percentage points (Fig. 3). In addition to external factors, the burning of composites is significantly influenced by the properties of the material itself, namely, the chemical composition (*i.e.*, lignin), filler content, moisture content, density and type of polymer [32]. Most likely, the reason that the sunflower-husk samples yielded inferior results was the lower moisture content in those composites. Among the above mentioned features that affect the flammability of NFCs, the filler content is also of note. The *OI* values decreased as the relative amount of components of natural origin increased. During the investigations, it was observed that the use of larger amounts of fillers reduced the spread of the flames. In the case of NFCs with larger amounts of filler, no burning drops were observed, while for the highest filler content, the material became carbonized. From the perspective of the course of the fire, the fillers favorably affect the burning of NFCs.

The analysis of $Q_{PCS}$ results shows that its value declines as the amount of filler in the NFC increases. The largest drop was recorded for composite PE-P55 (55 wt % of pistachio shell), whose $Q_{PCS}$ value were lower than that of the unmodified PE by 26 %. It should be borne in mind that a decline in the $Q_{PCS}$ value is accompanied by a decrease in the fire-load value in a given room, thus reducing the threat of fire. The difference in $Q_{PCS}$ value between samples PE-P35 and PE-S30 is only 3 %, which indicates that the type of filler does not significantly affect the combustion-heat values of the NFC.

The preparation of an NFC with a density of approximately 1 g/cm$^3$ was the result of the introduction of plant

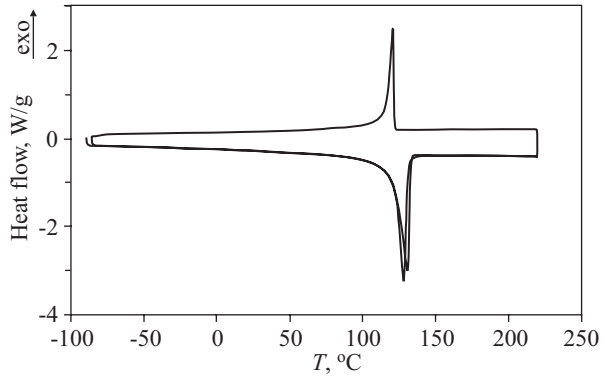


**Fig. 2. DSC curves of PE-S5 composite**

**T a b l e 4. The density of the composites (the values in parentheses are the standard deviations)**

| Sample name | $d$, g/cm$^3$ |
|---|---|
| PE | 0.9406 (0.0003) |
| PE-P15 | 0.9905 (0.0017) |
| PE-P35 | 1.0294 (0.0033) |
| PE-P55 | 1.0819 (0.0088) |
| PE-S5 | 0.9641 (0.0033) |
| PE-S15 | 0.9981 (0.0010) |
| PE-S30 | 1.0392 (0.0036) |

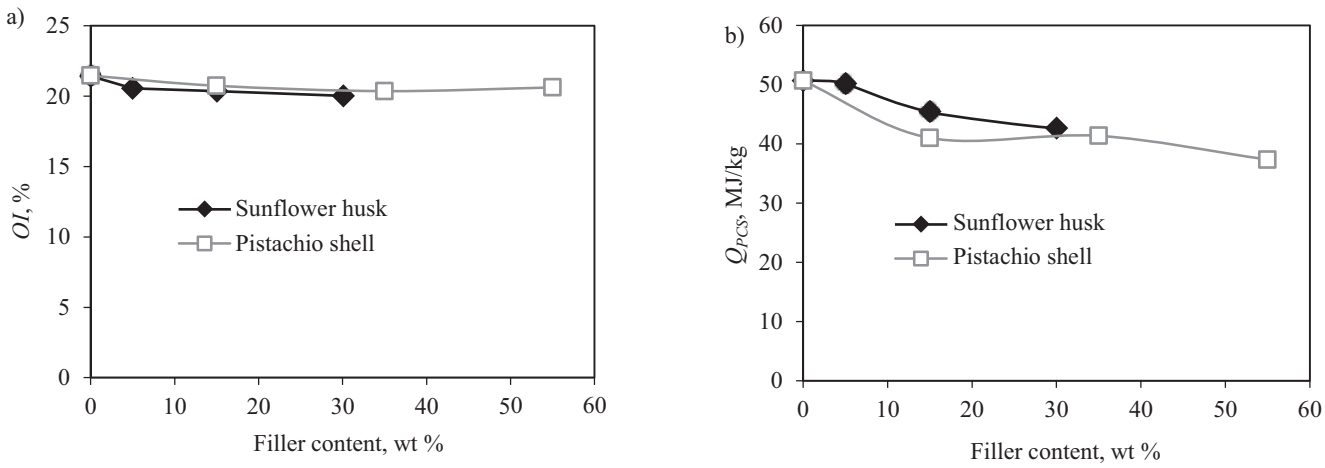


**Fig. 3. Effect of filler content on determined for PE composites values of: a) oxygen index (*OI*), b) combustion heat ($Q_{PCS}$)**

components (the density of each filler was $d$ = 1.4 g/cm$^3$) into the polymer matrix ($d$ = 0.94 g/cm$^3$). The densities of the prepared composites are listed in Table 4. Although the densities of both fillers are nearly identical, and the tested property increases almost linearly with the increase in the filler content, slightly lower values were obtained for the composites with pistachio shells. The greatest density increase, which was still no more than approximately 15 % with respect to the unfilled PE, was recorded for the sample PE-P55 with highest content of filler. However, a low density, though desirable because of the low weight of the product, may be unfavorable for this type of composite because it implies the presence of air voids in the NFC. The amount of air that is trapped in the material depends on the amount of moisture in the raw plant materials and/or the applied processing methods. A high initial moisture content in a plant component causes an increase in the porosity of the NFC and a decline in its density as a result of the evaporation of the water present in the filler, which occurs during the manufacture of the material. As demonstrated by Klyosov [32] for two groups of WPC boards that were manufactured from the same components but using different processing methods, composites of lower density exhibit a higher capacity for water uptake because of their higher porosity. The presence of pores may cause deterioration in the composites' mechanical properties, increase their ability to absorb a considerable amount of water and increase the likelihood of microbiological degradation of the plant fillers; it also affects the flammability of the NFC.

The presence of a considerable number of pores was confirmed by the analysis of SEM images, which are presented in Fig. 4. The numerous empty spaces that can be observed in the contact area between the hydrophobic matrix and the hydrophilic filler, which signify the limited adhesion of the components, were most likely formed during the cutting of the samples for analysis. This is indicated, *i.e.* by the delamination of the filler particles, which is visible in the images presented in Fig. 4c and 4d in the form of parallel lines. The images demonstrate that both NFC with pistachio shells are characterized by a weaker, than NFC with sunflower husk adhesion of their components, which resulted in the formation of numerous voids on the surfaces of the samples' cross sections. It was observed that the number of voids in the composites increased as the filler content increased. The microstructural images also illustrate the heterogeneous nature of the composite; the filler particles that are present in the matrix are characterized by an irregular distribution. Filler particles of various sizes and even single agglomerates are visible in the images. In the image shown in Fig. 4b, where considerably sized particles of finely ground pistachio shells are present, their rough surfaces are clearly visible.

To determine the porosity of the manufactured composites, their structures were analyzed using computer tomography. 2D images of selected NFCs and 3-dimensional models (3D) of the entire samples are presented in Fig. 5. The conducted analysis confirmed that the porosity of the NFCs increased as the plant-filler increased. However, the number of pores apparent in the SEM im-

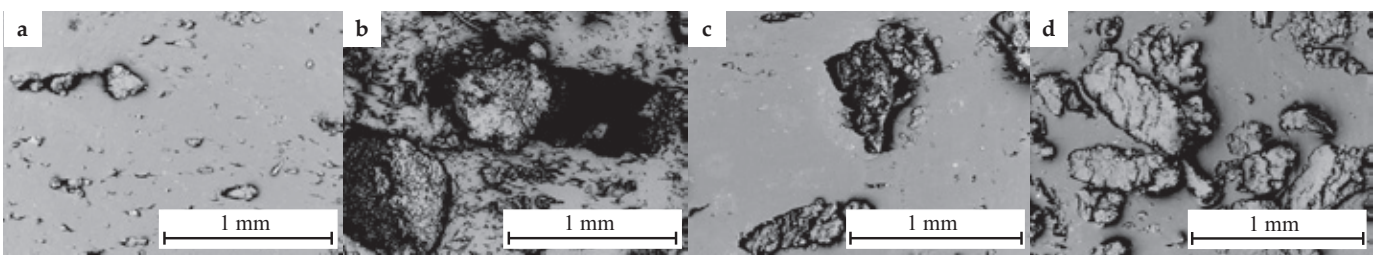


**Fig. 4. SEM images of composites: a) PE-P15, b) PE-P55, c) PE-S5, d) PE-S30**

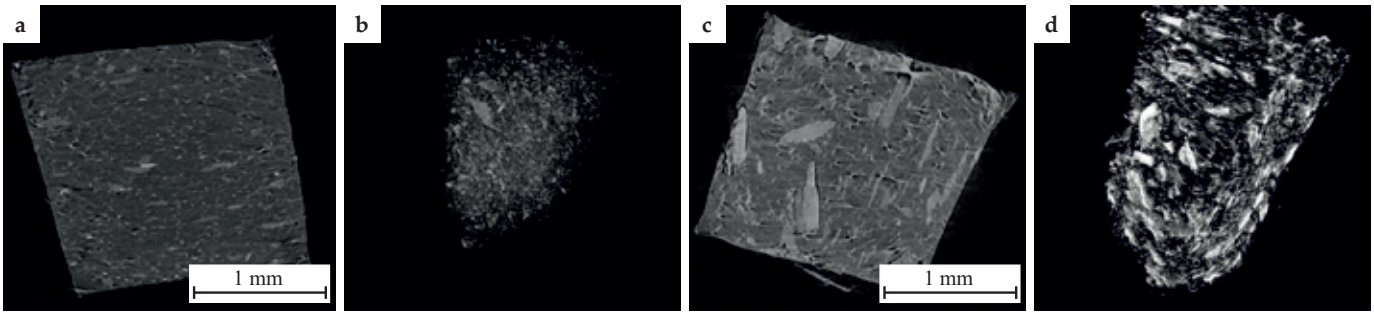


**Fig. 5. Thermographic images of the composites: a) 2D for PE-S15, b) 3D for PE-S15, c) 2D for PE-P30, d) 3D for PE-P30**

ages is significantly higher than the number detected by computer tomography, which confirms the above hypothesis concerning the formation of voids during the cutting of samples. For the subsequent composites with increasing content of pistachio shells, the porosity was 0.91, 1.56 and 2.89 %, while for the NFC samples with sunflower husks, it was 1.97, 2.83 and 4.22 %, respectively. The larger size of the filler particles (smaller specific surface of the filler) was the most probable cause of the higher porosity of the NFC samples with sunflower husks. In Fig. 5, we can clearly see the empty spaces present in the contact regions between the polymer matrix and the sunflower husk fragments, especially in the case of samples of a larger size.

Because of the similar densities of the used components, it was not possible to assess the porosity inside the filler. Despite the so-called large errors of the method that are related to the definition of the binarisation threshold, computer tomography is advantageous in this type of analysis because it offers the possibility of comparing a large number of cross-sectional images (over 1200 in the presented analyses) of a sample, free from the effect of damaging forces related to the preparation of the investigated material. Because of the resulting ability to obtain a higher-contrast image, a large differentiation in the size of the particles of the used nanofillers can be clearly observed. The computer tomography confirmed the presence of agglomerates, which were especially apparent in the case of the composites with pistachio shells.

The durability of the manufactured composites was assessed based on tests of swelling in length, width and thickness, as well as absorption after soaking in water, and the results determined after 1 and 28 days are listed in Table 5. The ability of the NFCs to take up a considerable amount of moisture depends, among others, on the plant-filler content and the porosity of the composite, in addition to environmental factors. In both series of materials, an increase in the amount of absorbed water was observed, which correlated with both the hydrophilic-filler content and the immersion time of the samples.

Similar relations have been previously described in the literature [26, 33, 34]. The composite PE-P55 exhibited the highest water absorption capacity, taking up 6.9 wt % of water after 28 days of soaking. The analysis of the obtained results was somewhat ambiguous regarding which composite series demonstrated a higher water absorption capacity. By extrapolating the results that corresponded to a filler content of 30 wt %, it was found that the NFC samples with sunflower husks demonstrated higher absorption. The cause of the increased absorption for the composites that contained the largest amount of finely ground sunflower husks was the increased porosity of the NFC materials. A comparison between the obtained values and the chemical compositions of the individual fillers revealed a linear relation, according to which the absorption capacity of the polymers increased with higher hemicellulose contents in the biomass. Based on a comparison of the results to those described in the literature, it can be concluded that the obtained results are worthy of interest. For comparison, PP-based composites that contained 30 wt % of ground wheat straw and 5 wt % clay, modified with maleic anhydride, exhib-

**T a b l e 5. Swelling and water absorption of composites after 1 and 28 days of immersion (the values in parentheses are the standard deviations)**

| Sample name | Water absorption, % | | Length swelling, % | | Width swelling, % | | Thickness swelling, % | |
|---|---|---|---|---|---|---|---|---|
| | 1 day | 28 days | 1 day | 28 days | 1 day | 28 days | 1 day | 28 days |
| PE | 0.0 (0.0) | 0.0 (0.0) | 0.0 (0.1) | 0.2 (0.1) | 0.2 (0.1) | 0.4 (0.2) | 0.1 (0.0) | 1.4 (0.1) |
| PE-P15 | 0.1 (0.0) | 0.9 (0.1) | 0.0 (0.0) | 0.4 (0.1) | 0.0 (0.1) | 0.4 (0.1) | 0.2 (0.1) | 2.8 (0.2) |
| PE-P35 | 0.1 (0.0) | 2.1 (0.0) | 0.1 (0.1) | 0.6 (0.0) | 0.2 (0.1) | 0.8 (0.0) | 0.2 (0.3) | 4.2 (0.6) |
| PE-P55 | 0.6 (0.0) | 6.9 (0.1) | 0.2 (0.2) | 1.8 (0.2) | 0.1 (0.0) | 2.2 (0.2) | 0.5 (0.3) | 8.4 (0.5) |
| PE-S5 | 0.0 (0.0) | 0.2 (0.1) | 0.0 (0.0) | 0.3 (0.1) | 0.1 (0.0) | 0.6 (0.3) | 0.4 (0.7) | 2.1 (1.0) |
| PE-S15 | 0.1 (0.0) | 0.7 (0.0) | 0.0 (0.1) | 0.3 (0.0) | 0.1 (0.1) | 0.5 (0.1) | 0.2 (0.2) | 2.6 (0.4) |
| PE-S30 | 0.5 (0.1) | 3.1 (0.2) | 0.1 (0.1) | 0.6 (0.0) | 0.2 (0.1) | 0.9 (0.3) | 0.3 (0.2) | 2.3 (0.8) |

ited a 6 wt % water uptake [35] after a 30-day immersion. A considerably lower absorption capacity than that of the produced NFC materials has been achieved only for composites containing modified cellulose fibers [30]. Similarly, for PE-HD composites filled with 25 wt % of dried distillers grains with solubles, after a 28-day immersion, the absorption amounted to 4.3 wt %, while in the case of an NFC that contained solvent-treated dried distillers grains with solubles, it declined almost by half. The use of polyethylene-*graft*-maleic anhydride had no effect on the observed results for the composites described above [36]. The greatest recorded increase in size for both series was in the thickness. Despite a discernible increase in size, especially after 28 days, the obtained results seem to be satisfactory. For instance, Adikary *et al*. [37] have reported that after 24 h, the growth in thickness for WPC manufactured from a PE-HD recyclate, which had filler contents of 30 or 50 wt %, was 0.42 and 1.85 %, respectively. The obtained results are also superior to those of the above mentioned composites, in which a factor was applied to improve the adhesion between components. A slight change in all three dimensions was also observed for the unmodified PE, and because the increase in the polymer's mass was close to 0, it was considered that a possible cause of this change was the deformation of the samples as a result of a long-lasting water effect.

Because the obtained results raised doubts concerning the possibilities of utilizing the composites in outdoor applications, moisture resistance under cyclic testing conditions that imitated changing environmental conditions was additionally conducted. The results achieved based on a static tensile test performed after the test was completed, which were then compared with the original values [38] determined for the tested NFC samples, are listed in Table 6. Despite the extreme conditions to which the composites were subjected, the manufactured materials retained their good mechanical properties. Similar results, which concern the mechanical properties of NFCs that were subjected to soaking only, have been reported previously in the literature [36] and are in conflict with results presented in other studies [26, 33]. While analyzing the changes in tensile strength ($\sigma_M$) of both material series and neat PE, a slight increase in the $\sigma_M$ value was observed, ranging between 0.29 and 1.05 MPa, in the case of the NFCs. Depending on the type of NFC, the Young's modulus ($E_t$) changed only slightly, whereas the elongation at break ($\varepsilon_r$), in most cases, oscillated within several percent points. A considerable difference was recorded for unmodified PE only, for which $\varepsilon_r$ reached 18 percent points. A detailed analysis of the mechanical properties of these materials was presented in another article [38] but it should be stated that the introduction of the investigated fillers, especially in the case of NFC with sunflower husks, positively affects the properties of the composites.

Apart from the loss of mechanical properties, absorbed water can also negatively impact the aesthetics of the composites and cause distortions, which is especially dangerous at locations where structural elements are connected. For this reason, the influence of variable conditions on the change in the thickness of the tested samples was investigated and the results are listed in Table 7. Slight changes, comparable to the calculation errors, in the investigated size dimensions were recorded for all materials. The thickness-swelling values that were obtained were unambiguously lower than those that were measured in the previous swelling and water-absorption tests. Most materials, with the exception of sample PE-P15, shrank with respect to their initial dimensions, which may have been caused by the washing out of the filler. These results are difficult to verify because thus far, no results regarding thickness swelling after cyclic testing have been presented in the literature.

**T a b l e 6. Mechanical properties of the composites after cyclic testing (according to [39], the values in parentheses are the standard deviations)**

| Sample name | Before test | | | After test | | |
|---|---|---|---|---|---|---|
| | $\sigma_M$, MPa | $E_t$, GPa | $\varepsilon_r$, % | $\sigma_M$, MPa | $E_t$, GPa | $\varepsilon_r$, % |
| PE | 21.8 (0.30) | 0.93 (0.08) | 26.4 (4.5) | 22.32 (0.45) | 0.86 (0.06) | 44.42 (15.01) |
| PE-P15 | 20.53 (0.63) | 1.21 (0.08) | 18.43 (1.44) | 21.58 (0.29) | 1.23 (0.09) | 19.17 (1.90) |
| PE-P35 | 14.13 (0.36) | 0.93 (0.13) | 10.71 (1.27) | 15.11 (0.58) | 0.96 (1.00) | 14.28 (1.42) |
| PE-P55 | 9.05 (0.15) | 0.68 (0.10) | 7.70 (2.65) | 9.34 (0.34) | 0.61 (0.02) | 8.77 (1.55) |
| PE-S5 | 24.22 (0.20) | 1.37 (0.03) | 14.5 (1.05) | 24.81 (0.17) | 1.36 (0.12) | 17.71 (0.43) |
| PE-S15 | 26.31 (0.78) | 1.92 (0.17) | 6.61 (0.65) | 27.01 (0.28) | 1.98 (0.11) | 6.03 (0.07) |
| PE-S30 | 22.74 (0.79) | 2.49 (0.11) | 3.93 (0.84) | 23.38 (0.85) | 2.58 (0.06) | 4.36 (0.77) |

**T a b l e 7. Swelling in thickness of the composites after cyclic testing (the values in parentheses are the standard deviations)**

| Sample name | Swelling in thickness, % |
|---|---|
| PE | 0.08 (0.14) |
| PE-P15 | 0.19 (2.1) |
| PE-P35 | -1.26 (1.0) |
| PE-P55 | -0.33 (0.14) |
| PE-S5 | -0.17 (0.14) |
| PE-S15 | -0.25 (0.0) |
| PE-S30 | -0.08 (0.14) |

## CONCLUSION

Within the framework of this study, NFC samples were produced from PE and two types of natural fillers. It was proven that, with the use of appropriate processing methods, it is possible to manufacture composites that are filled with waste products that can be obtained from the farm and food industries, namely, pistachio shells and sunflower husks, with properties similar to those of common WPCs.

The influence of the type and amount of plant fillers on the dimensional and thermal stability of the NFCs was assessed. Based on the achieved results, the following conclusions were drawn:

– The produced composites were considered to be solid materials, with porosities below 5 %. The NFC porosities increased with increasing filler content, and voids occurred primarily in the contact regions of the composites and were the result of their poor adhesion.

– The influence of the percentage of lignin and secondary components in the filler structure on the thermal stability of NFCs was confirmed. The composites that contained pistachio shells, which contained smaller amounts of the above mentioned substances, exhibited higher stability.

– The addition of plant materials caused a lowering of the degree of crystallinity of the NFC matrices. Pistachio-shell particles, which contain a larger percentage of fine particles, affect the lowering of the degree of crystallinity of the NFC matrix more than sunflower husks.

– The use of plant fillers causes a drop in *OI* value. Favorable changes were observed in the course of the NFC burning process in comparison with the polyethylene matrix. During NFC combustion, no burning drops fell and, with the addition of a larger amount of filler, the material became carbonized. The use of fillers causes a decline in $Q_{SPC}$ of the NFC, which, in the case of indoor applications, will lead to a lowering of the fire load.

– It was proven that the NFC ability to absorb considerable amounts of water is influenced by two main factors, namely, the porosity of the composites and the hemicellulose content in the filler.

– A test of moisture resistance under cyclic testing conditions confirmed that the investigated materials may be used in variable environmental conditions while retaining their good mechanical properties and shape of their structural elements.

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