STUDY ON BIODEGRADABLE MATERIALS FROM THERMOPLASTIC STARCH WITH THE ADDITION OF NUTS SHELL
/
BADANIE MATERIAŁÓW BIODEGRADOWALNYCH ZE SKROBI TERMOPLASTYCZNEJ Z DODATKIEM ŁUPIN ORZECHÓW

Tomasz ŻELAZIŃSKI[1)], Adam EKIELSKI[1)], Karol DURCZAK[2)], Magdalena MORAWSKA[3)]
[1)] Institute of Mechanical Engineering, Warsaw University of Life Sciences (SGGW) / Poland;
[2)] Faculty of Environmental and Mechanical Engineering, Poznan University of Life Sciences / Poland;
[3)] Faculty of Manufacturing Engineering, Warsaw University of Life Sciences / Poland
Tel 225934565; E-mail: tomasz_zelazinski@sggw.edu.pl (corresponding author).

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ABSTRACT
The paper presents the results of research on film biocomposites made of thermoplastic starch (TPS) and various types of nut shells. The research involved the use of thermally treated nut shells: hazelnuts, pistachios, walnuts and peanuts. TPS biocomposites were produced by the pour method using non-adherent moulds. The obtained samples were used to test the basic physical properties used in testing biodegradable materials. The following parameters were determined: mechanical strength, colour and colour difference, water contact angle, moisture absorption from water and atmospheric air. Images of biocomposite fractures were also taken using a scanning electron microscope (SEM). It was found that the addition of nut shells enabled the production of homogeneous materials and contributed to the improvement of their strength parameters. The research showed that nut shells can be a prospective raw material for the production of innovative biodegradable materials.

ABSTRACT
W pracy przedstawiono wyniki badań bikompozytów otrzymanych ze skrobi termoplastycznej (TPS) oraz różnego rodzaju łupin orzechów. Do badań wykorzystano poddane obróbce termicznej łupiny orzechów: laskowych, pistacji, włoskich i ziemnych. Biokompozyty TPS wytworzono metodą wylewową z wykorzystaniem form teflonowych. Uzyskane próbki posłużyły do zbadania podstawowych właściwości fizycznych stosowanych badaniach materiałów biodegradowalnych. Określono następujące parametry: wytrzymałość materiałów, barwę, różnicę barw, kąt zwilżania, absorpcję wilgoci z wody i powietrza atmosferycznego. Wykonano również zdjęcia pęknięć biokompozytów za pomocą skaningowego mikroskopu elektronowego (SEM). Stwierdzono, że dodatek łupin orzechów umożliwił uzyskanie materiałów jednorodnych i przyczynił się do poprawy ich parametrów wytrzymałościowych. Badania wykazały, że łupiny orzechów mogą być perspektywicznym surowcem do produkcji innowacyjnych materiałów biodegradowalnych.

INTRODUCTION
Pro-ecological activities observed in the global economy force the search for new solutions limiting the use of plastics in the agri-food industry *(Mangaraj et al., 2019).* At the same time, the constantly growing consumption causes an increasing demand for new and innovative products, including biodegradable materials *(Borowski et al., 2022).* Therefore, current biodegradable products cover a wider range of applications than just plates, drinking straws or other small everyday items. Scientists are increasingly trying to obtain structural biocomposites that could be used in various branches of the agri-food industry. Currently, these trends are widely promoted around the world, which opens up the possibility of implementing innovative biodegradable products on a global scale. There is also an effort to minimize energy consumption, which biocomposites perfectly fit in *(Borowski, 2021).* Therefore, the use of raw materials of completely natural origin and in accordance with the principles of sustainable development and the idea of "zero waste" is an important criterion for the production of modern biocomposites *(Nenciu et al., 2022a).* These raw materials include various by-products from technological processes related to agri-food processing. These can be, for example: fruit pomace, brewer's spent grains, pomace after oil extraction, waste from sugar cane processing and residues from processing nuts *(Ungureanu et al., 2022).* Some of such raw materials are also waste resulting from fruit and vegetables not sold in supermarkets *(Nenciu et al., 2022b).*

These raw materials are usually rich in many natural ingredients that strengthen the structure of biocomposites (e.g. lignocellulosic fibres, pectins, starch, proteins, etc.). The rational use of such raw materials for the production of biocomposites is therefore fully justified and prospective *(Rodriguez et al., 2020).*

Therefore, the essence of modern biocomposite production is to find the right ingredients from which innovative biomaterials can be easily produced. In general, some researchers argue that unsatisfactory physical and mechanical properties are one of the main limitations in the production of biodegradable materials *(Nanthananon et al., 2018).* Therefore, the solution seems to be the search for new components that will improve the properties of such materials as thermoplastic starch biocomposites (TPS). Such raw materials include waste from the processing of nuts. This waste is the shell after the edible part has been dehusked and consists mainly of lignocellulose.

According to some research, walnut shells contain 27.4-52.3% lignin, 25.6-34.5% cellulose and 22.1% hemicellulose *(Queirós et al., 2020)*. In the case of peanut shells, the percentage of these components is: lignin 35.4%; cellulose 26.7 - 40.5%; hemicellulose 12.1%. The composition of hazelnuts was as follows: lignin 27.2 - 40.3%; cellulose 26.7 - 40.5%, hemicellulose 30.4%.

The composition of pistachio shells according to *Kasiri and Fathi, (2018)* is lignin 23.6%, cellulose 38.1%, and hemicellulose 31.4%. An important feature of nut shells is low moisture content, which allows easy storage of shells without drying. This facilitates their use at very low costs. In addition, depending on the variety, the share of shells is from 10 to 70% of the total weight of the nut. Thus, the processing of nuts in industrial conditions leaves significant amounts of this raw material.

More than 3.7 million tons of walnuts are produced annually in the world. The largest producers are China 1.6 million tons, USA 0.6 million tons, Iran 0.4 million tons. In Poland, the production of walnut is about 0.1 million tons. Hazelnuts also account for a significant part of the production of nuts. In general, about 75% of the production of these nuts is produced in Turkey and Italy. The hazelnut shell makes up about 30% of the total weight of the nut. Another widely produced nut is the pistachio, which is produced around 0.6 million tonnes per year. Nearly 81% of total production is in Iran, USA and Iran. Pistachio shells account for over 30% of the dry weight of almond fruit. This means that the residues from nut processing may have great potential for their wider use. In general, the research conducted so far concerned the chemical properties of nut shells, including pistachio shells *(Yang et al., 2006).*

Research was also conducted on the use of almond peels as antioxidants (Mandalari et al., 2013). Nut shells have also been used as fillers for biocomposites for home applications *(Shaik et al., 2022*). Studies have also been conducted on the use of walnut shells as an additive to PLA polylactic acid *(Chaturvedi et al., 2021; Orue et al., 2020).*

Taking into account the above, no research has been carried out on their use in biocomposites made of TPS thermoplastic starch. The aim of this research is to produce a biocomposite from thermoplastic starch with the addition of various types of nut shells and to study their physical properties.

MATERIALS AND METHODS

Material

The following ingredients were used for the production of thermoplastic biocomposites: potato starch (PPZ Trzemeszno, Trzemeszno, Poland), purified vegetable glycerin (ERPOL, Warsaw, Poland) and nut shells: hazelnut, pistachio, walnut and peanut. Nut shells were obtained from purchased nuts on the local market in Poland. The obtained shells were ground into flour using an MKM 6000 impact mill (manufacturer: BOSCH, Gerlingen, Germany). Then the raw material was sieved on a sieve with a mesh size of 0.25 mm using a LPzE-2e screen (manufacturer: MULTISERW-Morek, Brzeźnica, Poland). Before adding the raw material for testing, it was thermally treated in a water bath for 60 s at 100 °C, and then drained on a sieve.

Production of biocomposite

The preparation of the test sample consisted in mixing 50 g of potato starch, 25 g of vegetable glycerin and the addition of nut shells in 500 ml of distilled water. Each time 2 wt% and 5 wt% of ground nut shells were added to the thermoplastic starch. The prepared suspension was placed on the heater and mixed with a CAT-30 stirrer (rotational speed of the stirrer 300 rpm) until the temperature of 85°C was reached. Then the obtained suspension was poured into di-Teflon moulds.

The sample prepared in this way was dried for 24 h at 45°C in a convection dryer Physical and chemical tests of the obtained materials included the determination of the basic parameters of the materials, such as: strength parameters, water contact angle, colour and colour difference, moisture absorption from water and air. The fractures of the samples were analysed using a scanning electron microscope (SEM).

Table 1

Parameters of the mixture for TPS biocomposites

Basic Components of TPS	Addition of Nut Shell to the Mixture (wt%)	Acronym of the Obtained Film/Biocomposite TPS
Starch 50 g + Glycerol 25 g	2 5	Haz_TPS (material with hazelnut shells)
	2 5	Pis_TPS (material with pistachio shells)
	2 5	Wal_TPS (material with walnut shells)
	2 5	Pean_TPS (material with peanut shells)
	0	TPS (thermoplastic starch)

Mechanical Properties

The following tests were selected to determine the strength parameters: elongation stress, elongation at break, Young's modulus and puncture force. Paddles of 6 mm x 80 mm were cut from the prepared TPS biocomposites (foil sheets). For the puncture tests, samples of 100 x 40 mm were prepared. The thickness of the TPS biocomposite in the analysed place was measured with an electronic caliper with an accuracy of 0.01 mm. The tests were performed in accordance with the standards *PN-EN ISO 527-1:2020-01, PN-EN ISO 527-2:2012.* The AXIS 500 universal testing machine with the FA 200 N (0.01 N) measuring head (manufacturer: AXIS, Gdansk, Poland) was used in the tests.

Water Contact Angle

Surface wettability was measured using the "sitting drop" method according to *Giri et al., (2019).* The test stand consisted of a digital camera A2500-14uc (5, Mpix), (manufacturer: Basler, Ahrensburg, Germany), an adjustable table and a syringe for dispensing distilled water. Each time, a drop of 15 µl was dosed on the surface of the tested material. Images were downloaded using the Pylon Viewer software (manufacturer: Basler, Ahrensburg, Germany). Wetting angle measurements were made in Autodesk Autocad Mechanical 2019. Product version: 23.0.46.0.

Colour

The images necessary for colour measurements were taken with an Optatech STX stereoscopic microscope equipped with a 5Mpx colour camera and a LED circular illuminator (colour temperature 7000K) (Opta-Tech, Warsaw, Poland). Prior to the study, the camera was calibrated using a Minolta white guide. CorelDRAW Home Version 17.1.0.572 software (Corel Corporation, Ottawa, Canada) was used in the colour studies, on which the L^*, a, $^*b^*$ colour space values were read.

Changes in the colour ΔE of TPS biocomposites, which occurred as a result of the addition of 2 wt% and 5 wt% nut shells, were also calculated.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{1}$$

where ΔL^*, Δa^*, Δb^* were changes in the colour value ΔE after increasing the addition of nut shells to TPS from 2 wt% to 5 wt%. Below in Fig. 1, exemplary photos of the produced TPS biocomposite samples are presented.

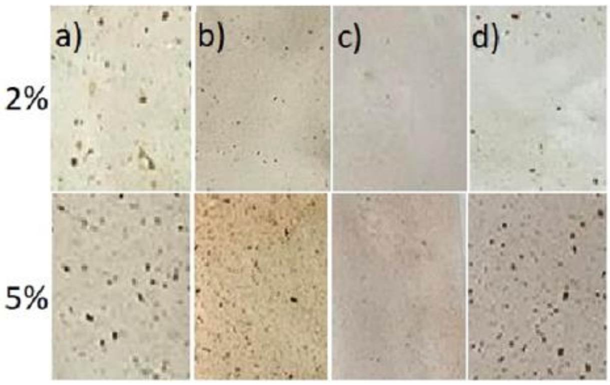

Fig. 1 - Example images of TPS biocomposites with the addition of:
a) peanut shells, b) hazelnut, c) pistachio, d) walnut

Scanning electron microscope (SEM)

Images of the structure of TPS biocomposites were made on a scanning electron microscope (SEM) HITACHI S-3400N at the Accelerating Voltage of 20 kV in a low vacuum of 70 Pa. The fracture of the composites after breaking the biocomposite was analysed.

Moisture absorption from water and air

Before starting the tests, the material samples were cut into pieces of 10 x 8 m and dried in a convection dryer to a constant weight. Then, the samples were placed in 50 ml flacons filled with distilled water at 21 °C. Each time after taking it out of the water, the sample was drained with a dry cloth and weighed on a laboratory scale with an accuracy of 0.001 g. During the test, the initial mass W_o and final mass W_t were recorded for each measurement. Measurements were made every hour for 8 hours.

The percentage absorption was determined on the basis of equation (2).

$$Moisture\ absorption = \frac{W_t - W_o}{W_o} \times 100\% \qquad (2)$$

Similarly, tests of moisture absorption from the air were carried out. In this study, samples were placed in a KBK-30 climatic chamber (manufacturer: Wamed, Warsaw, Poland), Relative humidity (RH): 75% at 25°C. The percentage absorption was also determined from equation (2).

Statistical analysis

Statistica 2013 software, version 13.3 (TIBCO Software Inc., Palo Alto, California, USA) was used for statistical analysis. Statistical analysis was performed in the tests of strength tests, wetting angle and general colour changes. The results from the experimental studies were obtained from 5 repetitions. The normality of the data distribution was tested with the Shapiro-Wilk test. The confidence level was 95% ($p < 0.05$). In the next step, the data was analysed by one-way ANOVA with Tukey's test. Significant and non-significant differences are shown in lowercase and uppercase letters above the error bars. Different upper-case letters, e.g., (C, B), indicate significant differences between the biocomposites (the same percentage of added digestate). Different lower-case letters, e.g., (c, d), indicate significant differences between samples with different percentages of components. Lack of significance between homogeneous groups is indicated by, e.g., (a, a, or B, B).

RESULTS

Analysing the results of strength tests, it can be concluded that the addition of crushed nut shells had a significant effect on changes in strength parameters. Observing the results of the elongation stress tests (Fig. 2a), it can be concluded that the TPS biocomposites with the addition of 5% of nut shells were characterized by the highest strength. The biocomposites with the addition of peanut shells (Pean_TPS) had the highest strength, which was 3.4 MPa. Biocomposites with the addition of walnut shells Wal_TPS, which was 3.0 MPa, were also characterized by high strength. Since the strength of a pure TPS sample was 2.6 MPa, the addition of these nuts increased the strength of biocomposites by over 30%. In the case of Pean_TPS biocomposites, the highest strength may result from a good connection of lignocellulosic fibres with the TPS matrix. Generally, lignocellulose was crushed mechanically and thermally treated, which could favour partial release of cellulose (*Delgenés et al., 2002*).

According to various studies, cellulose is a commonly used additive that strengthens the structure of various biocomposites *(Sirviö et al., 2018).*

The share of cellulose in peanut shells may even exceed 40%, which may explain the obtained strength parameters *(Queirós et al., 2020).* Biocomposites with the addition of Haz_TPS hazelnuts and Pis_TPS pistachio nuts had results similar to TPS thermoplastic starch films.

Analysing the results of the sample elongation tests (until breaking), it can be concluded that all samples had a lower elongation than biocomposites made of pure TPS (fig. 2b). This is one of the limitations of the use of lignocellulosic raw materials, which was also indicated *(Teixeira et al., 2012).*

Studies of Young's modulus YM presented in Fig. 2c showed an increase in elasticity for all biocomposites with the addition of nut shells. The highest YM values compared to TPS were found for peanuts (5 wt%) 109.2 MPa. For comparison, the lowest value for this test was 98 MPa for Haz_TPS. The addition of 2 wt% shells contributed to obtaining lower YM values, which ranged from 80.3 to 90.3 MPa.

Comparing these results to commercial foil tests, the obtained results are satisfactory. According to research by *Bilck et al., (2010),* a typical plant covering film has a Young's modulus of 81 - 122 MPa.

Promising results were also obtained when testing the puncture strength of TPS biocomposites (Fig. 2d). In this case, both the addition of 2 wt% and 5 wt% caused a significant increase in the force needed to pierce the sample. In this case, the biocomposite reinforced with peanut shells (5.1 N) was the most puncture resistant.

The puncture force values for the other shell-reinforced biocomposites were similar and ranged from 4.1 to 4.3 N with the shell addition of 5 wt%.

The strength of samples reinforced with 2 wt% of nut shells was lower by almost 1N for all samples. Despite the satisfactory results, the parameters obtained differ from commercial films, e.g. agricultural, whose puncture strength ranges from 8 to about 26 N *(Bilck et al., 2010).*

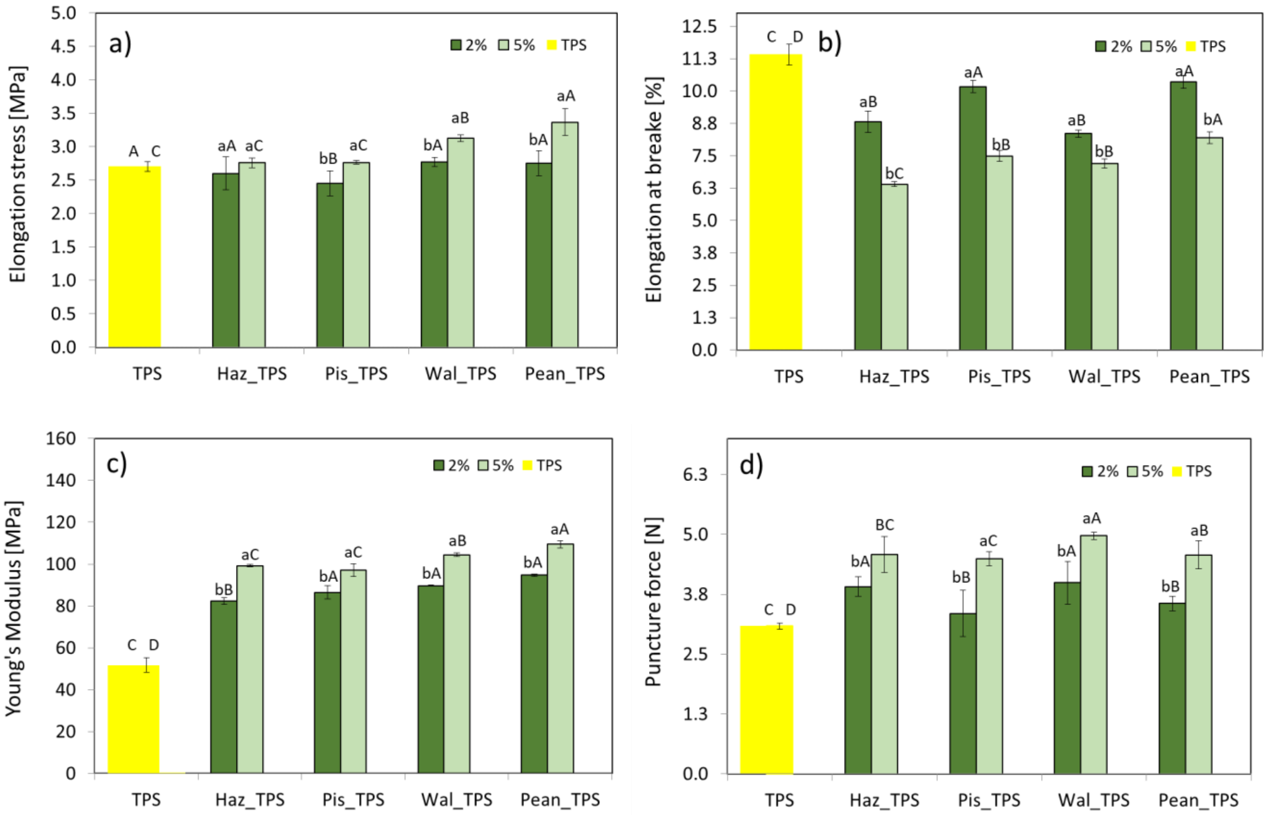

Fig. 2 - Strength tests of biocomposites

(a) elongation stress, (b) elongation at break, (c) Young's modulus, (d) puncture force.

Water contact angle

Analysis of the water contact angle (Fig. 3a) showed that all samples had a contact angle less than 0° < θ < 90°. According to *Valencia et al. (2018)* these samples are hydrophilic. The tests showed that the highest contact angle of 74° had samples with the addition of 2 wt% of Pean_TPS peanuts. Using a 5 wt% addition of these shells, a smaller contact angle of 70° was obtained. In general, all tested samples with 2 wt% shell added had higher values than samples with 5 wt% shell percentage. The samples with the addition of pistachio shells were characterized by the highest hydrophilicity.

The highest values of the contact angle for Pean_TPS may be related to the introduction of significant amounts of lignin found in peanuts into the biocomposite *(Martin et al., 2007).* Lignin is a component that can contribute to the reduction of the water absorption properties of the material.

Peanut shells also contain a small amount of hemicellulose (12%), which is generally considered hydrophilic, which may also contribute to the highest contact angle *(Demirbas, 2006; Aydin and Colakoglu, 2007).* Comparing the obtained results to the studies of other authors, PLA has a contact angle from about 70° to even 118° *(Lovinčić Milovanović et al., 2020; Bhasney et al., 2017).*

The most hydrophobic biodegradable material has a wetting angle of about 160° *(Liu et al., 2022).* It can therefore be concluded that in the case of the tested TPS biocomposites, the contact angle is low.

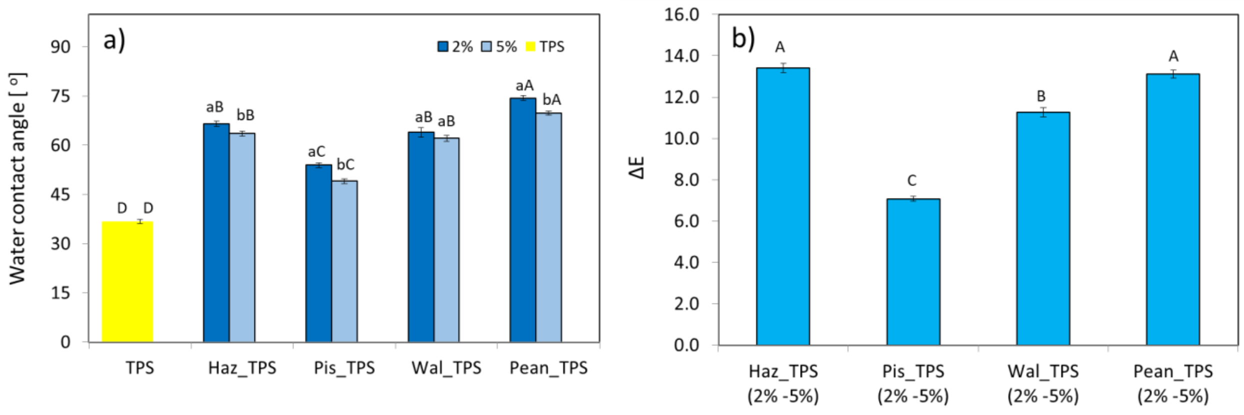

Fig. 3 - Water contact angle charts and colour tests

(a) mean values of the changes in the contact angle.

(b) Mean values of the difference in colour changes ∆E between the TPS with added 2% and 5% nuts shell.

Colour

Colour change studies showed that the TPS biocomposites were characterized by shades of yellow and light brown. This is confirmed by the results of colour changes a* and b*, which in the *L*, a, *b** colour space ranged from -2.02 to 30.22 (Table 2). The intensity of the colours was also affected by the high brightness of the L* samples, which ranged from 61.91 to 79%. By analysing the colour changes, it was found that in each case the addition of 5 wt% shells reduced the brightness of the obtained materials. In general, the overall colour change between the 2 wt% and 5 wt% shell samples was found to be from 7.07 to 13.42 (Figure 3a). Colour changes can therefore be observed even visually. The darkest samples were Haz_TPS and Wal_TPS, which can be explained by the darkest colour of these shells. According to the authors *Khir et al., (2014),* the colour may depend on the moisture content in the nuts and the temperature of the drying process. Therefore, it is to be expected that each batch of nut shells may slightly differ in colour, which may require inspection for industrial applications. The quality and stability of agri-food waste raw materials is one of the main limitations of their industrial use *(Farch et al., 2023).*

Table 2

Average values of *L, *a**, *b** colour components. Five-replicate measurements ($p<0.05$)**

Sample	Nuts shell addition 2 wt%			Nuts shell addition 5 wt%		
	*L**	*a**	*b**	*L**	*a**	*b**
Haz_TPS	69.41 (±0.21)	2.90 (±0.27)	21.11 (±0.15)	61.91 (±0.61)	9.38 (±0.14)	30.22 (±0.35)
Pis_TPS	78.52 (±0.65)	-1.58 (±0.22)	5.97 (±0.12)	77.54 (±0.36)	3.31 (±0.08)	11.02 (±0.43)
Wal_TPS	72.31 (±0.41)	0.93 (±0.32)	8.71 (±0.20)	64.87 (±0.54)	5.73 (±0.10)	15.67 (±0.46)
Pean_TPS	79.05 (±0.32)	-2.14 (±0.52)	7.23 (±0.18)	77.21 (±0.65)	1.11 (±0.08)	19.81 (±0.45)
TPS*	77.15 (±0.12)	-2.02 (±0.09)	4.92 (±0.16)	-	-	-

** - only TPS without the addition of nut shells.*

Moisture absorption in water

Analysing the obtained test results, it can be concluded that the water absorption of TPS biocomposites with the addition of nut shells changed with their addition (fig. 4a). For biocomposites with the addition of 2 wt% nuts, the moisture content increased from 56.5 to 96.3%. In the case of biocomposites with the addition of 5 wt% of nuts, the water absorption of the samples was in the range of 68.9 - 108.9%. Therefore, the research shows that with the increase in the addition of nut shells, the water absorption of the obtained TPS biocomposites also increases significantly. The highest water absorption was found in materials with the participation of Haz_TPS and Wal_TPS, whose water absorption increased from 96.3 to even 109.9%. Such high water absorption may be related to the high content of hemicellulose in these shells, which is considered a hydrophilic material *(Aydin and Colakoglu, 2007).*

In turn, the limitation of water absorption for these samples is lignocellulose, which is hydrophobic *(Gwon et al., 2010).* This may further explain the lowest water absorption for Pean_TPS and Pis_TPS, which have a low content of this component. High water absorption of the obtained materials is generally not a positive feature in the case of utility applications.

A solution to this problem could be to limit the availability of water to hemicellulose by minimizing, for example, thermal and pressure treatment of shells during drying *(Ciemniewska-Żytkiewicz et al., 2014; Bogumił, 2016).*

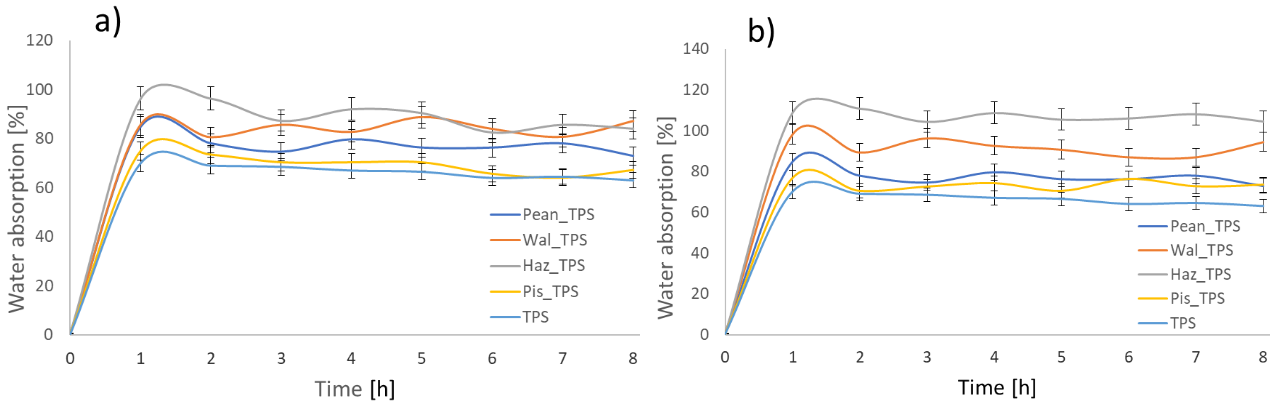

Fig. 4 - Water absorption results for samples with the addition of nut shells
a) 2 wt%, b) 5 wt%

Absorption of moisture from the air

Analysing the results of moisture absorption from the air, it was found that the addition of nut shells also influenced changes in this parameter. As in the above results, biocomposites with Haz_TPS had the highest moisture absorption. In the case of other nutshells, the differences between the obtained results were less visible. In this study, it was found that the water absorption of samples with the participation of Wal_TPS was significantly reduced, which was at the level of pure TPS material. The obtained values were even lower than Pean_TPS and Pis_TPS.

Generally, in this study the maximum moisture absorption was 35.8%. In the case of Wal_TPS it was only 26.7% with the share of this component of 5 wt%. Therefore, the nut components embedded in the TPS matrix did not have access to moisture, as in the case of complete immersion of the material in water. The TPS material, despite its significant hydrophilic properties *(Li et al., 2021),* is a protection against the absorption of moisture from the air for lignocellulosic materials rich in hemicellulose.

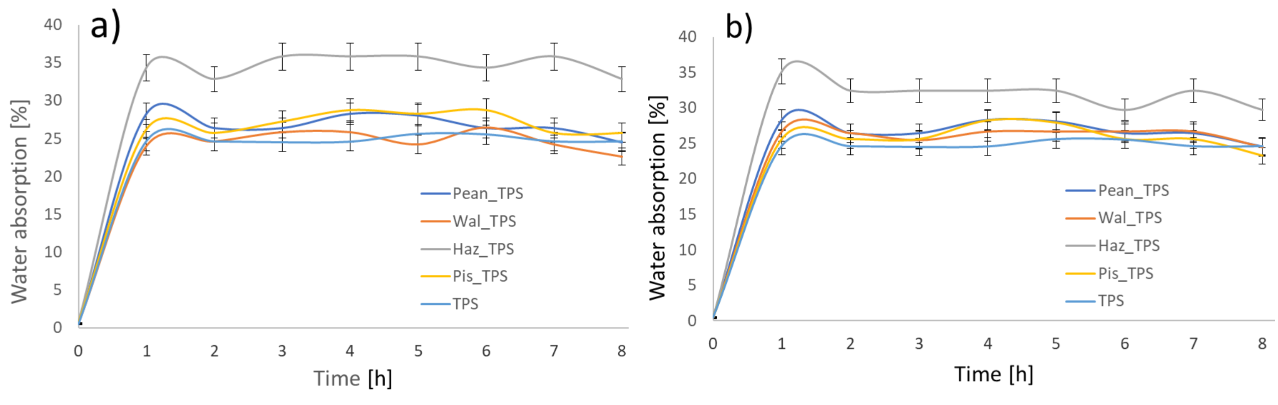

Fig. 5 - Results of moisture absorption from the air for samples with the addition of nut shells
a) 2 wt%, b) 5 wt%.

SEM

The analysis of SEM scanning electron micrographs (fig. 6) showed that all nut shells used as an additive for biocomposites were well embedded in the TPS matrixes. In general, raw materials rich in lignocellulose blend well into the TPS material at the stage of their production, which is confirmed by research *(Ekielski et al., 2021.*

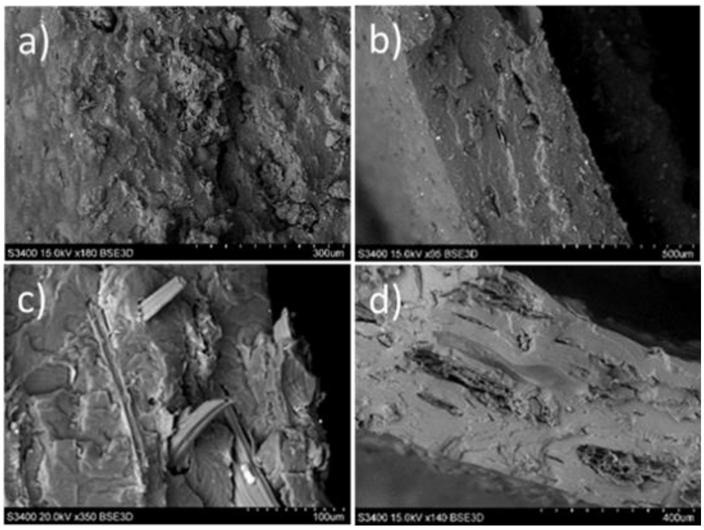

Fig. 6 - Images of fractures of TPS biocomposites
a) material with hazelnut shells, b) material with walnut shells,
c) material with pistachio shells, material with peanut shells

In Figure 6a, you can see the porous structure of hazelnut shells. This may explain the increased water absorption found during the tests. Fig. 6b shows the breakthrough of the biocomposite with the addition of walnut shells. The particles of these shells are perfectly embedded in the TPS matrix, and the pores are almost invisible, which may limit the sorption of moisture from the air by these shells. In Figure 6c, particles of pistachio shells that bind the biocomposite are visible, therefore these biocomposites have a high elongation until the sample breaks. In turn, in Fig. 6b, porous particles characteristic of peanut shells can be observed. The air pores that form these shells in the long run may adversely affect the sorption properties of such materials. On the other hand, the fibrous structure of these wastes improves the strength properties found during strength tests. The limitation of the use of these wastes may also be too high buoyancy of such particles, which makes it difficult to sink the shell particles in the TPS suspension. From an ecological point of view, this is beneficial, such materials can be more easily biodegraded *(Irwin, 2018).*

CONCLUSIONS

The obtained test results showed that it is possible to use nut shells as an additive to TPS biocomposites. However, in order to produce a material with a stable structure, previously heat-treated shells must be added to the thermoplastic starch. The raw material prepared in this way enables the use of various types of shells in the amount of 5 wt%, without reducing the quality of the biocomposite. Both the addition of shells 2% and 5% have a positive effect on increasing the puncturing force and increasing the modulus of elasticity YM. However, it is best to use the addition of peanut and walnut shells to improve these parameters. The addition of these shells changes the colour of biocomposites to the greatest extent, which can be observed even visually. The addition of nuts may make the materials more sensitive to moisture, which may limit the use of these materials. The lowest hydrophobicity can be obtained by adding peanut shells to TPS. To sum up, it is worth considering the use of crushed nut shells, especially ground and walnuts, as an addition to TPS biocomposites. When planning applications for these materials, their increased sorption properties should always be taken into account.

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