

WOOD DUST APPLICATION FOR IMPROVEMENT OF SELECTED PROPERTIES OF THERMOPLASTIC STARCH

WYKORZYSTANIE PYŁU DRZEWNEGO DO POPRAWY WYBRANYCH WŁAŚCIWOŚCI SKROBI TERMOPLASTYCZNEJ

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ABSTRACT

The objective of the paper was to examine the effect of changes of properties of biodegradable materials produced from thermoplastic starch (TPS) with pine wood dust (PWD) additive. Native potato starch, vegetable glycerine and pine wood dust (by-product of pine pellet production) were used for material production. The tests covered selected mechanical properties, i.e.: tensile strength, punching shear strength and Young's modulus. They also included the description of strength parameters changes in an environment with increased humidity for 5 days. The obtained results support application of cellulose additives to strengthen the structure of biodegradable materials.

STRESZCZENIE

Celem pracy było zbadanie wpływu zmian właściwości tworzyw biodegradowalnych wytworzonych ze skrobi termoplastycznej (TPS) z dodatkiem pyłu drzewnego (WD). Do wykonania tworzywa wykorzystano natywną skrobię ziemniaczaną, glicerynę roślinną i pył drzewny sosnowy (produkt uboczny przy produkcji pelletu sosnowego). Badania obejmowały wybrane właściwości mechaniczne tj.: wytrzymałość na rozciąganie i przebijanie oraz moduł Younga. Badania obejmowały również opis zmian parametrów wytrzymałościowych w środowisku o podwyższonej wilgotności przez 5 dni. Uzyskane wyniki są podparciem dla stosowania dodatków celulozowych do wzmocnienia struktury tworzyw biodegradowalnych.

INTRODUCTION

Many plastics are manufactured on the basis of the fossil materials obtained from depleting resources, mainly petroleum-derived, and which under naturally environmental conditions are non-biodegradable. This fact led to the accumulation of significant amounts of difficult-to-manage noxious waste, which also chemically pollute the natural environment (Borowski, 2019; Ekielski et al, 2018; Borowski, 2017; Fuzzi and Leal, 2016). Despite the implementation of modern utilization as well as recycling methods their application is not always economically justified (Carvalho et al. 2003; Encinar and González, 2008; Golub et al, 2018; Kamimura et al, 2014). It is therefore better to replace a part of products with modern biodegradable materials (Zhang et al, 2017). In particular, this is appropriate for packages employed in the food industry where products of a short life cycle are used (Ekielski and Wójcik, 2017).

The studies during the past several years show the replacement of artificial polymers with natural ones, such as: starch, polylactic acid and other (Musioł et al, 2018). The native starch, a component of numerous cultivated plants, is the most promising one from among available products. However, the manufacturing of the raw material on the basis of the starch plant requires use of additional plasticisers, as for example water and plant glycerine (Jiugao et al, 2005; Li and Huneault, 2011; Teixeira et al, 2007; Van Soest, 1996). Such products are widely described in the literature, however, the studies on this subject indicate many weaknesses of such products, e.g.: long stabilisation through water absorption, sensitivity to external environment, poor strength parameters and difficult processing (Pandya and Rathod, 2018).

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It is therefore reasonable to search for raw materials (fillers) which will effectively improve properties of such products and their use will be economically justified (Oniszczyk *et al*, 2016). Many studies on this subject indicate the use of lignocellulosic fibres which are the component of trees, straw and grass plants as well as many other plants (Fekete *et al*, 2018; Ekielski *et al*, 2017; Agnantopoulou *et al*, 2012). The available studies on this subject indicate the use of sawmill sawdust of various types of trees, cellulosic powders, micro-crystalline cellulose, natural fibres and other waste materials of wood processing and food industry in polymeric matrices (Girones *et al*, 2012; Hietala *et al*, 2017; Pérez *et al*, 2016; Saetun *et al*, 2017; Tulska *et al*, 2017; Yang *et al*, 2014). Generally, natural fibres in the TPS composite are not merely the filler, but improve the properties of the starch based composites. The addition of lignocellulose particles to TPS matrix, increase the moisture resistance and mechanical properties of obtained composites. It is therefore reasonable to search for new raw materials in order to improve the properties of thermoplastic starch (TPS). The aim of this study was to assess the addition of wood dust obtained as a by-product in the production of pine pellet which was used as an addition to the thermoplastic starch. In recent years the pellet production has continued to grow which is the additional support for the conducted study (Fuksa, 2016).

MATERIALS AND METHODS

The potato starch powder was provided by the company (PEPEES Group, Poland) and wood dust of the maximum size fraction equal to 250 µm obtained from the production of pine pellet (PWD – Pine Wood Dust) were the materials used in the study. The preparation of samples consisted in mixing 100 g of potato starch in 1000 ml of cold distilled water with an addition of 50 g of plant glycerine and various percentage share of PWD (0, 20, 25, 30 and 35%) in relation to the dry matter of starch.

Each of mixtures was heated to the temperature of 40°C for 5 minutes with the simultaneous intensive mixing by a mechanic stirrer R50 (producer CAT, USA) at the rotational speed of 400 rpm. Then, the speed of the stirrer was reduced to 200 rpm and the mixture was heated for 15 minutes until the temperature of 80°C was reached (the temperature was controlled by a J type thermocouple). The obtained solution of thermoplastic starch (TPS) with wood dust particles (PWD) was poured on the Teflon mould with a height of 1 mm and dried at the temperature of 50°C for 24 h. After drying, the thickness of the achieved composites was measured by means of an electronic micrometre (with the measurement error of ±0,001 mm). Then, specimens (so called paddle) with a total length of 60 mm ±1 mm and a working width of 6 mm ±0,5 mm according to the standards (PN-EN ISO 527- 1:2012, PN-EN ISO 527-2:2012, PN-EN ISO 527-3:2012) were prepared from the achieved plastics (composites). The parameters, such as tensile strength T_s [MPa], maximum stresses during puncture (puncture test [MPa]), Young's modulus [MPa], were examined. Young's modulus was calculated using formula 1. The puncture test was performed by using a round mandrel with a diameter of $D=1.5$ mm. The machine AXIS FA (producer: Poland) equipped with a head with a maximum force of 25 N and accuracy [0.01 N] was used for the strength tests. The speed of the head movement was 25 mm·min⁻¹.

$$E = \frac{F \cdot l}{A \cdot \Delta l} \quad [\text{MPa}] \quad (1)$$

where: E - Young's modulus, [MPa];

F - breaking force, [N];

A - the cross-sectional area of the sample, [m²];

l - original length, [m];

Δl - change in length, [m];



Fig. 1 - Selected test samples after being in a high humidity environment

Then, the samples were placed in a KBK-30W type climatic chamber (producer: Wamed, Poland) and stored for the period of 5 days at the temperature of 25°C (± 0.1 °C) and the air humidity of (RH – Relative Humidity) 90% ($\pm 0.1\%$). The strength tests were performed after 24, 48, 72, 96 and 120 h. The tests of the product mass changes were carried out concurrently during the aforementioned tests by using a weight WPS 610 (± 0.001 g), (producer: Radwag, Poland). Selected samples after being in a climatic chamber in an environment of high humidity are shown in Fig. 1. The measurements were taken in 5 repetitions.

RESULTS

The results of tensile tests T_s and puncture tests of the samples were presented in table 1. It was stated that both parameters substantially modified strength properties of the samples, as shown by the conducted analysis of variance ANOVA at the level of $p < 0.5$. It was observed that the strength T_s increased with the PWD share, however, the highest value of (6.77 MPa) was obtained with the 25% dust addition. Then, it was stated that the strength of the product decreased with the 35% share of PWD and reached the value equal to (5.19 MPa). Analysing the puncture test, a similar tendency could be observed, however, in this case, the maximum value of this parameter was (7.21 MPa) which was achieved with the 30% share of PWD. The further increase in the wood dust share resulted in the decrease of the strength parameters.

Table 1

The impact of PWD share on the strength changes to the manufactured products

No.	Pine wood dust [%]	T_s [MPa]	Puncture test [MPa]
1	0	3.58 (± 0.18)	3.72 (± 0.11)
2	20	4.42 (± 0.34)	6.69 (± 0.05)
3	25	6.77 (± 0.17)	6.82 (± 0.03)
4	30	5.75 (± 0.23)	7.17 (± 0.05)
5	35	5.19 (± 0.14)	5.35 (± 0.06)

Table 2

Coefficients of correlation

Variable	Pine wood dust [%]	T_s [MPa]	Young's modulus [MPa]	Puncture test [MPa]
Pine wood dust [%]	1.000	0.690*	0.621*	0.677*
T_s [MPa]		1.000	0.927*	0.717*
Young's modulus [MPa]			1.000	0.618*
Puncture test [MPa]				1.000

* Correlation coefficients are significant for $p < 0.05$.

Analysing the changes to the Young's modulus of elasticity (fig. 1), it was stated that this parameter reached the highest values of (6.42 MPa) with the 25% share of PWD and then it decreased. The results of the tests showed that in order to achieve the highest elasticity it was best to use an addition of dust at the level of 25%. The increase in the modulus of elasticity with the increase in the PWD share was strictly

connected with the decrease in deformations (Heidarian *et al*, 2017). The increase in the tensile strength is caused by the internal adhesion at water dust-starch matrix interfaces the chemical structure of which is similar (Fekete *et al*, 2018; Mischnick and Momcilovic, 2010). Chan *et al*. (2018) put this increase in the tensile strength down to the phenomenon of adhesion which contributes to the transfer of stresses from the polymer matrix to the particles of wood dust. Thus, the more particles in the cross section the greater strength of the composite, as observed by (Lodha *et al*, 2005; Agnantopoulou *et al*, 2012). However, it was observed in the conducted tests that there is the maximum limit of the PWD addition to TPS starting from which the decrease in the strength of the plastics is notable. The decrease in the strength of the achieved composites for the 30 and 35% share of PWD in the mixture may be connected yet with the less ability to absorb water by wood dust particle (PWD). From the utilitarian point of view such behaviour is favourable because the material losses its properties but it still does not crack. The substantial correlations between the share of wood dust and the analysed parameters (tab. 2) were also stated in the tests.

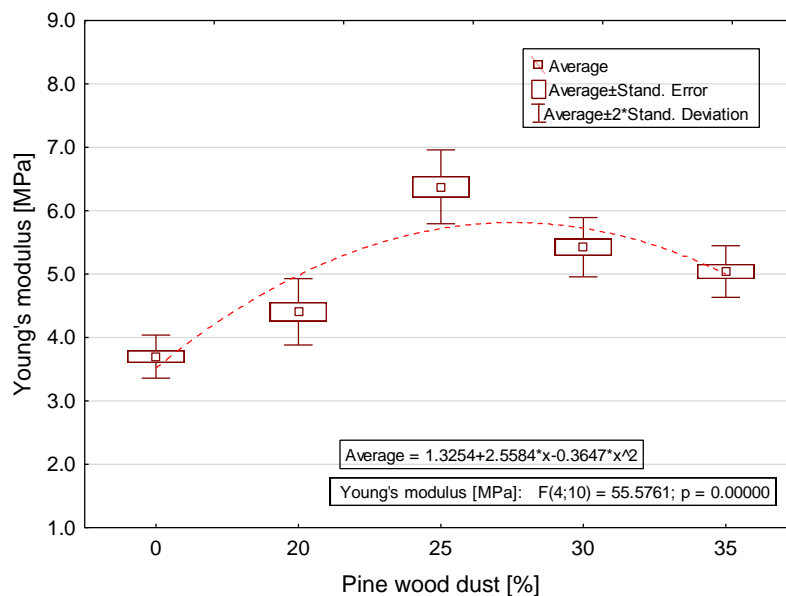


Fig. 2 - The impact of PWD share on the Young's modulus in the manufactured samples

Analysing the diagrams 3 and 4 on which the test results of strength parameters were presented it can be observed that the largest decrease in the strength of the samples was observed after the first 24 h of staying in the climatic chamber. The progressive decrease in the tensile strength of thermoplastic materials was also stated by (Saleh *et al*, 2017). Analysing diagram 2, it can be observed that after the next 24 h (i.e. after 48 h) all the samples, except (the one with the 30% PWD addition), reached the minimum levels of the tensile strength T_s . The longer staying of the samples under the conditions of the increased humidity (from 72 to 120 h) resulted in the insignificant increase in the tensile strength T_s . It seems that this phenomenon may be connected with the absorption of water by the PWD particles which additionally strengthen the structure of such material, as observed by (Agnantopoulou *et al*, 2012).

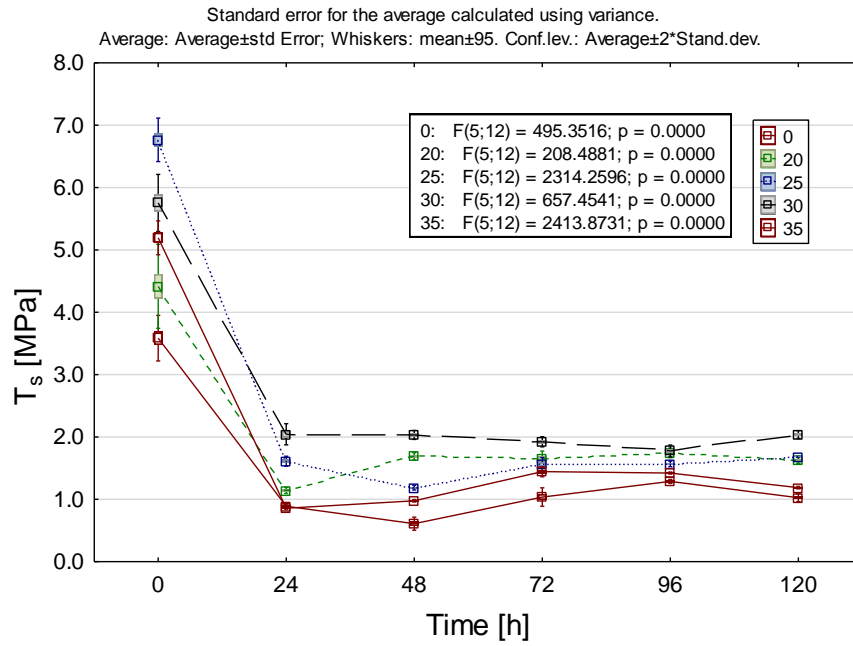


Fig. 3 - The impact of the staying time under the conditions of increased humidity on the changes to the tensile strength

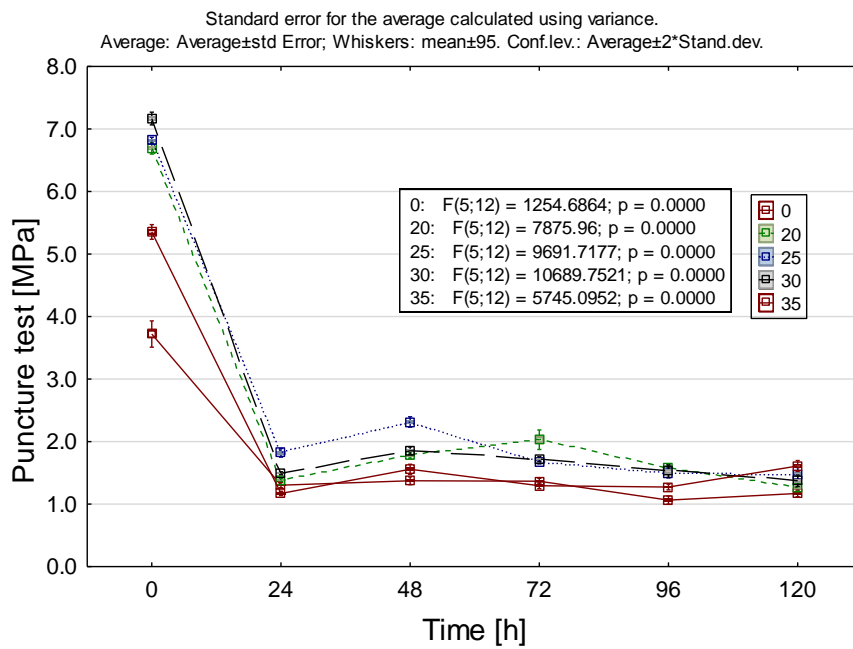


Fig. 4 - The impact of the staying time under the conditions of increased relative humidity on the resistance to puncture

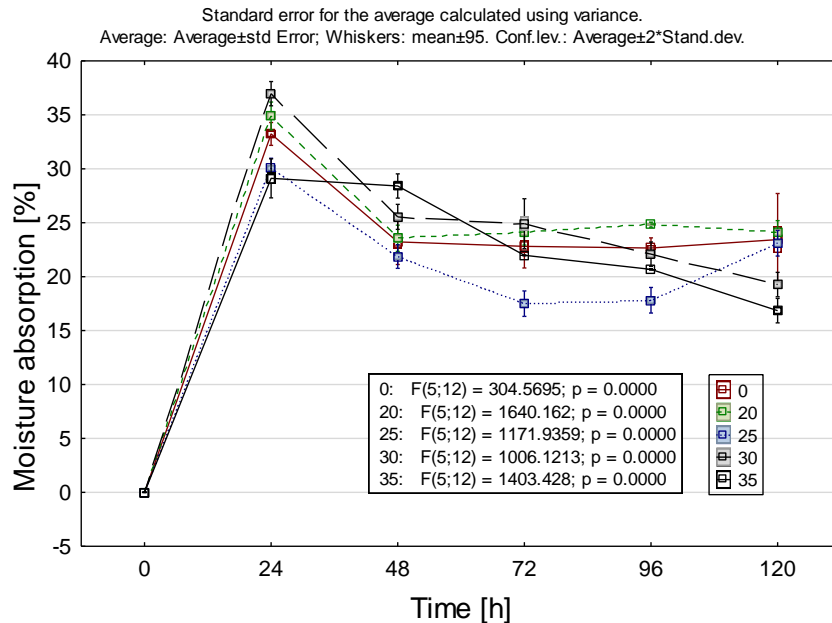


Fig. 5 - The impact of the staying time under the conditions of increased relative humidity on the moisture absorption

Analysing the changes to the puncture test (fig. 4) a sharp decrease in the strength of the composite after 24 h can also be observed. However, in this case, the insignificant decrease in the strength of the plastics over the entire staying of the sample in the climatic chamber can be observed. First of all, this demonstrates the progressive biodegradation of the product exposed to moisture (*Suriyatem et al, 2018*). Furthermore, it can be observed that the samples with the least PWD addition require the smaller force needed to puncture them with a round mandrel in comparison to the samples with the greatest PWD addition. This behaviour of the plastics can be explained by the significant dispersion of the particles of wood dust in the starch matrix which increases the vulnerability to puncture.

The behaviour of the samples under the conditions of the increased humidity is also shown in diagram 5 concerning the changes to the product mass as a result of the absorption of moisture from outside [%]. It can be observed in the diagram that the increase in the mass is very intensive initially, after which the mass of the product decreases in the following hours. This phenomenon confirms the properties of typical thermoplastic starch (TPS), described in the literature, consisting in the lasting stabilisation of the product (*Giuri et al, 2018*). This phenomenon also explains partially the changes to the strength parameters observed in diagrams 3 and 4. The products with the 25% PWD addition showed the smallest percentage decrease in the mass. Although the stated increase in the mass (water absorption) (between 24 and 120 h) is probably favourable, however, the intensity of the changes is too small for the product to maintain stability for a long period of time, in particular, outside the enclosed facility, under atmospheric conditions (*Giuri et al, 2018*). After 96 h, the first changes to the fungal growth were noticed on the sample which indicates the progressive biodegradation process.

CONCLUSIONS

The obtained results are promising and confirm that it is right to use PWD to strengthen the composites manufactured from TPS. The clear improvement of the strength properties of the product was observed in the test, in particular, when the PWD share did not exceed 25% of the dry matter of starch. The composites can be manufactured with the 30 and 35% PWD addition, however, the strength parameters (against the assumed recipe) of such products will decrease. The use of the greater PWD share, more than 35 of the dry matter of starch, requires use of additional components strengthening the matrix of the thermoplastic starch. The composites made of TPS and PWD are hydrophilic materials therefore, in order to increase their resistance to moisture, they require use of additional elements (components, barrier layers etc.) decreasing absorption.

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