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Selected mechanical properties of starch films

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Summary. This paper presents the results of measurements of selected mechanical properties of biodegradable starchy films (TPS), enriched by functional additives, produced at different screw rotation of the extruder. TPS granules were processed using a modified single screw extrusion-cooker TS-45 with L/D = 16. The following functional additives were used during the production: polylactide, polyvinyl alcohol and guar gum. Film blowing was carried out on the plastic extruder with L/D = 36. The obtained films were evaluated by mechanical properties test. Tensile strength, elongation, strain at break, elongation at break, work at tensile strength and work at break were measured. The best results were noticed for the film samples containing polyvinyl alcohol. The films with PLA addition were more brittle and weaker than the ones containing guar gum.

Key words: thermoplastic starch, extrusion-cooking, mechanical properties, PLA, polyvinyl alcohol, guar gum, film blowing.

INTRODUCTION

Application of biodegradable polymers, including starch, is becoming more and more popular during packaging production [2, 8]. Their use is important for ecological reasons, therefore innovative solutions aimed to reduce packaging waste are being searched. Studies on the possibility of increasing natural ingredients addition to produce more ecologic packaging are being carried out. The best, for economy and cost reasons, seems to be thermoplastic starch (TPS). Currently there are no chances to make pure starch material without plastic addition [4, 14, 17, 18]. Starch additive is only a filler, its content in the final materials is lower than 50%. During starch degradation to CO_2 and water, the materials disintegrate into smaller pieces.

Starch, as a biodegradable component of plastic materials, can fulfill the raw material function, it can also be physically or chemically connected with the synthetic polymer [7, 9]. It can be done using extrusion-cooking technique, which is one of the most commonly used methods for forming synthetic materials. That method has an important advantage – TPS can be produced using traditional machinery and equipment, typical for synthetic polymers manufacturing. Many publications and solutions presented on the international conferences confirm TPS functionality.

Oniszczuk et. al. [11] has described a wide application of TPS in biodegradable packaging materials production. It can be used as an additive which improves the degradation of plastics or as a stand-alone packing material. Starch biodegrades to CO_2 and water in a relatively short time. To improve the flexibility of ready materials and improve the production process, plasticizers are used. The most popular is glycerol. For improving the mechanical properties of the rigid forms of packaging based on TPS, the functional additives are used such as emulsifiers, cellulose, plant fiber, bark, kaolin or pectin [10].

In numerous scientific centers of the world scientists are searching for polymers based on natural raw materials. Recently, polylactide (PLA) is used as one of the most popular functional additives or as a stand-alone packaging material.

PLA is an aliphatic polyester obtained by condensation of milk acid [6, 19, 20]. Its production is carried out on a massive scale. PLA, due to its properties, is particularly useful in the manufacture of food packaging. The polymer can be used for packing fruit and food. From PLA thermoformed trays, containers are made. It can be also used to produce shopping bags and labels. Packaging from PLA is compostable. The advantage of this material is its ecologic aspect. PLA is based on natural raw ingredients , so the requirements of environment are achieved, e.g. natural biological processes to obtain half-ready product, use of renewable raw materials, reduction of CO_2 emissions, organic recycling of packaging waste. The disadvantages of PLA are: price, tenderness and stiffness. However, there is the possibility of using PLA in the packaging industry through other functional additives [5].

MATERIALS AND METHODS

The basic raw material used for TPS production was potato starch Superior produced by PPZ Bronislaw Sp. z o.o. During the production the plasticizer – glycerol of 99.5% purity, was used. In order to obtain a film with similar properties to typical synthetic material, 3 functional additives were used: polylactide 2003D Ingeo ™ Biopolymer (NatureWorks LLC), polyvinyl alcohol and guar gum.

Potato starch, glycerol and functional additives were mixed in a batch mixer accordingly to the recipe presented in Table 1. PLA was added to pure TPS after extrusion-cooking before film blowing.

Table 1. Recipes of TPS applied for biodegradable film blowing

Sample	Potato starch [%]	Glycerine [%]	Ingeo™ 2003D [%]	Polyvinyl alcohol [%]	Guar gum [%]
a4	58	22	20	-	-
c4	76	22	-	2	-
e4	77	22	-	-	1

In order to enhance penetration of glycerol and additives into starch, the obtained blends were kept in sealed plastic bags for 24 hours before processing, than processed on a modified single screw extrusion-cooker TS-45 (Polish design) with L/D = 16 (see Fig. 1) in the temperature range of 85-100°C and a screw rotation of 80 rpm. Extrudates were cut using high-speed cutter, adapted to achieve small size granules. Further cooling was used to avoid the sticking together of granulates. Dried TPS granules, a half product for film blowing, were stored in plastic containers.

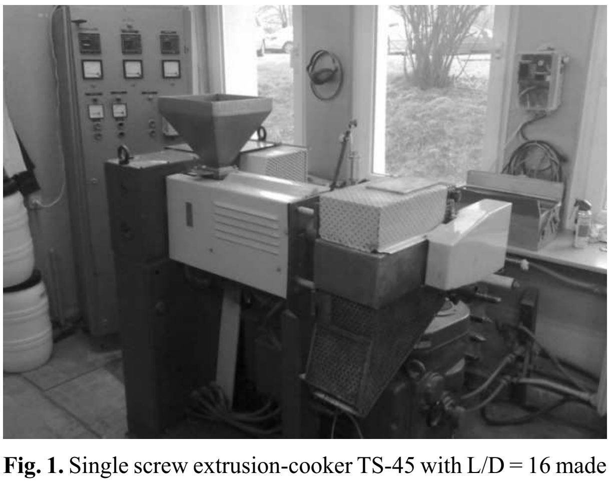

Fig. 1. Single screw extrusion-cooker TS-45 with L/D = 16 made by Z.M.Ch. Metalchem

Film blowing was carried out on a plastic extruder with L/D = 36. During extrusion the die-mold with a nozzle diameter of 80 mm and the working slot of 0.6 mm was used. The applied screw rotation was variable: 50, 60, 70 and 80 rpm. Each sample of the collected products (film sleeve about 200 cm lengths) was dried for 24 hours at ambient temperature (Fig. 2). After that it was cut into pieces of film (15 cm length and 2 cm width), assembled and stored in the open containers.

Fig. 2. TPS film slave sample

The mechanical properties of the film samples were measured on the Zwick Universal Testing Machine type BDO-FBO0.5TH (Fig 3). The samples were cut longitudinally and transversely to the direction of extrusion blown film. The tensile strength, elongation, strain at break, elongation at break and work done to achieve the targets were measured according to the Polish standards and methodology described by Rejak et al. [1, 3, 12, 13, 15, 16]. The results were statistically analyzed using *Statistica 6* tool.

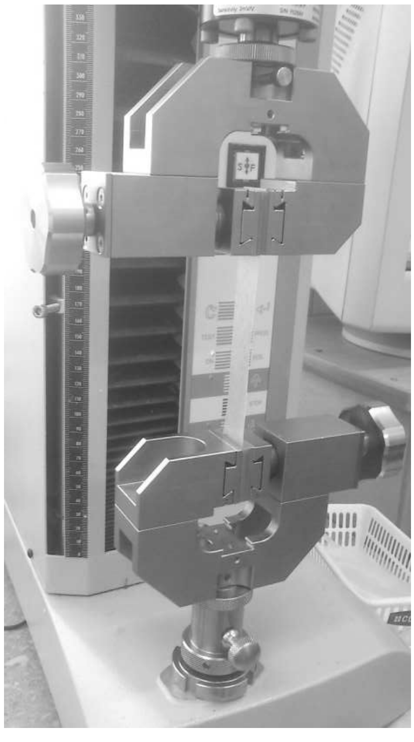

Fig. 3. Universal Testing Machine Zwick BDO-FBO0.5TH

RESULTS

The results of measurement of the tensile strength of samples processed with different extruder screw rotations are presented in Fig. 4. Maximum values of the tensile strength (the maximum value of the tensile force) were obtained for c4 samples processed at 80 rpm (72.65 N – sample cut longitudinally; 63.88 N – sample cut transversely). The lowest values of tensile strength occurred in the film samples produced at 70 rpm (13.26 N – a4 longitudinally; 16.07 N – c4 transversely). The statistical analysis showed that the tensile strength of samples which were cut longitudinally and contained the polyvinyl alcohol increased with higher rotation of the screw (correlation coefficient 0.75). To the contrary, the tensile strength of samples with the addition of PLA cut transversely decreased (correlation coefficient -0.93). In the remaining samples, statistical analysis showed no relationship between the speed rotation and the value of the test.

Elongation at tensile strength is the value of the elongation at the maximum value of the tensile force. Results of elongation measurement are shown in Figure 5. The highest elongation values occurred in the samples enriched by polyvinyl alcohol, processed at 70 rpm (value of 5.88% for samples cut longitudinally and 22.55% for samples cut transversely). Samples cut transversely had a larger elongation. The lowest value of elongation was observed for the samples containing polylactide (1.63% – samples cut longitudinally produced at 70 rpm, 1.51% – samples cut transversely produced at 60 rpm). Unfortunately, the low values of correlation coefficients indicated a lack of correlation between the screw speed and elongation.

The strain at break is defined as the value of tensile force at maximum elongation at break. The obtained results are shown in Figure 6. The highest values were reported for samples with guar gum addition (20.34 MPa and 20.50 MPa for the samples produced at 70 rpm cut longitudinally and transversely). The lowest values of strain at break were noticed for film samples containing a polyvinyl alcohol, processed at 70 rpm (3.88 MPa – samples cut longitudinally, 2.70 MPa – samples cut transversely). Only for the films produced at 80 rpm and cut lengthwise the inverse relationship was noted – the highest value of strain at break occurred in sample c4 (16.52 MPa) and the lowest in sample e4 (7.83 MPa). The statistical analyzes showed no significant relationship between the screw rotation and strain at break of the films.

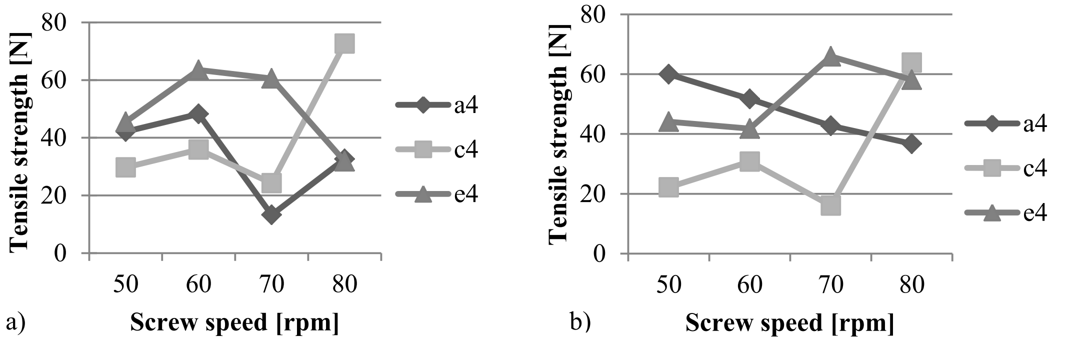

Fig. 4. Tensile strength of the film samples produced at different screw rotations (a – sample cut longitudinally, b – sample cut transversely)

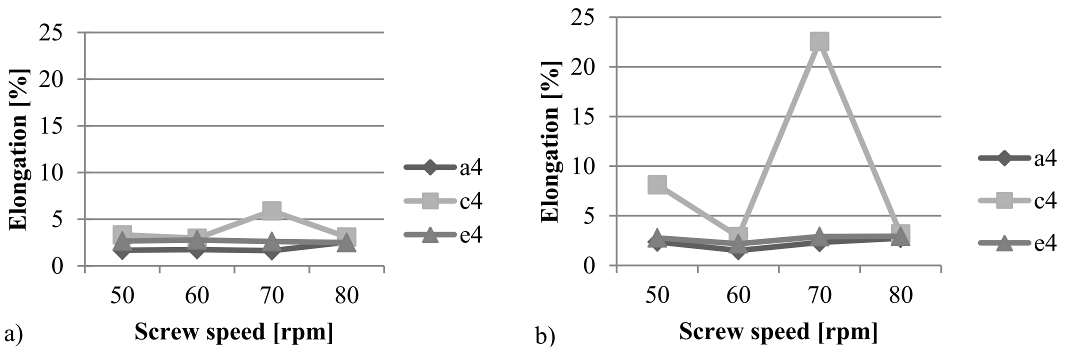

Fig. 5. Elongation of the film samples processed at different screw rotation (a – sample cut longitudinally, b – sample cut transversely)

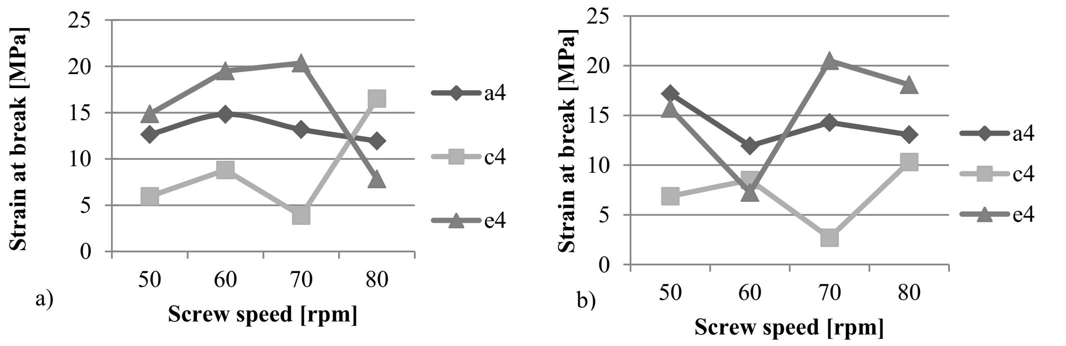

Fig. 6. Strain at break of the film samples processed at different screw rotation(a – sample cut longitudinally, b – sample cut transversely)

Elongation at break is the maximum tensile elongation. Figure 7 shows the results of measurement of that mechanical parameter. The samples a4 and e4 did not show an impact value of the screw speed on these characteristics. For samples cut longitudinally and transversely similar results were noted. The lowest values of elongation at break were reported for samples with PLA addition (1.66% at 70 rpm –samples cut longitudinally, 1.54% at 60 rpm –samples cut transversely). The highest value was observed for the samples c4 prepared at 70 speed (19.80% – samples cut longitudinally; 26.87% – samples cut transversely). Unfortunately, a low value f correlation coefficients was noticed during the measurements, which did not allow to estimate clear relationship between the screw rotation and the screw rotation and elongation at break.

Work at tensile strength defines value of the area under the curve of the maximum tensile force. Results of the measurement of this parameter are shown in Figure 8. The highest value was noticed for the film samples containing the polyvinyl alcohol (137.46 mJ at 80 rpm – samples cut longitudinally; 283.26 mJ at 70 rpm – samples cut transversely). The lowest results were noted for sample a4 (37.30 mJ at 50 rpm – longitudinally, and 38.75 mJ at 60 rpm – transversely). Looking for the relationship between the value of work at tensile strength and the applied screw rotation, only the measurements of the films with the polyvinyl alcohol cut transversely showed satisfactory value of the correlation coefficients (0.88). For the other results values of the correlation coefficients were too low.

Work at break is the value of area under the entire curve of the tensile force to break. The screw speed had the impact on the value of work at break in the case of films with the addition of polyvinyl alcohol (Figure 9). For samples c4 the highest values of the work at break was noticed (429.57 mJ at 70 rpm – lengthwise; 475.37 mJ at 80rpm – transversely). The film samples containing PLA were characterized by

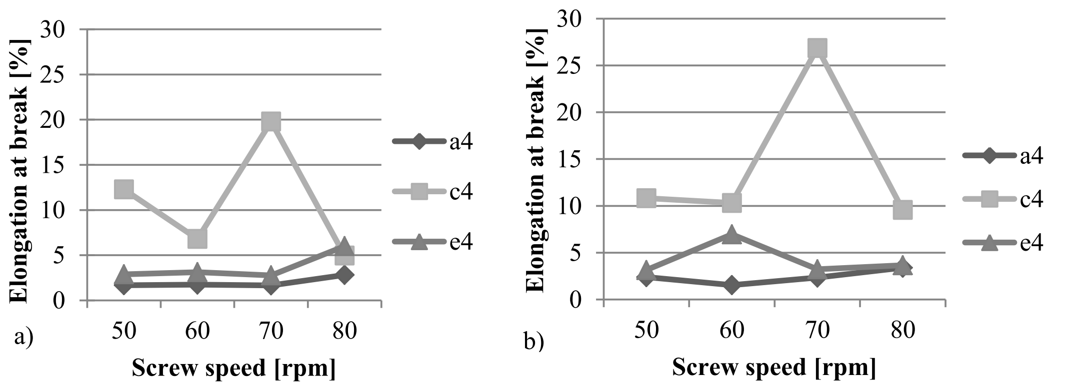

Fig. 7. Elongation at break of films with functional additives produced at different speeds (a – sample cut longitudinally, b – sample cut transversely)

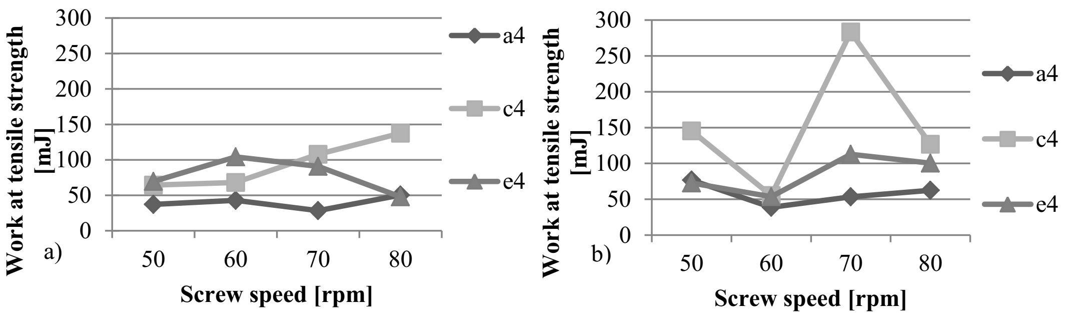

Fig. 8. Work at tensile strength of the film samples processed at different screw rotation (a – sample cut longitudinally, b – sample cut transversely)

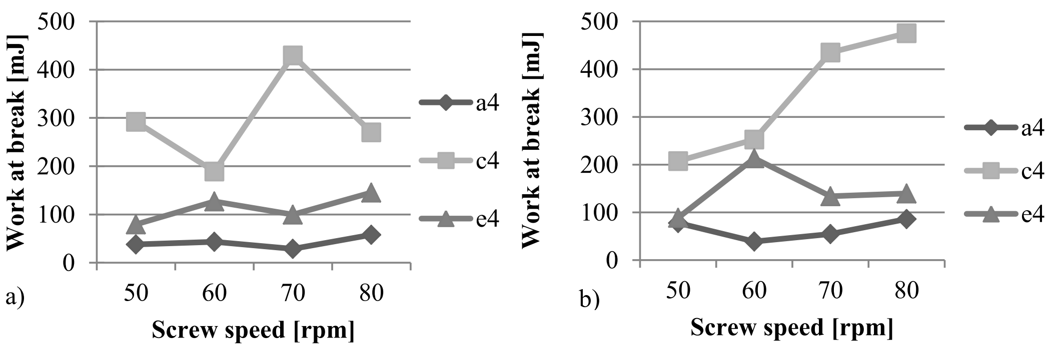

Fig. 9. Work at break of the film samples processed at different screw rotation (a – sample cut longitudinally, b – sample cut transversely)

the lowest value of the measured parameter (28.66 mJ at 70 rpm – lengthwise; 39.09 mJ at 60 rpm – transversely). The highest value of the correlation coefficient (0.77) was obtained for the films containing the polyvinyl alcohol and cut transversely (the value of work at break grew with the increase almost linearly with the screw speed).

CONCLUSIONS

Application of variable screw rotation speed during TPS films blowing influenced their mechanical properties. Samples containing PLA were characterized by average strength properties compared to the films produced from other blends. The best results for the films with PLA were obtained only during the tensile strength test.

The films containing the guar gum were the most elastic, which allowed obtaining a packaging material of better mechanical characteristics than the one containing 20 % of PLA.

The best results of mechanical properties were shown by the film samples containing 2 % of polyvinyl alcohol. The statistical analysis indicated that during this type of film processing, the screw rotation speed had a significant, positive influence on its mechanical properties. The combined application of the extrusion-cooking technique and typical “plastic” film blowing has allowed for the conclusion that TPS processing in order to produce biodegradable packaging materials is promising and gives acceptable results. However, further studies are needed to improve the stability of both the process and physical parameters of the obtained products.

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WYBRANE WŁAŚCIWOŚCI MECHANICZNE SKROBIOWYCH FOLII

Streszczenie. W pracy zaprezentowano wyniki pomiarów wybranych właściwości mechanicznych biodegradowalnych folii skrobiowych wzbogaconych dodatkami funkcjonalnymi wyprodukowanych przy różnych obrotach wytłaczarki. Granulat skrobi TPS wytworzono na jednoślimakowym, zmodyfikowanym ekstruderze TS-45 o L/D=16. Zastosowano dodatki funkcjonalne w postaci polilaktydu, alkoholu poliwinylowego oraz gumy guar. Proces wytłaczania folii z rozdmuchem wykonywano na wytłaczarce o L/D = 36. Wytworzone folie poddano testom na

rozciąganie. Zbadano cechy wytrzymałościowe folii, tj. wydłużenie przy wytrzymałości na rozciąganie i wydłużenie niszczące, wytrzymałość na rozciąganie i naprężenie przy zniszczeniu oraz pracę przy wytrzymałości na rozciąganie i pracę zniszczenia. Najlepsze wyniki odnotowano w przypadku folii z dodatkiem alkoholu poliwinylowego. Folie z dodatkiem PLA odznaczały się większą kruchością i gorszą wytrzymałością niż folie z dodatkiem gumy guar.
Słowa kluczowe: skrobia termoplastyczna, ekstruzja, właściwości mechaniczne, PLA, alkohol poliwinylowy, guma guar.