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Influence of keratin addition on selected mechanical properties of TPS film

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Summary. The aim of this study was to investigate the influence of process parameters of extrusion-cooking of thermoplastic starch (TPS) enriched with keratin hydrolyzate on selected physical properties of packaging films obtained. TPS granulates were processed using single screw extrusion-cooker TS-45 (Polish design). The mixtures of raw materials contained: starch, glycerin and hydrolyzed keratin. The obtained granulates were finally processed by film blowing process in a plastic extruder, especially designed in the Department of Food Process Engineering of University of Life Sciences in Lublin. Mechanical tests of films were performed to evaluate strain and elongation during extension tests.

Key words: starch, film, keratin, extrusion, blowing, strain, elongation.

INTRODUCTION

The increasing demand for disposable packaging contributed to the significant development of the packaging market, but also created a problem with its utilization after use. A particular difficulty makes plastic materials, whose large amounts are polluting the natural environment. The antidote is recycling, but it carries a large cost and requires adequate segregation of waste.

Nowadays, the problem of ecology is the leading theme in EU countries. There is a clear trend that aims to replace a variety of materials for their organic counterparts. This phenomenon is reflected also in packaging sector. Currently the leading product as packaging material is a plastic film, whose main ingredients are polypropylene, polyethylene and other plastics, which are totally indecomposable in the environment. The solution to the problem of disposals of such material is the use of biodegradable materials through photochemical transformation with chemical or biological reagents. More and more scientists are looking for materials that are both degradable and durable and have become an alternative to plastics.

The best ecological way to reduce packaging waste is the production of biodegradable packaging materials [6, 8]. The initial step in the process of biodegradation of conventional plastics packaging can be done by modifying the material or the additive having the capacity to absorb solar radiation [9, 21]. Recently has been introduced on an industrial scale production of packaging materials made from polyolefin polymers with modified starch, otherwise known as thermoplastic starch (TPS) [1, 2 3]. They belong to a generation of biodegradable materials based on natural resources.

Starch is relatively cheap raw material and completely biodegradable [3, 4]. Materials from the starch exhibit a tendency to brittleness unfortunately, are not resistant to water and over time lose their mechanical properties due to the process of recrystallization [11]. Starch may be plasticity by baro-thermal treatment provided with the appropriate mix of plasticizers [12, 13, 18, 19, 20].

MATERIALS AND METHODS

Tests of TPS film blowing and its physical properties measurements were conducted in the laboratories of Department of Food Process Engineering (DFPE) of University of Life Sciences. The obtained granulates were finally processed on a laboratory production lines, specially designed in FPED, produced by SAVO Wiązowna, using a film blowing technique (Fig. 1).

The basic raw materials for production of biodegradable films were: potato starch “Superior” of ZPZ Łomża, technical glycerin of ZPCH Lublin and an emulsifier - keratin hydrolyzate produced by “Proteins” Łódź. Compositions of mixtures used in the experiments are presented in Table 1.

Fig. 1. Film blowing equipment [8]

TPS granulates were processed using a modified single screw extrusion-cooker TS-45 (Polish design), with L/D = 16, the screw speed varied from 40 to 80 rpm and the temperature in the range 70–120°C. Determination of selected physical properties of TPS granulates was helpful in order to establish the range of temperatures and screw speed during film extrusion.

Table 1. Recipes of granulates applied for biodegradable film blowing

Sample	Potato starch [%]	Glycerine [%]	Keratin [%]
SGK-1	78	20	2
SGK-2	75	20	5
SGK-3	70	20	10

During the extrusion with blowing of TPS the film sleeves were obtained with different diameters and thicknesses, depending on the composition of the TPS granulates, extrusion-blowing temperature range (59-130°C) and the screw rotation (60, 70 and 80 rpm). During the tests the die-mold with a nozzle diameter of 80 mm and the working slot of 1 mm was used.

The obtained films were evaluated to mechanical properties tests, during which the specified breaking force and elongation were measured [15, 16, 17]. Strength tests were carried out on Zwick universal testing machine type BDO-FBO0.5TH (Ulm, Germany) (Fig. 2). During multiple measurements followed properties of film samples were determined: σM - maximum strain, σB - strain at break, εM - elongation at maximum strain, and εB - elongation at break [5, 7, 14]. Test strips (length of 100 mm and width of 20 mm) were cut from the film depend on recipe. Tests samples were prepared longitudinal and transversal to the direction of film blowing. The measurements were conducted in five replications. Results were analyzed with Statistica 6.0 [10] according to keratin addition and screw speed used..

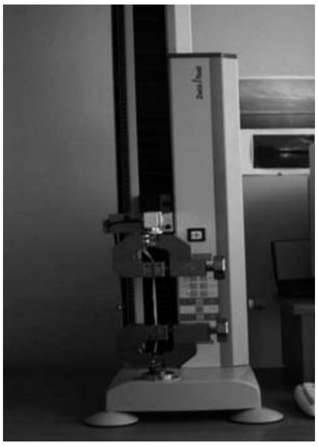

Fig. 2. Universal testing machine type Zwick BDO-FB0.5TH.

RESULTS

Different film sleeves were obtained depending on the composition of TPS granulates and process parameters. Film extrusion-blowing conditions depend on keratin addition are shown in Table 2.

Table 2. Processing parameters of biodegradable film blowing

Sample	Screw speed [rpm]	Motor load [A]	Temperature of extruder sections [°C]						
			Barrel				Die-head		
			I	II	III	IV	1	2	3
SGK-1	60	8.6	59	76	118	109	92	112	111
	70	8.6	69	73	117	119	115	107	103
	80	9.7	67	73	117	119	120	122	110
SGK-2	60	9.1	61	72	120	124	120	120	108
	70	9.1	62	71	122	123	114	119	104
	80	9.1	61	70	120	121	112	117	103
SGK-3	60	8.2	60	75	124	123	118	119	107
	70	8.2	65	80	128	120	110	110	105
	80	9.3	61	75	128	123	115	108	107

All the obtained films were flexible; very good properties presented films processed with different screw rotation on the base of SGK-1 and SGK-2 granulates, in which the keratin was added respectively in 2 and 5%. Films obtained from these granulate characterized good flexibility during blowing, had a semi-transparent color and after cooling remained relatively resilient, with no crumbling. Satisfactory results were also obtained during the extrusion-blowing of films with application of granulates with 10% of keratin, however the film was very soft, which greatly impeded their blow.

After blowing, all the film samples were tested to determine a tensile strain and elongation during extension. Film samples were analyzed not only according to keratin addition level and varied screw speed during the extrusion-blowing, but also depend on direction of cutting of samples for tensile tests: longitudinal and transversely to the direction of film blowing. Films obtained from SGK-1 and SGK-2 granulates were characterized by good flexibility as well during blowing as the tests of strength. These films have high resistance to rupture, as evidenced by the breaking force values are illustrated in Figure 3, higher than in other examined samples of films, both the tensile samples cut transversely and longitudinally to the direction of extrusion.

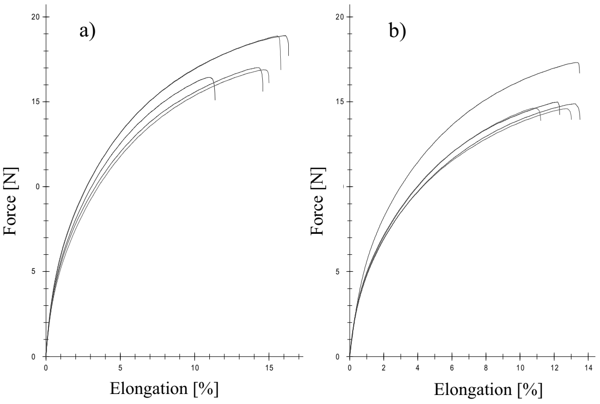

Fig. 3. Breaking force and elongation during extension test of a) longitudinal and b) transversal samples of SGK-1 film processed at 60 rpm

The results of measurements of maximum tensile strain of the transversal film samples during extension tests depending on the screw rotation used and keratin participation in a mixture of raw materials are shown on the Figure 4. Maximum strain values were 4.23-4.67 MPa in the transversal samples of films with 2% of keratin in the formulation of TPS granulates. Increasing the amount of keratin to 10% decreased the maximum strain to the level of 1.75-2.28 MPa. The significant dependence of screw speed during extrusion the maximum strain on the was not observed in this case.

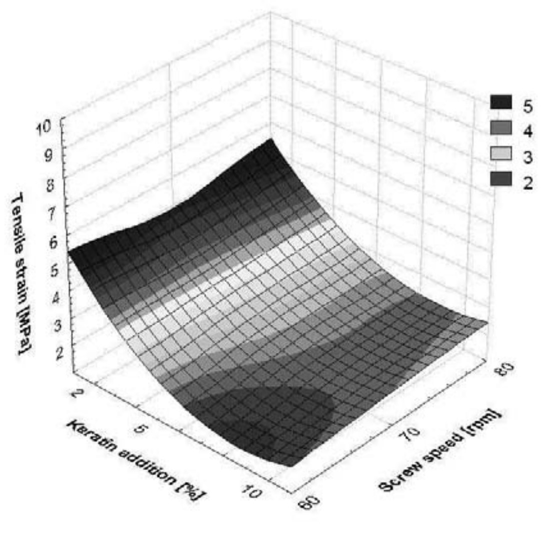

Fig. 4. Maximum tensile strain σM at extension test of transversal samples

Maximum tensile strain valuesdetermined by extension test of the longitudinal samples were similar, ranged from 1.61-2.08 MPa for films SGK-3 with 10% addition of keratin to 3.31-5.24 MPa for films SGK-1 with 2% addition of keratin (Fig. 5). Increasing share of keratin in the formulations caused a decrease in the maximum strain of the samples. The use of high screw rpm increased the maximum strain of the longitudinal film samples during extension.

Figure 6 shows the results of measurements of the strain at break during extension test of transversal film samples. The values of this parameter were slightly lower than the maximum strain and ranged from 1.57 to 4.40 MPa, depending on the screw rotation used during the extrusion and the amount of keratin in TPS granulates.

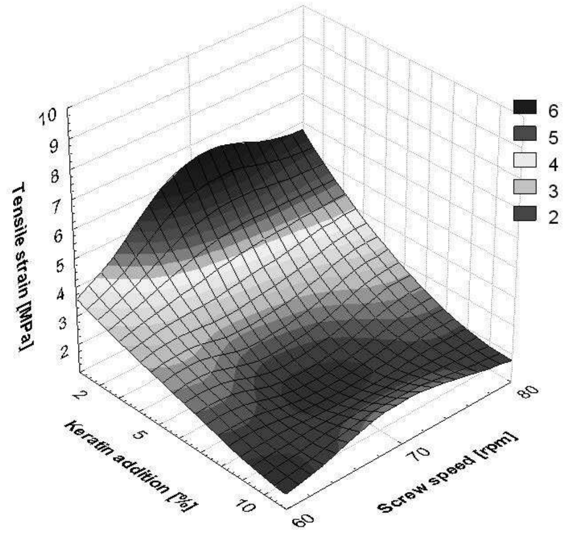

Fig. 5. Maximum tensile strain σM at longitudinal samples during extension test

There was a tendency to reduce strain during breaking with increasing addition of keratin, as evidenced by negative correlation coefficients determined for this feature.

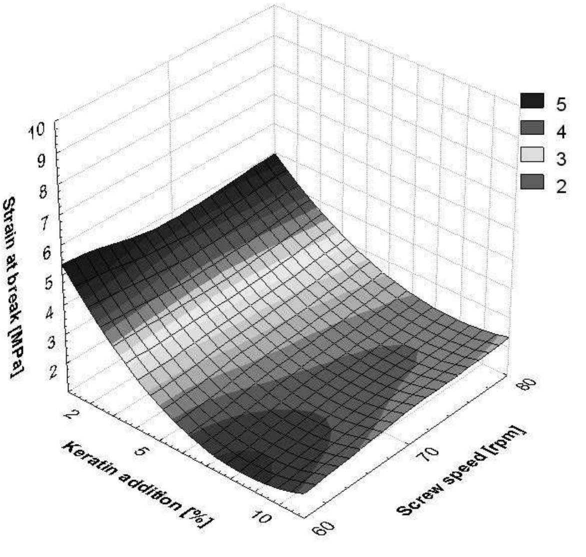

Fig. 6. Tensile strain at break σB at extension test of transversal samples

The results of measurements of film strain at break during longitudinal extension in the direction of extrusion-blowing are summarized in Figure 7. For longitudinal samples higher values were indicated than for transversal samples. In attempts at SGK-1 containing 2% of keratin, decrease of a strain at break was observed with increasing screw speed during extrusion. The opposite tendency was observed for other samples, when a small increase in strain was noted at higher screw speed applied during film production.

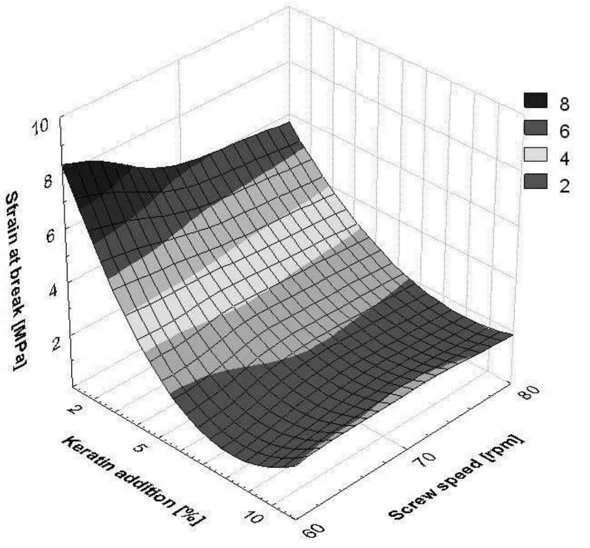

Fig. 7. Tensile strain at break σB at longitudinal samples during extension test

Differentiated relationships were observed during determination of the film elongation, according to the sample direction, the content of keratin and screw rotation used during production. Figure 8 shows the results of measurements of the maximum film elongation for transversal samples to the direction of its extrusion-blowing.

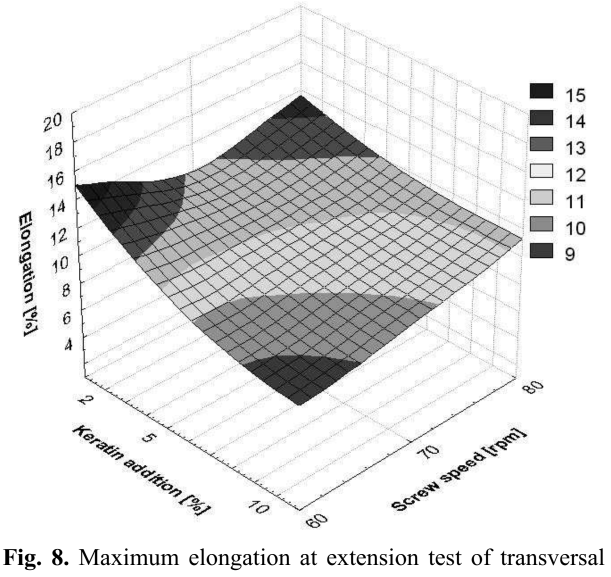

Fig. 8. Maximum elongation at extension test of transversal samples

Elongation of the films ranged from 8.62 to 13.83%, and the maximum flexibility was measured for SGK-1 film containing 2% addition of keratin, produced at low screw speed. Similar results of maximum elongation of film samples cut longitudinal to the extrusion direction were obtained (see Figure 9). The values obtained according to the addition of keratin and screw rotation used during extrusion showed that again, the lowest keratin addition in the recipe allowed for greater flexibility of films. The elongation for this sample ranged from 10.89% when using 60 rpm during extrusion to 13.84% at a maximum screw speed. The results obtained for the sample of SGK-3 are presented on the Figure 10.

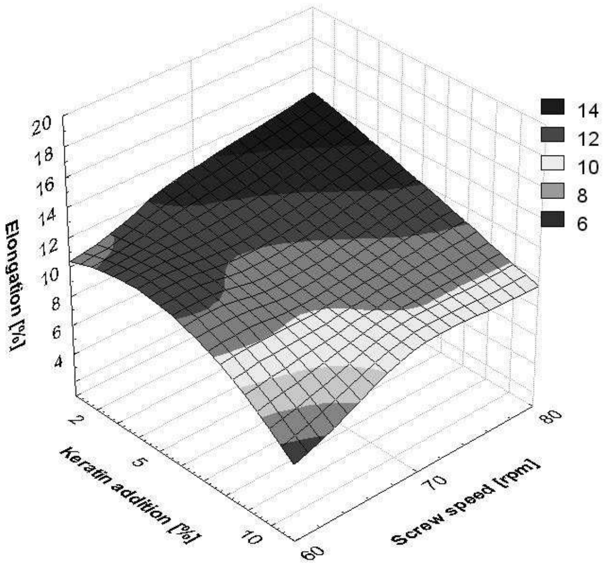

Fig. 9. Maximum elongation at extension test of longitudinal samples

The lowest elongation both for samples selected across and along the direction of extrusion was noted with a film obtained by using low screw rotation and with the greatest participation of keratin in the formulation. Also for this film the lowest value of the breaking force was measured (not exceeding 10 N). Large keratin addition weakened the internal structure of the film that was less flexible (elongation 6-8%) and less resistant to damage.

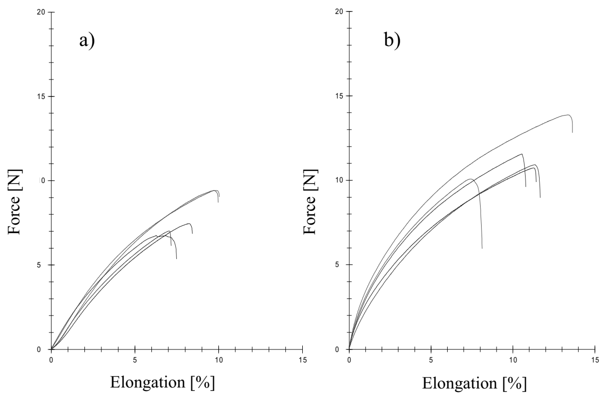

Fig. 10. Breaking force and elongation of a) longitudinal and b) transversal samples during extension test of SGK-3 film processed at 60 rpm

The results of measurements of the film elongation at break during extension of transversal samples depended on the applied processing screw speed and the amount of the additive are presented on the Figure 11. Elongation at break ranged from 8.22 to 13.75%, as previously the highest elongation characterized films produced at the highest screw speed and the lowest addition of keratin. Increasing the screw speed during extrusion-blowing affected the flexibility of film and higher elongation values of all the samples reached for longitudinal samples along the direction of film extrusion.

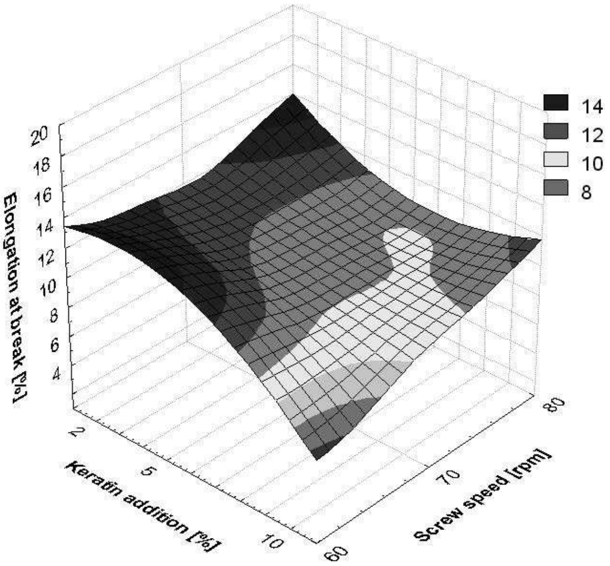

Fig. 11. Elongation at break εB at transversal samples during extension test

The values of this parameter were slightly lower than for samples cut transversal to the film sleeve blowing direction. The results of the elongation at break of film are summarized on the Figure 12.

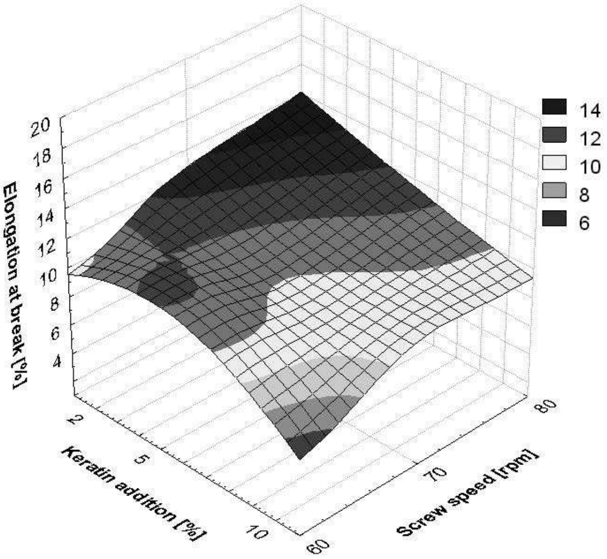

Fig. 12. Elongation at break εB at longitudinal samples during extension test

Analysis of the results showed that at 5 and 10% addition of keratin increasing maximum strain - σM and strain at break - σM for transversal films during extension tests were observed with increasing a screw speed during extrusion, as evidenced by high values of correlation coefficients in Table 3.

For the film samples containing 2% of keratin there was unclear effect of the screw rotation speed on the studied properties. While the results of elongation during extension tests indicated an increase the maximum elongation - εM and elongation at break - εB during tests of longitudinal samples of blow film with increasing screw speed.Increasing content of keratin in the blends of raw materials affected the lowering of the value of all parameters, as evidenced by negative correlation coeffi-

Table 3. Correlation coefficients of the mechanical properties of TPS film depending on the content of keratin

Keratin [%]	σM at trans-versal extension	σM at longitudinal extension	σB at trans-versal extension	σB at longitudinal extension	εM at trans-versal extension	εM at longitudinal extension	εB at trans-versal extension	εB at longitudinal extension
2	0,397	0,797	-0,309	-0,952	-0,318	0,990	-0,364	0,995
5	0,945	0,676	0,990	0,427	0,911	0,717	-0,873	0,578
10	0,969	0,402	0,971	0,488	0,990	0,875	0,990	0,877

Table 4. Correlation coefficients of the mechanical properties of TPS film depending on the screw rotation during extrusion

Screw speed [rpm]	σM at trans-versal extension	σM at longitudinal extension	σB at trans-versal extension	σB at longitudinal extension	εM at trans-versal extension	εM at longitudinal extension	εB at trans-versal extension	εB at longitudinal extension
60	-0,918	-0,990	-0,909	-0,886	-0,977	-0,884	-0,940	-0,818
70	-0,952	-0,838	-0,918	-0,932	-0,990	-0,975	-0,998	-0,932
80	-0,927	-0,985	-0,929	-0,936	-0,954	-0,999	-0,635	-0,999

cients with high values (above 0.8) determined for whole range of the screw rotation used [22]. Data summarized in Table 4 demonstrates the negative impact of increasing amount of keratin on the mechanical properties of the obtained TPS films, irrespective on the screw speed used during extrusion.

CONCLUSIONS

The detailed study and analysis of the obtained results have allowed for the following conclusions:

It is possible to produce biodegradable starchy films of satisfactory properties while using extrusion-cooking process for the production of TPS granulates (half-product) and extrusion-blowing technique for films (final product), however implementing carefully selected process conditions.

Addition of keratin in amounts up to 5% significantly improved the ability of film elongation (film SGK-1, SGK-2).

Addition of keratin at 10% resulted in excessive softness of the film, substantially reduced its strength.

The screw speed had a significant impact on the physical properties of TPS films.

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WPŁYW DODATKU KERATYNY NA WYBRANE WŁAŚCIWOŚCI FIZYCZNE FOLII ZE SKROBI TERMOPLASTYCZNEJ

Streszczenie. Celem pracy było zbadanie wpływu wybranych parametrów procesu wytłaczania folii z granulatu skrobi termoplastycznej z dodatkiem hydrolizatu keratyny, na podstawowe właściwości fizyczne otrzymywanych folii opakowaniowych. Do produkcji folii skrobiowej zastosowano granulat otrzymany w procesie ekstruzji na ekstruderze jednoślimakowym TS-45 o L/D=16. Do wytworzenia granulatu użyto skrobię, glicerynę oraz polimer hydrolizat keratyny. W trakcie procesu wytwarzania granulatu stosowano obroty ślimaka ekstrudera w zakresie od 40 do 80 obr.min^{-1} oraz temperaturę w zakresie 70 – 120°C. Następnie z uzyskanego granulatu wytłaczano folię metodą rozdmuchu na specjalnie do tego celu wytłaczarce, zaprojektowanej w Katedrze Inżynierii Procesowej UP w Lublinie. Badano cechy wytrzymałościowe folii tj. naprężenie i wydłużenie podczas testów na rozciąganie.

Słowa kluczowe: skrobia, folia, keratyna, ekstruzja, wytłaczanie, naprężenie, wydłużenie.