

Impact of bioethanol additive on the properties of stretchable starch films

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Abstract: *Impact of bioethanol additive on the properties of stretchable starch films.* The objective of the study was to examine the impact of bioethanol additive on mechanical properties of stretchable starch films. The test consisted of adding bioethanol to the plasticizer, constituting a mixture of water and glycerol. Mass proportion of plasticizer to raw starch was 8 : 1 (800 g/100 g). Bioethanol used for the tests was a raw distillate, obtained directly from an agricultural distillery, containing 90% ethanol. The mixture obtained from these ingredients was heated to the temperature of 80°C, and then poured into Petri dishes and dried. The quality of starch coating obtained was assessed by calculating the Young's modulus and the maximum puncture force with a cylindrical penetrometer. The strength tests were conducted for dried samples and for samples exposed directly to water. For this purpose, the samples were kept in an aqueous environment for 6 h and 6 days, and strength tests were conducted every 1 h and 24 h, respectively. It was found that under exposure to water, the quality of products changed over time, and increase in alcohol content resulted in increase in the value of Young's modulus of the starch coating.

Key words: thermoplastic starch, coatings, glycerol

INTRODUCTION

Interest in production of biodegradable packaging is, to some extent, due to growing awareness of the recipients, but mostly by economic conditions. Biodegradable packaging can be made of highly processed natural products. In comparison with artificial packaging, it is relatively costly despite their competitive performance. At the other end of the spectrum, there are packaging products made directly of biodegradable or low-processed materials, which is compensated by relatively low production cost. These packaging items are also well received by the market as being “environment-friendly”.

Improvement in the quality of low-processed materials is implemented by using additives to processed materials to improve their specific characteristics [Lisowski et al. 2015] without a substantial increase in their production costs. The material used for food packaging

should have the appropriate strength and barrier properties, as well as prevent transfer of particles contained in the packaging to the product being protected [Ghasemlou et al. 2013, Rompothi et al. 2017]. One of the materials, which meet the requirements of biodegradability and originating from renewable sources is TPS (thermoplastic starch), obtained using extruders [Mościski and Oniszczyk 2008] or casting. Many publications have presented the impact of the type of plasticizer on usable properties of the material obtained [González-Seligra 2017]. One of the most popular plasticizers added to obtain TPS is glycerol [Laohakunjit and Noomhorm 2004, Combrzyński 2012]. Glycerol added to extruded starch mix ensures the proper elasticity of the extrudate obtained. Glycerol limits the process of crushing of extrudates by dynamic forces, which is typical for extrudates obtained using water as a plasticizer [Ekielski et al. 2016].

Unfortunately, thermoplastic starch obtained in this manner has two basic flaws in comparison with popular artificial plastics. One of these is water absorbability, the other – relatively poor mechanical properties [Pushpadass et al. 2009]. These properties can be improved by adding substances to reinforce the TPS structure or by using a proper combination of plasticizers for production of TPS [Tachaphiboonsap 2013]. A significant additive, which improves the usable properties of the TPS, is raw spirit obtained directly from agricultural

distilleries, the so-called raw distillate, or other alcohol [Gilfillan et al. 2016]. Raw distillate is a semi-finished product, obtained directly from distillation columns of alcohol content of 88–92% (PN-A-79523:2002). It is a crude product, which is then subjected to further purification and dehydration. These processes are characterized by high energy consumption. There is no exhaustive information in the available literature on impact of adding the relatively cheap raw distillate, on the properties of thermoplastic starch.

The objective of the study was to assess the impact of adding of raw spirit on the mechanical properties of starch coatings, used as barrier coatings for disposable packaging materials.

MATERIAL AND METHODS

The study was conducted using potato starch and alcohol solution, the so-called raw distillate, obtained from an agricultural distillery. The study consisted of mixing 100 g of potato starch in 800 cm³ of a mixture of glycerol and bioethanol solution (the table). Alcohol concentration in raw distillate was 90.5 ± 0.5%. Alcohol content was determined by measurement of density of the sample tested using a pycnometer and comparison with alcohol solution density tables. The measurement points were prepared using the central composition plan (DOE) in Statistica v. 12 software. The range of variability of external factors introduced has been presented in the table.

TABLE. Study plan 2/3/9 generated in Statistica v. 12

Sample number	Glycerol index [%]	Alcohol index [%]	Glycerol mass [g/100 g of starch]	Alcohol concentration [%]
1	0	1	30	30
2	1	0	50	15
3	-1	-1	10	0
4	-1	0	10	20
5	1	1	50	30
6	0	-1	30	0
7	1	-1	50	0
8	-1	1	10	30
9	0	0	30	15

The mixture was heated to the temperature of 80°C and stirred intensively at the same time. Modified thermoplastic starch was poured onto Petri dishes and dried in the temperature of 40°C, until achieving moisture content of 7%. After drying the film obtained, its thickness was measured at seven random points using a slide caliper with accuracy of ±0.01 mm. Film, in which thickness differences exceeded 10% in relation to the average, was rejected. Samples to be used for further tests were prepared in accordance with the conditions and modes specified in standards PN-EN ISO 527-1:2012, PN-EN ISO 527-2:2012 and PN-EN ISO 527-3:2012, of width of 10 mm and length of 40 mm.

The material samples obtained were exposed to water for the period up to 6 h (strength measurement every 1 h) and then for the period of 6 days (strength measurement every 24 h). Prior to measurements, excess water was removed from the sample by drying on tissue paper and its mass was measured using a scales WPS 610 (Radwag, Radom, Poland) with the accuracy level of ±0.01 g.

The samples obtained in this manner were subjected to strength tests.

For this purpose, tensile strength tests were conducted (Young's modulus), and the maximum force F_{\max} [N] was determined, necessary to puncture the sample with a round mandrel of diameter $D = 1.5$ mm. Strength tests were performed using AXIS FA testing machine, equipped with a head of maximum 25 N. The head movement speed was 25 mm/min.

The strength-displacement charts during tensile and pull tests made it possible to determine the value of Young's modulus (E) as the curve gradient on the stress-elongation chart. The Young's modulus value was determined in accordance with the standards: ISO 527-1, ISO 527-2 and ASTM D 638.

$$E = \frac{F_1}{s-d} \cdot \frac{l_1}{l_0}$$

where:

- E – value of Young's modulus [MPa];
- F_1 – value of force causing linear strain-ing [N];
- s – initial sample width [mm];
- d – initial sample thickness [mm];

l_1 – sample length at tensile force F_1 [mm];
 l_0 – initial sample length [mm];

During tests measurements of each of the variables were repeated five times. The test results were processed using statistical methods of software Statistica v. 12.

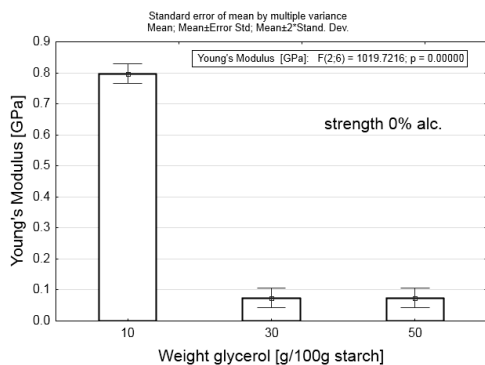
TEST RESULTS AND ANALYSIS

Analyzing the test results, it was found that both addition of glycerol and alcohol to the sample exerted significant impact on the quality parameters of the samples

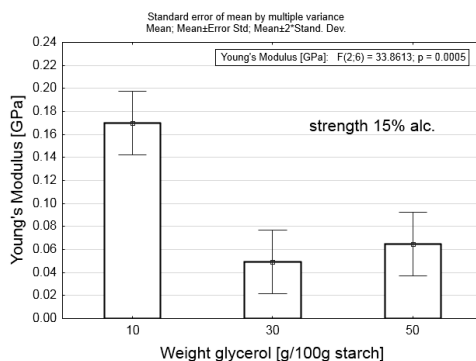
being analyzed. On the basis of charts (Fig. 1), it can be stated that the smallest addition of glycerol to the mixture (10 g per 100 g of starch) resulted in obtaining of a product, for which the Young's modulus value was the highest, within the range of 0.17–1.2 GPa depending on alcohol concentration in the mixture.

Presumably, alcohol particles partially replace the glycerin particles, making the amylopectin chains more rigid. Increasing of glycerol concentration in the mixture to the value of (30 and 50 g/100 g of starch), on the other hand, resulted in a substantial decrease in the value of

a



b



c

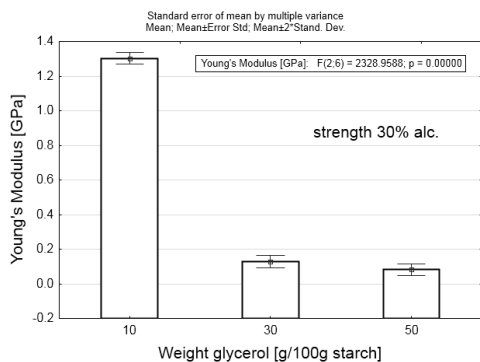


FIGURE 1. Impact of glycerol concentration on the Young's modulus value in samples at alcohol concentration of: a – 0%, b – 15%, c – 30%

Young's modulus to 0.05–0.12 GPa, indicating higher elasticity of these products. It was also observed that the differences in glycerol content in starch mix 30 g/100 g and 50 g/100 g were insignificant.

The charts (Fig. 2) illustrate results of tests of changes of quality parameters of the samples obtained, exposed directly to water in the time of 6 h. It was found that all samples exposed to water changed their properties substantially after the defined period of time.

During strength tests of the samples, it was found that their hardness decreased

after the first hour of exposure to water; no statistically significant changes were observed earlier. Such phenomenon was observed for all mixtures with alcohol content of 0, 15 and 30%. Charts 2a and 2b also indicate that increase in glycerol content in the mix leads to visible reduction in strength of the product. Comparing the charts being analyzed, it can also be concluded that as alcohol content in the mixture increases, sample strength decreases visibly (Fig. 2b). The obtained results of tests on the impact of alcohol on the strength of thermoplastic starch have been observed also during produc-

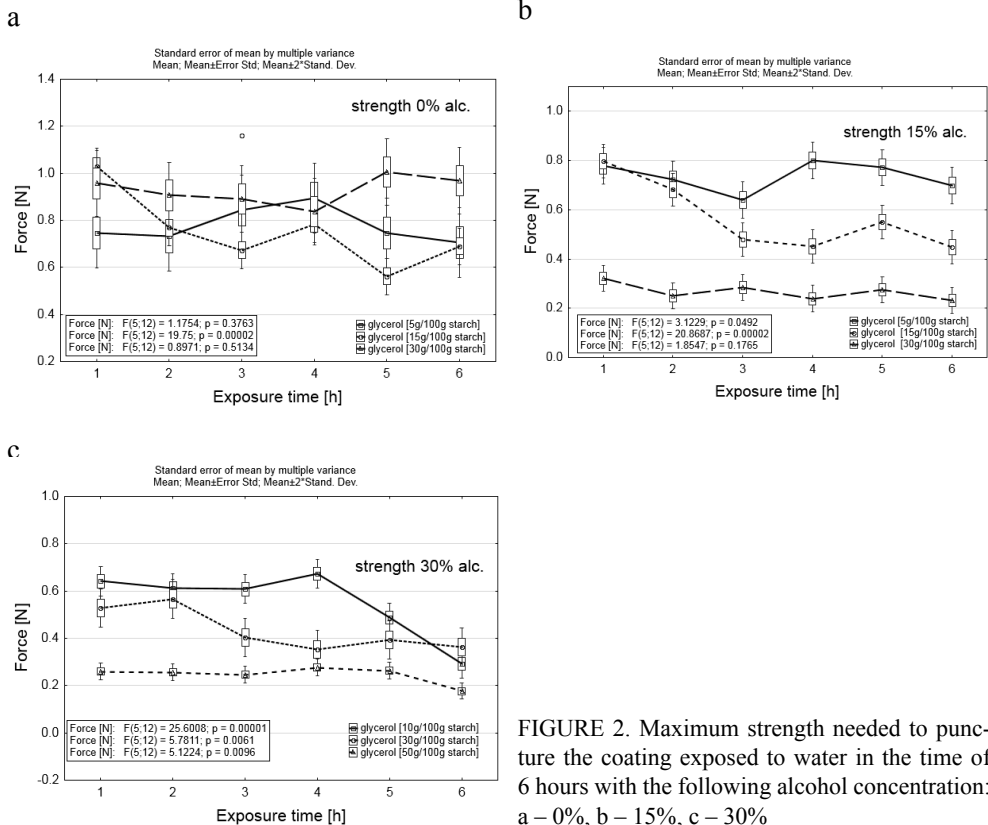


FIGURE 2. Maximum strength needed to puncture the coating exposed to water in the time of 6 hours with the following alcohol concentration: a – 0%, b – 15%, c – 30%

tion of TPS using the extrusion process [Gillfillan et al. 2016].

The charts illustrating changes in sample mass produced different results (Fig. 3). At 0% alcohol content, the sample mass was visibly reduced as the time of exposure to water increased. Addition of alcohol led each time to main-

During the next stage of the study, then, further exposure of the samples to water for the period of 6 days was undertaken. Analyzing the results for samples exposed to long-term impact of the solvent (Fig. 4), it was found that the strength reduction trend was maintained, and the samples reached their lowest

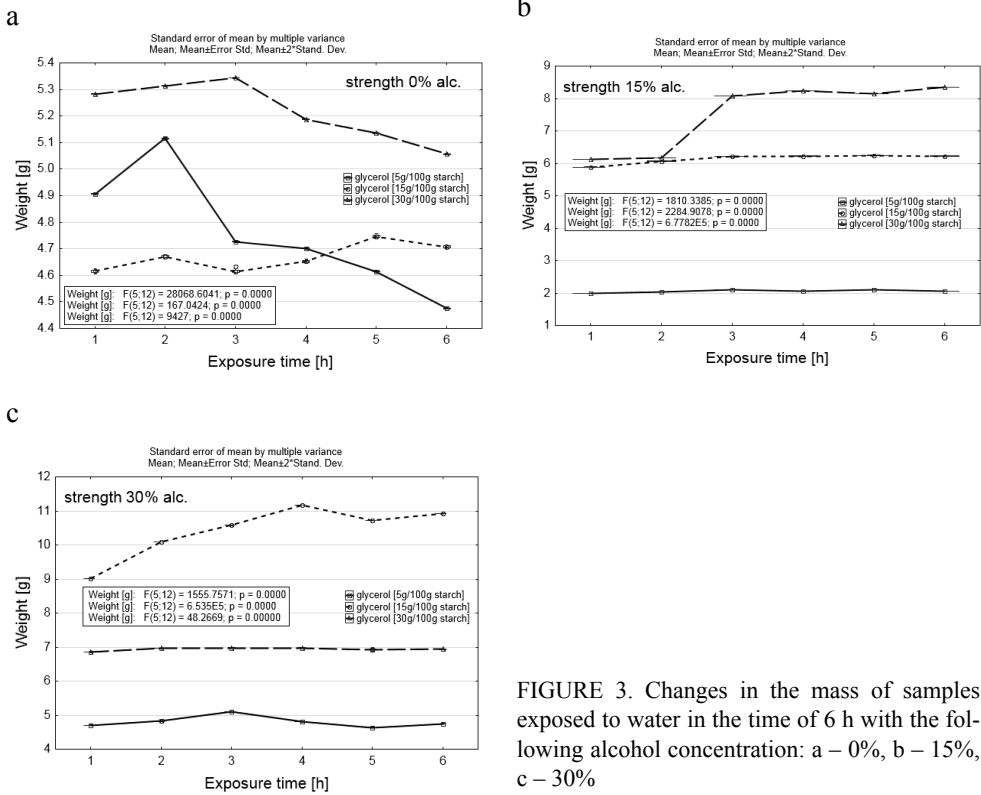


FIGURE 3. Changes in the mass of samples exposed to water in the time of 6 h with the following alcohol concentration: a – 0%, b – 15%, c – 30%

taining or a small increase in the product mass. During 6 h of exposure, it was also possible to observe the impact of glycerol content in the mixture on the product mass; however, at this stage of research, it was difficult to interpret the cause of such change.

strength value after 6 days. It can also be observed that for samples with alcohol content 15 and 30%, with 30 and 50 g of glycerol per 100 g of starch, reduction in product strength was observed along with reduction of glycerol content. On the other hand, a sample made of mix-

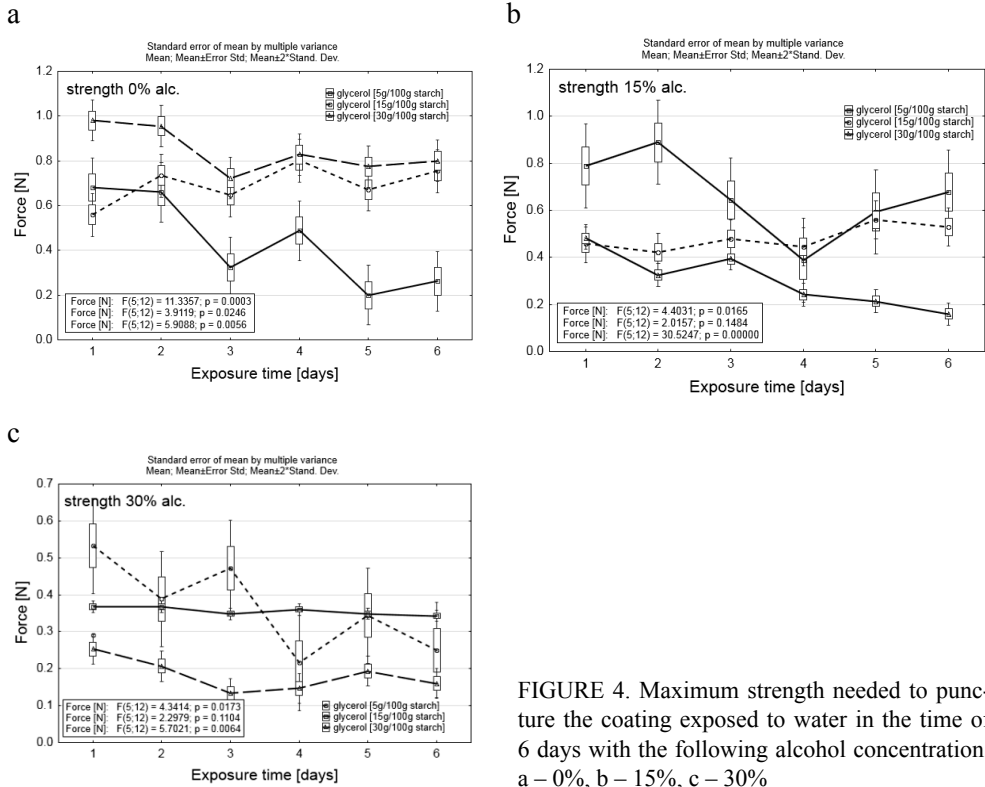


FIGURE 4. Maximum strength needed to puncture the coating exposed to water in the time of 6 days with the following alcohol concentration: a – 0%, b – 15%, c – 30%

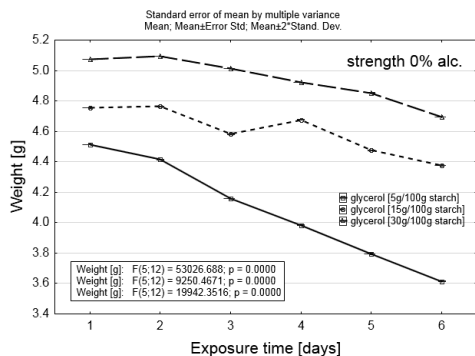
ture with the lowest glycerol content initially showed increasing strength, which then dropped quickly. This could be the result of biodegradation of the product.

Such behavior of the samples is confirmed by results of changes in their mass (Fig. 5), which indicated clearly that mass of products with the lowest glycerol content in the mixture lost decreased the fastest, which was probably associated with dissolution of gelatinized starch in water due to lesser impact of glycerol particles built into their structure. This decrease was most visible when the alcohol content in the mixture was 0%. Like in the first 6 h, also after 6 days, reduction in mass of individual

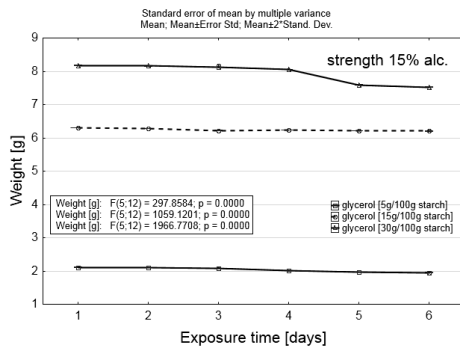
samples decreased as the alcohol content in the raw material increased.

Changes in physical properties of the samples examined may indicate that alcohol used for production has some properties, which protect the product by reducing its susceptibility to biodegradation in the aqueous environment. It can also be concluded that lack of alcohol in the mixture will result in intense and quick solving of the sample in the aqueous environment. Comparing the results for different values of alcohol content in the sample, it can also be stated that even the smallest addition of alcohol to the mixture will improve resistance of starch material to water.

a



b



c

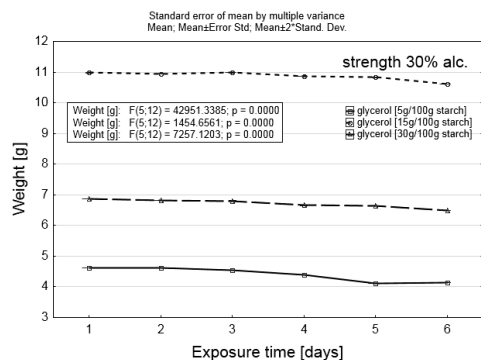


FIGURE 5. Changes in the mass of samples exposed to water in the time of 6 days with the following alcohol concentration: a – 0%, b – 15%, c – 30%

CONCLUSIONS

1. The examined quality parameters of starch coatings changed under exposure to water, regardless of the quantity of glycerol and alcohol additives used. Their quality (strength parameters) decreases significantly in the first 6 h of being in the water environment. The next 6 days in the water cause a further decrease in the quality of these materials, but the changes are no longer so intense.
2. Increase in the alcohol content in the mixture results in increasing of the value of Young's modulus of the

starch coatings examined in all samples tested.

3. Adding of alcohol to the mixture results in increase in resistance of the starch coating to puncture. It is important in the case of coatings used for packaging purposes (e.g. disposable dishes).
4. Samples containing alcohol, after 6 days of direct exposure to water, do not dissolve, and their water absorbability increases. Presumably, taking the place of glycerol particles, alcohol blocks the remaining glycerol molecules, thus limiting solubility of the coating.

5. In order to improve the mechanical properties of starch coating, it is possible to use non-purified bioethanol, thus shortening the energy chain in the production process, improving the functional parameters of the products while reducing energy consumption.

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Streszczenie: *Wpływ dodatku bioetanolu na właściwości elastycznych powłok skrobiowych. Opakowania biodegradowalne mogą być wytwarzane z naturalnych produktów o wysokim stopniu przetworzenia. W porównaniu do opakowań z tworzyw sztucznych są one jednak stosunkowo drogie pomimo konkurencyjnych cech użytkowych. Dla poprawy jakości tych wyrobów stale poszukuje się dodatków poprawiających ich określone cechy bez znacznego podnoszenia kosztów wytwarzania. Celem badań była ocena wpływu dodatku bioetanolu na właściwości mechaniczne*

powłok skrobiowych, które mogą być wykorzystywane jako powłoki barierowe do opakowań jednorazowego użytku. Badanie polegało na dobraniu i wymieszaniu w odpowiedniej proporcji mieszaniny glicerolu i roztworu bioetanolu. Użyty bioetanol był tzw. surówką pozyskaną z gorzelni rolniczej. Uzyskana z powyższych składników mieszanina była podgrzewana do temperatury 80°C, a następnie rozlewana na płytki Petriego i suszona. Do oceny jakości powłok skrobiowych wykorzystywano wskaźnik modułu Younga i siłę maksymalną przebiccia produktu. Próbkę poddano ekspozycji środowiska wodnego, a wyniki przeanalizowano w trakcie pierwszych 6 h, a następnie przez kolejne 6 dni. Stwierdzono, że po poddaniu działania wody jakość produktów zmienia się w czasie, a wzrost udziału alkoholu wpływa na zwiększenie wartości modułu Younga powłok skrobiowych.

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