Evaluation of Water Vapor Permeability of Biodegradable Starch-Based Films

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Summary. Packaging is an integral part of food – meets both security features to packaged food and marketing to encourage potential consumers to purchase. In the era of sustainable development, which produced materials to be environmentally friendly, a lot of attention is paid to the biodegradable packaging. The aim of this study was to evaluate the water vapor permeability of starch films on the basis of gravimetric method. Permeability tests were performed for various compositions of raw materials and processed at different screw speeds during film blowing. Tests results showed that water vapor permeability values ranged from $2{,}63 \cdot 10^{-9}$ to $0{,}65 \cdot 10^{-9}$ g/(m·s·Pa) depending on recipe of granulate and processing conditions. Lower permeability of water vapor occurred in starch film with 20% of glycerol and 4% of poly(vinyl) alcohol processed at 80 rpm.
Key words: starch, biodegradable packaging, film blowing, water vapor permeability.

INTRODUCTION

Packaging material is an integral part of food products which has to fulfil a number of important functions. First of all, it is to protect the product, facilitate storage and sale. Packaging should prevent spoilage, discoloration, contamination or damage of the product. In view of the widespread use of plastics and because of the environmental problems there are increasingly higher requirements for the packaging to be "environmentally friendly". For this purpose, some additional agents can be easily incorporated into the packaging materials or biodegradable plastics are designed, which are able to degrade in a short time [3, 21]. However, due to the food safety, these materials require the detailed research for their quality and properties.

Popularity of plastics as packaging materials for food is the result of beneficial properties, such as the mechanical tensile strength, high barrier properties against oxygen, carbon dioxide, anhydrides and aromas or good sealing features. Used over the years synthetic plastics have led to serious environmental problems. At the same time such a situation led to intensive research on the development of biodegradable materials.

For biodegradable packaging materials from renewable resources starch is primarily applied [1, 14, 16, 18]. However, if the biodegradable materials are designed to be used as food packaging they must meet the requirements for materials intended for contact with food. These concerns mainly the protection of the product from physical damage, contamination or deterioration and the maintaining of the quality of the product. From the viewpoint of the packaging industry, starch-based materials have an enormous potential due to the biodegradability, compostability, but also the availability of large quantities of starch and its renewability [3, 4, 15]. Furthermore, due to their relatively low cost, they could be an attractive alternative to polymers based on petrochemical raw materials [22]. Starch-based packaging materials have been used as films for wrapping food, food containers such as bowls, plates, cups, egg wrappings. Thermoplastic starch has good oxygen barrier properties, but the hygroscopic nature of starch makes this material unsuitable for liquid products and for high-moisture food [5, 9, 18, 20, 23].

The aim of the study was to determine the water vapor permeability of starch-based films with different additives depending on granulates composition and film-blowing conditions.

MATERIALS AND METHODS

The scope of work included measuring the water vapor permeability of biodegradable starch-based films with gravimetric method. The material used in experiments included the starch-based biodegradable films, processed from granulates with composition shown in Table 1. The films were produced at the Department of Process Engineering, Faculty of Production Engineering, University of Life Sciences in

Lublin in the two-step process: biopolymer granulates were processed using the extrusion-cooking equipment, and the films were made from granulates using film-blowing device at various screw rotational speed of 50, 60, 70 and 80 rpm, depending on the granulates applied [18]. Water vapor permeability through the packaging starch-based material was tested in the Department of Food Engineering and Process Management, Faculty of Food Sciences, SGGW in Warsaw using gravimetric method described by Jamshidian and coworkers [8].

The films were placed between two gaskets and sealed in specially prepared glass containers with an opening and twist-off cap. Glass containers were filled with distilled water, which has a water activity equal to 1 and 3167 Pa pressure. Measuring containers were placed in a desiccator with a solution of $MgCl_2$ for conditions ensuring constant relative humidity at 30%. The testing was carried out at room temperature. Measurements of the sample mass were performed once a day for 7 days. The tests were performed in duplicate. To determine the permeability it was necessary to perform film thickness measurement, which was realized using the thickness gauge A400 Ultrametr Metrison with accuracy of 1 micron. The measurement was performed in six replicates.

Water vapor permeability was calculated from the formula:

$$P = \frac{\Delta m \cdot e}{A \cdot \Delta t \cdot \Delta p}, \quad (1)$$

where:
P – water vapor permeability, g/(m·s·Pa),
Δm/Δt – sample weight loss in time function , g/s,
e – film thickness, m,
A – permeability area, $8.55 \cdot 10^{-4}$ m²,
Δp – pressure difference under the film and outside, Pa.

Changes of sample mass during the time were calculated by use of linear regression. The data were analyzed by ANOVA using Statgraphics Plus 4.1 software. Fishers test was used for the analysis. Verification was made at the significance level of 0.05 [11]. An analysis of the detailed comparisons was performed at the significance level α = 0.05, which divided the means of results into homogeneous groups.

Table 1. Composition of starch films

Lp.	Material*	Potato starch [%]	Glycerol [%]	Poly(vinyl) alcohol [%]	Keratin [%]	Flax oil [%]
1	SGA I	78.0	20	2.0	-	-
2	SGA II	76.0	20	4.0	-	-
3	SGA III	74.0	20	6.0	-	-
4	SGAK II	77.0	20	2.0	1.0	-
5	SGAK III	76.0	20	3.0	1.0	-
6	SGAK IV	75.5	20	3.5	1.0	-
7	SGK III	79.75	20	-	0.25	-
8	SGO II	78.5	20	-	-	1.5

* symbol explanation:
S – potato starch K – keratin
A – poly(vinyl) alcohol O – flax oil

RESULTS

One function of packaging materials is the formation of barrier for water between the food and the environment. It was observed that before the expiry of seven days of research, some attempts of starchy materials have been overgrown with mold such as SGA II 80, SGA III 80, SGK III 60, SGK III 50, SGK III 70, SGAK III 70. A similar phenomenon was observed for starch films by Bergenholtz and Nielsen [2].

Figure 1 shows the water vapor permeability results of SGA films containing starch with addition of poly(vinyl) alcohol. Permeability for this group of materials varied in the range of $0.65^{\cdot 10\text{-}9}$ for the SGA II 80 to $2.63^{\cdot 10\text{-}9}$ g/(m·s·Pa) for the SGA I 80. Increasing the content of poly(vinyl) alcohol from 2 up to 4% resulted in a 4-fold reduction in the water vapor permeability of film processed at 80 rpm, and almost three times using 50 rpm during film-blowing of starch granulates with this agent.

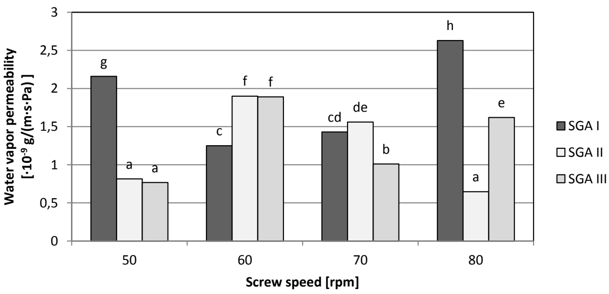

Fig. 1. Water vapor permeability of starch films SGA processed with film-blowing at various screw speed (numbers I, II, III marked poly(vinyl) alcohol amount: 2, 4 and 6%, respectively); a – h – similar letters showed homogeneous groups of means

Also for starch-based films SGAK with the addition of poly(vinyl) alcohol and keratin diversified results were obtained (Fig. 2). The material, which was characterized by the highest permeability with mean result of $2.29 \cdot 10^{-9}$ g/(m·s·Pa) was film processed with SGAK IV recipe using 80 rpm during film-blowing. In contrast, the film prepared from the same recipe but processed using 60 rpm screw speed was characterized by the lowest water vapor permeability at the level of $0.72 \cdot 10^{-9}$ g/(m·s·Pa).

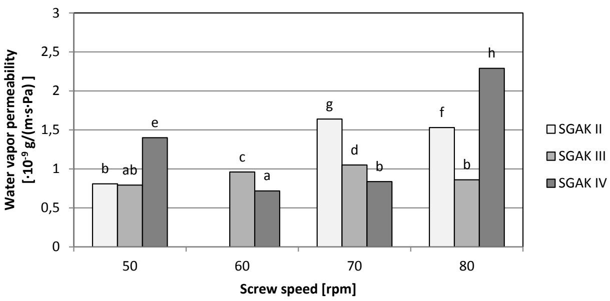

Fig. 2. Water vapor permeability of starch films SGAK processed with film-blowing at various screw speed (numbers II, III, IV marked poly(vinyl) alcohol amount: 2, 3 and 3.5%, respectively, K is 1% of keratin); a – h – similar letters showed homogeneous groups of means

During the tests of film materials containing starch and addition of keratin (the material symbol SGK), the lowest permeability ($0.778 \cdot 10^{-9}$ g/(m·s·Pa) was evaluated for the material processed at 70 rpm screw speed (Fig. 3). For the same screw speed applied during film-blowing of SGO material with flaxseed oil addition also low permeability at the level of $0.889 \cdot 10^{-9}$ g/(m·s·Pa) was determined.

Analysis of the results presented in the paper showed statistically significant differences in water vapor permeability between samples (Tab. 2).

Both the material composition and the processing conditions affected the level of water vapor permeability. There was no linear relationship between the number of screw speed used in the production of starch-based films and the level of water vapor permeability. Additionally, it was shown that both the formulation and production parameters could affect the film water vapor permeability. It was noted that even a small addition of substances such as 0.25% of keratin or up to 6% of poly(vinyl) alcohol, and variation in screw speed during starch-based film processing can cause significant changes in water vapor permeability of the packaging. The appropriate selection of additives for the preparation of raw material mixtures and proper selection of production parameters can produce a film with satisfactory parameters of permeability.

Confirmation of significantly altering the barrier to water vapor by the addition of various substances are tests results presented by Galdeano et al. [7], who conducted the study of the oat starch film produced by casting with the addition of various plasticizers: glycerol, sorbitol, and mixtures of glycerol, sorbitol, sucrose and urea. It was shown that the water vapor permeability (WVP) of the film with the addition of the plasticizer was significantly lower than without the additive. Plasticizers prevent cracking of the film during cargo handling and storage, but their greater additive reduces the barrier to gases, water vapor and solutes. This behavior is probably due to the structural modification of the starch, which may become less dense, due to the addition of substances with hydrophilic character which promote absorption and desorption of water [1].

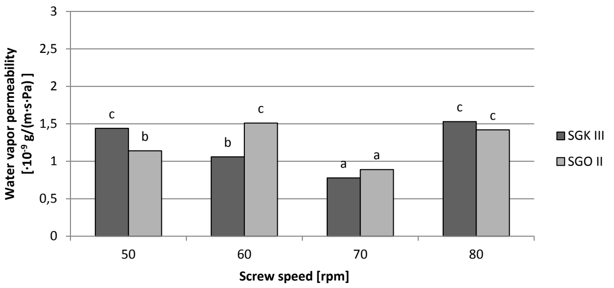

Fig. 3. Water vapor permeability of starch films SGK and SGO processed with film-blowing at various screw speed (K is 0.25% of keratin, O is 1.5% of flax oil); a – c – similar letters showed homogeneous groups of means

Galdeano et al. [6] observed the opposite situation, probably due to the antiplasticizing effect exerted by plasticizers used in specific experimental conditions in which they were tested. The values of water vapor permeability of plasticized films ranged from 2.317 to $4.211 \cdot 10^{-12}$ g/(m·s·Pa), whereby the lowest permeability was evaluated during tests of film with sucrose addition. Sucrose molecules, as a result of crystal formation, influenced the film matrix and increased the barrier properties [24]. In contrast, the highest permeability was obtained for film with glycerol, as expected. Glycerol is an effective plasticizer having high ability to interact with water, facilitating its solubility and penetration through the membrane [12]. This is so, because of easy penetration of glycerol inside the film structure and the presence of hydroxyl groups, thereby producing a highly hydrophilic material [13].

Table. 2. Analysis of variance of water vapor permeability results of starch-based films

Source of variation SGA	Degree of freedom df	Mean square MS	F	p-value
Between groups	11	0	104,54	0,0000
Inside groups (error)	12	0		
Total	23			
Source of variation SGAK	Degree of freedom df	Mean square MS	F	p-value
Between groups	10	0	320,04	0,0000
Inside groups (error)	11	0		
Total	21			
Source of variation SGK	Degree of freedom df	Mean square MS	F	p-value
Between groups	3	0	107,64	0,0003
Inside groups (error)	4	0		
Total	7			
Source of variation SGO	Degree of freedom df	Mean square MS	F	p-value
Between groups	3	0	128,43	0,0002
Inside groups (error)	4	0		
Total	7			

According to the results presented by Sobral and coworkers [19] the more plasticizer is used, the lesser density of network is formed and consequently the film is more permeable. The value obtained by these authors for film with glycerol was lower than that of starch materials tested with various additional substances. This may be due to various origins of the starch or additional substances, which caused an increase in permeability. An increased lipid content in oat may help to reduce the water vapor permeability of the film, presumably because lipids influence the barrier properties.

Similarly, Kechichian and coworkers [10] showed that the addition of antimicrobial constituents significantly affects the properties of the film based on manioc starch produced by casting. Films with the average content of cinnamon powder (0.2 g/100g) presented the lowest value of the water vapor permeability (WVP), probably because these components affect the improvement of barrier to water vapor of biodegradable film matrix. Addition of more antibacterial component caused the opposite effect and water vapor permeability (WVP) increased, which indicates that there is limited range of application of this additive to improve the barrier properties against water vapor.

Comparing the results for starch-based materials with literature data for the film produced on the basis of petroleum raw materials, or for some biopolymers, it can be stated that the starch-based materials have a lower barrier properties. Presented in this study potato starch-based films were characterized by low water vapor permeability, i.e. SGA II 80, received a similar value as for materials with manioc starch plasticized with glycerol (40g/100g of starch) – $6.25 \cdot 10^{-10}$ g/(m·s·Pa) and maize starch plasticized with glycerol (40g/100g of starch) – $6.7 \cdot 10^{-10}$ g/m·s·Pa [12]. The film prepared with low density polyethylene LDPE exhibits higher barrier properties with values of water vapor permeability from $0.9 \cdot 10^{-12}$ to $1.3 \cdot 10^{-12}$ g/(m·s·Pa) [17].

CONCLUSIONS

Starch-based biodegradable materials with the addition of glycerol, poly(vinyl) alcohol, keratin and flax oil tested in this work failed to meet the requirements for the food contact packaging materials. During the water vapor permeability tests absorption of water vapor was observed, and thus the use of such packages in contact with food is unsuitable. Water vapor permeability of starch-based packaging materials ranged from $2.63^{\cdot 10-9}$ to $0.65^{\cdot 10-9}$ g/(m·s·Pa). The lowest water vapor permeability was evaluated for SGA II 80 – potato starch-based film containing 20% of glycerol and 4% of poly(vinyl) alcohol addition, processed with film-blowing at 80 rpm screw rotational speed.

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OCENA PRZEPUSZCZALNOŚCI PARY WODNEJ SKROBIOWYCH FOLII BIODEGRADOWALNYCH

Streszczenie. Opakowanie stanowi nieodłączny element żywności – spełnia zarówno funkcje ochronne wobec zapakowanej żywności, jak i marketingowe, mające zachęcić potencjalnego konsumenta do zakupu. W dobie zrównoważonego rozwoju, gdzie wytwarzane materiały mają być przyjazne środowisku, wiele uwagi poświęca się opakowaniom biodegradowalnym. Celem pracy było określenie przepuszczalności pary wodnej materiałów przyjaznych środowisku w oparciu o metodę grawimetryczną. W pracy badano przepuszczalność pary wodnej folii skrobiowych wykonanych z różnych mieszanek surowcowych oraz z zastosowaniem zróżnicowanych obrotów ślimaka podczas wytłaczania folii z rozdmuchem. Przeprowadzone badania wykazały, że przepuszczalność pary wodnej dla opakowań skrobiowych wynosiła od $2,63 \cdot 10^{-9}$ do $0,65 \cdot 10^{-9}$ g/(m·s·Pa). Najniższą przepuszczalnością wobec pary wodnej charakteryzowała się folia skrobiowa z 20% zawartością gliceryny oraz 4% dodatkiem alkoholu poliwinylowego wyprodukowana przy prędkości obrotowej ślimaka 80 obr·min^{-1}.

Słowa kluczowe: skrobia, wytłaczanie, opakowania biodegradowalne, przepuszczalność pary wodnej.