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Preliminary studies of the influence of starch irradiation on physicochemical properties of films prepared using starch and starch-surfactant systems*

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Abstract. The influence was studied of potato and wheat starch irradiation on physicochemical properties of films, prepared using either starch alone or a composition of potato starch with three surfactants: sodium laurate, sodium palmitate and cetyl-trimethyl-ammonium bromide (CTAB). The surfactants were introduced at a level of 0.038÷0.075 g per 1 g of starch. This corresponds to 0.136–0.222 mmol/g, depending on the surfactant type and its amount used. Irradiations were carried out using ^{60}Co radiation with doses of 5, 10, 20 and 30 kGy. Films were prepared with addition of glycerol (0, 20 or 30% in terms of starch mass) by means of casting from the gelatinized starch or starch-surfactant solutions. With the purpose to characterize the films, mechanical tests (using an Instron instrument) and the wetting angle measurements were performed. The effect was determined of the storage and conditioning in an atmosphere characterized by the various moisture content on the properties of films with various compositions. The results show the radiation-induced improvement of hydrophobic properties of the films prepared using potato and wheat starch, and the selected potato starch-surfactant compositions. Improvement of strength and flexibility was obtained in the case of potato starch films, while in the case of wheat starch films the increase of strength was accompanied by a decrease in flexibility. Improvement of the functional properties of potato starch films corresponds to the improvement of their structural properties, found by scanning electron microscopy (SEM). The possibilities of modification of the films properties by modification of composition and radiation treatment were discussed.

Key words: starch films • starch-surfactants films • gamma irradiation • mechanical properties • barrier properties • hydrophobic

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Introduction

Problem of the increasing amount of non-degradable plastic waste induces interest to substitute such plastics by materials based on natural resources [14, 17, 19]. Edible and biodegradable films and coatings based on proteins, polysaccharides and some hydrophobic materials serve as a barrier for liquid and gas transfer in the food system and might participate in the drug delivery systems [9, 10, 12, 14, 17]. Using such packaging enables to prolong shelf-life of food and to fulfil a demand of environmental protection at a relatively low cost. Moreover, the possible application for preparation of such materials of some agricultural bi-products as well as the products that are produced in excess in relation to the possible implementation, might grow the economy of agricultural production and, therefore, participate in the increase of the added value.

The materials that might be used as edible and biodegradable packaging should reveal appropriate

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mechanical and barrier properties. In order to improve these properties, the new film compositions are tested and a number of methods are applied for material modification.

Development of the methods of biopolymers modification that apply ionizing radiation is observed during the last decade. Gamma irradiation was already found to be an effective method for improvement of barrier and mechanical properties of the edible and biodegradable films and coatings based on food proteins [3, 7, 8, 18, 29]. Accordingly, it appears interesting to check also the possibility to use gamma irradiation for modification of the properties of the appropriate starch based material. The radiation technology seems to be more promising as it was already found that irradiation induces improvement of the properties of the films based on bean protein–bean starch systems [31, 32]. Moreover, substitution of the non-irradiated starch by the irradiated one in the composition of the films based on bean proteins was found to improve the properties of such films [15].

Starch is an abundant and cheap biopolymer containing two polysaccharides: amylose constituting a linear chain of D-glucose units, and a branched amylopectin. Native starches (excluding those genetically modified) contain normally 20–30 wt.% of amylose. For example, the average amylose content in potato starch reaches ca. 23 wt.% and in wheat starch 26–31 wt.% [2]. The average polymerization degree of potato amylose is equal to ca. 3200 and that of wheat starch to ca. 2100, while amylopectin molecule might contain several dozen thousands of glucose units, with the branch chains length of 15–40 glucose molecules [2].

Starch, in particular high amylose starch, is known to have a good film forming properties and forms films with a good mechanical resistance [10, 14, 17, 19]. In particular, potato starch is the appropriate material for preparation of the edible and biodegradable films and coatings. Such materials are widely applied in both food industries and technical industries. Disadvantage of the films based on native starches is, however, their high hydrophilicity [10, 14, 17]. Moreover, elastic properties of starch films might be insufficient [14, 17, 19]. As film forming capability and the quality of the resulting films depend on the molecular structure of starch, modifications of starch are performed applying various physical and chemical methods. Among others, it was discovered that the better starch-based films that found practical application can be obtained when starch hydrolizates (i.e. dextrins) [14, 17, 19] are used, as well as simultaneously oxidized and partially degraded starches [1, 13, 17]. Therefore, while both the processes: degradation and oxidation might be induced under the influence of irradiation, it appears possible to adopt radiation treatment for improvement of the starch films properties.

Principal process occurring in starch under the influence of gamma irradiation is polysaccharide degradation occurring due to break down of glicosidic linkages [11, 26, 27]. Apart from the formation of smaller macromolecules, the small molecular products are formed as a result of disruption the glicosidic linkages near the macromolecules endings [26, 27]. Simultaneously, oxidization processes taking place in the resulting smaller macromolecules as well as in the water soluble dextrins and sugars, lead to the formation of carboxylic acids, aldehydes and alcohols. Additionally, water, hydrogen peroxide and some gaseous products are formed (CO_2, H_2) [16, 25]. The content of water-soluble dextrins and total acidicity of the products obtained after irradiation of the native starches have revealed a linear dependence on the dose applied in the range 1–20 kGy [22, 24, 26, 27]. In general, the content of water-soluble products formed after application of such doses is not very high. However, using a 50 kGy dose leads to the formation of ca. 6.5% of water-soluble products composed in 76% of glucose [22]. It was also found that the carboxylic acid content was the highest in the products when the water content in the solid starch was nearest to that labeled at the equilibrium with air [26, 28].

Raffi *et al*. [27] and Michel *et al*. [22] have proved the linear dependence between the radiation dose and the inverse of logarithm of the starch gels viscosity (connected with a decrease in the macromolecules weight). Following their results we have discovered a linear decrease in swelling power of starch accompanied with an increase of the dose [4, 5]. Decrease in volume of gel (prepared under the same conditions using irradiated and non-irradiated samples) reached ca. 2.8 and 1.5 fold in the case of potato and wheat starches, respectively, after irradiation performed using a dose of 30 kGy [4, 5]. Simultaneously, a ca. 6 fold increase of the absorbance of the polyiodine complexes formed by water-soluble products (blue value) observed in both cases [5] indicated the essential presence of such products in the irradiated species.

Improvement of the barrier properties of biopolymer films might be achieved by addition of hydrophobic compounds, for example, lipids or surfactants to their composition [9, 10, 12, 14]. Furthermore, it was found that the films containing homogeneously distributed lipids might appear a better barrier as compared to the laminated ones [14], and in some cases also mechanically stronger [33]. Thus, it seems possible to reduce also hydrophilicity of starch films applying the appropriate starch-lipid or starch-surfactant composition. On discussing that problem, it is worthy of mention, however, that the addition of hydrophobic compounds (lipids) to the biopolymer films composition is reported to results in the increased flexibility of the films [30, 34], as well as in the increased brittleness [35].

The present studies concerned the effect of irradiation performed for starch on the properties of the films, prepared using that starch with a various content of glycerol as a plasticizer (0, 20 or 30% in terms of starch mass). The potato starch representing B type starch (crystalline fraction of B type, free of lipids) and wheat starch, containing naturally occurring lipids (A type starch) were selected. It was found that a decrease in molecular weight induced after irradiation performed at a 10 kGy dose for those particular samples, causes respectively, a 5.5 fold and 2.7 fold decrease of the viscosity of the gels prepared using these starches [4]. When a dose of 20 kGy was applied, ca. a 5.5 fold decrease in viscosity of wheat starch gels was already detected [4]. Apart from the starch-glycerol systems, the films based on potato starch, glycerol and the admixed surfactants were examined. The following compounds

were selected: sodium laurate, sodium palmitate and CTAB. Two fatty acid salts represent anionic surfactants while CTAB is a cationic surfactant. With the purpose to obtain appropriate homogeneity of material, complexation of surfactant with starch was carried out before the preparation of the films. The influence of the prolonged storage and conditioning in an atmosphere characterized by varying humidity was determined on the properties of the films with modified compositions.

With the purpose to select appropriate conditions for comparative testing of the film properties, examination of the influence of atmosphere humidity applied during conditioning (relative humidity RH = 56, 43 or 33%) on the results of the mechanical tests were performed in the preliminary stage of experiments. This regards the sensitivity of the properties of the films, in particular, those containing surfactants, to the storage atmosphere. On the one hand, it appears advisable to secure in the sample the appropriate high content of moisture, acting as plastificator and enabling to perform the mechanical tests. On the other hand, conditioning in the atmosphere with humidity similar to that of the laboratory, enables to avoid changes of the sample properties directly before the measurements. Such tests were performed for the selected films, prepared using the non-irradiated potato starch and that irradiated applying a 30 kGy dose, as well as for the appropriate films containing the addition of sodium laurate. It was then decided to carry out further experiments for the samples conditioned at RH = 56%, with minimizing of the time when the sample was kept in air before the measurements. The reason of such a choice was the fact that some films conditioned in the atmosphere of lower humidity became rather brittle, especially after prolonged storage. In the last stage of experiments, mechanical tests and wetting angle measurements were performed simultaneously for the selected series of the films, prepared using starches irradiated applying various doses (5÷30 kGy) and conditioned at RH = 56%.

Experimental

Materials, irradiation and the preparation of films

Potato and wheat starch of Sigma production (S-4251 and S-5127, respectively) were used for the films preparation. Wheat starch contains ca. 11.7 wt.% of adsorbed water and potato starch contains ca. 14.8 wt.% of adsorbed water. Sodium laurate and sodium palmitate from Fluka, CTAB from Aldrich and the analytical grade glycerol were also used, as well as deionized water.

Irradiations of starch were carried out with Co-60 gamma radiation in air at ambient temperature in a gamma cell Issledovatel placed in the Centre for Radiation Research and Technology, Institute of Nuclear Chemistry and Technology (INCT), Warsaw. The starch samples closed tightly in polyethylene bags were irradiated with doses of 5, 10, 20 and 30 kGy applying a dose rate of 0.36 $Gy \cdot s^{-1}$. The average dose rate in the source was determined using a Fricke dosimeter. The dose absorbed by material was determined using an alanine dosimeter analysed by the EPR method.

Surfactant complexation and the films preparation

Films were prepared by casting from the gelatinized starch or starch surfactant solutions. With the purpose to improve the flexibility of the films, glycerol was added into their compositions (0, 20 or 30 wt.% of glycerol in terms of starch mass). Glycerol was introduced to the film forming solution after gelatinization and complexation prior to the films casting (procedure I) or before starch gelatinization (procedure II). Procedure I was applied in the case of all films prepared without surfactant addition. The aliqout of 11 ml of the final starch solution (2%) or 13 ml of starch-surfactant solution (1.69%) were pipetted on polystyrene Petri dishes with a diameter of 90 mm and allowed to dry at ambient temperature. Then, the films were peeled from the substrate, dried and conditioned before the mechanical as well as wetting angle testing for 6 days at the required relative humidity (RH = 33, 43 or 56%; in a dessicators over saturated solutions of $MgCl_2$, Na_2CO_3 or NaBr, respectively).

With the purpose of preparation of potato or wheat starch films, gelatinization was performed by heating of starch suspensions (2 wt.%), with intermediate mixing during 2 h in a heating chamber kept at 100°C.

In order to obtain starch-surfactant connections, potato starch-surfactant solutions containing 0.038÷0.075 g of the surfactant per 1 g of starch (g/g) were prepared. This corresponds to 0.136–0.222 mmol/g, depending of the surfactant and its amount used. Starch was pregelatinized in the heating chamber at a temperature of 90°C for 1.5 h. The surfactant solution was then added slowly during intensive mixing with a magnetic stirrer at 80°C, and mixed for the next 2 h. Heating at 90°C was continued afterwards in a heating chamber during 6 h. The selected starch-surfactant ratios used enable to obtain a homogeneous system after performing the procedure with no surfactant excess observed either visually or röntgenographically [4]. An example of the typical X-ray diffraction pattern recorded for the potato starch-surfactant systems is shown in Fig. 1.

The films thickness was equal to ca. 95±15 μm.

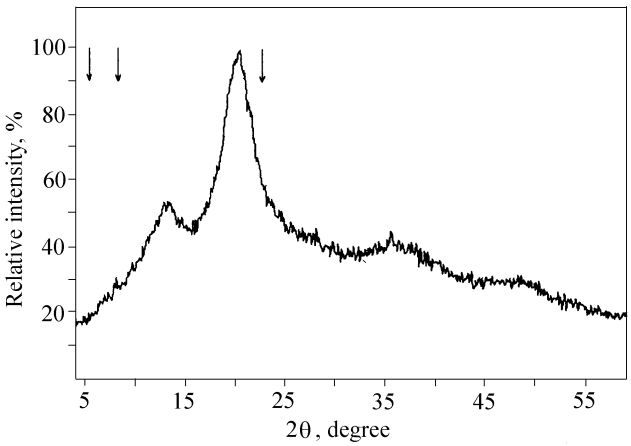

Fig. 1. X-ray diffraction pattern recorded for the connections of potato starch with sodium laurate (0.049 g/g corresponding to 0.222 mmol/g), prepared basing on non-irradiated potato starch and used for the films production. The arrows shows possible positions of the strong and narrow reflections of the crystalline sodium laurate.

Methods

Mechanical tests

Mechanical tests (determination of tensile strength, elongation at break and Young Modulus) were carried out using the Instron testing machine, type 5565, for pieces of films with dimensions ca. 70 × 9 mm. The ramp velocity was 5 mm/min. The appropriate parameters were calculated on the basis of 4–6 measurements (depending of reproducity) performed for the pieces of films of each composition, cut from three separate samples. The low value of Young Modulus shows a high film elasticity.

In the next sections terms "higher flexibility" or "lower flexibility" are used with the purpose to express a higher or lower elongation at break (Δl, (%)).

The wetting angle measurements

The wetting angle measurements (enabling to evaluate the hydrophilic/hydrophobic properties) were done using the instrument constructed in the Laboratory of Materials Research, INCT. A water drop (volume of 5 μl) was placed on the film surface and the drop shape was analysed. The wetting angle was calculated for each individual drop accordingly to the following equation:

$$(1) \qquad \upsilon = \text{arc} \cdot \cos \cdot \{[1 - (h/r)^2] / [1 + (h/r)^2]\}$$

where h and r mean the height and radius of the drop basis, measured for its magnified image.

The average values were then calculated on the basis of 12–15 measurements, performed for three separate samples of each composition.

In the next sections, the terms "hydrophilicity" or "hydrophobicity" as well as "hydrophilic" or "hydrophobic" properties are used with the purpose to describe the comprehensive capability of the films for wetting with water.

Scanning electron microscopy (SEM)

SEM studies were conducted using a DSM 942 Scanning Electron Microscope (Zeiss-Leo production) at ambient temperature for the samples covered with a thin gold layer. The films were submitted to chemical treatment with glutaraldehyde, dehydrated in water-ethanol solution and kept in acetone at 4°C prior to the SEM examinations. SEM photos (at magnification 1000×) were taken for the fracture of the films placed in a holder in such a way that the surface of the film was parallel to the top of the picture.

X-ray diffraction

Studies were performed using a URD6 diffractometer (Carl Zeiss Jena) with an IRYS-3M generator. CuK_α radiation (Ni filtered, $\lambda = 1.54178$ Å) was employed with a tube voltage of 34 kV and a tube current of 18 mA. The measurements were carried out using the step scanning method with a step of $2\theta = 0.1$ and a counting time of 10 s.

Results

Potato starch films

Table 1 presents the results of the comparative mechanical tests, performed for the films prepared basing on potato starch, non-irradiated and that irradiated applying a 30 kGy dose, after simultaneous storage followed by conditioning at a modified relative humidity. The films formed after irradiation were characterized generally by the higher tensile strength and higher flexibility (shown by the higher values of Δl), as compared to the non-irradiated films submitted to the same treatment. It happens independently of the atmosphere of conditioning applied before the measurements.

The values of Young Modulus of potato starch films were in the range predicted for this type of material [20].

Table 1. Comparison of the mechanical properties of the films, prepared using the non-irradiated potato starch and the starch irradiated with the 30 kGy dose and stored simultaneously in the same condition of the relative humidity. The measurements were performed: 8 weeks[a]; 10 weeks[b]; 12 weeks[c]; 14 weeks[d] – after peeling of the films

No	Dose (kGy)	Relative humidity, RH (%)	Tensile strength (MPa)	Elongation at break, Δl (%)	The average value of the Young Modulus (MPa)
I	II	III	IV	V	VI
			20% of glycerol		
1[b]	0	33	34.3 ± 4.0*	4.6 ± 1.0*	1079
2[b]	30	33	52.4 ± 1.2	7.5 ± 0.5	1113
3[c]	0	43	44.2 ± 2.0	9.1 ± 1.0	1151
4[c]	30	43	56.3 ± 1.2	7.4 ± 0.5	1488
5[a]	0	56	25.4 ± 0.7	6.8 ± 0.4	1000
6[a]	30	56	34.6 ± 0.7	7.1 ± 0.6	813
			30% of glycerol		
7[b]	0	33	31.6 ± 2.0	5.30 ± 0.3	856
8[b]	30	33	37.5 ± 0.5	7.60 ± 0.0	998
9[d]	0	56	22.2 ± 1.0	6.50 ± 1.0	763
10[d]	30	56	26.8 ± 1.0	11.40 ± 0.2	810

* – The data present only terminal value, achieved before the brittle failure of the material.

Table 2. The results of the mechanical tests performed for the films, prepared basing on potato starch, non-irradiated and irradiated using doses in the range 5–30 kGy. Prior to measurements the films were conditioned several days at a relative humidity of 56%. The measurements were done 5 months after the films preparation

No	Dose (kGy)	20% of glycerol		30% of glycerol	
		Tensile strength (MPa)	Elongation at break, Δl (%)	Tensile strength (MPa)	Elongation at break, Δl (%)
I	II	III	IV	V	VI
1	0	32.3 ± 1.1	6.4 ± 0.5	24.9 ± 1.9	7.8 ± 0.6
2	5	40.6 ± 3.3	7.4 ± 0.5	28.3 ± 1.2	8.6 ± 0.9
3	10	36.8 ± 1.2	8.2 ± 0.4	31.0 ± 1.1	9.5 ± 1.1
4	20	41.4 ± 0.8	9.3 ± 0.8	27.9 ± 1.7	8.9 ± 0.3
5	30	nd*	nd*	28.1 ± 0.3	9.6 ± 0.4

* – not determined, because of the film breaking.

These values varies from 763 to 1488 MPa, depending on the glycerol content and conditions of storage and appear slightly higher in the cases of the irradiated samples, indicating a slightly decreased film elasticity (examples in Table 1).

Mechanical tests, performed after 5 months of storage simultaneously for the films, prepared using starch irradiated with doses in the range 5–30 kGy, have confirmed, in general, the conclusion concerning the increase in tensile strength and flexibility of the films, occurring due to irradiation (Table 2). Simultaneously, comparison of the data presented in Tables 1 and 2 showed that the films, irradiated with a 30 kGy dose and characterized by a high flexibility in a short period after casting, lost this property during storage and, as a result, became rather brittle. On the contrary, none noticeable modification of the films flexibility was detected in the case of non-irradiated starch.

Storage at low as well as high humidity for the period longer than 3 months does not induce essential modification of the tensile strength of the films (Table 1, column IV, points 9, 10 and Table 2, column V, points 1 and 5). The increase in tensile strength occurs, however, after a shorter storage (i.e. Table 1, column IV point 5 and Table 2, column III, point 1).

Mali *et a*l. [20] have attributed the similar modification mechanical properties of starch films, occurring during storage in an atmosphere of high humidity, to the starch recrystallization. However, this explanation seems to need verification, considering that the crystalline phase content in starch might be controlled in a reversible way by conditioning in the atmosphere of the required humidity [6, 23]. Moreover, it appears possible that the properties alteration occurs due to evacuation of the plasticizing agents and that the process might be facilitated in the case of the irradiated samples, as compared to the non-irradiated ones [4].

As a result, the optimal mechanical properties after 5 months of storage have revealed the films prepared basing on the starch irradiated with a dose of 20 kGy and containing 20% of glycerol (Table 2).

The results of wetting angle measurements, carried out after 5 months of storage, have indicated that irradiation causes a decrease in hydrophilic properties of potato starch films. The υ values obtained for the films, prepared basing on the non-irradiated starch and that irradiated using a 30 kGy dose, both containing 30% of glycerol, were equal to 42.0° ± 3.4° and to 63.3° ± 1.2°.

The improvement of the films properties due to irradiation can be related to the improvement of the compactness of the irradiated species, as compared to the non-irradiated ones [4]. In the SEM images of the fracture of the films based on the non-irradiated starch, the rectangular blocks might be noticed with the cracks parallel to the film surface (the example in Fig. 2). No cracks were observed in the fracture of the

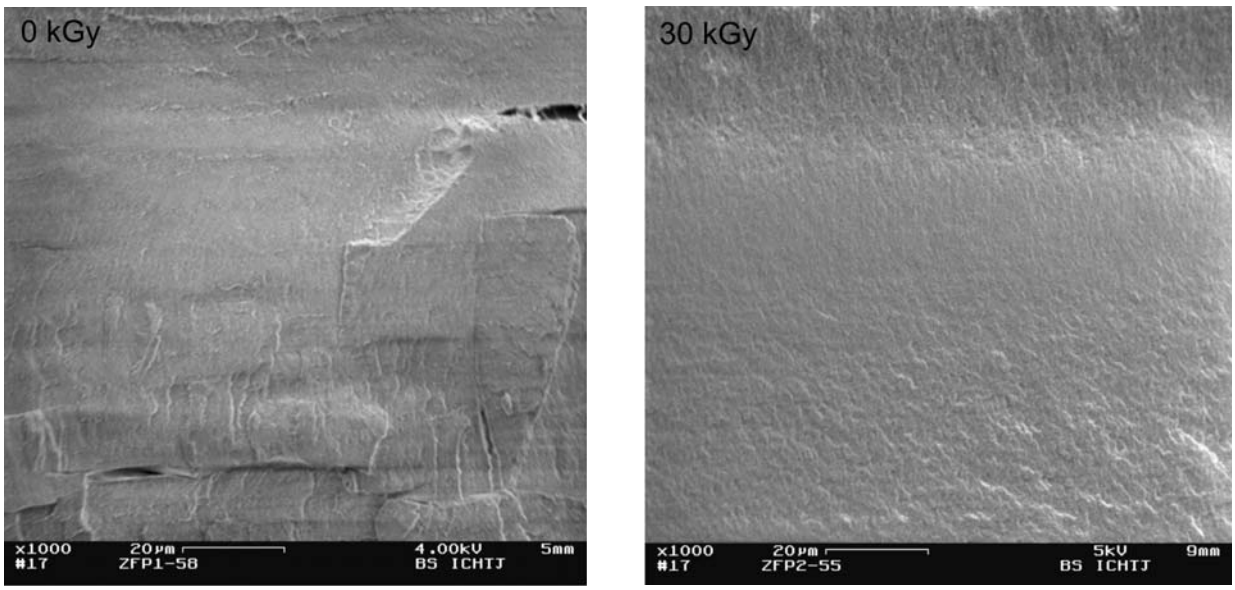

Fig. 2. SEM images of the fracture of the films prepared using potato starch and 30% of glycerol.

irradiated specimen (Fig. 2). The irradiated films appear smoother, more homogeneous and reveal more particulate structure, with only slight orientation of the very small structural elements. Accordingly, the denser packing of material might be concluded in the case of the irradiated films, as compared to the non-irradiated ones.

The films prepared basing on potato starch-surfactant systems

The films based on the irradiated starch, in particular those with high glycerol content, revealed considerably stronger adhesion to the polystyrene surface as compared to the appropriate non-irradiated products. These films stayed also longer on the substrate, in regard to the difficulties with peeling. After peeling and drying, however, a majority of the films prepared basing on the irradiated starch, became more brittle than the non-irradiated films. In general, the irradiated films were characterized by a high flexibility in the conditions of high humidity, however the loss of flexibility in air was observed the sooner the higher was the radiation dose.

Small elongation at break of the films containing surfactants (both lipid derivatives or CTAB) and submitted to drying and prolonged storage, corresponds to the data showing that addition of the lipids led to the preparation of brittle biopolymer films [35]. On the other hand, high Δl values determined for the newly obtained films are indicative of the plasticizing effect of lipids on the polysaccharides films [30, 34].

Potato starch-sodium laurate films

Films of a good quality were obtained with addition of 0.049 g/g of sodium laurate (0.222 mmol/g of starch). Within a week after peeling and conditioning at RH = 56%, the films formed using both the non-irradiated and the irradiated starch with addition of 30% of glycerol (applying the I experimental procedure) have appear less "hydrophilic" as compared to the appropriate films, prepared without the surfactant addition. The films irradiated using a 30 kGy dose revealed a considerably higher flexibility and lower hydrophilicity than the films prepared basing on the non-irradiated starch, with a slightly decreased tensile strength. Accordingly, the irradiated films have appeared "hydrophobic" (Table 3, points 1 and 2).

The results of examination repeated 5 months after preparation of the films indicated an increase in tensile strength of the both films accompanied by a decrease in flexibility (Table 3, points 3 and 7), similar to the cases of the films prepared without surfactant addition. Simultaneously, a decrease in the capability of the films for wetting with water took place.

As a result of the occurring changes, the films prepared basing on the irradiated starch have appeared less flexible than the films prepared basing on the non-irradiated starch. However, the irradiated films still revealed stronger hydrophobic properties than the non-irradiated ones.

Table 3. The results of the mechanical and wetting angle tests performed for the films, prepared basing on potato starch with addition of sodium laurate (0.049 g/g corresponding to 0.222 mmol/g), non-irradiated and irradiated. The films were simultaneously stored and conditioned at a relative humidity of 56%

No	Dose (kGy)	Tensile strength (MPa)	Elongation at break, Δl (%)	The average value of the Young Modulus (MPa)	The average υ value (°)
I	II	III	IV	V	VI
		I experimental procedure, 30% of glycerol, 1 week after preparation of films			
1	0	3.57 ± 0.54	18.4 ± 1.4	156	58.4
2	30	2.56 ± 0.20	32.6 ± 2.7	88	100.4
		I experimental procedure, 30% glycerol, 5 months after preparation of films			
3	0	24.0 ± 3.0	3.9 ± 0.8	862	84.3
4	5	16.6 ± 0.9	3.2 ± 0.2	841	108.2
5	10	17.4 ± 2.0	3.2 ± 0.3	789	108.2
6	20	8.8 ± 0.6	2.8 ± 0.5	516	110.2
7	30	6.6 ± 1.0	1.5 ± 0.3	448	109.6
		I experimental procedure, 20% glycerol, 5 months after preparation of films			
8	0	28.8 ± 1.9	4.4 ± 0.1	819	84.7
9	5	27.4 ± 1.3	3.4 ± 0.2	1191	–
10	10	26.4 ± 1.1	2.8 ± 0.2	1164	91.9
11	20	16.1 ± 1.0	2.0 ± 0.1	1272	92.4
12	30	10.7 ± 3.4	1.4 ± 0.1	1538	102.8
		II experimental procedure, 30% glycerol, 5 months after preparation of films			
13	0	25.8 ± 1.0	4.5 ± 0.2	1106	93.9
14	5	14.7 ± 1.0	3.4 ± 0.1	612	104.3
15	10	15.3 ± 1.3	3.6 ± 0.3	805	111.1
16	30	9.2* ± 0.3	1.4* ± 0.5	756	–

* – The data present terminal values achieved before the brittle failure of the films. In the cases of the films containing 20% of glycerol the plateau step was not observed on the curves elongation – strength before breaking of the films. The υ value equal to 115.4° was determined for the film prepared applying to the second experimental procedure basing on the starch irradiated with 20 kGy dose.

Table 4. The results of the mechanical and wetting angle tests performed for the films, prepared basing on potato starch with addition of CTAB (0.075 g/g corresponding to 0.206 mmol/g). The measurements were done 5 months after preparation for the films conditioned at RH = 56%

No	Dose (kGy)	Glycerol content (wt.%)	Tensile strength (MPa)	Elongation at break, Δl (%)	The average υ value (°)
I	II	III	IV	V	VI
1	0	20	14.4 ± 1.0	4.80 ± 0.5	43.3
2	30	20	12.0 ± 1.3	3.20 ± 0.3	63.8
3	0	30	5.0 ± 0.4	8.30 ± 1.0	40.0
4	30	30	1.1 ± 0.2	12.00 ± 0.5	73.3

The studies were continued for the films irradiated with doses in the range 5–30 kGy (prepared applying experimental procedures I and II) and stored before the measurements during 5 months. Tensile strength and elongation at break of the films have appeared to be lower when the irradiation dose was higher, as well in the case of the films containing 20 and 30% of glycerol (Table 3, points 3–7), and independently whether the glycerol was introduced before or after the complexation procedure (Table 3, points 3–7 and 13–16). The Young Modulus value decreased in the case of the films containing 20% of glycerol, following the increase in a dose applied for the starch irradiation, but increased in the case of the films containing 30% of glycerol.

The results of measurements performed at the same time have confirmed an increase in hydrophobic properties of the films, induced by starch irradiation (Table 3).

Potato starch-CTAB films

The films were prepared applying experimental procedure I, basing on potato starch irradiated with a 30 kGy dose and the non-irradiated starch with CTAB addition of 0.075 g/g (0.206 mmol/g). These films have revealed a strong adhesion to the polystyrene surface and peeling of the films containing 30% of glycerol was realized only after drying in vacuum. The films containing 30% of glycerol, irradiated or non-irradiated, preserve a high flexibility even after few months of storage (Table 4), and the irradiated sample was still more flexible as compared to the non-irradiated one.

Irradiation led also to decrease in "hydrophilic" properties of these films (Table 4).

Potato starch-sodium palmitate films

Experimental procedure I was applied for the preparation of films containing palmitate addition of 0.061, 0.046 and 0.038 g/g (corresponding to 0.219, 0.165 and 0.136 mmol/g) and potato starch irradiated with a 30 kGy dose and non-irradiated.

It was noticed that the direction of the irradiation influence on the properties of the potato starch-sodium palmitate films depends on the surfactant content and glycerol content. For example, in the case of the non-irradiated films containing palmitate at a level of 0.038 g/g, the wetting angle value was the lower, the higher was the glycerol content. On the contrary, in the case of films based on the irradiated starch, the higher υ value was associated with the higher glycerol content (Table 5). The "hydrophobic" films were obtained basing on this system after irradiation and addition of 30% of glycerol. These films have revealed better hydrophobic properties than the film of the same surfactant content and prepared basing on the non-irradiated starch without addition of glycerol (Table 5, columns III and V).

The higher wetting angle value (equal to 104.2°) was also observed for films prepared with 30% of glycerol basing on potato starch and the palmitate addition of 0.038 g/g, as compared to the value of 47.8° obtained for the films of larger palmitate content (0.061 g/g) (Table 5). Moreover, a comparison of the data shown in Table 5 leads to the conclusion, that it is possible to obtain "hydrophobic" films basing on the irradiated starch with a smaller content of palmitate than the possible "hydrophobic" films prepared using the non-irradiated starch (Table 5, column V, point 2 and column VI, point 1).

The above composition effects seem to be connected to the tendency of the films for breaking (observed visually). In fact, in the case of the brittle films the water drop does not swell on the surface but penetrates through the pores. Therefore, the higher υ values correspond to the lower tendency for breaking, thus to the smaller porosity induced in the films.

Wheat starch films

Films of good quality were obtained with addition of 30% of glycerol. The measurements were performed 5 months after preparation of the films which were

Table 5. The average υ values, determined for the films containing potato starch and sodium palmitate

Lipid:starch (g/g)		0.038	0.038	0.038	0.061	0.046
No	Dose (kGy)	Glycerol content				
		0%	20%	30%	30%	0%
I	II	III	IV	V	VI	VII
1	0	87.0	75.5	71.1	115.1	79.4
2	30	75.2	90.4	104.2	47.8	80.5

Table 6. The results of mechanical tests, performed for the films prepared basing on wheat starch, non-irradiated and irradiated. The measurements were performed 5 months after preparation for the films conditioned at a relative humidity of 56%

No	Dose (kGy)	Tensile strength (MPa)	Elongation at break, Δl (%)
I	II	III	IV
		30% of glycerol	
1	0	6.5 ± 1.9	26.5 ± 1.6
2	5	6.4 ± 0.9	18.0 ± 2.2
3	10	7.1 ± 0.8	23.8 ± 1.1
4	20	9.6 ± 0.7	10.2 ± 1.7
5	30	14.3 ± 1.6	8.0 ± 1.2
		20% of glycerol	
6	0	18.2 ± 2.5	4.0 ± 0.6

conditioned at RH = 56%. The higher values of tensile strength were determined for those films for which the irradiation dose was higher. Although the increase in the films strength was accompanied by a decrease in flexibility, those films were still quite flexible even after applying an irradiation dose of 30 kGy (shown by a relatively high Δl values). The irradiated films were also less "hydrophilic" than the non-irradiated ones. The average υ values, determined in the case of the non-irradiated films and those irradiated with a 30 kGy dose were equal to 57.2° and to 83.9°.

Mechanical data obtained for the wheat starch films containing 0 or 20% of glycerol are not reported, because of the brittleness failure occurring during the measurements (excluding the films based on non-irradiated starch, characterized by a relatively high strength and low Δl value, Table 6 point 6).

Discussion

Dependence of the direction of the irradiation influence on the hydrophilic/hydrophobic properties of the potato starch-surfactant films and on the surfactant content and glycerol content indicates that the compactness of the films is a major factor influencing their capability for wetting with water. In fact, the wetting angle data might not correspond in the case of brittle films to the hydrophilic/hydrophobic properties of raw material, because of the facilitated permeability of the water drop through the induced cracks. Although the higher content of plastificator is expected to result in an increase of hydrophilic properties of the starch films and the increased capability for water adsorption [21], it was stated at present that the films containing irradiated starch and surfactant might be characterized by the reduced capability for wetting with water when glycerol content was the higher. Similarly, application of the composition characterized by a minor content of hydrophobic compound (i.e. sodium palmitate) might appear profitable for obtaining more "hydrophobic" films, as compared to the composition with a higher content of such compound, in regard to the smaller brittleness of the resulting material.

It was confirmed that the improved compactness of potato starch films, resulting due to irradiation (shown by SEM), constitutes the reason of reduction of their capability for wetting with water [4], despite that radiation processes led to the formation of hydrophilic carboxyl groups in the starch. On the other hand, reduced comprehensive "hydrophilic" properties of those films might be related to the reduced ability of native starch for water adsorption, accompanied by a decrease of the crystalline ordering, discovered after irradiation [6].

Moreover, it seems worthy of mention, that the better compactness of the films was observed after irradiation for the films prepared basing on the selected starch-surfactant systems [4].

Confrontation of the results, obtained after prolonged storage for wheat starch films with data obtained for potato starch and potato starch-admixed fatty acid salt systems, suggests that the decrease in flexibility of wheat starch films, resulting due to irradiation, is probably connected to the presence in those films of naturally occurring fatty acids. On the contrary, a simultaneous increase in tensile strength of wheat starch films remind the increase of tensile strength observed in the case of the films prepared using potato starch alone (thus containing no lipids nor surfactants) while irradiation induces a decrease in tensile strength of potato starch containing surfactants.

Analysis of the presented data concerning the properties of the starch and starch-surfactant films shows the possibilities of modification of the film parameters by modification of their composition and the irradiation conditions. For example, in the films containing CTAB and 20% of glycerol (Table 4, points 1 and 2) it was possible to reduce their "hydrophilic" properties by irradiation (30 kGy) without an essential modification of the mechanical properties. On the other hand, reduction of "hydrophilicity" after irradiation of the films containing 30% of glycerol accompanies a considerable improvement of their flexibility and deterioration of strength (Table 4, points 3 and 4). Possibilities of modification of the properties of potato starch-sodium palmitate films are discussed in the 'Results' section.

Irradiation seems to be helpful, in particular, for improvement of the flexibility of the starch-hydrophobic compound barrier acting in the condition of high humidity. A high "hydrophobicity" as well as a high adhesion to the substrate and a high flexibility, preserved even after a prolonged storage in atmosphere of high humidity, might predestine the films, prepared using the irradiated starch and possible surfactant (and probably

as well lipid) addition for application as coatings for the products, characterized by a relatively high humidity and/or a short time of serviceableness (determined as a shelf-time), thus such as a low-moisture food.

Conclusion

The results show the radiation-induced improvement of hydrophobic properties of the films prepared using potato and wheat starch, and the selected potato starch--surfactant composition. The films prepared basing on the irradiated potato starch have revealed improved both the strength and flexibility, as compared to the non-irradiated ones, during several weeks of storage. In the case of wheat starch films, the increase of strength was accompanied by a decrease in flexibility. As wheat starch films (with 30% of glycerol) reveal after irradiation still a good flexibility, radiation treatment might appear a proper method for improvement also of those film properties and, consequently, for possible qualifying of wheat starch for edible packaging.

The improvement of the functional properties of potato starch films achieved due to irradiation are connected to the improvement of their compactness and homogeneity (indicated by SEM).

Introduction of sodium laurate to the composition of potato starch films results in decreased "hydrophilicity" and application of the irradiated starch lead to preparation of the "hydrophobic" films. The increase in the plasticizer content might result in a decrease in "hydrophilic" properties of starch-surfactant films, in regard to their reduced brittleness and therefore, to the limited induced porosity.

Decrease in flexibility leading to general deterioration of the mechanical resistance of the films might occur faster in some films based on the irradiated starch than in the cases of the appropriate non-irradiated specimens.

The sensitivity to storage conditions of mechanical properties of the "hydrophobic" films based on the irradiated potato starch and sodium laurate suggests that these materials can be useful for packaging of the products stored at a high moisture level and/or during a relatively short time, thus the films appear appropriate for food systems.

Analysis of the results obtained in the present studies might be helpful for further preparation of films revealing the parameters required for particular applications of the appropriate modification of their composition and the control of irradiation conditions.

For more detailed explanation concerning the relationship between physicochemical and functional properties of the films and the films microstructure further studies are needed.

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