



# The influence of ionizing radiation on the properties of starch-PVA films

Anna Abramowska,  
Krystyna A. Cieśla,  
Marek J. Buczkowski,  
Andrzej Nowicki,  
Wojciech Głuszewski

**Abstract.** The cornstarch: poly(vinyl alcohol) (PVA) films characterized by the alternating ratio of starch:PVA (100:0, 80:20, 60:40, 40:60, 20:80, and 0:100) and containing 30% of glycerol were prepared by solution casting. The films were irradiated with an absorbed dose of 25 kGy with gamma rays in a vacuum and with fast electrons in the air. The films characterized by a high content of starch appeared stiff, while the films characterized by a high content of PVA were highly flexible. The tensile strength and flexibility, as well as swelling and hydrophilicity, increased with the increase in the PVA content in the films. However, the tensile strength and wetting angle values achieved a minimum at an intermediate composition. It was found that irradiation enables to reduce hydrophilicity of the films accompanied by a decrease in their flexibility. No general conclusion concerning the effect of irradiation on tensile strength and swelling behavior can be derived. An increase in the homogeneity of the films and an increase in the compatibility of their components was found by scanning electron microscopy (SEM). Strong interactions of the starch and the PVA components were discovered by diffuse reflectance spectroscopy. Degradation was found to be the prevailing process occurring in the films under the influence of irradiation. The possible accompanying crosslinking is discussed in terms of the gel content in the samples. Creation of various oxidation products in the films characterized by the modified composition was observed under the influence of irradiation carried out in the air. Basing on the obtained results it can be supposed that the selected starch-PVA compositions might appear useful as packagings of the products predicted for radiation decontamination.

**Key words:** starch • poly(vinyl alcohol) • films • ionizing radiation • mechanical properties • physicochemical properties

A. Abramowska, K. A. Cieśla✉, M. J. Buczkowski,  
A. Nowicki, W. Głuszewski  
Institute of Nuclear Chemistry and Technology,  
16 Dorodna Str., 03-195 Warsaw, Poland,  
Tel.: +48 22 504 1106, Fax: +48 22 811 1532,  
E-mail: k.ciesla@ichtj.waw.pl

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## Introduction

The increasing interest in substitution of traditional packagings (films, foams and coatings) by the materials prepared basing on the natural and biodegradable polymers rises the need for searching for new and more environmentally friendly products. Preparation of such materials basing on the systems composed from various natural polymers (polysaccharides and proteins) and the mixtures of natural and biodegradable artificial polymers seems to be the perspective possibility. A variety of commercial biodegradable plastics are proposed at present on the market. The composition of these materials is often based on starch, chitosan, poly(vinyl alcohol) (PVA), poly(lactic acid) (PLLA), aliphatic-aromatic copolyesters (AAC) or polyhydroxybutyrate) (PHB).

Starch is an abundant and cheap biopolymer with a good film forming ability and therefore it appears to be an appropriate source for manufacturing of

cheap biodegradable packaging [1–8]. Thermo-plastic starch (TPS) (plasticized by presence of the components alike water or polyols) can be already processed alike synthetic polymers. However, although starch forms relatively strong films, mechanical properties of these materials are still worse as compared to artificial plastic, in particular that the higher strength of these films is connected with their insufficient elasticity. A serious disadvantage of such materials is their high affinity to water. Therefore, modified starches are commonly used to obtain better films as well as the trials for further surface modifications are conducted. Processes such as degradation, crosslinking, oxidation, etherification or esterification are usually induced by chemical or enzymatic methods. In particular, degradation of the starch (accompanied by oxidation) appears to be a desirable process enabling to obtain homogeneous and good quality coatings and films.

The other possibility is to blend starch with other natural polymers or with artificial biodegradable polymers. PVA is a biocompatible polymer with an excellent film forming ability [8–20] and a number of commercial PVA films are available in the market. Moreover, PVA forms films with perfect mechanical and gas barrier properties. PVA reveals also excellent compatibility with starch [8–20]. Although PVA is a hydrophilic polymer, similarly as starch, blending PVA with starch (or other biopolymers) produces better films as compared to the materials prepared using each component alone. Crosslinking technologies (with using crosslinking agents), or photocrosslinking are applied for reinforcing and reducing hydrophilicity of TPS or TPS/PVA blends or for their surface modification [16–18].

Ionizing radiation appears to be the appropriate techniques for modifying natural polymers as well as biodegradable artificial polymers. Ionizing radiation might be applied to induce degradation, crosslinking or grafting in the systems containing polysaccharide or PVA [18–31]. It is known that these processes (carried out for solution, paste-like state or for ready films) might lead to an improvement of the properties of the resulting films. Our previous results have also shown that radiation treatment might be adopted for altering the properties of the films formed using starch or a composition of starch with hydrophobic compounds [5, 6]. Modifications induced by irradiation allow to limit the use of strong chemicals and thus the processes are more friendly for the environment than chemical methods and less expensive as compared to enzymatic methods. Irradiation of the 'ready' films seems to have at present a high practical impact. This is because a sterile packaging material is obtained [29]. Simultaneously, the development of the methods of radiation decontamination of various commercial products involves requirements for appropriate resistance against irradiation of the materials applied for such products packing [32, 33].

Accordingly, the evaluation of the effect of irradiation on the possible packaging material appears to be highly important in relation to both: the search of new radiation based technologies for biodegradable

polymers modification and the search of appropriate resistant biodegradable packaging materials for the products subjected to radiation decontamination.

Single trials for improvement of the properties of the starch-PVA packaging by irradiation of the ready films with gamma rays were already carried out [19, 20]. In dependence on the films composition (starch and PVA substrate, starch to PVA ratio, plasticizer type and content, presence of the additives) and the condition of irradiation various irradiation effects on their mechanical properties were discovered. Senna *et al.* [19] have reported that an increase in the dose till 50 kGy results in an improvement of both the strength and the flexibility of the films formed at the starch:PVA ratio in the range from 75:25 to 95:5. However, the data presented by Parvin *et al.* [20] show that irradiation might induce a deterioration as well as an improvement of the films properties and that the application of the doses of ca. 20 kGy allows to obtain better material (characterized by the starch to PVA ratio of 35:65) as compared to the lower or the higher doses.

It was concluded that the improvement in the integrity of the starch-PVA blends resulting from gamma (or UV) irradiation [9, 17, 19] is caused by the formation of the hydrogen bonds between the OH groups of the starch (bound to C6) and the OH groups of the PVA macromolecules [9].

Our previous results have shown that, in regard to radiation induced oxidative degradation processes, the usage of the starches pre-irradiated with gamma rays enables to obtain films characterized by a higher homogeneity and better mechanical and barrier properties as compared to the films based on the native starches [5]. The improvement of the films' homogeneity resulted due to decreased viscosities of the gels obtained basing the irradiated starches [34, 35] at the intermediate step of preparation while oxidation seemed to be the crucial process improving the moisture barrier properties [5]. Moreover, the doses in the range of 10–20 kGy seemed to be optimal and the application of the dose of ca. 10 kGy has been sufficient for preparing films with good properties.

Our present study concerns the evaluation of the properties of the films formed in the starch-PVA system characterized by various starch:PVA ratios. Starch pre-irradiated with the dose of 10 kGy was applied for the films preparation. Furthermore, the influence of gamma and electron irradiation on the properties of the resulting films was evaluated. The absorbed dose of 25 kGy was selected in both cases for the films irradiation. This dose was chosen due to the fact that it was expected to be in the range of doses enabling to improve the films properties and, simultaneously, because such a dose is applied in the technological conditions for sterilization purposes. Therefore, the application of this dose allows to evaluate the effect of radiation sterilization on the potential packaging material. Mechanical properties of the films as well as their interaction with water (wetting angle to water and swelling) were examined and related to the films microstructure, possible interaction of the films components and to the occurring chemical processes.

## Experimental

### Materials and irradiation

#### Materials

Cornstarch (Sigma product S412) poly(vinyl alcohol) PVA (Merck 8148941001) with a mean molecular mass of 145 kDa and analytical grade glycerol (Chempur, Poland) were used. To induce starch degradation, solid specimen was pre-irradiated before the syntheses with  $^{60}\text{Co}$  gamma rays in the air with the absorbed dose of 10 kGy applying a dose rate of 5 kGy/h (see below).

#### Films preparation

Films with the content of starch-PVA in percentage ratios: 0:100, 20:80, 40:60, 50:50, 60:40, 80:20 and 100:0 were prepared by solution casting after the addition of glycerol as a plasticizer at the level of 30% in terms of the total polymer mass (altogether starch and PVA). PVA was dissolved in distilled water on the way of heating during 4 h at the temperature of 90°C. A 1.64% solution was obtained. Gelatinized cornstarch solutions (1.96 wt%) were obtained in the process of heating at the temperature of 90°C during 40 min. Using the starch pre-irradiated with a dose of 10 kGy has appeared the appropriate procedure for preparing the homogeneous starch gel solutions characterized by a sufficiently low viscosity, leading in consequence to the preparation of homogeneous films. To the contrary, using the non-irradiated starch caused the preparation of viscous starch gels even at such a low concentration (1.96%), and resulted in casting of the nonhomogeneous films. Glycerol was introduced into the starch suspension before starch gelatinization. PVA solutions were then added stepwise into the gelatinized starch dispersions and heated with a continuous stirring within the subsequent 1 hour. Afterwards, the films were cast onto polystyrene Petri dishes, dried during 20 h in the heating chamber at a temperature of 50°C and afterwards allowed to dry in the air at room temperature. The dried films were cast from the substrate and kept at room temperature at the relative humidity of 43% (in a desiccator above the saturated  $\text{K}_2\text{CO}_3$  solution) before further processing.

The films were then irradiated and conditioned before testing at a relative humidity of 43%.

#### Irradiation

Irradiations of the films were carried out at ambient temperature with the gamma rays ( $^{60}\text{Co}$ ) in a vacuum and by fast electrons in the air. The films packed in polyethylene bags were irradiated with the electron beam (EB). In both cases the absorbed doses were equal to 25 kGy.

Gamma irradiation was realized in the Gamma Chamber GC 5000 applying a dose rate of 5 kGy/h, while irradiation with electrons was carried out in the Elektronika 10/10 accelerator generating 10 MeV electron beam at an average dose rate of

approx. 3 kGy/min. Both these devices are installed in the Centre for Radiation Research and Technology, INCT.

### Methods

#### Mechanical tests

Mechanical tests (determination of tensile strength, elongation at break and Young modulus) were carried out using a Universal Testing Machine (Instron Model 5565) for pieces of films with dimensions ca.  $60 \times 10$  mm. The ramp velocity was 20 mm/min. The appropriate parameters were calculated on the basis of six to eight measurements (in dependence of reproducibility) performed for the pieces of films of each composition, cut from three separate samples. Low value of Young modulus shows high films elasticity.

In the next sections, terms 'higher flexibility' or 'lower flexibility' are used to express the higher or the lower elongation at break ( $\Delta l$ , %).

#### 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 Material Research, INCT. A water drop (volume of 5  $\mu\text{l}$ ) was placed on the film surface and the drop shape was analyzed. The wetting angle was calculated for each individual drop using the following equation:

$$\text{Wetting angle} = \arccos\{[1 - (h/r)^2]/[1 + (h/r)^2]\}$$

where  $h$  and  $r$  mean 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 at least three separate samples of each composition.

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

#### Swelling behavior

The pieces of films (with dimensions of  $10 \times 10$  mm) were weighted, immersed in the distilled water and kept for 24 h at a temperature of 25°C. Afterwards, they were drained with a blotting paper, re-weighted and dried at a temperature of 110°C (till constant mass was achieved). Swelling percentage was calculated applying the following formula:

$$\text{Swelling} = 100 \times (W_s - W_d)/W_d$$

where  $W_s$  and  $W_d$  mean the weight of the swollen sample (solid sample with the captured water) and the dried sample, respectively.

### Determination of gel fraction

The weight portions of the samples (ca. 150 mg) were cut into small pieces, immersed in distilled water and heated at a temperature of 105°C for 2 h, with intermediate stirring. The gel was then separated from the liquid phase by centrifugation. Liquid phase was transferred into the pre-weighted tube. Both the gel fraction and the liquid phase were dried at a temperature of 110°C till the constant mass was achieved, and re-weighted. The mass of the dried soluble part (Ws) and the mass of dried gel (Wg) were then calculated. The content of gel fraction [wt%] was determined accordingly to the following formula

$$\text{Gel fraction} = 100 \times (W_g)/(W_g + W_s).$$

### Diffuse reflectance spectroscopy

DRS studies were carried out applying Jasco V-670 Spectrophotometer equipped with the reflection device (Model ISN-723, integrating sphere 60 mm). Prior to the measurements, the films were irradiated with gamma rays in the air at ambient temperature with the absorbed dose of 25 kGy applying a dose rate of 5 kGy/h.

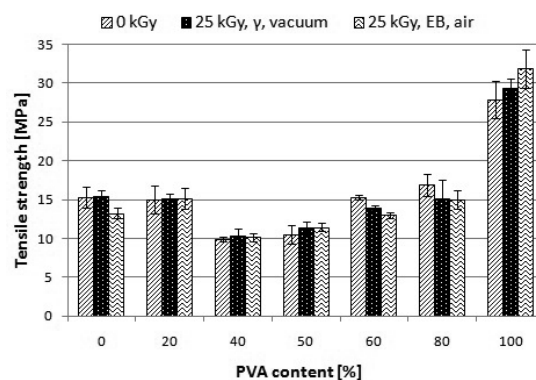
### Scanning electron microscopy

Scanning electron microscopy studies were conducted using the DSM 942 Scanning Electron Microscope (Zeiss-Leo production) at ambient temperature for the samples covered with thin gold layer. SEM photos (magnification of 1000×) were taken for fracture of the films placed in the holder in such a way that the surface of the film was parallel to the top of the picture.

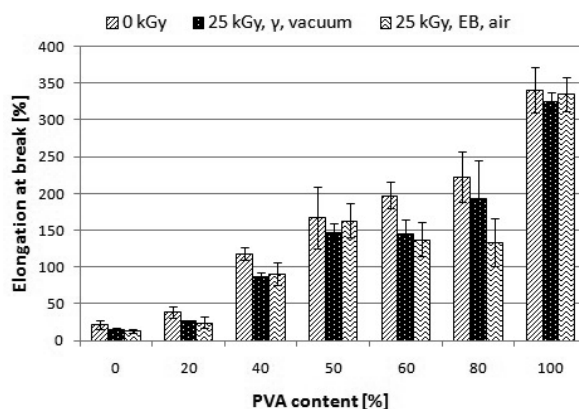
## Results and discussion

### Mechanical properties of the films

PVA films have revealed high tensile strength and high flexibility (Figs. 1 and 2). To the contrary, both these parameters were essentially lower in the case of starch films. Accordingly strength and flexibility of the starch films containing addition of PVA were higher as compared to the starch films while those of the PVA films containing addition of starch were lower as compared to the PVA films. Flexibility of the films decreased with the increase in the



**Fig. 1.** Tensile strength of the starch-PVA films, nonirradiated and irradiated with  $\gamma$ -rays (vacuum) or fast electrons (air) applying a dose of 25 kGy.



**Fig. 2.** Elongation at break of the starch-PVA films, nonirradiated and irradiated with  $\gamma$ -rays (vacuum) or fast electrons (air) applying a dose of 25 kGy.

content of starch in all the composition range, while tensile strength reached minimum values at the intermediate starch content (50–60% of starch) and then increased with the further increase of the starch addition. This probably occurs due to specific interaction between both the components leading just to physical blending or to formation of the hydrogen bonding in the system during the films preparation. Beside, participation of glycerol in formation of such a network should be considered. High values of the average Young modulus were calculated for the starch films and low modulus values were found for the PVA films and those characterized by a high PVA content (Table 1). This result might be related to the high stiffness of the starch films and to the high elasticity of the PVA rich materials. The Young modulus values decreased gradually with the increase of the content of PVA component.

**Table 1.** The values of Young modulus determined for the nonirradiated and the irradiated starch-PVA films

PVA content [wt%]	Young modulus		
	0 kGy	25 kGy, $\gamma$ , vacuum	25 kGy, EB, air
0	817 $\pm$ 67	809 $\pm$ 51	678 $\pm$ 61
20	736 $\pm$ 69	695 $\pm$ 20	703 $\pm$ 64
40	338 $\pm$ 11	391 $\pm$ 22	400 $\pm$ 23
50	255 $\pm$ 6	303 $\pm$ 22	291 $\pm$ 17
60	348 $\pm$ 20	377 $\pm$ 22	345 $\pm$ 20
80	195 $\pm$ 8	203 $\pm$ 19	256 $\pm$ 21
100	157 $\pm$ 10	180 $\pm$ 11	195 $\pm$ 13

There are a number of structural factors influencing mechanical properties of the polymers. Besides the structure of the macromolecules, the physical state dependent, i.e., on the material crystallinity might have the important impact on these properties. PVA is the linear polymer and forms fibrinous macrostructure. It is also known to have excellent mechanical properties. Starch contains a number of the branched (beside to linear) chains built from the glucose units and is characterized by a granular structure. Addition of starch into the mixed polymer system play a role of the filler [36], whereas PVA is used as a plasticizer [19].

Accordingly, the increase of the flexibility with no particular effect on tensile strength observed by us after addition of 20% of PVA to starch in relation to that of the starch films might be explained in terms of the plasticizing effect of PVA and to the formation of the hydrogen bonds between starch and PVA. Deterioration of tensile strength and flexibility of the PVA films caused by addition of starch might be related to the results obtained by Chen *et al.* (at starch addition on the level till 40%) [12]. The authors explained the strong compositional effect in terms of the insufficient compatibility between starch and PVA.

None of the general conclusion concerning the effect of irradiation carried out in vacuum as well as in air on tensile strength might be derived (Fig. 1). It was stated, however, that irradiation, both conducted with gamma rays (at vacuum) as well as in EB (in air) induces decrease in flexibility of all the films. Simultaneously, it can be noticed that the Young modulus is slightly lower after irradiation in the case of the films characterized by the high content of starch but slightly higher in the case of the films with the high content of PVA. This suggests an increase in elasticity of the starch rich films but a decrease in elasticity of the PVA rich materials.

The observed changes might be related to the possible radiation induced degradation of the starch component, crosslinking accompanied by degradation of the PVA component and to the formation of the crosslinks between starch and PVA macromolecules, as well as scission of such crosslinks formed on the step of the films preparation. Participation of those processes might differ in the case of the particular compositions. Decrease in flexibility might be related to the possible formation of some crosslinks in the material. However, Parvin *et al.* [20] suggested that decrease in flexibility at doses above 20 kGy results rather due to chain scission. Similar to the now observed effect of irradiation on the Young modulus in the cases of the starch rich specimens, we have already observed in the cases of the films prepared basing on the pre-irradiated starch (alone), due to radiation induced starch degradation [5]. It can also be supposed that a slight increase in the Young modulus (showing decrease in elasticity) occurring in the case of the PVA rich films after gamma irradiation might be caused by formation of crosslinks between the particular PVA macromolecules.

## Wetting angle

Wetting angle constitutes the parameter that delivers information concerning mainly hydrophilic/hydrophobic properties of the surface of the films.

Starch films reveal only low hydrophilicity while PVA films have appeared highly hydrophilic. It is shown by the high wetting angle value determined for the starch films and the low value found for the PVA films (Fig. 3). The differences between hydrophilicity of the both types of the films arise due to the differences in their molecular structure determining the availability of the hydroxyl groups on the surface of the films. It seems worth to mention that cornstarch as the A-type starch contains some lipids and thus can form the starch-lipid complexes during gelatinization. It should be also pointed out that even such a small presence of hydrophobic components is expected to weaken hydrophilic nature of the starch. However, it can be also expected that low hydrophilicity of the starch films might partially results due to pre-irradiation of the starch substrate before the syntheses. This process is accompanied by oxidation leading to substitution of some hydroxyl groups by less hydrophilic carbonyl and carboxyl groups. Our previous data have indicated that using the pre-irradiated starch enables to prepare the starch films with the essentially decreased hydrophilicity as compared to the films formed by the nonirradiated starch [5].

Accordingly, the films containing high amount of starch were generally characterized by the higher values of the wetting angle as compared to those containing high amount of PVA. The wetting angle values decreased with the increase of PVA addition. However, at the intermediate starch content (ca. 60% of PVA) hydrophilicity of the films considerable increased (wetting angle decreased) as compared to that of the films with the larger or the smaller PVA contribution (Fig. 3). As in the case of tensile strength, this effect is probably connected to the specific interaction between starch and PVA (and glycerol) components in the system.

In general, irradiation carried out in a gamma chamber as well as in an EB induced essential decreases in the hydrophilicity of most of the films

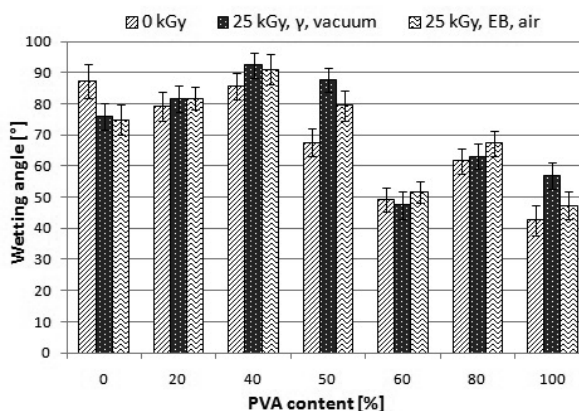
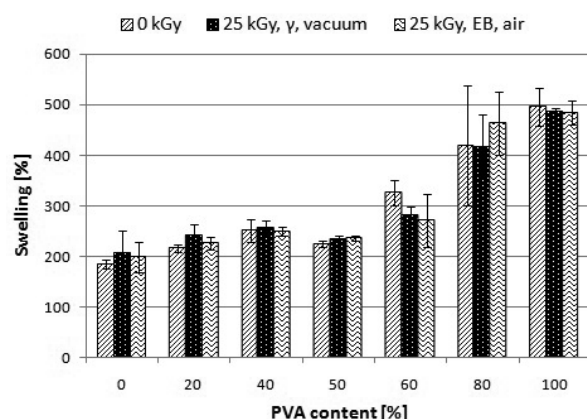


Fig. 3. The values of wetting angle determined for the starch-PVA films, nonirradiated and irradiated with  $\gamma$ -rays (vacuum) or fast electrons (air) applying a dose of 25 kGy.



**Fig. 4.** The values of swelling parameter determined for the starch-PVA films, nonirradiated and irradiated with  $\gamma$ -rays (vacuum) or fast electrons (air) applying a dose of 25 kGy.

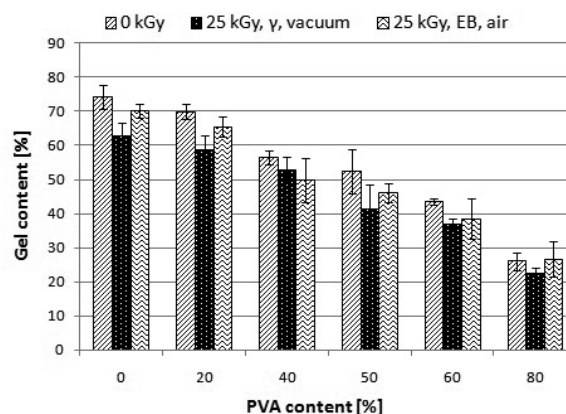
(shown by the increase in the wetting angle value, Fig. 3). The exceptions were starch films. This effect was, particularly, clearly observed in the cases of the films characterized by a high content of starch or PVA.

### Swelling

Swelling concerns the interaction of the surface as well as the bulk material with water.

The starch films are characterized by moderate swelling properties while a strong swelling in water of the PVA films was observed (Fig. 4). It was also difficult to determine exactly the swelling parameter in the cases of the films with a high PVA content because of the high instability of mechanical properties of these films immersed in water and a possible loss of material during the subsequent operations.

A small influence of irradiation on the swelling of the films in water was observed (Fig. 4). However, it can be noticed that rather a higher swelling occurred in the case of a majority of the films containing a high amount of starch as compared to the nonirradiated ones, while in the cases of some films characterized by the higher PVA content, rather a decrease in the swelling parameter took place.



**Fig. 5.** Comparison of the content of gel fraction in the starch-PVA films irradiated with  $\gamma$ -rays (vacuum) or fast electrons (air) applying a dose of 25 kGy with those nonirradiated.

### Gel content

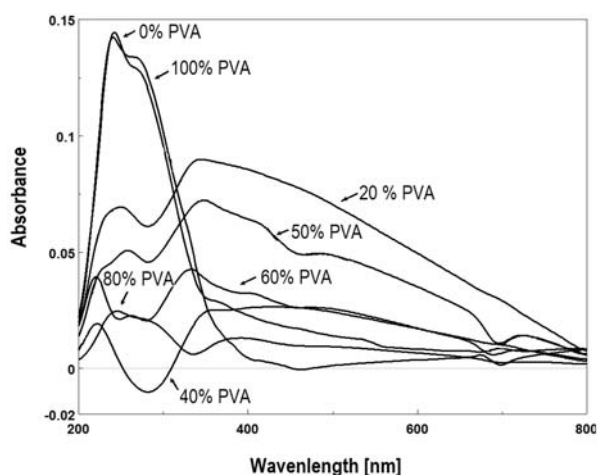
A high gel content on the level of  $74 \pm 2\%$  was determined in the cases of the starch films (Fig. 5). Gel content in the films decreased with the increasing addition of PVA. It might be stated, moreover, that the dependence of the gel content on the PVA content might be described as almost linear in the range of 20–80% PVA (not shown).

A lower gel content was determined in the cases of the irradiated films as compared to the nonirradiated ones. These results indicated that degradation was the prevailing process resulting from irradiation. It can be noticed, however, that the gel content in the irradiated films was still relatively high and reached the values of 0.79–1.00 of these determined for the nonirradiated films (Table 2 with footnote; the highest value was determined due to the justified experimental errors). For comparison, when the starch substrate was irradiated under the same conditions, the content of the gel fraction decreased to the level of 32–33% of that determined before this process (Table 2). This result might be considered in terms of the crosslinking processes accompanying the degradation in the starch-PVA-glycerol system under the influence of irradiation, although it is also possible that some crosslinks were created formerly during the films' syntheses, and the crosslinked material is more resistant to irradiation as compared to granular starch.

**Table 2.** The average value of the gel fraction determined for the irradiated films expressed in terms of the gel fraction found for the nonirradiated films compared to the gel fraction determined for the irradiated starch substrate

Composition	Gamma, vacuum	Electron beam, air
Starch-PVA films prepared basing cornstarch irradiated using a dose of 10 kGy and containing 30% of glycerol		
0% PVA	0.85	0.95
20% PVA	0.84	0.94
40% PVA	0.93	0.88
50% PVA	0.79	0.88
55% PVA	0.86	0.89
60% PVA	0.85	0.88
80% PVA	0.86	1.00*
Starch substrate		
Pre-irradiated cornstarch (10 kGy)	0.32	0.33

\* High value might result due to the small gel content resulting in the relatively high experimental error.



**Fig. 6.** Diffuse reflectance spectroscopy spectra of the starch-PVA films irradiated with  $\gamma$ -rays in air applying a dose of 25 kGy.

No presence of the gel fraction was detected in the PVA films, whether nonirradiated or irradiated. This result confirms that starch constitutes at least the major component participating in the formation of the gel fraction under the applied conditions, while no or only a small contribution of PVA (connected to the possible formation of the crosslinked starch-PVA-glycerol network) can be expected.

#### Diffuse reflectance spectroscopy

The bands in the DRS spectrum (Fig. 6) indicated a formation of various oxidation products induced by the irradiation carried out in the air. Similar patterns were recorded for the starch and the PVA films. All the patterns recorded for the films containing simultaneously both components with the modified starch:PVA ratio differ considerably from those recorded for the single-component films. This result indicates a strong interaction of the components in the mixed system, alternating in relation to the compositional changes.

The band around 245 nm (a major band in the patterns of the starch films and the PVA films) was identified as the band of the carboxyl groups in the middle of polymer chains (ketone groups) [37, 38]. Bands at 295–320 nm were assigned to the C=O groups at the end of chains (aldehyde groups con-

nected to the presence of the products of degradation of the polymer chain) and peaks in the range of 210 nm are acquired to the presence of peroxides and hydroperoxides [37, 38] (strong bands at this position are observed in the case of the films containing 40 and 60% of PVA). It can be also supposed that several bands of absorption in the range of the higher wavelength can be assigned to carboxyl groups at different positions.

It might be supposed that the decrease in the surface hydrophilicity of the films observed after irradiation carried out in the air can be partially attributed to the appearance of the C=O groups resulting from substitution of the more hydrophilic OH groups. However, due to the fact that a decrease in hydrophilicity was observed also after irradiation carried out in the vacuum, the other processes influencing this property should be also considered.

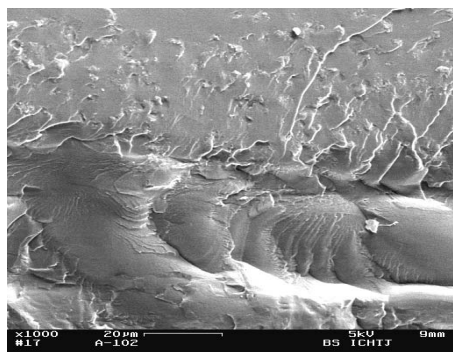
#### Scanning electron microscopy

The SEM images of the nonirradiated films are characterized by a presence of the block system connected probably to the presence of the starch component [39] strongly influencing the appearance of the starch-PVA system (Fig. 7). Moreover, the occurrence of the veins (white) can be observed supposedly regarding inclusion of the PVA component partially non-solubilized in the starch-PVA matrix.

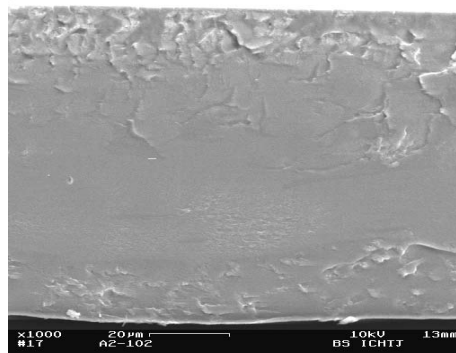
Smooth areas were observed in the fractures of the irradiated films accompanied by the disappearance of the veins (Fig. 7). This shows an improvement of the homogeneity of the films and compactness of their components connected to irradiation.

#### Conclusion

The films characterized by a high content of starch have appeared stiff, while the films characterized by a high content of PVA were highly flexible. Tensile strength of the films characterized by a high content of PVA was higher than that of the starch rich films. Tensile strength and flexibility, as well as swelling and hydrophilicity, increased gradually with the increase in the PVA content in the films. This indicates an improvement of the mechanical prop-



0 kGy



25 kGy

**Fig. 7.** The examples of images of the fractures of starch-PVA films (50:50), nonirradiated and irradiated with  $\gamma$ -rays in vacuum with a dose of 25 kGy.

erties accompanied by a deterioration of the films' resistance against moisture, both connected to the increase of PVA content. However, tensile strength and wetting angle values achieved a minimum at the intermediate composition. This phenomenon showed specific interaction between the components taking place on the step of the films preparation.

In general, irradiation enables to reduce hydrophobicity of the films (shown by the increase the wetting angle values) accompanied by a decrease in their flexibility. No general conclusion concerning the effect of irradiation on tensile strength and swelling behavior can be derived basing on the present preliminary data. The occurring changes are connected to the increase in the homogeneity of the films (as shown by SEM) related to the increase in the compatibility of the components in the PVA-starch-glycerol systems taking place under gamma radiation. This can be also referred to the occurrence of a strong interaction of the starch and the PVA components discovered in the mixed starch-PVA films by DRS. Degradation was found to be the prevailing process taking place in the films as well under influence of irradiation carried out in the air (with fast electrons) as in the vacuum (with gamma rays), however, it seems possible that crosslinking accompanies degradation. Simultaneously, the creation of various oxidation products in the films characterized by the modified composition was observed under the influence of ionizing radiation performed in air.

Although the deterioration of the films flexibility occurs under the influence of gamma and electron radiation, mechanical properties of the selected materials appear still acceptable after the radiation treatment. This statement connected with an observation of a simultaneous improvement of the hydrophobic properties (a decrease in hydrophilicity) suggests that the materials might appear appropriate for packing the products predicted for radiation decontamination.

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