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The effect of poly(vinyl alcohol) type and radiation treatment on the properties of starch-poly(vinyl alcohol) films

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ABSTRACT

Our present study concerns the effect of application of various PVA substrates and the influence of ionising radiation on the properties of films based on starch and PVA. Four PVAs revealing various molecular masses (in the range of 11–145 kDa) were selected for this purpose. The films characterized by starch: PVA ratios of 40:60 were prepared by solution casting and irradiated with ^{60}Co gamma rays (under nitrogen) and with fast electrons (under air) applying the absorbed dose of 25 kGy. Mechanical properties of the films (tensile strength, elongation at break and Young Modulus) were examined, as well as the contact angle to water and swelling in water, in regard for evaluation of the hydrophilic/hydrophobic properties. Gel content in the samples was also determined.

Physicochemical properties of the films and their sensitivity to irradiation strongly depend on the applied PVA substrate. This can be related to differences in the capability of particular PVAs for forming the crosslinked starch-PVA network during the films' synthesis and future treatment. In particular, the usage of the PVA characterized by the high molecular mass has appeared more rewarding as compared to those based on the low molecular mass PVAs. Additionally, properties of these films were not affected or improved after irradiation.

1. Introduction

The increasing problem of environmental pollution induces interest in substituting traditional packaging by biodegradable plastics from renewable resources and in the development of more environmentally-friendly methods for their manufacturing. Mixed systems composed from a variety of natural polymers (polysaccharides or proteins) as well as from natural polymers and synthetic biodegradable polymers were proposed in the last years for these purposes.

Starch appears to be the appropriate source for preparation of cheap biodegradable packaging due to its abundance, low costs and good film forming capabilities (Cieśla et al., 2010, 2014a, 2016a, Tang and Alavi, 2011, Ryzhkova et al., 2011). However, films prepared based on natural starches alone have rather moderate mechanical properties and relatively low resistance to moisture. Therefore, in purpose to improve the properties of starch films various methods are applied as: usage of modified starches, blending starch with other natural polymers or with artificial biodegradable polymers, introduction of reinforcing or plasticizing agents (Aydin and Ilberg, 2016, Naznin et al., 2012, Frone et al., 2015, Jiang et al., 2012, 2016, Rahmat et al., 2009, Tang et al., 2008, Yao et al., 2011, Yoon et al., 2012) and application of various physical and chemical treatments.

Poly(vinyl alcohol) (PVA) can be used for packaging purposes and is known to be an appropriate polymer for blending with starch (Abramowska et al., 2015; Cano et al., 2015; Chen et al., 2008; Frone et al., 2015; Ishigaki et al., 1999; Jiang et al., 2016; Luo et al., 2012; Russo et al., 2009, Tang and Alavi, 2011; Yoon et al., 2012). It is a biodegradable polymer with excellent film forming abilities. Moreover, PVA films have splendid mechanical properties, although their resistance to water is rather poor. However, it was discovered that blending of starch with PVA results in improvement of physicochemical properties of materials (Rahmat et al., 2009)

Simultaneously, radiation techniques appear as the perspective methodology for modifying polymers and biopolymers (including the films), enabling to reduce the use of strong chemicals. These methods were also applied successfully for the starch-PVA systems (Senna et al., 2011; Parvin et al., 2011; Naznin et al., 2012; Ryzhkova et al., 2011; Khan et al., 2006; Zhou et al., 2009).

Development of sterilization/decontamination techniques that involve ionising radiation induces the need for search of appropriate packaging for the decontaminated products (Chmielewski, 2006; Haji-Saeid et al., 2007; Silvestre et al., 2014, 2017). At present, the search is carried out also for modern biodegradable packaging that can be used for products subjected to radiation sterilization/decontamination.

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Obviously, it is required that irradiation cannot deteriorate functional properties of such packaging material. A potential improvement of the material properties after irradiation might be considered as an additional benefit that arises from such processing.

The possible desired modification of the films' structure and properties as well as the potential for packing the products subjected to radiation decontamination make it interesting to study the effect of ionising radiation on biodegradable films.

Properties of the polymer films might depend on the substrates used and the procedure applied for the films' preparation (Chai et al., 2012; Chen et al., 2008). In particular, Chai et al. (2012) examined the effect of using PVAs characterized by different molecular masses on some properties of the starch-PVA blends. However, although, these studies covers degradability and mechanical properties, the effect of the PVA substrate on the other properties of the films was not recognized. There is also missing information concerning the relation between using various PVA components and the influence of irradiation on the resulting films' properties. In relation to the fact that considerable differences arise between the effects of ionising radiation on the starch-PVA films reported by various authors (Senna et al., 2012, Parvin et al., 2011), it can be supposed that these differences might be partially caused by the usage of different PVA and starch substrates for the films syntheses.

It is considered that blending of starch with PVA occurs via a formation of a network built from starch macromolecules with crosslinked PVA molecules during heating of the gel solution (Rahmat et al., 2009). This phenomenon was explained in terms of hydrogen bonding interaction between starch and PVA (Rahmat et al., 2009). It is also announced that crosslinking of starch with PVA takes place during the heating of the samples in regard to drying (Tang et al., 2008; Yao et al., 2011). On the other hand, it is acquired that crosslinks formation might be induced by ionising radiation together with degradation (Senna et al., 2011, Parvin et al., 2011).

It can be thus supposed that the capability of PVAs for formation of the crosslinks with starch leading to the more crosslinked phases in result of heating the gel solutions and films as well as of irradiation might depend on the chain length of PVAs.

Our previous results have already shown that the usage of irradiated starch enables to obtain the starch films with better properties as compared to those prepared basing on the native starch (Cieśla et al., 2010, 2014a, 2016). This occurs due to the fact that starch degradation taking place under gamma irradiation permits to obtain gels with decreased viscosity and improved homogeneity at the intermediate step of preparation, and this leads to preparation of more homogeneous films. Oxidation accompanying to degradation and resulting in substitution of some hydroxyl groups by carbonyl or carboxyl groups lead simultaneously to films with decreased hydrophilicity. Additionally, the data obtained for the starch-PVA system characterized by various starch: PVA ratios show the increase in the compatibility of the components taking place under gamma radiation (Abramowska et al., 2015). Moreover, it was discovered that irradiation permits to reduce also the hydrophilicity of starch-PVA films with a selected composition (Abramowska et al., 2015, Cieśla et al., 2014b; Cieśla and Sartowska, 2016).

The purpose of present work is to evaluate the effect of using various preparations of PVA differing in the molecular mass on the properties of the starch-PVA films and the effects of irradiation on the films prepared basing on those particular PVAs. Basing on our previous results (Abramowska et al., 2015), the composition with starch: PVA ratio equal to 40:60 was selected for the present studies. The films with this composition were characterized by a relatively high tensile strength, sufficient flexibility and a moderate swelling parameter.

2. Experimental

2.1. Materials

The following PVA specimens characterized by various molecular masses were used for the films preparation: PVA1: characterized by Mw c.a 145 kDa (Merck product 8148941001), PVA2: Mw 88–98 kDa (product of Alfa Aesar, *A Johnson Mattey Company,* 41243,); PVA3: Mw ca. 60 kDa (Merck, S651446623 (843866)), and PVA4 Mw 11 – 31 kDa (Alfa Aesar *A Johnson Mattey Company,* 41241). Both Alfa Aesar products ((PVA2 and PVA4) were indicated by the producer as incompatible with a strong oxidizing agent).

Moreover, cornstarch (Sigma product *S412*) and analytical grade glycerol (Chempur, Poland), were applied. The starch was degraded before use on the way of irradiation with an absorbed dose of 10 kGy, in purpose to reduce it's viscosity (Cieśla et al., 2010).

2.2. Films preparation

Films with the content of starch -PVA in percentage ratio 40:60 were prepared by solution casting accordingly to the procedure described in (Abramowska et al., 2015). The glycerol was introduced 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 starch solutions (1.96 wt%) were obtained on the way of heating at the temperature of 90 °C during 40 min. Glycerol was added into the starch suspension before gelatinization. The starch pre-irradiated with a dose of 10 kGy has appeared as a suitable substrate for preparing homogeneous starch gel solutions characterized by an adequate low viscosity and consequently enabled casting homogeneous films. To the contrary, applying the non-irradiated starch resulted in a preparation of viscous gels even at such a low concentration, and lead to preparation of non-homogeneous films. PVA solutions were then introduced step-wise into the gelatinized starch dispersions with a continuous stirring and then heated within the subsequent 1 h. Afterwards, the films were cast onto polystyrene Petri dishes, dried during 20 h in the heating chamber at a temperature of 50 °C, then allowed to dry at ambient temperature, and afterwards cast from the substrate.

The films were conditioned before irradiation and before testing at room temperature at a relative humidity of 43%.

2.3. Irradiation

Irradiations of the films were carried out at ambient temperature with the absorbed doses equal to 25 kGy. Irradiation with the gamma rays (^{60}Co) was conducted under nitrogen atmosphere in the Gamma Chamber GC 5000 applying a dose rate of 5.00 kGy/h. Irradiation with fast electrons was carried out under air for the films packed in polyethylene bags in the Elektronika 10/10 accelerator generating 10 MeV electron beam at an average dose rate of approximately 3 kGy/min.

Gamma irradiations chamber in oxygen free atmosphere with a low dose rate (thus within a prolonged time) seemed to be preferable conditions for involving possible crosslinking processes. On the other hand, irradiations in e-beam under air with a high dose rate were carried out in relation to conditions applied in INCT for sterilization and modification of polymers on technological scale. Thus, the results showing resistance of the potential packaging material based on starch: PVA system might be related both to capability for usage of such packaging for the products subjected to radiation decontamination, as well as to suitability of particular radiation techniques for the films' modification.

2.4. Mechanical tests of the films

Mechanical tests were performed using of an Instrom testing machine types 5565 applying the ramp velocity 20 mm/min. The