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Effect of gamma irradiation on thermophysical properties of plasticized starch and starch surfactant films

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H I G H L I G H T S

- The films were prepared basing starch, surfactant and glycerol.
- Two glass transitions were observed showing an existence of two phase system.
- The first T_g of the starch-CTAB films shifts after irradiation to lower temperature.
- In all the other cases it shifts after irradiation to higher temperature.
- Differences in volatile fractions content are not important for the temperature shift.

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In this work the influence of gamma irradiation on the thermomechanical properties of the films formed in potato starch-glycerol and potato starch-glycerol-surfactant systems were examined by Dynamic Mechanical Analysis, DMA, and Differential Scanning Calorimetry, DSC, and the results were correlated to the amount of the volatile fraction in the films.

The starch was irradiated with a dose of 30 kGy. The films were prepared by casting from solutions with addition of 0, 20 and 30 wt% of glycerol. Two endotherms attributed to glass transitions were observed in water or glycerol plasticised samples, the first one shifting to higher temperature after irradiation. A similar shift was observed after irradiation of films prepared from starch-sodium laurate and starch-sodium palmitate systems, while a decrease in glass transition temperature was observed in the case of starch-cetyltrimethylammonium bromide films. Small differences in the content of the volatile fraction reached after the appropriate conditioning had no impact on the direction of temperature shift of T_g observed after irradiation.

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1. Introduction

Starch is an abundant and cheap biopolymer and potato starch is the proper material for preparation of edible and biodegradable films and coatings, appropriate for food systems and for technical industries (Kester and Fennema, 1986; Mali et al., 2006; Arvanitoyannis et al., 1996, 1998; Lazaridou and Biliaderis, 2002). To improve the barrier properties hydrophobic compounds might be introduced into such packaging compositions (Kester and Fennema, 1986). As film forming capability and the quality of the resulting films depend on the molecular structure of starch, modifications of native starch are performed, applying various physical and chemical methods.

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Gamma irradiation induces chemical changes in starch macromolecules (Raffi et al., 1981; Cieřła, 2009). The major process occurring in starch is degradation of the macromolecules with an accompanying oxidation by atmospheric oxygen and leading to the formation of carbonyl and carboxyl derivatives. Apart from formation of macromolecules with shorter molecular chains, water-soluble molecules are formed, due to disruption of the glycosidic linkages near the macromolecules endings.

Development of methods of biopolymer modifications that apply ionising radiation is observed in the last decade (Cieřła, 2009). This also concerns starch based plastics (Zhai et al., 2003; Lepifre et al., 2004; Cieřła, 2009; Cieřła et al., 2010; Ryzhkova et al., 2011).

As the amorphous fraction in starch is high, its thermomechanical properties largely depend upon the position of its glass to rubber transition (glass transition, T_g), compared to the application temperature. T_g thus determines the process ability. Especially in the case of biochemical systems and plastics based on

natural components the position of T_g is of special importance as the factor determining the effect of storage conditions on the quality of such materials. Consequently, the position of T_g compared to room temperature will decide about the possible application for the material, in particular in food systems and in packaging. In general, the stability of such systems is higher when their T_g is higher. This is because the material even at rubbery state transforms slower when the difference between storage temperature and its T_g is smaller. Moreover, the mobility of the molecular chains below its glass transition is expected to influence the stability of such materials. In the case of starch and thermo-plastic starch, recrystallisation occurs during storage at temperatures above T_g (De Meuter et al., 1999; Mali et al., 2006; Jimenez et al., 2012). On the other hand, storage of the material at high humidity even at a temperature below T_g leads to the uptake of water and consequently a further lowering of T_g (Mali et al., 2006).

The glass transition of anhydrous starch is expected at 220–250 °C (Karel et al., 1994). It is known that the presence of plasticizers like water or glycerol leads to a decrease of the glass transition temperature (Arvanitoyannis et al., 1996, 1998; Lazaridou and Biliaderis, 2002; Mali et al., 2006), while the water content in biochemical systems strongly depends on the conditions of storage (humidity and temperature).

Our previous results have shown that radiation treatment might be adopted for improvement of the properties of films formed using potato and wheat starch as well as compositions of potato starch with several surfactants, all plasticized by glycerol and water (Cieřla, 2009; Cieřla et al., 2010). This occurred due to the fact that starch degradation and oxidation (both major processes induced by irradiation) appeared useful for improvement of the film properties (Kester and Fennema, 1986). Our previous results have also already proven that the glass transition of the starch irradiated applying a dose of 20 kGy occurs at slightly lower temperature, as compared to the non-irradiated starch (Cieřla et al., 2003). Accordingly, it appeared interesting also to examine thermophysical properties of the multi-component starch based systems useful for film production.

Our present study concerns the effect of irradiation on the glass transition of films prepared from potato starch–glycerol and potato starch–glycerol–surfactant. The study was performed on systems containing two anionic surfactants (sodium laurate and sodium palmitate) and one cationic surfactant (cetyltrimethylammonium bromide). Due to the known sensitivity of T_g of the films to the storage conditions, our results were collected on samples subjected to the appropriate conditioning at a controlled humidity. This conditioning will determine the presence of total volatile fraction in the films.

2. Experimental

2.1. Materials and irradiation

Potato starch (S-4251, Sigma) as well as sodium laurate (NaLau, Fluka) and sodium palmitate (NaPam, Fluka), cetyltrimethylammonium bromide (CTAB, Aldrich), analytical grade glycerol and deionised water have been used for the film preparation. Irradiation with Co-60 gamma radiation was carried out for native potato starch in the gamma cell *Issledovatel* placed in the Centre for Radiation Chemistry and Technology in the Institute of Nuclear Chemistry and Technology. A dose of 30 kGy was applied.

2.2. Film preparation

The films were prepared by casting the gelatinised starch solutions (Cieřla et al., 2010).

Gelatinisation of starch was performed by heating the starch suspensions (2 wt%) during 2 h in a heating chamber kept at

100 °C. Glycerol was introduced into the film forming solution prior to casting (procedure I) or at the very beginning, before starch gelatinization (procedure II). A glycerol content of 0, 20 or 30% (in terms of starch mass) was used as a plasticizer.

The surfactants were introduced on the following levels expressed in terms of g per 1 g of starch: NaLau – 0.049 g/g, NaPam – 0.038 g/g and CTAB – 0.075 g/g. This corresponds to 0.222, 0.136 and 0.206 mmol per 1 g of starch, respectively. The following procedure enabling the formation of starch–surfactant complexes was used (Cieřla et al., 2010). Starch was pregelatinized in the heating chamber at the temperature 90 °C for 1.5 h. The surfactant solution (1.2 wt%, 0.9 wt% and 2.0 wt% in the cases of NaLau, NaPam and CTAB, respectively) 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.

An aliquot of 11 ml of the final starch solution (2.0%) or 13 ml of starch–surfactant solution (1.7%) was pipetted in the polystyrene Petri dishes with a diameter of 90 mm and allow to dry at ambient temperature. The dried films were peeled from the substrate and conditioned before the examinations at ambient temperature and a relative humidity RH of 56% or ca. 30%. The film thickness was equal to ca $95 \pm 15 \mu\text{m}$.

Determination of T_g was performed two weeks after the films preparation.

2.3. Methods

Dynamic mechanical analysis (DMA) was carried out with a heating rate of $2.5 \text{ }^\circ\text{C min}^{-1}$ using the PerkinElmer DMA7 in tension (vertical) as well as in compression (horizontal geometry). In the case of compression, several layers of the film were stacked tightly in Al foil to obtain a thicker sample. Prior to heating, the samples were cooled till $-120 \text{ }^\circ\text{C}$ at 5 or at $3 \text{ }^\circ\text{C min}^{-1}$ (in the case of vertical or horizontal system, respectively). The temperature of the maximum of $\tan\delta$ was selected as a characteristic point of the glass transition. In order to avoid drying of the films during measurements, a container with water was placed under the experimental cell, creating a relative humidity of 100%. Several measurements were carried out for each of the selected film compositions. Non-irradiated as well as irradiated samples were measured: starch, starch–glycerol (30%) and starch–NaLau–glycerol (30%).

DSC studies were carried out during heating with a rate of $10 \text{ }^\circ\text{C min}^{-1}$ between -150 and $110 \text{ }^\circ\text{C}$ using a Q2000 DSC from TA Instruments. The midpoint on the DSC curve (determined on the basis of the minimum on its derivative (dDSC)) was taken as a characteristic temperature of the glass transition. However, in some cases when blurred dDSC peaks were detected, T_g was determined on the basis of both dDSC and DSC curves. Three measurements were performed for each film composition and the mean value was taken.

The content of the volatile fraction was determined from the residues obtained after DSC analyses as a mass loss occurring after drying. Drying was carried out at ambient temperature over silica gel during 1 month and afterwards over P_2O_5 for the next 2 months.

3. Results and discussion

3.1. Appearance of the glass transition

Typical DMA curves are presented in Fig. 1. At least two phenomena are observed in the temperature range from $-100 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$, in the cases of the films containing glycerol and water as well as in the cases of the films containing only water as a plasticizer. The first one (lower temperature) was detected in the range of -90 to $-30 \text{ }^\circ\text{C}$ and the second one above $-30 \text{ }^\circ\text{C}$. The

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