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SEM studies of the structure of the gels prepared from untreated and radiation modified potato starch

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HIGHLIGHTS

- Four procedures of the preservation of starch gels for SEM studies were applied.
- The ability to observe the radiation effect by SEM was assessed for each method.
- Dose dependent changes in the gel structure were discovered.
- It was related to decrease in the swelling power and decreased viscosity of the gels.
- A hot-stage microscope was applied in order to follow the gelatinization process.

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ABSTRACT

Potato starch was irradiated with a ^{60}Co gamma rays using doses of 5, 10, 20 and 30 kGy. Gels containing ca. 9.1% of starch were prepared by heating the starch suspensions in the heating chamber stabilized at 100 °C. Four procedures were applied for preparation of the samples in regard to SEM studies and the ability to observe the radiation effect by SEM was assessed for each method. Differences were observed between the SEM images recorded for the non-irradiated samples prepared using all the methods, and those irradiated. Images of the non-irradiated gels indicate generally a honey-comb structure, while smooth areas but with oriented fractures has appeared after irradiation. Modification of gel structure corresponds to the applied dose. The results were related to the process of gel formation (as observed by means of the hot stage microscope) to decrease in swelling power of the irradiated starch and to decreased viscosity of the resulting gels. It can be concluded that the differences in structural properties of gels shown by SEM result probably due to the better homogenization of the gels formed after radiation induced degradation.

1. Introduction

Natural polymers of plant and animal origin are widely applied as hydrocolloids in the food industry. The increase in interest in environmental protection led to the increasing interest in application of such materials also in technical industries, as well as in development of the more friendly for environment "green" technologies enabling to limit the use of strong and toxic chemicals. Radiation modification appears to be an alternative perspective method that might substitute chemical and enzymatic procedures, applied till now on an industrial scale.

Potato starch is an abundant and cheap raw material widely applied in various food, pharmaceutical and technical industries. Gelling properties of starch and viscosity and stability of its' gels appear to be the crucial factors that affect possible application of starch in a number of industrial products. Accordingly development of the methods of starch modification and testing of the products that contain newer starch modificates appear to be the important task.

Degradation and oxidation (consisted on formation of carbonyl and carboxyl groups) are desirable processes that enable us to obtain starches forming gels with reduced viscosity, in relation to those formed by the native starch. Such species are widely applied as components of packaging materials (films and coatings), coatings and glues in technical industries, and as functional additives in the instant food products (Cieśla, 2009). Decrease in molecular weight of starch accompanied by oxidation are common processes induced by ionizing radiation (Raffi et al., 1981; Sharpatyi, 1995, Korotchenko and Sharpatyi, 2004, Henry et al., 2010). The irradiated starch and flour reveal essentially lower swelling power (Ferdes et al., 1996; Bao and Corke, 2002; Cieśla and Eliasson,

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2007; Lu et al., 2012) and the resulting gels are less viscous as compared to those of the reference non-irradiated species (Raffi et al., 1981; Bao and Corke, 2002; Cieśla, 2003; Wang, 2007; Wu et al., 2002; Lee et al., 2008; Chung and Liu, 2010).

Several trials for preparation of the radiation modified starches were carried out. Among the others, it was found that applying of ionizing radiation to starch might lead to modification of the properties of the films prepared basing the starch systems (Zhai et al., 2003; Bhat and Karim, 2009; Cieśla, 2009; Cieśla et al., 2010, 2014). As gels appear to be the important semi-products formed on the intermediate stage in the production of the starch-based films and coatings, it might be expected that the structural properties of the gels influence the physico-chemical properties of the final material, alike in the case of the films based on food proteins (Cieśla et al., 2006). However, gelling properties of the irradiated starches or flours and physico-chemical properties of the resulting gels have gained an interest also because of the possible application of the radiation modified hydrocolloids in food or even direct modification of food's functional properties (Yu and Wang, 2007; Nemţanu et al., 2007; Lee et al., 2008; Yoon et al., 2010).

It can be considered that the methods applied for gel preparation strongly influence its' structure. Several procedures have been applied till now in order to observe the starch gels using light or electron microscopy (SEM). The most standard procedure was prolonged cooling of the gels at 4 °C followed by chemical fixation (Kaczyńska et al., 1993) or storage of the gels at room temperature with further smearing on the glass slide (Byars et al., 2006). Freeze-drying of swollen granules (Chemeris et al., 2007) and direct observation of the frozen gels using SEM or TEM methods were also carried out (Eliasson, 1985; Chemeris et al., 2007).

The present studies dealing with influence of gamma irradiation on the structure of starch gels were initiated applying SEM. Accordingly, four procedures of gels preparation and preservation were tested and evaluated in relation to ability for detection of the differences between SEM images obtained for the non-irradiated species and those irradiated applying various doses, and the influence of each procedure on the resulting images was analysed. SEM data were related to the process of gel formation (as observed by means of the hot-stage microscope), to the swelling power of the non-irradiated and the particular irradiated starches and to the viscous properties of the gels.

2. Experimental

2.1. Materials and irradiation

Potato starch was extracted in the laboratory from potato of Fauna type. The starch contained ca. 14 wt% of moisture, and pH of the 20% suspension was estimated as being equal to 7.0. Solid starch was irradiated with ^{60}Co gamma rays in the gamma cell Issledovatiel installed in the Centre for Radiation Research and Technology (CeBaTeRad), Institute of Nuclear Chemistry and Technology. Doses of 5, 10, 20 and 30 kGy were used, applying a dose rate of 1.00 $\pm$ 0.05 Gy s^{-1}.

2.2. Preparation of gels for SEM observations

The starch suspensions (100 mg of starch per 1 ml of water) were placed in glass tubes and heated for 45 min in the heating chamber stabilized at 100 °C. The final gels contained 9.1% of starch (ca. 7.7% in terms of dry matter). The hot specimens (liquid state) were subjected to the following four experimental procedures:

Procedure I: The hot liquids were rapidly frozen in liquid nitrogen. A drop of gel was placed on the frozen metallic stunt and stored in liquid nitrogen during 3 h before SEM studies. SEM examinations were carried out directly for the frozen gels.
Procedure II: The hot liquids were also rapidly frozen in liquid nitrogen but afterwards lyophilized.
Procedure III: The hot liquids were rapidly frozen in liquid nitrogen, kept at −18 °C for two weeks and then subjected to chemical fixation followed by drying at critical point (CO_2).
Procedure IV: The specimens were slowly cooled at ambient temperature, stored at 4 °C for 2 days and subjected to chemical fixation and critical point drying.

Chemical fixation was performed accordingly to the modified procedure of Kaczyńska et al. (1985). The samples were kept in a solution of glutaraldehyde (1 wt%) at 4 °C during 20 h, and washed several times with distilled water. Then the procedure enabling us to substitute water with acetone was applied (washing with water: ethanol solutions, ethanol and acetone). The obtained specimens were stored in acetone and then dried at critical point drying apparatus Polaron CPD 7501).

The sections and the surfaces were examined in the case of the gels obtained with regard to procedure I, while fractions and surfaces of the gels were examined in the case of the second, third and fourth preparation procedures.

2.3. Scanning electron microscopy (SEM)

SEM studies of the dried samples (obtained due to procedures II–IV) were carried out at ambient temperature using the DSM 942 Scanning Electron Microscope (Zeiss-Leo production) installed in the Institute of Nuclear Chemistry and Technology. The samples were covered with a thin gold layer. The fractures and surfaces of gels were examined with magnifications of 150, 500 and 1000×. The images taken at a magnification of 1000× or 500× were selected for visualization of the most typical areas in the case of the samples obtained using procedures II–IV.

The Quanta 200 Microscope (FEI) installed in Analytical Centre, Warsaw Agricultural University was involved for SEM studies conducted at depressed temperature (procedure I). The pieces of these gels were directly placed into the microscope at medium vacuum (0.98 Torr) and depressed temperature (−18 °C). Magnifications of the images were 100, 300, 600, 1200, 1600 and 2400. The best visualization of the typical areas were selected at a magnification of 600× and the particularities were shown at a magnification of 1200×.

2.4. Light microscopy

The light microscope with a hot stage (Optimus) installed in the Department of Food Technology, Chemical Centre, Lund University was used. Observations were done with magnifications of 80× and 250× for the non-irradiated starch and the starch irradiated using a 30 kGy dose. Diluted starch suspensions (containing initially less than 0.5 wt% of starch) were placed on the plate of the microscope. Several experiments were conducted for each sample during heating with a rate of 10, 5 or 3 °C/min and the temperature fixed at 50, 60. 70, 80 and 90 °C for 1 or 2 min. However, the images were taken also at the intermediate temperature. The course of gelatinization of the selected granules was monitored till evaporation of the excess water has occurred. Dimensions of these selected granules (length and width of the oval shaped granules) were also measured.

Statistical analysis of the granules' dimensions was done for both the samples at room temperature. The lengths of the oval-shaped granules or diameters of the round-shaped granules were measured and then the granules were grouped into several categories according to their dimensions (5–10, 11–20, 21–30,