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The structure and properties of different types of starch exposed to UV radiation: A comparative study

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ABSTRACT

The effect of UV-irradiation on four different types of native starch (corn, waxy corn, wheat and potato) have been investigated. Although the changes in the chemical structure of starch specimens were small, indicating good photostability, the samples lost adsorbed water and their crystallinity degree decreased after irradiation. Moreover, a drop in average molecular weight occurred in samples (with the exception of potato starch) as a result of main chain scission. The variations in the properties of investigated specimens of various origin were related to the differences in their structure and macromolecular arrangement. The lowest photostability among the four starches was exhibited by potato starch.

1. Introduction

Polymers from renewable resources, namely proteins and polysaccharides have recently attracted increasing attention. Starch and its derivatives are readily available, cheap and environmentally friendly materials. This is a reason for their increasing use in the packaging industry (including food packaging) and many other branches of the economy.

Besides many useful properties (e.g. hydrophilicity, biodegradability, gelatinization), starch has disadvantages–one of them is poor processability, thus, modification is needed for some industrial applications. Therefore, investigations on starch often focus on modifications to ensure its optimum use in modern technologies e.g. in food industry, bioengineering, pharmacy or agriculture (Singh, Nath, & Singh, 2010).

Although the chemical structure of starch is known, materials obtained from various sources differ distinctly in molecular order, average molecular weight and polydisperisty. Moreover, the methods and conditions of isolation (dry or wet milling) influences the starch yield, molecular structure, granule size and shape (Correia & Beirão-da-Costa, 2011; Hoover, Hughes, Chung, & Liu, 2010).

A comparison of the changes in properties of various types of starches under the same conditions (e.g. upon heat, UV-irradiation, or chemical treatment) could be useful for potential manufacturers and should allow them to estimate the applicability of treated starches in the special fields (Bhat & Karim, 2009).

This work concerns the characterization of four types of native starches of different origin and comparison of their resistance to UV-irradiation. The basic properties such as content of water, amount of amylose, molecular weight and crystallinity degree have been determined. Irradiation is often used to extend the shelf life and increase the safety of food (Kizil & Irudayaraj, 2006). Moreover, the results will allow determination of studied starches in applications where resistance to ultraviolet radiation is needed, for example, in UV-sterilized materials for controlled drug release or biodegradable food packaging.

2. Experimental

2.1. Materials

Four types of native starch in the powder form were supplied by Cargil-AKV I/S, Denmark: corn starch – **CSt**, waxy corn starch – **WCSt**, wheat starch – **WSt** and potato starch – **PSt**. All starches were used without any purification. Standard amylose from potato starch, Sigma–Aldrich, was used for quantitative determination of its content in starch specimens. All other reagents (analytical grade): NaOH, CH_3COOH, ethanol, I_2, KI were supplied by POCh, Poland.

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2.2. Characterization of starch properties

2.2.1. Content of moisture

Before estimation of moisture content (MC) all samples (weitght of ~5 g) were stored at the same conditions (constant humidity and room temperature) for 48 h. This time is necessary to reach the mixture equilibrium.

MC (%) has been determined by the drying of starch at 95 °C to a constant weight using analytical balance. Before weighing, the samples were cooled to room temperature at vacuum. The amount of moisture (%) was calculated according to the formula:

$$MC = \frac{W - W_0}{W} \times 100\%$$

where W is the weight of the sample before drying, W_0 is the weight of dried samples.

2.2.2. Apparent amylose content

Apparent amylose content in starch was determined by visible (VIS) spectrophotometry using the procedure of Juliano (1971). Spectra of starch aqueous solutions with a concentration of 0.5 wt% were obtained using UV-1601 PC spectrophotometer (Shimadzu, Japan) in the range of 200–800 nm.

Each starch sample (100 mg) was solubilized in 9.0 mL of 1 M NaOH and 1.0 mL of 95% ethanol and heated for 10 minutes in a boiling water bath, then cooled and made up the volume to 100 mL with distilled water. 5.0 mL of obtained solution was pipetted out to another 100 mL volumetric flask. First, 1.0 mL of 1 M acetic acid, then 2.0 mL of iodine/potassium iodide solution (0.26 g of iodine dissolved in 10.0 mL of potassium iodine containing 2.6 g KI to obtain iodine/potassium iodide solution) were added. Next, the solution was made up to volume with 100 mL with distilled water and mixed.

In the same way standard amylose solutions of nine concentrations and amylose–iodine complexes were prepared. All of flasks with obtained solutions were covered with aluminum foil to prevent direct light exposure, as I–KI disintegrates on exposure to light. After 20 min, the absorption spectra of formed complexes were recorded, and absorbances at 620 nm (including blank) were read from VIS spectra and plotted against amylose concentration.

The calibration plot can be described by straight line function:

$$A_{620} = 0.0217c + 0.0068$$

where c is amylose concentration ($R^2 = 0.9987$).

Moreover, the absorptivity constant (a) for starches at 620 nm were calculated by dividing the absorbance by starch concentration expressed in μg/ml.

2.2.3. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra (with resolution of 4 cm^{-1} and accumulation of 64 scans) of starch powders were recorded with a Genesis II FTIR spectrophotometer (Mattson, USA) equipped with ATR device – MiracleTM Pike Technologies containing zinc-selenide crystal. The spectra were base-line corrected and then deconvoluted (gamma factor 10, increment 0.1, peak width 20 cm^{-1}) using Grams/AI 8.0 software, avoiding the essential changes in spectrum shape.

2.2.4. X-ray diffraction (XRD)

X-ray diffraction patterns of starch powders were obtained by means of X'PertPRO, Philips (Panalytical, Holland) operating at voltage 40 kV, current 30 mA; scanning speed 7.5×10^{-3} °/s. The applied radiation from target CuKα was nickel filtered (λ = 1.540 Å). The range of scattering angles (2θ) was 4–40°. The obtained curves have been mathematically elaborated using Hpert High Score software (supplied by producer).

Table 1
The water and amylose content (before and after 8 h UV-irradiation) and absorptivity coefficients (from UV–vis spectroscopy) for four native starches.

Starch source	Water content, %		Amylose content, %		Absorptivity at 620 nm
	0 h	8 h	0 h	8 h	
Corn	11.7	5.4	24.3	22.0	10.69×10^{-3}
Waxy corn	12.9	4.9	8.00	6.50	3.400×10^{-3}
Wheat	13.3	4.3	24.0	22.2	10.51×10^{-3}
Potato	19.2	4.1	26.1	24.0	11.38×10^{-3}

The relative degree of crystallinity (X_c, %) has been calculated as the ratio between the area of crystalline signals (A_{cryst}) and the total area (A_{total}) of the diffractogram:

$$X_c = \frac{A_{cryst}}{A_{total}} \times 100\%$$

2.2.5. UV-irradiation

Thin layers of starch powders (about 0.1 mm thick) were exposed to low-pressure mercury vapor lamp TUV-30W (Philips, Holland) at room temperature and in air atmosphere. The wavelength and intensity of emitted radiation was 254 nm and 33.4 W/m^2, respectively. Maximal time of exposure was 16 h.

2.2.6. Size exclusion chromatography (HPSEC)

Average molecular weights ($\overline{M}_w, \overline{M}_n$) and molecular weight distribution (polydispersity, $P = \overline{M}_w/\overline{M}_n$) have been determined using high-performance liquid chromatography (HPSEC) equipped in two detectors: Multiple Angle Laser Light Scattering (MALLS) Detector type Dawn-DSP-F (Wyatt, Santa Barbara CA, USA) and Merck L-7290 refractive index detector. The system contained Shimadzu 10AP pump, Rheodyne 7021 valve and two columns: TSK Gel GMPWXL and TSK Gel 2000 PW (7.8 mm × 300 mm), Tosoh Corporation, Tokyo, Japan.

The starch samples were dissloved in DMSO, boiled for 2 h, intensively stirred and then filtered through a 5 μm filter before injection.

The mobile phase was 0.15 M solution of sodium nitrate. The flow rate was 0.4 ml/min, volume of injected solution was 500 μl and the temperature of columns was 50 °C. The molecular weights and polydispersity were calculated using Astra 4.73.04 software (Wyatt, Santa Barbara, CA, USA). The Berry method was used for results extrapolation. The standard error was lower than 1%. The details of GPC analysis have been described earlier (Fiedorowicz, Tomasik, & Li, 2001).

3. Results and discussion

The samples of 4 types of starch have been subjected to UV-irradiation within 1–16 h. Systematically, after each hour of the process, the FTIR and Vis spectra as well as XRD patterns were registered. The greatest changes in the measured parameters arose within the first 8 h of irradiation. After this time further changes were within the measurement error so only the changes after 8 h treatments were discussed. This time refers to a total irradiation dose equals to 962 kJ/m^2.

3.1. Moisture content

The moisture content (Table 1), which has an important effect on starch properties, is about 12–13 wt% in **CSt**, **WCSt** and **WSt** specimens but a few % higher in **PSt** (19.2%). The adsorbed water plasticizes the macrochains enhancing their mobility. Moreover, water molecules participate in hydrogen bonding and helix

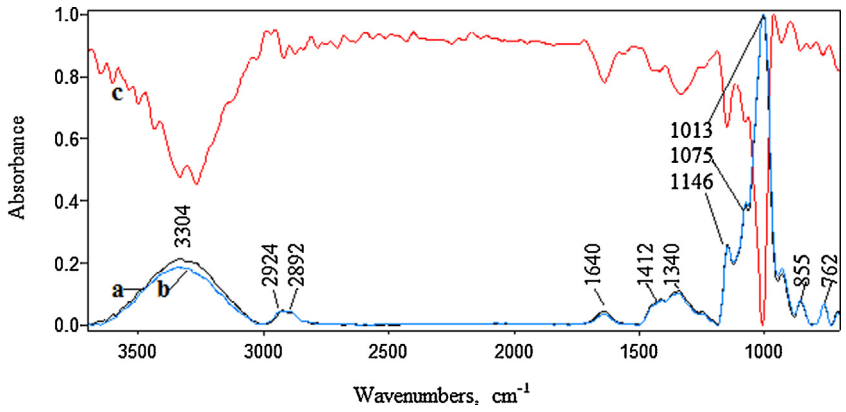

Fig. 1. ATR-FTIR spectra of corn starch: (a) untreated, (b) 8 h UV-irradiated and (c) difference spectrum.

formation. Thus, water plays an important role in crystallization process of polysaccharides (Bayer, Cagiao, & Balta Calleja, 2006).

In all UV-irradiated starches, stored at the same conditions as unexposed specimens, the amount of water systematically decreased. As can be seen from Table 1, after 8 h of exposure the content of moisture is similar in all types of starch (ca. 4–5wt%). Because there were no further changes of sample weight at temperature chosen for drying (95 °C), one can conclude, that only strongly bounded water remains and its content is independent on the starch type.

The smaller values of MC in exposed samples suggest that part of bound water was eliminated during UV-irradiation.

3.2. Apparent amylose content measured by visible spectroscopy

The numerous techniques have been proposed for quantitative estimation of amylose (for instance, Correia & Beirão-da-Costa, 2011; Das, Singh, Singh, & Riar, 2010). The result depends not only on the method used but also on the procedure applied and sample preparation. We decided to use the spectroscopic method owing to its availability and simplicity.

UV-irradiation of starch powders causes negligible changes in apparent amylose content, which indicates that both components have similar resistance to UV exposure (Table 1). The small decrease of apparent amylose content (about 2%) suggests its somewhat lower photostability comparing to amylopectin.

Probably linear amylose chains, which are more flexible, undergo partial photocrosslinking, mainly at the surface of starch granules. Such crosslinks can enhance the polysaccharide structure and protect further deterioration.

It is known, that amylose content affects the nutritional and technological properties (Gerard et al., 2001).

3.3. Structure characterization by ATR-FTIR spectroscopy

An example of ATR-FTIR spectrum of unexposed and 8 h UV-irradiated corn starch is presented in Fig. 1. The main absorption bands appear in the ranges characteristic for polysaccharides: 3000–3500 cm^{-1}, attributed to hydroxyl groups and adsorbed water vibrations (broad, very intensive); 2800–3000 cm^{-1}, C—H stretching vibrations (medium intensity); 1640 cm^{-1}, bending mode of adsorbed water (low intensity); 900–1200 cm^{-1}, arising from (C—O—C stretching vibrations in glycosidic linkages and in glucose rings). Moreover, some other specific peaks with medium intensity in 400–1500 cm^{-1}, i.e. in fingerprint region, are observed.

C—O—C band delivers information concerning content of crystal and amorphous phase in tested samples (Bernazzani, Peyyavuala, Agarwal, & Tatikonda, 2008). This band in the 800–1300 cm^{-1}, called "saccharide band" is sensitive to conformational changes. The band at 995 cm^{-1}, which is due to C—OH bending vibrations (also in hydrogen bonds), is particularly sensitive to water content in starch.

There are no significant differences between FTIR spectra recorded for samples from various origins (**CSt**, **WCSt**, **WSt**, **PSt**). Nevertheless, the comparison of absorbance of particular bands exhibits some alterations. In C—H stretching region two unresolved bands exist at 2926 cm^{-1} and 2890 cm^{-1}, with absorbance ratio similar for **CSt**, **WCSt** and **WSt** (~1.2), whereas A_{2926}/A_{2890} is somewhat higher for **PSt** (~1.5).

The detailed analysis of C—O—C band enables to point out the difference in structure of starch samples before and after irradiation. To determine thoroughly those changes, this band has been subjected to deconvolution (Fig. 2). After this numerical procedure, the weak bands are amplified, thus, they can be partially separated. The calculated ratios of absorbance at 1040 cm^{-1} and 1012 cm^{-1} ($R = A_{1040}/A_{1012}$) are similar for samples of **CSt** and **WCSt** but somewhat higher for **WSt** and **PSt** (Table 2). UV-irradiation leads to small changes of these values: slight increase in **CSt** and **WCSt** but decrease in **WSt** and **PSt** specimens.

It was reported that the ratio of absorbance at 1047 cm^{-1} and 1032 cm^{-1} or 1045 cm^{-1} and 1022 cm^{-1} increases with the increasing content of short range alignment of helices (Dithal, Shrestha, Flanagan, Hasjim, & Gidley, 2011; Rindlav, Hulleman, & Gatenholm, 1997). Thus, this proportion is often interpreted as the ratio of crystalline and amorphous phase fractions. It was also proved that bands at 1000 cm^{-1}, 1022 cm^{-1} and 1047 cm^{-1} are sensitive to starch crosslinking and transition from helix to random coil (Ispas-Szabo, Ravenelle, Hassan, Preda, & Mateescu, 2000). Thus, changes observed in this region are due to the complex conformational and rearrangement photophysical processes as well as possible photochemical reactions.

Besides the changes in the adsorption ratio R, the integral intensity of hydroxyl and C—O—C bands drops after UV-irradiation of the samples, indicating the macromolecules photolysis. The observed

Table 2
Ratio of intensities at 1040 cm^{-1} and 1012 cm^{-1} (obtained from FTIR spectra) and relative crystallinity degree (X_c, %, from XRD) of starch samples before and after 8 h UV-irradiation. In brackets – the percentage changes of X_c after 8 h UV.

Starch source	$R = A_{1040}/A_{1012}$		X_c, %	
	0 h	8 h	0 h	8 h
Corn	0.5869	0.5902	25.91	21.47 (17%)
Waxy corn	0.5848	0.6136	33.20	29.25 (12%)
Wheat	0.6260	0.6180	19.88	15.24 (23%)
Potato	0.6506	0.6136	17.62	8.750 (50%)

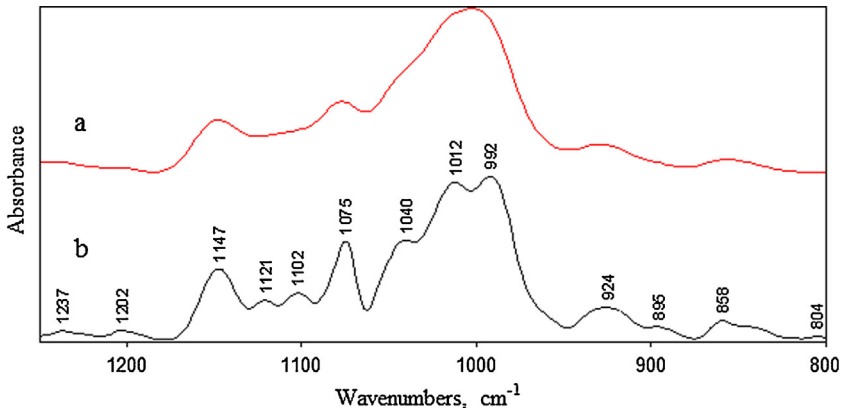

Fig. 2. ATR-FTIR spectrum of corn starch in 800–1250 cm^{-1} range: (a) original spectrum and (b) deconvoluted.

changes are irregular suggesting some reversibility of the photo-processes.

Fig. 3 shows the relative changes of intensities of chosen characteristic bands at: 3000–3620 cm^{-1}, 1550–1700 cm^{-1} and 900–1100 cm^{-1} ranges after 8 h exposure. Exposed potato starch exhibits the highest changes indicating its instability comparing to other starches.

It should be added that formation of carbonyl groups was not observed, thus, photooxidation with formation of such moieties does not occur in the starches studied.

3.4. X-ray diffraction

The crystals types (A, B, C and V) existing in starch have been described in literature (Avérous & Halley, 2009; Myllärinen, Buleon, Lahtinen, & Forssell, 2002; Tester, Karkalas, & Qi, 2004).

The X-ray diffraction patterns of our samples are presented in Fig. 4. All starches are characterized by the partial crystallinity (Table 2). The strongest reflections (at 2θ ~15, 17, 18 and 23°) appearing in the diffraction spectra of **CSt**, **WCSt** and **WSt**, indicate the presence of A-type structures (Fig. 4a, b,and c). The signal at 17–18° is a weakly separated doublet. The small variations in the peak position and intensity arise from the different macromolecules arrangement determined by amylose/amylopectin ratio and content of water in the samples.

Only **PSt** pattern varies considerably from three other starches. Characteristic signals at 2θ ~6, 17, 20, 22 and 24° (Fig. 4d) can be assigned to the B-type crystallities. It was stated that the degree of crystallinity is inversely proportional to the amylose content (Cheetham & Tao, 1998; Frost, Kaminski, Kirwan, Lascaris, & Shanks, 2009).

Very weak peak detected at about 20° in pattern of **CSt**, **WSt** and **PSt** samples (but not present in starch **WSt**) can be attributed to small amount of V-type crystallities (single helical complexes). All parameters obtained from XRD for all four starches before and after exposure to UV are listed in supplementary materials.

The unexposed sample **WCSt** has the highest X_c, whereas starch **PSt** is characterized by the lowest X_c among studied specimens.

UV-irradiation caused insignificant alteration of X-ray diffractograms of **CSt** and **WCSt** as well. Somewhat higher changes (but still negligible) have been observed in **WSt**.

The largest effect on crystallinity after UV treatment is in **PSt** – the diffraction reflections become broader and less intensive, which indicates that the efficient amorphization takes place in this sample. The peak at $2\theta = 5.5°$ characteristic only for this starch disappears completely after UV-irradiation. It suggests the lower

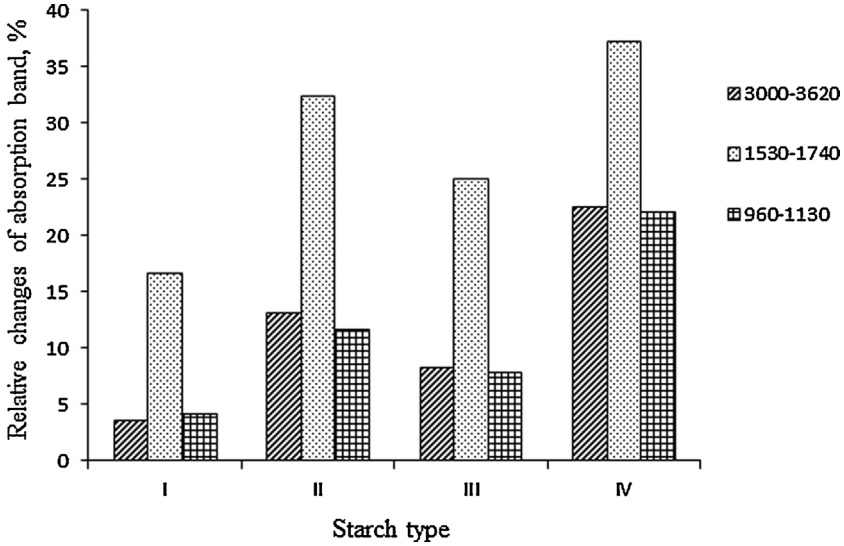

Fig. 3. The relative changes of band at 3000–3620, 1530–1740 and 960–1130 cm^{-1} in FTIR spectra of starches after 8 h irradiation; expressed in % (changes were calculated by dividing the integral intensity of chosen peaks by area of standard band at 2800–3000 cm^{-1} range due to C—H stretching vibrations).

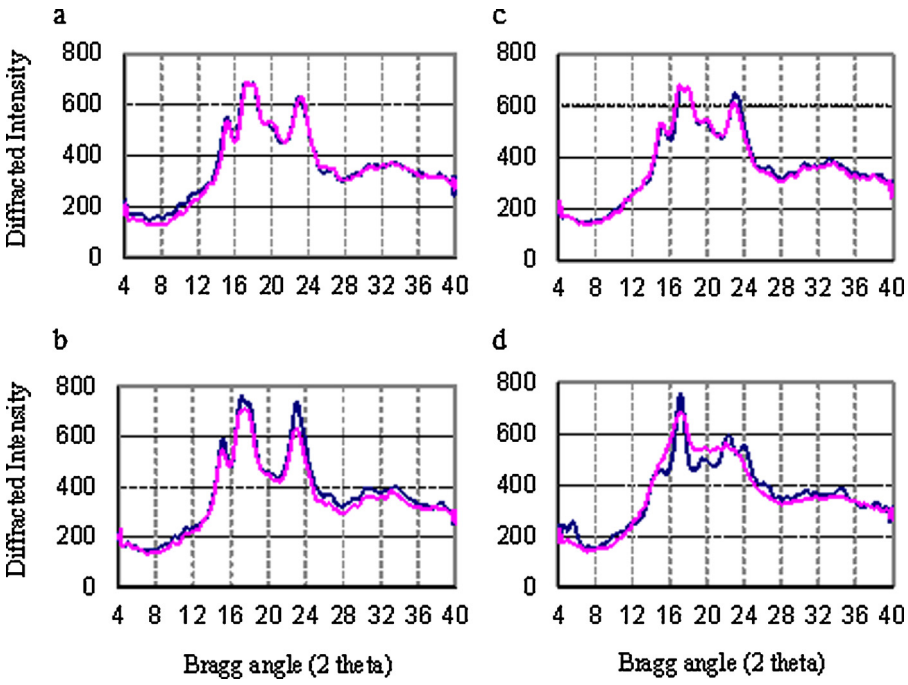

Fig. 4. X-ray diffraction patterns of unexposed (blue) and 8 h (pink) UV-irradiated specimens: corn (a), waxy corn (b), wheat (c) and potato (d) starches.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photostability of B-type structure comparing to A-type crystallities, which are strongly dependent on the amount of water. Probably, B → A transformation can occur, which is opposite process to described by Soest during storage of starch at 70 and 90% relative humidity (Van Soest, Benes, de Witt, & Vligenthart, 1996).

The significant drop of crystallinity degree (50%) in potato starch after exposure to UV can be explained by the both photochemical reactions and the photophysical processes (such as conformational changes). It explains the lowest photostability of this sample monitored by FTIR among studied starches. Moreover, the loss of water during exposure leads to the changes in macromolecules arrangement, too. It is known that water plays an important role in intermolecular interactions in starch crystallities. Some water molecules directly participate in hydrogen bonding with OH groups from polysaccharide. Thus, H_2O removal and partial destruction of hydrogen bonds leads to destabilization of structure. furthermore, the water loss can cause conformational transitions and finally change the crystallinity degree. A similar effect of water has been observed in the case of dehydrated, dried starch (Shorgen et al., 2006).

It should be mentioned that potato starch contained the highest amount of moisture, thus, its elimination during irradiation may be one of the reasons for the changes in molecular order compared with the other starches.

These observed results are consistent with the previously published data (Tester, Karkalas, & Qi, 2004). The crystallinity has the decisive impact on the functional properties of starch including stability, barrier properties and enzymatic behavior.

3.5. Size exclusion chromatography

The chromatograms of native starches did not show clear separation between amylose and amylopectin peaks, thus, it was impossible to calculate the molecular weights of both components. This means the results are some mean of the that amylose and amylopectin fractions.

8 h UV-irradiation caused the significant drop of both molecular weights in **CSt**, **WCSt** and **WSt**, which is an evidence of main chain scission (Fig. 5). The other trend was observed in **PSt**, where the increase of average molecular weights was found, suggesting that photoaggregation or even photocrosslinking occurs. It is possible, that aggregates are formed in **PSt** during retrogradation because potato starch contains the more linear chains (owing to higher amylose content) susceptible to rearrangement upon UV radiation.

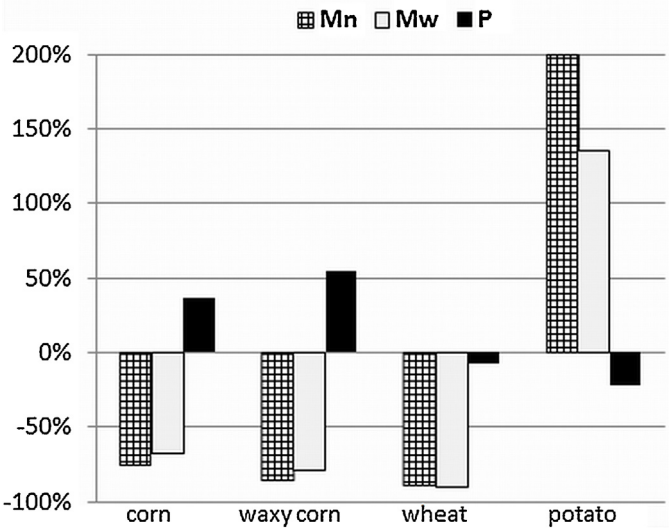

Fig. 5. The percentage changes of average molecular weights and polydispersity of four native starches after 8 h UV-irradiation (obtained from SEC analysis).

The increase of molecular weight and viscosity on corn starch photocrosslinking was also reported by Fiedorowicz, Tomasik and Li, 2001.

The polydispersity (P) increased in samples **CSt** and **WCSt**, but decreased in **WSt** (slightly) and **PSt** (significantly) after exposure. The rise of polydispersity is an evidence of competing reactions: chain scission and macroradical recombination. A drop in P indicates that starch becomes more uniform after UV-irradiation.

3.6. Discussion of mechanism of starch photodegradation

The general mechanism of photo-oxidative degradation of polysaccharides is considered as a free radical process. Main photochemical reactions involved in starch are chain scission, dehydroxylation, dehydrogenation and glycoside ring opening (Bertolini, Mestres, Colonna, & Raffi, 2001a; Bertolini et al., 2001b; Fiedorowicz et al., 2001). All of them lead to formation of free radicals ($P^{\bullet}$), which can then react with atmospheric oxygen giving peroxyradicals ($POO^{\bullet}$) or abstract hydrogen atoms from the neighboring units. The peroxy and alkyl radicals participate in secondary processes resulting in a complex mixture of photo-products is formed. However, their content in starch is usually very low and difficult to detect. The termination step of photodegradation is a result of recombination or disproportionation of free radicals.

The main chain scission in UV-irradiated starch has also been proved by viscometric measurements (Bertolini et al., 2001a,b). The formation of free radicals has been confirmed by electronic spin resonance. It has been ascertained, that radicals formed in starch during photo- and thermal-degradation as well as upon gamma irradiation are the same.

4. Conclusions

UV irradiation of starches causes mainly the physical changes: the loss of water, which is responsible for the conformational transformation and formation of less ordered structures than those in native polysaccharides. FTIR and SEC indicate that photolysis with breaking of glycoside bonds also takes place in studied starches. VIS spectroscopy proves slightly lower photostability of amylose comparing to amylopectin.

It was found that potato starch differs significantly from three others polysaccharides – it contains the highest amount of water and the lowest degree of crystallinity. It is less photostable as well as more susceptible to amorphization during exposure to UV than other samples. Only in potato starch the aggregation (or macroradicals recombination) dominates, contrary to three other starches, where the main chain scission is more efficient. On the other hand, waxy corn starch is characterized by high content of amylopectin and the highest crystallinity but its photostability almost does not differ from corn starch.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.05.090.

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