Preparation and properties of hydrogen peroxide oxidized starch for industrial use

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Abstract

Oxidized starch, an additive used in paper manufacturing and products for construction industry, is usually produced using harmful oxidant, such as hypochlorites or periodates. In this study, a simple and efficient eco-friendly laboratory and industrial procedures for starch oxidation were developed. The procedure involves application of small amounts of more environmentally friendly oxidant, hydrogen peroxide, a novel special metal complex catalyst such as copper(II) citrate and copper(II) ricinoleate and biobased plasticizers. Optimization procedure, with respect to the quantity of hydrogen peroxide and temperature in the presence of iron(II) sulphate catalyst, was performed by using the response surface methodology. Comparative analysis of the use of the other catalysts that is copper(II) sulphate, copper(II) citrate and copper(II) ricinoleate, indicated copper(II) citrate as the catalyst of choice. Improvement of starch is achieved using three plasticizers: ricinoleic acid (RA), diisopropyl tartarate, as well as epoxidized soybean, linseed and sunflower oils. The effects of hydrogen peroxide and catalyst concentrations, as well as the reaction temperature in the presence of naturally based plasticizers on the physicochemical, thermal and morphological properties of oxidized starch are presented. According to the results obtained in initial experiments, the optimal industrial process is based on the use of copper(II) citrate (0.1 %) as a catalyst and RA (3 %) as a plasticizer.

Keywords: starch oxidation, environmentally friendly process, carboxyl and carbonyl groups, structure, technological properties

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1. INTRODUCTION

Starch is a naturally occurring, biodegradable, biocompatible, non-toxic, renewable, low cost and abundantly available polysaccharide [1-5]. It is widely distributed in the form of tiny granules that contain linear amylose and branched amylopectine, which represent approximately 98–99 % of the dry weight [6]. Starch powder also contains small amounts of proteins, lipids, water, and traces of phosphorus, magnesium, and calcium compounds [7-8]. There are myriad of hydroxyl groups within the starch structure, two secondary at C-2 and C-3 of each glucose residue, as well as one primary at carbon C-6 [7]. The presence of numerous surface hydroxyl groups makes it susceptible to substitution reactions, which enable tuning the material properties for various application fields.

Modification of starch is carried out to overcome shortcomings of native starch and increase its usefulness for industrial applications [9] especially in respect to the evolution of new processing technologies and market trends [10]. Basically, there are four widely used approaches for starch modification: chemical, physical, enzymatic and genetic modifications [9,11-12]. Chemical modification provokes structural alteration and introduction of oxygen containing functional groups, thus affecting the physicochemical properties of the starch and making it suitable for various industrial uses. Recently, oxidized starches have been widely used in paper, textile, construction and food industries [13-14].

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Starch oxidation involves oxidation of primary or secondary hydroxyl to carbonyl or carboxyl surface groups [7,15], whereas the number of these groups indicates the modification efficacy [16]. Oxidized starch exhibits lower viscosity and tendency for structure deterioration, while better clarity, film forming, and binding properties than the native starch [17-19]. Oxidized starch is commonly prepared by starch reaction with a specified amount of an oxidant under controlled temperature and pH [20-21]. Several oxidants have been applied including hydrogen peroxide, oxygen, ozone, bromine, chromic acid, permanganate, nitrogen dioxide and hypochlorite.

The use of hydrogen peroxide has become widespread due to its low price, high oxidation potential and beneficial environment-friendly qualities like safety of use and production of non-toxic wastes. Lacks in the use of hydrogen peroxide are low reactivity towards most organic functional groups and the fact that in the presence of the compounds with electrophilic character it behaves as a nucleophile, not exhibiting oxidizing properties. This unfavorable property of hydrogen peroxide can be overcome by using catalysts such as metal ions: Cu(II), Fe(II), Fe(III), Co(II), Ti(III), W(VI) or V(V) [7]. The most promising catalysts for starch oxidation are copper and iron ions, especially when they are combined [22]. Iron ions promote starch oxidation while copper ions enhance the effect of Fe(II) ions. Mechanisms of the reaction between hydrogen peroxide and starch are very complex and depend on the reaction conditions (pH, temperature, concentration, *etc.*), type of the oxidant and starch resource [23]. It is shown that the efficacy of starch oxidation, expressed as a number of carbonyl and carboxyl groups, and depolymerization are favored in alkaline medium [22]. Additionally, the content of carboxyl and carbonyl groups is higher as the temperature of starch oxidation by hydrogen peroxide, increases [18]. Selection of the appropriate catalyst as well as its concentration have the essential impact on duration of the oxidation reaction and the quality of the targeted product. It was reported that implementation of 0.5% of $CuSO_4$ is sufficient to reduce the reaction time from 72 h to just 1 h [2].

Besides oxidation, esterification is commonly taken into consideration in order to expand the starch usefulness in industrial applications and improve its processability [24-25]. Generally, modifiers used for this purpose are high fatty acids, with superb hydrophobicity and biodegradability, which are commonly mixed with starch in an organic solvent to obtain the targeted end-product [26]. However, utilization of organic solvents has been recently disapproved due to economic, environmental and safety drawbacks [27]. Solvent-free procedures, such as solid phase synthesis (SPS) and mechanical activation, simplify the reaction process [28-29]. The advantage of such technique is environmental safety since it excludes the use of potentially hazardous organic solvents and generation of wastewater [25]. All of these aspects make this process attractive for further innovative improvements and scale-up to the industrial level.

To avoid the use of harmful oxidants such as hypochlorites or periodates and adopt the environmental concerns and regulations it is necessary to develop new technologies having low environmental impact, high performance products and stability with short periods for the return of investments. Therefore, the aim of this work was to develop a process for industrial starch oxidation with reduced generation of inorganic by-products by replacing harmful oxidants with an environmentally friendly oxidant *i.e.* hydrogen peroxide, and the use of a novel metal complex catalyst. Also the aim was to achieve high efficiency and improved processability by using biobased plasticizers. Further, the objective was to evaluate the developed SPS starch oxidization process and determine the effects of different process parameters on physicochemical, structural, thermal and morphological properties of the obtained oxidized starch. These parameters include the hydrogen peroxide concentration, temperature (20 and 80 °C), different special catalysts (iron(II) sulphate, copper(II) sulphate, copper(II) citrate and copper(II) ricinoleate) and the addition of natural plasticizers/modifiers within the material structure (ricinoleic acid (R-(Z))-12-hydroxy-9-octadecenoic acid) (RA), diisopropyl tartarate (dipropan-2-yl 2,3-dihydroxybutanedioate) (DIPT) as well as epoxidized soybean, linseed and sunflower oil (ESO, ELO and ESFO, respectively)) on the extent of oxidation and properties of the obtained products.

2. EXPERIMENTAL

2. 1. Materials and methods

Details on materials, laboratory isolation and characterization of ricinoleic acid, epoxidation of soybean, linseed and sunflower oil and synthesis of diisopropyl tartarate, copper citrate and copper ricinoleate are given in the Supplementary material.

2. 1. 1. Laboratory preparation of oxidized starch by the SPS method

Starch was oxidized by using hydrogen peroxide with or without plasticizers and metal catalysts at different temperatures. In a typical experiment, wheat starch and synthesized plasticizers (sections 1.2.1-1.2.3 – Supplementary material), were vigorously grinded/homogenized at room temperature for 15 min. After that, in the obtained mixture a catalyst ($FeSO_4 \cdot 7H_2O$, copper citrate or copper ricinoleate) was added at the quantity shown in Table 1 and grinded additionally for 10 min in a mortar. When a fine material was obtained, hydrogen peroxide was sprayed over the mixture at vigorous mixing at room temperature for 30 min, and then at 80 °C for 30 min. Experiments 1-8, 14, 15 and 17 (Table 1) were performed to investigate the influence of the metal catalyst, hydrogen peroxide amount and reaction temperature on the degree of the starch oxidation. Experiments 9-13 and 16 (Table 1) were performed to investigate the influence of the plasticizer type on the efficiency of starch oxidation, *i.e.* improvement of material processability. Plasticizers were introduced before catalyst addition in order to achieve effective catalyst distribution into starch material. Moreover, a range of experiments was performed with copper(II) sulfate to evaluate the catalytic efficacy with respect to iron(II) sulphate and similar results were obtained (data not presented). Table 1 shows the amounts of used reactants and experimental conditions in Exps 1-17. Figure D3 shows mechanisms of starch oxidation by using hydrogen peroxide [21-22].

Table 1. Quantities of reactants and reaction conditions used in experiments at the laboratory level

Sample	Starch mass, g	Plasticizer	Plasticizer volume, cm^3	H_2O_2, volume, cm^3	Catalyst	Catalyst mass, g	T / °C
Exp 1	20	-	-	3.6	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 2	20	-	-	3.6	$FeSO_4 \cdot 7H_2O$	0.01	80
Exp 3	20	-	-	1.9	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 4	20	-	-	1.9	$FeSO_4 \cdot 7H_2O$	0.01	80
Exp 5	20	-	-	1.5	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 6	20	-	-	1.5	$FeSO_4 \cdot 7H_2O$	0.01	80
Exp 7	20	-	-	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 8	20	-	-	1.2	$FeSO_4 \cdot 7H_2O$	0.01	80
Exp 9	20	RA	0.4	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 10	20	DIPT	0.4	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 11	20	ESO	0.4	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 12	20	ELO	0.4	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 13	20	ESFO	0.4	1.2	$FeSO_4 \cdot 7H_2O$	0.01	20
Exp 14	20	-	-	1.2	-	-	20
Exp 15	20	-	-	1.2	Cu citrate	0.01	20
Exp 16	20	RA	0.4	1.2	Cu citrate	0.01	20
Exp 17	20	-	-	1.2	Cu ricinoleate	0.35	20

2. 2. Industrial starch oxidation by the SPS method

Oxidized starch at the industrial level was obtained by using hydrogen peroxide and copper(II) citrate as a catalyst in a horizontal countercurrent mixer. A schematic overview of the technological process for the starch oxidation is shown in Figure D4 (Supplementary material). The procedure was as follows: 200 kg of starch (dozer #1 – Fig. D4) and 0.01 kg of the copper(II) citrate catalyst (position #6 – Fig. D4) were mixed for 15 min at room temperature. The plasticizer/modifying agent (ESO or RA) (position #9 or #12 – Fig. D4) was added in the mixture under stirring during 15 min. After that, 20 dm^3 of 10% H_2O_2 solution (dozer #2 – Fig. D4) was continuously sprayed for 30 min at 50 °C. The pH value of the starch dispersion was set between 7 and 8 by using sodium hydroxide solution (position #13 – Fig.D4). The dispersion was mixed for 5 h at 50 °C. Regulation of viscosity of the oxidized starch was achieved by addition of 0.4 kg of hydroquinone (dozer #14 – Fig. D4) under stirring during 15 min. Afterwards, the mixture was extruded (position #15 – Fig. D4) according to the following technological parameters:

- retention time in the extruder of 50 s,
- first zone temperature of 100 °C,

- second zone temperature of 120 °C and
- third zone temperature of 80 °C.

Thereafter, the mixture was dried (position #16 – Fig. D4) and at the end, the oxidized starch was milled (position #17 – Fig. D4) and the final product was obtained, which can be used in paper industry. The industrial batches were produced in the production facility of the HI Župa, Kruševac (Serbia). Three experimental conditions were applied each using 200 kg of starch, 20 dm^3 of the 10 % H_2O_2 solution, 10 g copper(II) citrate as a catalyst, and 0.4 kg hydroquinone: Exp 18 without a plasticizer, Exp 19 with 0.4 kg RA as a plasticizer and Exp 20 with 0.4 kg ESO as a plasticizer.

2. 3. Characterization

Details of characterization methods are given in the Supplementary material.

3. RESULTS AND DISCUSSION

3. 1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the synthesized plasticizers RA, ESO and DIPT are shown in Figure D5 (Supplementary material). Oxidation leads to the replacement of hydroxyl groups with carboxyl and carbonyl groups in the starch molecules, which could be confirmed by FTIR spectroscopy. The FTIR spectra of native and oxidized starches are shown in Figure 1. The absorption peak at 3344 cm^{-1} originates from the –OH stretch vibration of the glucose unit. This band becomes broader after starch oxidation (Table 1, Exps 1, 8, 10 and 16) due to contribution of –OH vibration from carboxylic groups, indicating successfulness of the starch oxidation process.

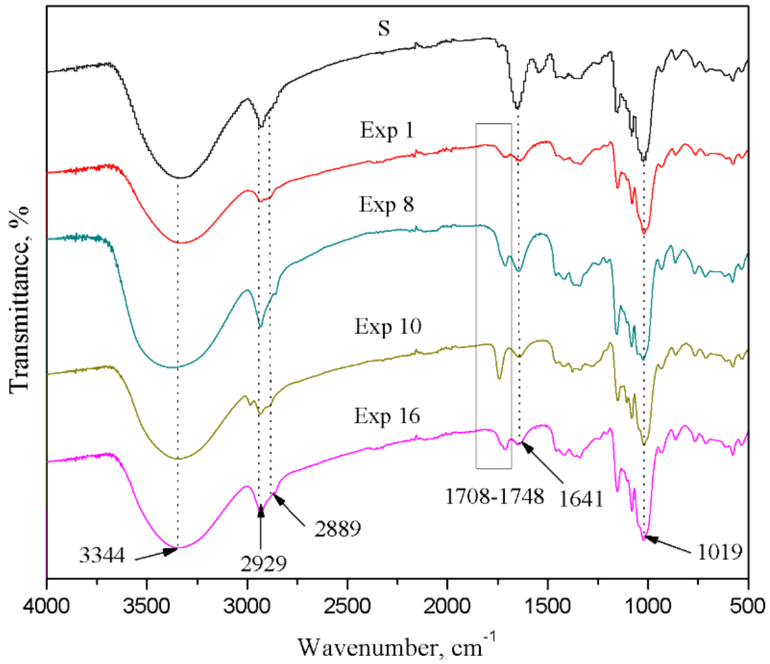

Figure 1. FTIR spectra of native starch (S) and oxidized starch samples obtained in the experiments 1, 8, 10 and 16 (Exp1, Exp 8, Exp 10 and Exp 16, respectively; Table 1)

The bands related to asymmetric and symmetric stretching vibration of methylene groups can be observed at 2927 and 2889 cm^{-1}. The peak at 1641 cm^{-1} is a typical band residing in the spectra of starch and its derivatives, which is attributed to -OH bending vibration originating from adsorbed water molecules [30-31]. After oxidation the intensity of this peak decreases. The absorbance at 1019 cm^{-1} reflects the asymmetric deformation vibrations of C–OH and CH_2 groups [16,32-33].

A new absorption band appearing in the region from 1748 to 1708 cm^{-1} in the spectra of the oxidized starch samples can be assigned to the C=O stretching vibration of oxygen containing functionalities [34-36]. In order to determine contribution of carbonyl, carboxyl and ester C=O groups in the overlapped bands in the region 1600-1770 cm^{-1}, deconvolution is performed, and results are presented in Figure 2 and Table D1 (Supplementary material). A broad peak, in all oxidized starch samples, at ~1726 cm^{-1} corresponds to stretching vibrations of carbonyl (aldehyde) groups. These peaks, overlapped with intensive stretching vibrations observed at 1708 to 1719 cm^{-1} indicate introduction of a significant amount of carboxyl groups onto oxidized starch molecules. Moreover, in the presence of DIPT and RA (Exps 10 and 16), peaks at 1744 and 1748 cm^{-1} are observed indicating the DIPT presence or formation of an RA ester, respectively. Areas of the carbonyl and carboxyl groups peaks (Table D1, Supplementary material) are in accordance with carboxyl and carbonyl contents determined by titration methods (Table D1, Supplementary material). Overall, the FTIR spectra indicate that native starch was successfully oxidized by hydrogen peroxide*, i.e.* hydroxyl groups were successfully converted to carboxyl and/or carbonyl groups.

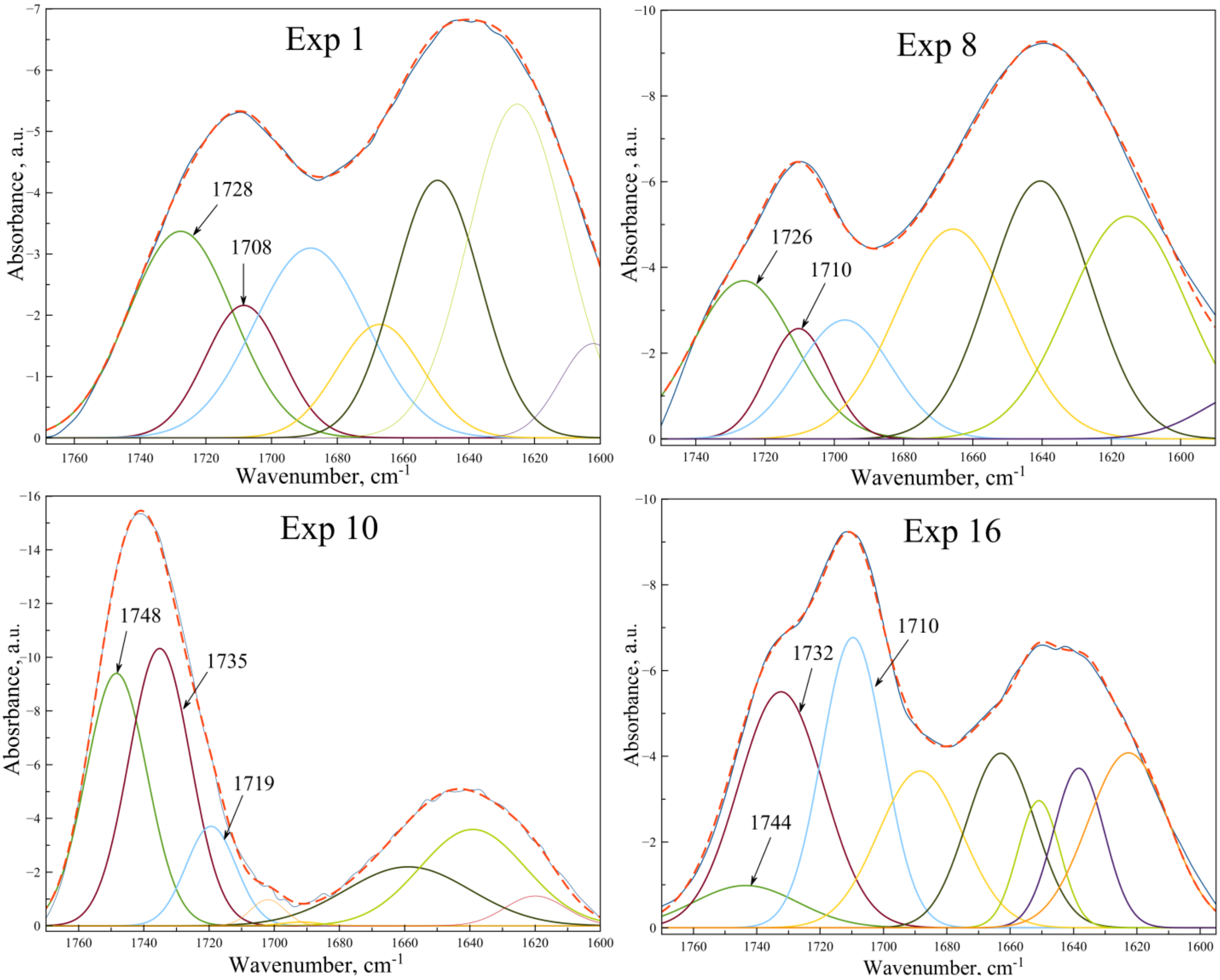

Figure 2. Deconvolution of the CO band (1708-1748 cm^{-1}*) of Exp 1, Exp 8, Exp 10 and Exp 16*

3. 2. Contents of carboxyl and carbonyl groups

The carboxyl/carbonyl content express the success of hydroxyl groups oxidation to carboxyl and carbonyl groups per 100 glucose units (COOH/100 GU and CO/100 GU, %). Amounts of carboxyl and carbonyl groups within the structure of native and oxidized starch samples obtained at the laboratory and industrial levels are shown in Tables D2 and D3, respectively (Supplementary material). In both cases starch oxidization using hydrogen peroxide was successful as indicated by the presence of carbonyl and carboxyl groups. A lower content of carboxyl groups is only obtained in the absence of the catalyst (Exp 14). Results of the starch oxidation optimization by the response surface methodology

(RSM) [37-38], presented in the Supplementary material (Table D4 and Fig. D6), indicate that the H_2O_2 concentration, reaction temperature and the presence of a plasticizer (*i.e.* RA/DIPT/ESO/ELO/ESFO) have significant effects on carboxyl and carbonyl contents. The obtained values of carboxyl and carbonyl groups contents are ranging between 0.018 and 0.258, and 0.126 and 0.468, respectively, which is in the excellent agreement with the results of previous studies [19,22]. The increase in the carboxyl group content is remarkable, up to 1300 % (Exp 2), while enhancement in the carbonyl group amount is lower but still significant (about 270 % - Exp 14), in comparison to the values determined in native starch. Such results mostly depended on the H_2O_2 concentration and applied temperature. It is noted that lowering the H_2O_2 concentration leads to the reduction of the carboxyl group content with a slight increase in the amount of carbonyl groups. This finding is particularly emphasized in Exps 7 and 8, which suggests that the used H_2O_2 concentration is not sufficient for complete oxidation of surface hydroxyl groups. Decomposition of hydrogen peroxide, *i.e.* creation of hydroxyl radicals, which oxidize the hydroxyl group in the glucose unit, significantly depends on the reaction temperature [19]. Hereupon, the increasing of temperature from 20 °C to 80 °C accelerates oxidation of native starch for about 50 % [18].

The addition of plasticizers into the oxidized starch formulation has a positive effect on conversion of hydroxyl to carbonyl/carboxyl groups. Steric hindrance, potentially occurring due to the presence of branched plasticizers, is overcome by improved processability, which enables a better contact between the oxidizing agent and native starch. Still, starch hydroxyl groups are more available when the flexible structure of RA is used as a plasticizer (Exp 9), which is evidenced by the higher amount of carboxyl groups obtained in this case (Table D2 , Exp 9). There were negligible differences in the oxidation degree between the experiments 11-13 since the structures/conformation of ESO, ELO and ESFO are quite similar.

A known limitation in the oxidation process is the material processability so that the extent of oxidation is strongly related to the homogeneity of the starch mixture (exterior *versus* interior oxidation of a starch grain). We have tried to solve this problem by application of RA, DIPT, ESO, ELO and ESFO plasticizers (Exps 9-13). Except of DIPT, the other plasticizers are reactive and provide both plastification and reactivity by creating a grafted moiety on the starch chain, so incorporating in that way the internal non-migrating plasticizer in the final product. Similar behavior shows DIPT by establishing hydrogen bonds with the main starch polymeric chain. In addition to the improvement of oxidized starch properties (Table D2), easier processability is achieved by using plasticizers, which provided transmission of the most of the final product properties to the industrial level.

By taking into consideration customer quality requests two synthesized catalyst have been selected in laboratory development of the starch oxidation process: copper(II) citrate and copper(II) ricinoleate (Exps 15-17). The benefit of the use of these two catalysts lies in the compatibility of organic ligands with starch functionalities (better accessibility to the internal starch structure) and plasticizing properties of the non-reacted ricinoleic acid in the copper(II) ricinoleate catalyst. The obtained results indicate the possibility for starch oxidation at lower temperatures (20-40 °C), which could provide processing without heating as a desirable technology as well as improved starch processability. This is an acceptable option for application at the industrial level.

Among these two catalysts better activity is obtained by using copper(II) citrate at lower temperatures (20-40 °C), which is a beneficial processing parameter and provides lower energy consumption. In addition to this finding, the possibility to achieve the necessary extent of starch oxidation (in accordance to the market demand) designated copper(II) citrate in the combination with the RA plasticizer as an optimal choice to be used at the industrial production level.

3. 3. Swelling capacity (SC), water solubility (WS) and viscosity (η)

Tables D5 and D6 (Supplementary material) show that the SC and WS values of oxidized/modified starch are significantly increased (ranged from 15.4 % (Exp 14) to 25.2 % (Exp 2) and from 25.6 % (Exp 14) to 42.8 % (Exp 2), respectively) in comparison to SC and WS values of native starch (11.8 and 19.2 %, respectively). These results are expected for starch which is only oxidized, since hydrogen peroxide disrupts the crystalline structure (due to the breakage of hydrogen bonds in amylose domain) aiding permeation and increasing the active surface available for water penetration into the starch granulates [39]. Conversely, introduction of hydrophobic segments within the starch structure, by esterification with fatty acids/epoxidized oil, should reduce swelling of such modified starch samples. Quite opposite phenomena occur due to appearance of repulsion forces between starch molecules, which increase the free volume available for water penetration into the amorphous region, reflected in a higher SC value. Likewise, the WS of modified samples probably increases due to the structural reorganization, which causes weakening of the starch grains and favors amylose leaching [40]. Contrary to SC and WS values, Tables D5 and D6 show that the starch viscosity is remarkably decreased, in comparison to native starch (~ 1.06 Pa·s), which is primarily due to the reduced content of hydroxyl groups in the oxidized/modified starch structure. In addition, there are additional factors which cause a decrease in the starch viscosity: mechanical treatment, oxidation and modification. Mechanical treatment causes breakage of inter- and intramolecular hydrogen bonds and deterioration of crystalline amylose domains within the starch grain structure [25]. Further on, during the starch treatment by hydrogen peroxide, along with the oxidation of hydroxyl groups to carboxyl and carbonyl groups, carbohydrate chains cleavage also occurs, which could induce a decrease in viscosity of oxidized starch [2]. Introduction of long alkyl chains, by modification, may cause steric hindrance inducing weakening of hydrogen bonds between starch molecules and thus decreasing the viscosity [25]. Lower viscosity leads to better flowability and processability, which can significantly broaden potential uses of the obtained materials.

Viscosity of oxidized starch obtained at the industrial level is in the range of values requested by the customer (<100 mPa·s) (determined by the B Method, Supplementary material), while after one week of storage, a high viscosity build up is observed. This phenomenon may be the effect of additional starch oxidation/cross-linking processes due to the presence of non-terminated reactive oxidative species. The problem is solved by the addition of 0.2% hydroquinone at the end of the oxidation process. The viscosity values of oxidized starch (determined by the B Method, Supplementary material) are lower than 50 mPa·s (Table D6 , Supplementary material), which is a requirement for the application in the paper industry. A similar approach is applied to the procedures according to Exps 1-13 but a significantly higher amount of hidroquinone is necessary, which resulted in brownish coloration of the final product. This drawback eliminates these operating conditions from further consideration for industrial production.

3. 4. Thermogravimetric analysis

Thermogravimetric (TG) analysis has been the conventional and most popular technique used to study thermal stability of starches [41-44]. Thermal properties of native and selected oxidized starches are shown in Figure 3 and Table D7 (Supplementary material). Selection of the samples for thermal analysis is made with the aim to examine the influence of different treatment parameters on the thermal stability: H_2O_2 concentration (Exp 1), temperature (Exp 6) and the type of modifier/plasticizer (Exps 10 and 16). Generally, there is a similar, two-step degradation pattern observed for all analyzed samples (Fig. 3a). Modified starches exhibit somewhat higher thermal stability within the applied temperature range in comparison to the native starch. In the first step, between 25 and 250 °C, the mass loss originates from residue moisture and traces of low-boiling reactants [45]. The second mass loss interval, in the temperature range between 250 and 340 °C, is mainly attributed to starch decomposition processes [46], which intensively occur. The temperature at which 5 % mass loss is occurred (T_5) of the native starch and the oxidized starch obtained in the experiment 1 (Exp 1) are lower as compared to those of the other analyzed samples. These phenomena are related to the dehydration process within native starch as well as to depolymerization of polymer chains by oxidation, which causes a decrease in the molecular weight with the increase in the oxidation degree (Table D2 -Exp 1, Supplementary material) [2]. Additionally, the increased carbonyl content, established by the partial oxidation of hydroxyl groups, weakened hydrogen bonds, resulting in the lower energy demand for degradation of the starch structure obtained in the Exp 1. Conversely, there are negligible differences in the values of the temperature at which 50 % mass loss is occurred (T_{50}), which suggests that the degradation pattern mainly manifests thermal properties of the basic starch structure [47]. The obtained results indicate that the investigated starches can be thermally processed, since the processing temperature is significantly lower than 248 °C.

The somewhat greater thermal stability of oxidized and modified starches is potentially related to the lower amount of remaining hydroxyl groups, *i.e.* the increased content of carboxyl and carbonyl groups [28]. Moreover, the presence of longer carbon chains within the modified starch structure increases its thermal stability (Table D7, Exp 16, Supplementary material) [24]. DTG curves (Fig. 3b) exhibit similar trends with one peak determined for all materials, which reflects decomposition of the starch structure with the maximum at 314 °C for Exp 1 and about 305-307 °C for the other samples.

DSC profiles of both, native and oxidized/modified starches, display one value at about 310 °C (Fig. 3c), which represents the endothermic peak of thermal starch degradation [24].

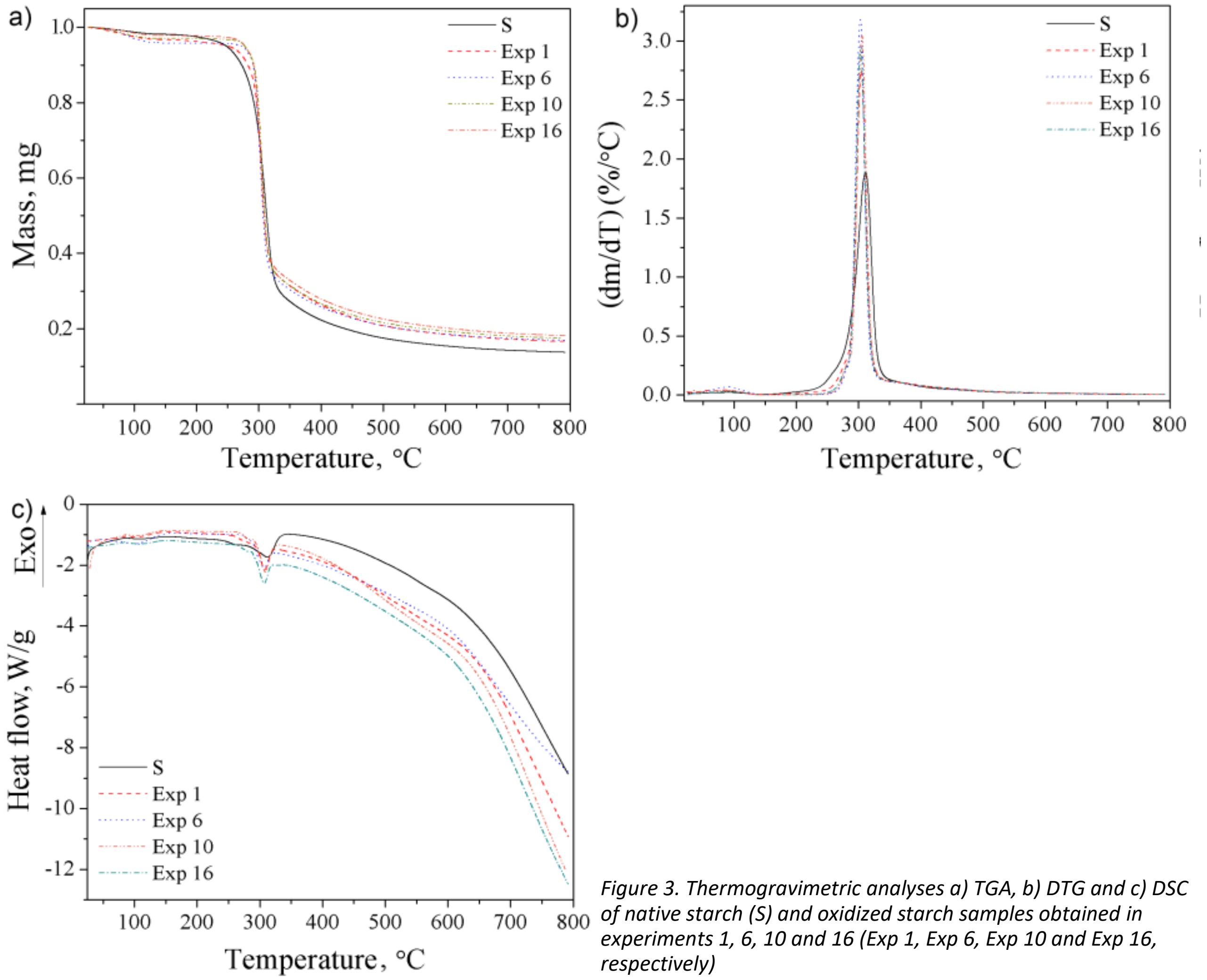

Figure 3. Thermogravimetric analyses a) TGA, b) DTG and c) DSC of native starch (S) and oxidized starch samples obtained in experiments 1, 6, 10 and 16 (Exp 1, Exp 6, Exp 10 and Exp 16, respectively)

3. 5. Scanning electron microscopy (SEM)

Surface morphology micrographs of native and oxidized/modified starches determined by SEM are shown in Figure 4. Native starch appears as large-sized, irregularly shaped granules, somewhat aggregated with smaller ones (Fig. 4a).

The SEM analysis shows that there is no obvious change in granule size, indicating that oxidation mainly causes the changes on the surface of starch particles [48]. However, mechanical activation somewhat caused structural deterioration of starch particles whereby agglomeration occurs to some extent [25], while the influence of oxidation is not clearly seen (Figs 4b-e). Such phenomenon is potentially related to application of the dry method, conducted under anhydrous conditions, which does not cause starch gelatinization. Introduction of RA segments leads to obtaining smooth surfaces of starch granules (Fig. 4e) due to their coverage by coiled hydrocarbon chains additionally anchored by covalent bonding. This implies that mechanical treatment deteriorates the stable amylose crystalline domain, providing an easy access to the oxidizer, which enhances the reactivity of starch and thus the esterification with RA [25]. Presence of DIPT within the starch structure shows a similar effect as RA, but less pronounced (Fig. 4d). DIPT possesses smaller hydrocarbon segments, which are not capable of successful coating of the starch granules and providing such smoothness and gloss as those treated with RA.

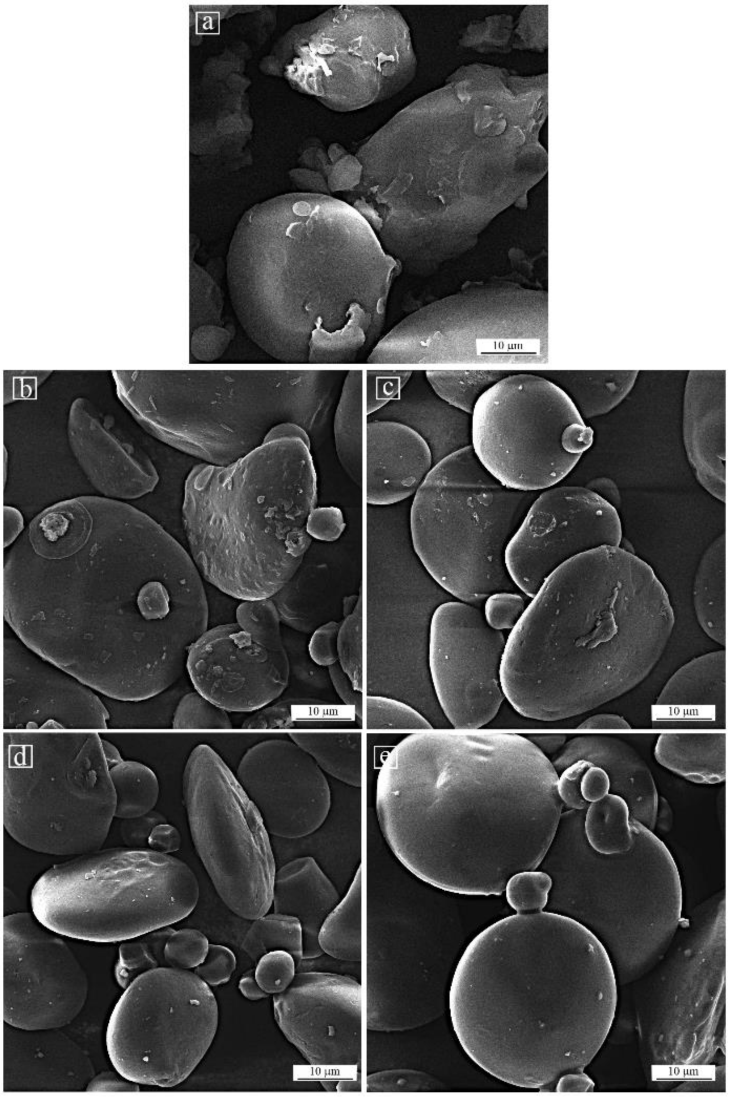

Figure 4. FEG-SEM micrographs of a) native starch, and oxidized starch samples obtained in experiments: b) 1, c) 6, d) 10 and e) 16 (Exp 1, Exp 6, Exp 10 and Exp 16, respectively) (scale bar: 10 µm)

4. CONCLUSION

Development of starch oxidation technology at laboratory and industrial levels was successfully performed based on an environmentally friendly method using hydrogen peroxide. The main intention of the optimization procedure and technology development was establishment of processes, which resulted in maximal oxidation of hydroxyl to carboxyl groups. The obtained values of carbonyl (0.126–0.368 % / 100 GU) and carboxyl (0.060–0.258 % / 100 GU) group contents showed that the increase in these values led to increases in swelling capacity and solubility while viscosity decreased as compared to the values obtained for native starch. Also, starch oxidation results in a small increase in thermal stability as compared to the native starch. The analysis of FTIR spectra, especially the region of carbonyl/carboxyl groups revealed large influences of process parameters on the oxidation degree and band structures. Results of deconvolution and quantification of the peaks in the range 1708-1748 cm^{-1} were in good agreement with the results obtained by volumetric titrations. Morphology of native and oxidized starches, as revealed by SEM analysis, showed that after oxidation the starch particle surfaces become smoother than those of the native starch with aggregation of small and large-sized granules. Obtained results showed that hydrogen peroxide as an environmentally friendly oxidant, combined with biobased plasticizers and novel metal complex catalyst can be successfully used for starch oxidation achieving high oxidation efficiency and improved processability with reduced generation of inorganic by-products.

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SAŽETAK

Priprema i svojstva oksidovanog skroba dobijenog pomoću vodonik-peroksida za industrijsku primenu

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Oksidovani skrob, aditiv koji se koristi u proizvodnji papira i proizvoda za građevinsku industriju, obično se proizvodi korišćenjem štetnih oksidanata kao što su hipohloriti ili perjodati. U ovom radu, razvijen je jednostavan i efikasan ekološki prihvatljiv laboratorijski i industrijski proces za dobijenje oksidovanog skroba. Postupak uključuje primenu malih količina eko-oksidanta, vodonik-peroksida, inovativnih katalizatora na bazi metalnih kompleksa kao što su: bakar(II)-citrat i bakar(II)-ricinoleat, kao i prirodnih plastifikatora. Optimizacija postupka posmatrana u odnosu na količinu vodonik-peroksida i temperaturu u prisustvu katalizatora gvožđe(II) sulfata, izvedena je metodom odgovora površine (*eng*. response surface methodology, RSM). Korišćeni su i drugi katalizatori, bakar(II)-sulfat, bakar(II)-citrat i bakar(II)-ricinoleati uporednom analizom utvrđeno je da je bakar(II)-citrat optimalan katalizator. Poboljšana obrada skroba postignuta je korišćenjem tri plastifikatora: ricinolne kiseline(RK), diizopropil-tartarata, kao i epoksidovanog sojinog, lanenog i suncokretovog ulja. Prikazani su efekti koncentracije vodonik-peroksida, katalizatora i reakcione temperature u prisustvu plastifikatora na prirodnoj bazi na fizičko-hemijska, termička i morfološka svojstva oksidovanih skrobova. Prema rezultatima dobijenim u eksperimentima, dalja implementacija optimalnog industrijskog postupka bazirana je na korišćenju katalizatora bakra(II)-citrata (0,1 %) i RK (3 %) kao plastifikatora.

Ključne reči: oksidacija skroba, ekološki prihvatljiv process, karboksilene i karbonilne grupe, struktura, tehnološka svojstva