

[E0004]

## Microwave assisted starch oxidation – a ‘green’ way for polysaccharide modification.

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### Abstract

The aim of the study is to summarize our investigations on combined action of microwave irradiation (2.45 GHz) and hydrogen peroxide to starch. Depending of oxidation condition (microwave power and temperature) a various products can be obtained – from slightly oxidized to deep degraded starches. Possible mechanisms of the microwave assisted processes were outlined.

### Keywords

Starch, oxidation, hydrogen peroxide, green chemistry, microwave irradiation

### Introduction

Starch as a one of the most common and easy to recover biopolymer become in the scope of many research [1]. Only a few purposes have been found for raw, "native" starch. Most of the material is modified by various methods i.e. physical, enzymatic or chemical. Oxidation of starch may be carried out using different oxidants but most common industrial processes employ sodium hypochlorite and potassium periodate. Such processes suffer from non environmental reaction conditions e.g. large amount of NaCl production and a risk of chlorine by-product formation. Hydrogen peroxide seems to be very promising as the oxidant of organic molecules in terms of non-toxic side products (i.e. water) and high oxidation potential. In fact, oxidation reaction of many organic compounds by H<sub>2</sub>O<sub>2</sub> requires some kind of activation. It is known that starch can be oxidized by hydrogen peroxide, mostly by catalyst based on d metal compounds e.g. Cu (II), Fe(II), Fe(III), Co(II), Ti(III), W(VI) or V(VI) [2]. Based on our previous research concerning microwave assisted organic synthesis [3-6] and especially microwave assisted oxidation of alcohols by hydrogen peroxide [7], we have decided to apply microwave irradiation to improve starch oxidation process. Nowadays, microwave synthesis of organic compounds attracts a lot o researches because of the shortening in the reaction time, which is very often followed by the development in the yield and selectivity [8]. However, these phenomenon's are still beyond the clear explanation; some hypotheses have already been emphasize using dielectric and conducting mechanism of microwave dielectric heating as well as (in some cases) by interphase polarization. The so called "non-thermal" effects have also been suggested by some scientists [8]. Recent research clearly shows that starch strongly interacts with microwave irradiation. A microwave heated starch has different properties than conventionally heated one. Microwave heating might change starch gelatinization mechanism [9-10] and influences on both thermal and pasting properties of starch [11].

### Experimental

Potato starch was purchased from a local market. Hypochlorite oxidized potato starch – E1404 (WPPZ Lubon S.A., Poland), 30% H<sub>2</sub>O<sub>2</sub> (POCH, Poland) and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (POCH, Poland) were used as received. Starch oxidation was carried out in the multimode microwave reactor Moulinet FM A945GS. Temperature was measured by means of two-channel fiberoptic thermometer Reflex RFX-2, Neoptix, Canada. Measurements of microwave absorption and reflexion of starch paste were done on monomode

microwave reactor, Plazmatronika, Poland. Oxidation of starch was conducted as follows: 8.5g (correspondents to 50 mmol anhydrous glucose units) of native potato starch was put into the 170mL of water. The mixture was pasted at 90°C during 15min. The paste was cooled down to 30°C and then for catalytic process 0.9g (3 mmol) of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was added. After 15min of intensive stirring hydrogen peroxide was added (30mL of 30% water solution, 0.3 mol) and sample was irradiated by microwaves at various power or placed into a water bath to heat conventionally. Reaction was stopped when conversion of the oxidant ( $\text{H}_2\text{O}_2$ ) reached more than 90% (manganometric titration). After the reaction was finished - typically up to 0,5h - the solution was cooled down and the starch was recovered by precipitation in cold MeOH. Precipitated starch was centrifuged and dried. Carboxyl content was estimated based on cation-exchanger method [12] with some modification as follows: 1g of starch was pasted in 100ml of deionized water at 130°C (0.2MPa) for 20 min. Next, the sample was cooled down and passed through a column filled with strong cation exchange resin (Amberlite IR120, H+ form). The effluent was titrated by 0.02M NaOH to pH 8.3. A blank sample was titrated as well. Hydroxylamine method to carbonyl groups estimation was applied [13]. Dextrose equivalent (DE) was determined by standard procedure with 3,5-dinitrosalicylic acid (DNS) [13]. Molecular weight distributions were performed by means of Gel Permeation Chromatography (GPC). The system of two columns Ultrahydrogel-2000 and Ultrahydrogel-500 (Waters) connected in a series and RI detector (Knauer) was used. As an eluent 0.1 mol/L  $\text{NaNO}_3$  and 0.02%  $\text{NaN}_3$  solution in water was applied. Flow rate was set to 0.6ml/min and sample volume of 100µl was injected. The sample concentration was c.a. 5mg/ml. A calibration using pullulan standards was performed.

## Results and discussion

Depending on temperature and microwave power product with different oxidation level can be obtained (Fig. 1 and Tab. 1). At lower temperature, oxidation of the polysaccharide is a dominant process. When temperature (microwave power) increases, the polymer depolymerisation (degradation) plays more crucial role in the modification reaction - average molecular weights decrease and DE increase. It should be noted (results not presented) that elimination of tungstate catalyst does not significantly change the properties of the product, thus metal-free variant of the process is a valuable, truly 'green' procedure.

Tab. 1. Yields of microwave assisted epoxidation (MW) with comparison to reactions carried out in conventional condition.

Processing condition	-COOH, mmol/100g	-CHO, mmol/100g	DE, %	Mw, mol/g	Mn, mol/g	Color of the product
1	39	16	2	780000	26400	White-transparent
2	39	26	2	139000	26000	White
3	34	17	3	99000	26800	Brownish

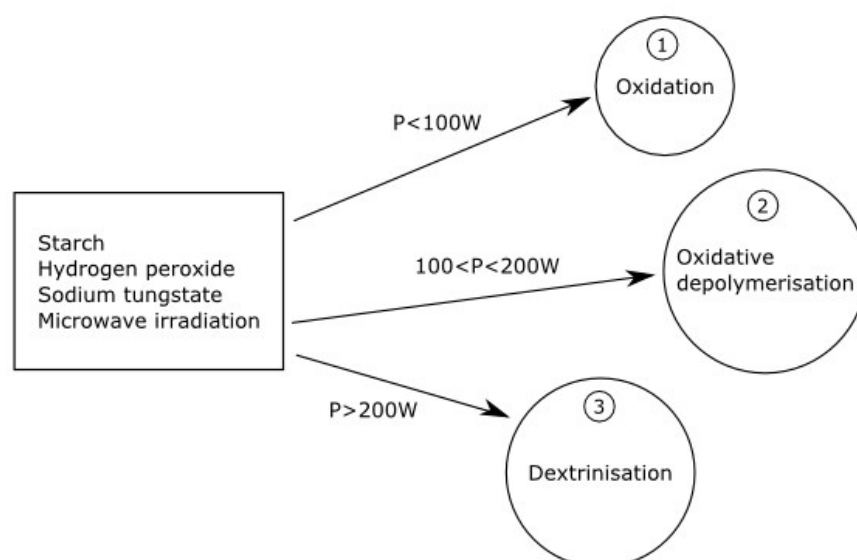


Fig. 1. A brief overview of processes occurred during microwave assisted starch oxidation.

The action of microwave irradiation can be explained by following hypotheses:

- Superheating

Starch paste is a viscous medium thus heat convection is hindered. When microwave irradiation is applied, especially at higher power, formation of hot-spots is possible. Generation of heat might be faster than its dissipation in the paste.

- Microwave induced starch granule destruction

Starch granules contain c.a. 20% of water. During microwave heating the water may evaporate and a pressure generated inside the granule can break it down ('popcorn' effect) (Fig. 2). The residue parts of the granule swell and gelatize rapidly and polysaccharides chains (amylose and amylopectin) transfer to solvent (water) where are easily available for reagents (oxidant). In the case of influence of microwave irradiation on pasted starch (at 90°C for 15min, see experimental part), the effect might be less significant, due to thermal destruction of granules. However, the paste obtained in conventional condition (see above) still contains certain amount of not destroyed granules, which can interact with the electromagnetic waves.

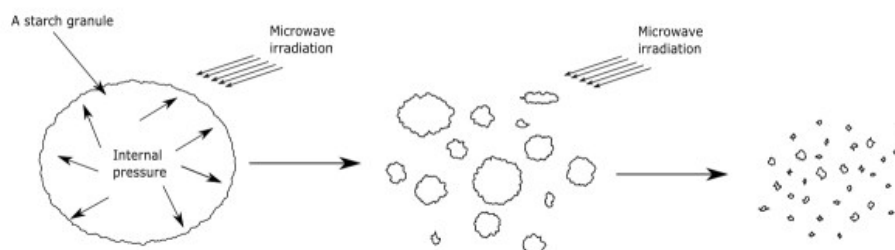


Fig. 2. Microwave induced starch granule destruction.

- Specific starch activation

Starch is a polar polysaccharide with hydroxyl groups capable to interact with microwave irradiation. A specific, non-thermal effect is possible to occur, but difficult to prove. A strict temperature control during the process is needed [3].

The properties of microwave assisted oxidized starches i.e. high yield of carboxyl and carbonyl group and significant depolymerization are comparable to those of obtained by reactive extrusion process [14]. A mechanical stress with action of hydrogen peroxide/Fe(II) system causes, in this case, similar effect to those observed when application of microwave irradiation is jointed with action of hydrogen peroxide even without any metal salt. According to application of microwave oxidized starch it is worth to point out that it may be used as obtained (in the paste form) as well as after precipitation and separation. The pastes are transparent and form strong coatings adhere to e.g. a glass surfaces. It suggests potential application of such product in both paper and textile industry. Additionally, described oxidation process could be easily scaled-up, both on microwave batch reactor or even continuous microwave reactor with rotating quartz tube [4]. More detailed study on mechanical properties of microwave assisted oxidized starches (e.g. rheological behavior) will be subject of further investigations.

## Conclusion

In the conclusion, we would like to point out that application of microwave heating for oxidation of potato starch guides to the high conversion by means of carboxyl content and high polysaccharide depolymerisation. The developed process has clean variant without addition of any heavy metal salt and the product has generally similar or better properties to commercially available one.

## Acknowledgment

The Polish State Committee supported the research for Scientific Research Grant No. N31200731/0848.

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