

Microwave-Assisted Oxidation of Starch using Hydrogen Peroxide

Marcin Lukaszewicz¹, Bohdan Achremowicz¹, Szczepan Bednarz²

¹Department of Carbohydrate, University of Agricultural,
ul. Balicka 122 30-149 Krakow, Poland
e-mail: rmlukasi@cyf-kr.edu.pl

²Department of Engineering and Machinery for Food Industry, University of Agricultural,
ul. Balicka 122 30-149 Krakow, Poland

Abstract Keywords Introduction Experimental Results and Discussion Literature

ABSTRACT

The oxidations of native starch by hydrogen peroxide using microwaves as an energy source is described. The reaction results in oxidation of some primary hydroxyl group into corresponding aldehyde or carboxylic group. The observed differences in the degree of oxidation (monitored by analysis of carbonyl and carboxyl group content) as well as the changes in molecular mass of biopolymer comparing to those found at conventional conditions were showed.

KEYWORDS

microwaves, hydrogen peroxide, oxidation, starch, microwave.

INTRODUCTION

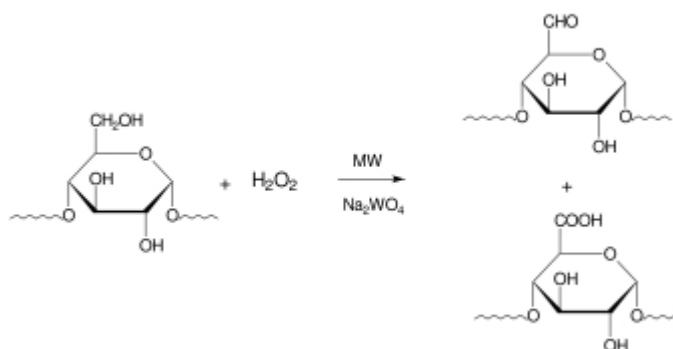
The application of microwaves at the field of synthetic organic chemistry has already been described in many publications [1]. The conclusions from the research, state that such kind of energy may have an influence on both rate and selectivity of the reaction [2]. The phenomenon may be a consequence of the interaction of microwaves with the matter by means of dielectric and conducting mechanism [3]. In the accelerating of the reaction the interphase polarization could also be an important factor [4].

Starch as a one of the most common and easy to recover biopolymer become in the scope of many research [5]. Its application ranges from typical agricultural ones through food industry and, especially nowadays, far beyond its classical perception in modern non-food application [6]. Only a few purposes have been found for raw, "native" starch. Most of the material is modified by various methods i.e. physical, chemical or enzymic. Because of its chemical structure starch could be modified on different ways mostly by reaction at primary or secondary hydroxyl groups. Oxidation of starch may be carried out using different oxidants but most common processes using sodium hypochlorite and potassium periodate suffer from non environmental reaction conditions [7].

Because starch might be described as a polyalcohol we can stated that the described procedure is a continuation of our earlier research on microwave assisted synthesis [8]. The described reaction was conducted applying hydrogen peroxide as the oxidant and Na_2WO_4 as the catalyst, the system similar to those applied for oxidation of low molecular alcohols [9].

EXPERIMENTAL

According to Scheme 1 the oxidation of starch was conducted as follows: 2,5g of "native" maize starch was put into the 50mL of water. The mixture was pasted at 90°C during 15min. Obtained paste was cooled down to 60°C and the 0,06g of Na_2WO_4 was added. After the 15min of intensive stirring hydrogen peroxide was added (14,7mmol, 1,5mL of 30% water solution) and sample was irradiated by microwaves (Moulinet FM A945GS) at the power of 85W or placed into the water bath to heat in the conventional way (at 70°C). After reaction was finished the solution was poured into the well stirred methanol in order to precipitate the polymer.



Scheme 1. Oxidation of Starch by Hydrogen Peroxide.

Starch was then centrifuged and dried. For the product carbonyl (by means of titration by hydroxylomine) and carboxyl (by means of titration with HCl) group content was calculated. The main investigation was focused on the changes in molecular mass of the starch during the reaction progress. The molecular mass was estimated using gel permeation chromatography (the system of two columns was used: 380mmx16mm and 460mmx16mm both filled with S-200 and S-500 Sephadex gels). As the eluent the 0,003mol/L Na_2CO_3 was used with the flow rate 0,128mL/min. The analysis was done at 20°C using RI detection. Collected fraction allowed determining the sum of carbohydrates in the sample by means of anthron method [10]. Molecular mass of amylose and amylopectine polymers were determined by means of potassium-iodide complex analysis of collected fractions [11]

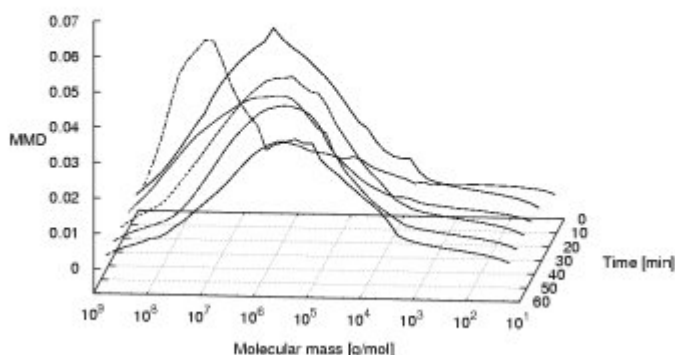
RESULTS AND DISCUSSION

As a results of our experiments we have obtained a series of oxidized starches which differ with the oxidation level what was measured by the analysis of carbonyl and carboxyl compound. Looking into results (Table 1) it may be stated that the amount of carbonyl group (the product of the first stage of oxidation of -OH) drops in the case of conventional heating during the whole process. From the other hand in microwave assisted reaction the amount of C=O group remains constant during the reaction time. At conventional heating the COOH content remains at almost the same level during the process while the grows of the carboxylic group content could be seen in microwave assisted process. Such phenomenon could be the result of some changes in selectivity of the reaction in microwaves.

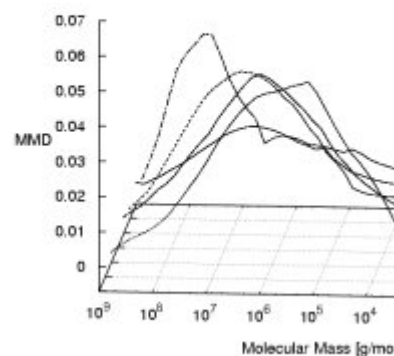
Table 1. Carbonyl and carboxyl group content in oxidized starch.

Reaction Time [min]	Conventional heating	Microwave	Conventional heating	Microwave
	Carbonyl group contents [%]	Carbonyl group contents [%]	Carboxyl group contents [%]	Carboxyl group contents [%]
10	0,161	0,161	0,002	0,003
20	0,158	0,161	0,002	0,003
30	0,157	0,164	0,002	0,003
40	0,154	0,161	0,002	0,004
50	0,150	0,161	0,002	0,004

As it is known almost each modification of starch guides to the decrease of the molecular weight of the polymer. Sometimes as in the case of acid or enzymic hydrolysis the phenomenon is very useful. But in plenty of modification reaction the shortening of polymer chains is unfavorable side reaction which needs to be reduced. During the investigation of changes in molecular mass and its distribution we have found that both processes i.e. conventional and microwave assisted oxidation of starch causes the decrease in Mn and Mw which, by the way, is linked with the strong decrease in polydispersity of the polymer (Scheme 2). However the changes in polydispersity observed for both kind of oxidations differ by means of time depending changes. In each case i.e. in changes of Mn and Mw value of starch (Scheme 3) and its components (Scheme 4 and 5) the microwave assisted process is much gentle than the conventional ones. The values of described factors observed up to 40min of the reaction time is grater for microwave process. The degradation of carbohydrate chains become stronger only at the end of the process but even there the molecular mass still becomes higher than observed in conventional condition.

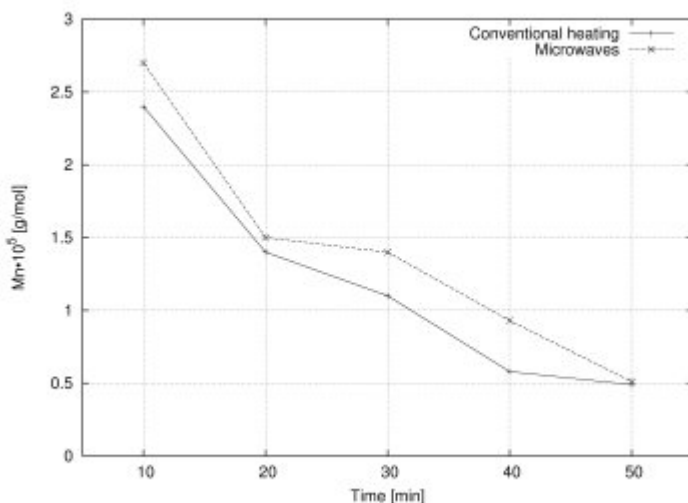


a) Conventional heating

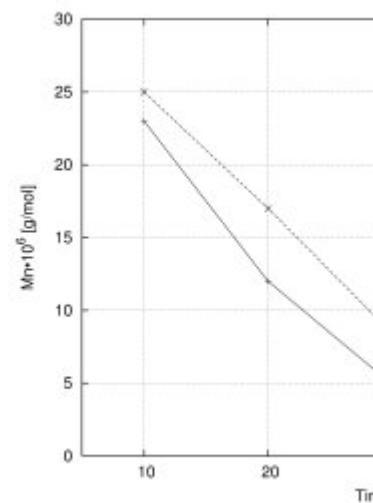


b) microwav

Scheme 2. Molecular Mass Distribution of Starch oxidised at different tim

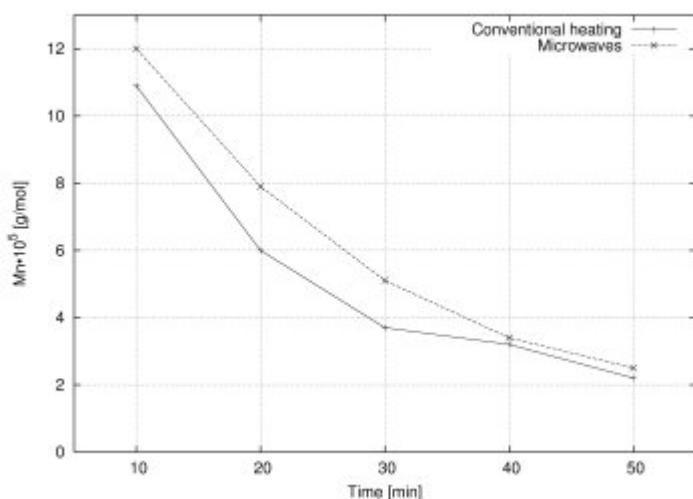


a) Number Average Molecular Weight

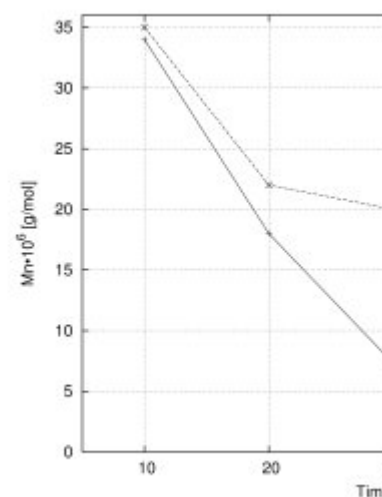


b) Weight Average

Scheme 3. Time dependent Changes in Molecular Mass of Starch

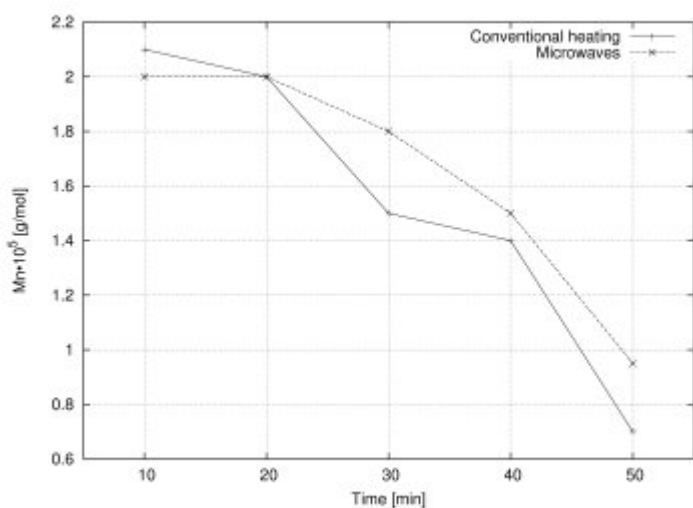


a) Number Average Molecular Weight

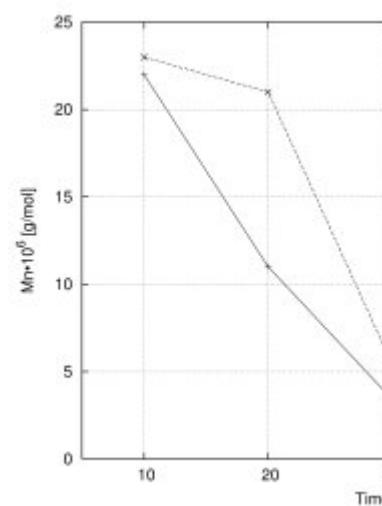


b) Weight Average

Scheme 4. Time dependent Changes in Molecular Mass of Amylos



a) Number Average Molecular Weight



b) Weight Average

Scheme 5. Time dependent Changes in Molecular Mass of Amylopec

As a conclusion we can state that presented preliminary studies on microwave assisted oxidation of starch look promising as the alternative for the conventional process. The changes in the oxidation level observed at the same time for microwave and conventional reaction as well as the alteration of molecular mass guides to the point that such kind of starch modification after appropriate improvement could be the good alternative for other polysaccharide oxidation processes conducted at both laboratory and industrial scale.

LITERATURE

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