DIALDEHYDE STARCH – CROSS-LINKING AGENT FOR BIOMEDICAL APPLICATIONS

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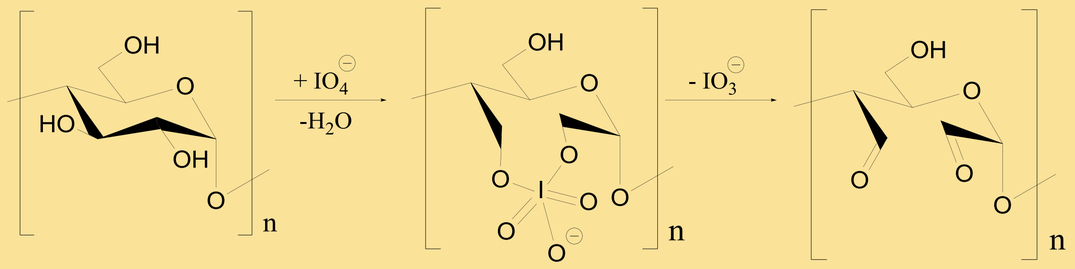
INTRODUCTION

Starch is a polymer consisting residue of α-D-glucose units. It consists of unbranched amylose and branched amylopectin. Starch can undergo numerous modifications, including oxidation. Controlled periodate oxidation of polysaccharides results in partial oxidation of the hydroxyl groups on carbons 2 and 3. The partial oxidation of these groups leads to the repture of bond between carbons 2 and 3 and to the formation of two aldehyde groups in each oxidized monomeric units.



Mechanism of starch oxidation with sodium periodate

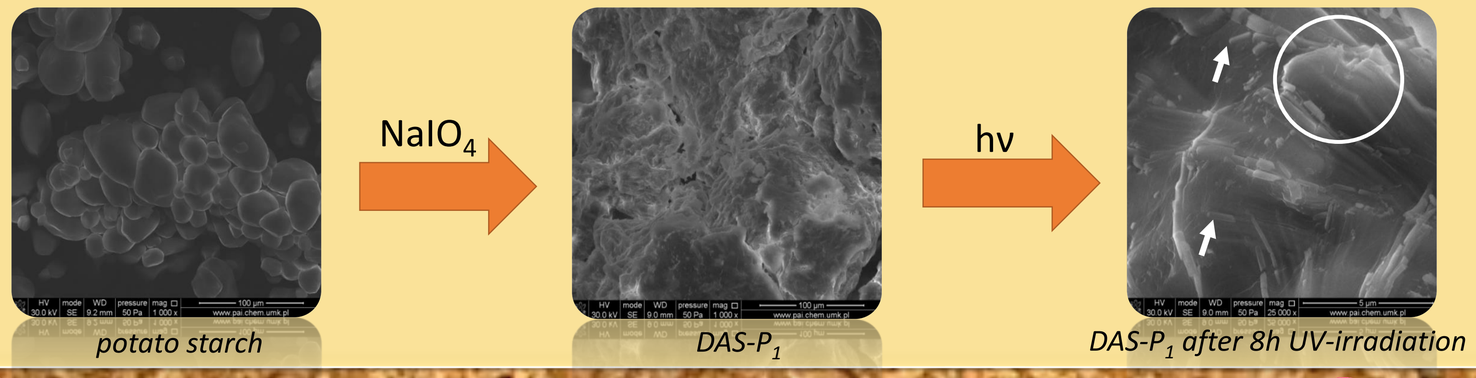
Dialdehyde starch has found wide application in tissue engineering (design of implants), the food industry (preparation of films for food packing), and in biomedical applications (immobilization ofbioligands), where they perform the function of cross-linking agent.

DETERMINATION OF UNITS CONTAINING ALDEHYDE GROUPS

Sample	ALD, %	Sample	ALD, %
DAS-C_1	**25**	DAS-P_1	**21**
DAS-C_2	**29**	DAS-P_2	**25**
DAS-C_3	**37**	DAS-P_3	**29**
DAS-C_4	**67**	DAS-P_4	**33**
DAS-C_5	**45**	DAS-P_5	**33**

As can be seen, the highest oxidation degree can be achieved at equal proportions of starch and periodate (1:1). Moreover, corn starch, at the 1:1 ratio, is more susceptible to oxidation than potato starch, which was confirmed by the highest percentage content of dialdehyde groups (67%). It can result from different content of amylose in two starches. A higher content of amylose in corn starch than in potato starch promotes the modification process.

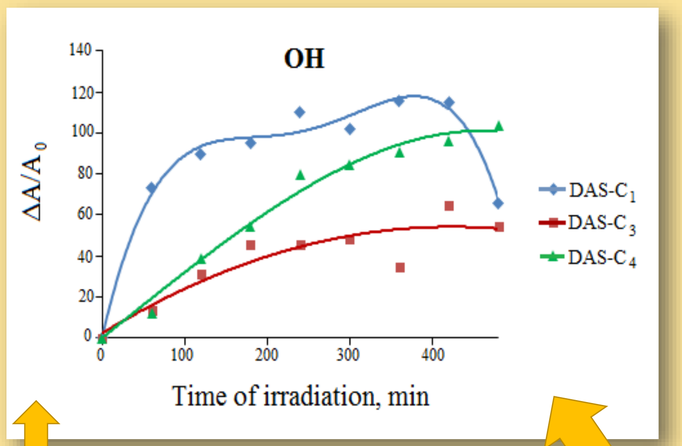
SCANNING ELECTRON MICROSCOPY



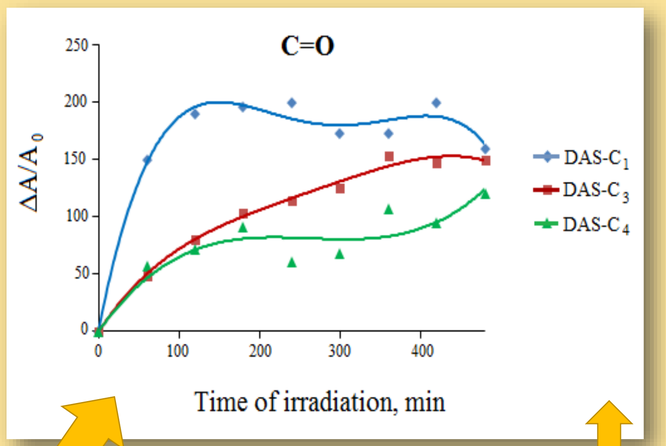
potato starch — *DAS-P_1* — *DAS-P_1 after 8h UV-irradiation*

Potato starch form agglomerates consisting of loosely-bound grains. The globular structure disappears after oxidation in most specimens independently from oxidant content. The images of the exposed potato starch exhibit altered structure with numerous holes. Higher magnification allows us to observe sticks and plates scattered in disordered polysaccharide bulk. Some of these plates are arranged parallel, forming packages. This partially ordered structure may be a result of photodestruction of amorphous phase in the sample.

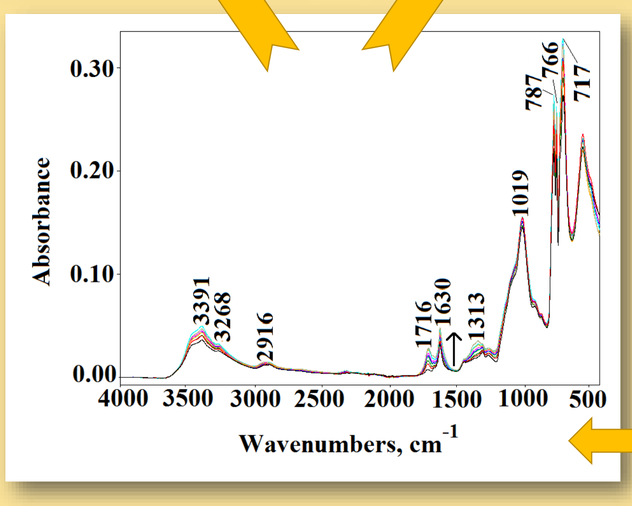
ATR-FTIR ANALYSIS



Changes in the relative absorbance of hydroxyl bands for dialdehyde corn starches versus irradiation time



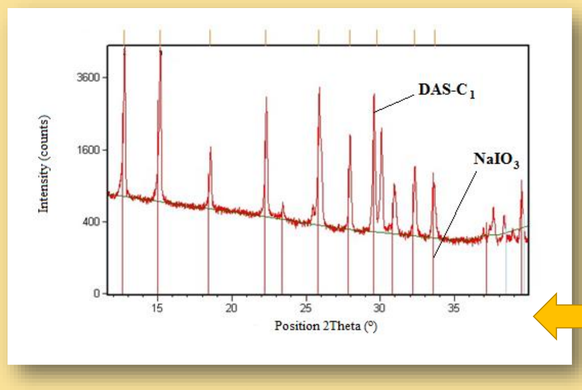
Changes in the relative absorbance of carbonyl bands for dialdehyde corn starches versus irradiation time



DAS-C_1 exposed for UV-irradiation for 480 minutes

In order to compare the behavior of the samples during UV-irradiation, absorbance value (A) of the selected bands and the relative absorbance changes were calculated. Subsequently, the relative changes, ΔA, were divided by the absorbance of the band at 2920 cm^{-1}, chosen as the internal standard. An increase in efficiency of formation of hydroxyl and carbonyl groups indicates that UV radiation causes a further oxidation of dialdehyde starch.

XRD ANALYSIS



X-ray diffraction pattern of DAS-C with overlapped signals of pure $NaIO_3$

XRD pattern with many narrow intensive signals demonstrates the presence of the crystalline product. It turned out that these signals came from the oxidant reduced to iodate(V) indicating a relatively stable combination of DAS and iodate.

SUMMARY

Dialdehyde starch with different content of dialdehyde groups was obtained by chemical oxidation of native corn or potato starch. Spectroscopic results showed a systematic increase in the amount of functional groups for DAS, what is causes a further oxidation due to the further oxidation of these groups. The SEM images of the exposed potato starch exhibit altered structure with numerous holes. The dialdehyde starch obtained from PST (i.e., DAS-P) is less photostable than that obtained from CST (i.e., DAS-C), that may be caused by the differences in the structure and chemical composition of the native polysaccharides.

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