EFFECT OF ESTERIFICATION AGENT AND SUBSTITUTION DEGREE ON HYDROFOBICITY AND THERMAL PROPERTIES OF STARCH

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INTRODUCTION

The use of biodegradable polymers represent a solution to the problems of contamination caused by conventional synthetic polymers. One of such polymers is starch, which occurs widely in nature and is the second largest biomass on earth after cellulose and one of the most abundant bio-renewable materials. However, the intermolecular forces and hydrogen bonds in starch granules prevent the processing of starch in the way typical to thermoplastic materials. By reducing those interactions, the thermal properties of starch could be changed. The aim of this study was to synthesize starch esters with controllable thermal properties by using different organic anhydrides and varying the degree of substitution (DS).

EXPERIMENTAL

Potato starch was modified with acetic (Ac) and/or octenyl succinic (OSA) anhydrides (Fig. 1) and characterized by Fourier-transform infrared spectroscopy (Fig. 2) and scanning electron microscopy (Fig. 3). The thermal properties of the modified starches were evaluated by thermogravimetry and differential scanning calorimetry (Table 1).

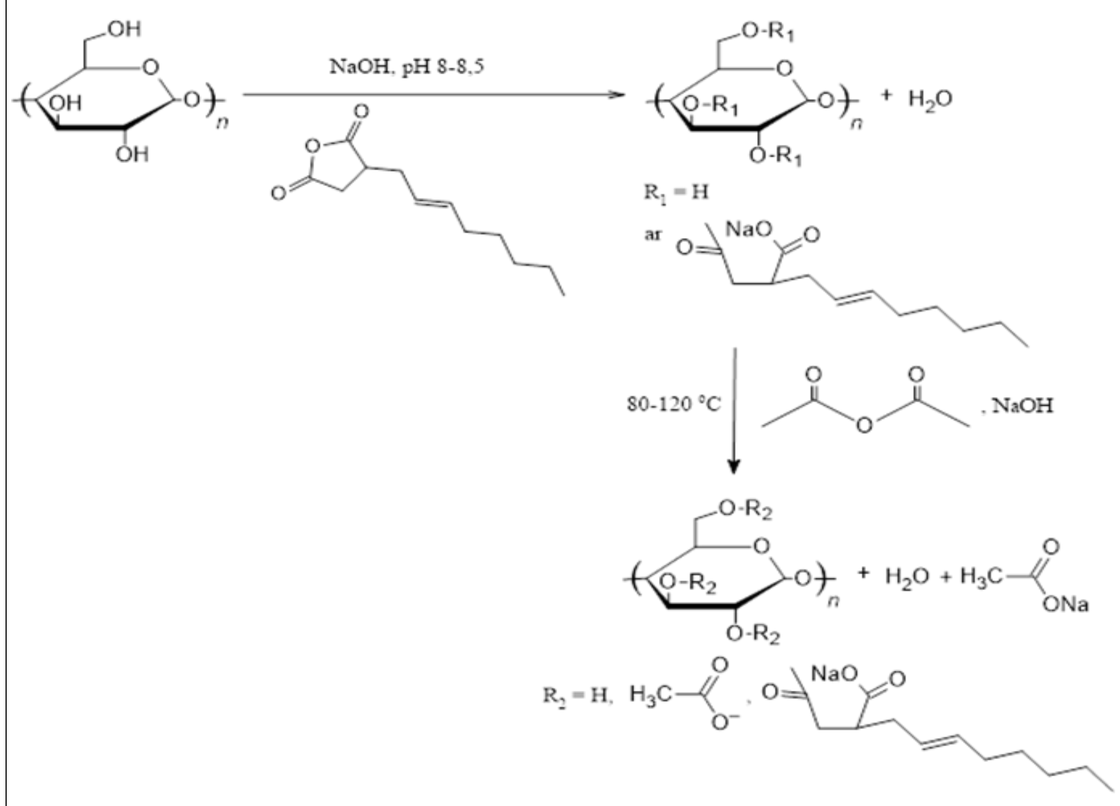

Fig. 1 Starch modification scheme.

Disruption of starch granules occurred during modification with acetic anhydride. But granular structure maintained during acetylation of starch octenyl succinate.

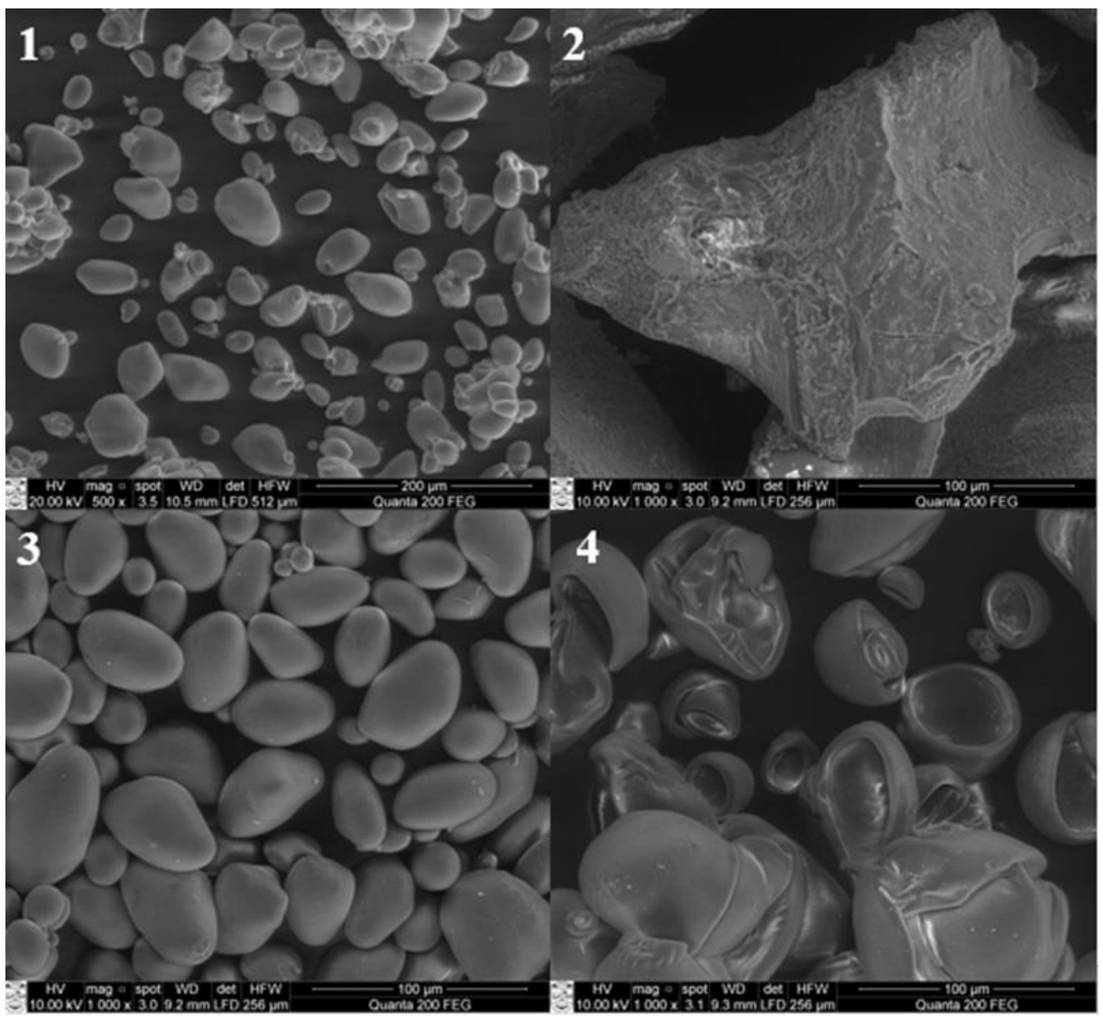

Fig. 3 SEM micrographs of starch (1), starch acetate with DS – 1,67 (2), starch octenylsuccinate with DS – 0,06 (3), starch acetate octenyl succinate with DS – $0{,}06_{OSA}/1{,}68_{Ac}$ (4).

RESULTS

The FTIR spectra of native potato starch, starch octenyl succinate, starch succinate and starch acetates are presented in Fig 2. Compared with native potato starch, a new peak was found at 1720 cm^{-1} for OSA-modified starch can be attributed to the formation of ester carbonyl groups. Acetylated and dual modified starches had absorption band at 1730 - 1737 cm^{-1} which intensity increase with increasment of DS.

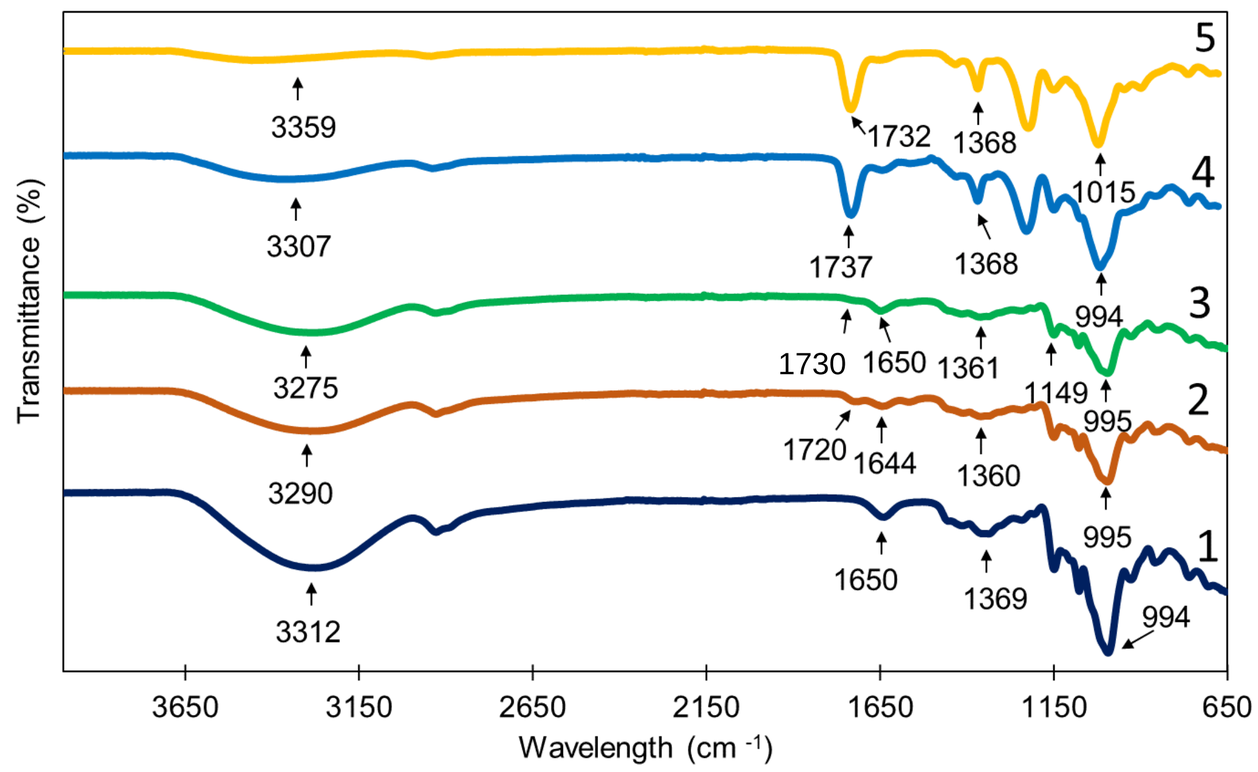

Fig. 2 FTIR spectra of native starch (1), starch octenyl succinate with DS 0.06 (2), starch acetate with DS 0.06 (3) and starch acetates with DS values of 1.67 (4) and starch acetate octenyl succinate with DS – $0{,}06_{OSA}/1{,}68_{Ac}$ (5).

When starch was modified with octenyl succinic or acetic anhydride at low degree of substitution, DS being up to 0.62, the glass transition (T_g) temperature was not observed (Table 1) and destruction temperature (T_d) of derivatives decreased with increasing DS. T_g of starch acetate with high DS higher than 0.8 was detected in the interval of 162-167 °C and T_d was increasing with increasing DS. T_g was also observed for starches dual modified with both Ac and OSA even at low DS values, which was increasing with increasing DS_{Ac}. When DS_{Ac} was higher than 1.06 the T_g dependence on DS was no longer valid. Meanwhile T_g was affected by molecular weight of modified starch. The T_d of dual modified starch increased with increased DS_{Ac}.

Table 1. Thermal properties of modified starches

DS_{Ac}	DS_{OSA}	T_d, °C	T_g, °C
0	0	291	-
0	0.06	272	-
0.30	0	292	-
0.62	0	240	-
0.8	0	249	162
1.10	0	249	162
1.67	0	278	167
1.88	0	312	165
0.03	0.06	287	162
0.44	0.06	279	163
0.53	0.06	302	164
1.06	0.06	318	175
1.23	0.06	316	171
1.58	0.06	315	167
1.68	0.06	312	171