Optimized Synthesis of Acetylated Starch Octenyl Succinates and Study of Thermal Properties

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Introduction

Chemical modification has been exploited as one of the most common method for enhancing starch properties mainly due to the high reactivity of its glucose hydroxyl groups which serve as key site for chemical modification (Si and Zhang 2024). Herein we report the optimization and controlled acetylation of succinylated corn starch using response surface methodology. The initial modification was carried out with octenyl succinic anhydride (OSA) as the esterifying agent using previously optimized conditions while selected reaction parameters for the second modification (acetylation) were optimized using central composite design. Furthermore, changes in the structural and thermal properties of the different starch deriavatives were investigated via SEM, FTIR, XRD, DSC and TGA. We hypothesized that the double chemical modification of native starch would allow for enhanced functional properties, especially the thermal properties.

Experimental

Synthesis of Starch Octenyl Succinate (OSA-St):

A 30% starch slurry was prepared in distilled water and adjusted to pH 8.5 with 3% NaOH. OSA (0.02 mol per mol starch) was added gradually while maintaining pH 8.5–9.0, afterwards, The reaction mixture was left to stir at room temperature for 12 h. Subsequently, the mixture was neutralized to pH 6.5 using 2% HCl, washed and firstly dried at 40°C for 24 h and then at 105°C for 2 h. The degree of substitution (DS) of OSA was determined to be 0.026 via alkali saponification and back titration.

Synthesis of Acetylated Starch Derivatives (St-OSA-Ac):

Acetylation of OSA-starch was carried out using acetic anhydride as the esterifying agent under alkali conditions. The reaction conditions for the acetylation were based on central composite design (CCD) as summarised in Table 1. The DS of acetyl group was determined via saponification and titration, using St-DDSA as the blank.

Characterization of Starch Derivatives

The structural modifications elicited in the starch deriavatives were elucidated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction crystallography (XRD) proton nuclear magnetic resonance (H-NMR), while changes in the thermal properties were investigated using Differential Scanning Calorimetry (DSC) and TGA (Thermogravimetric analysis).

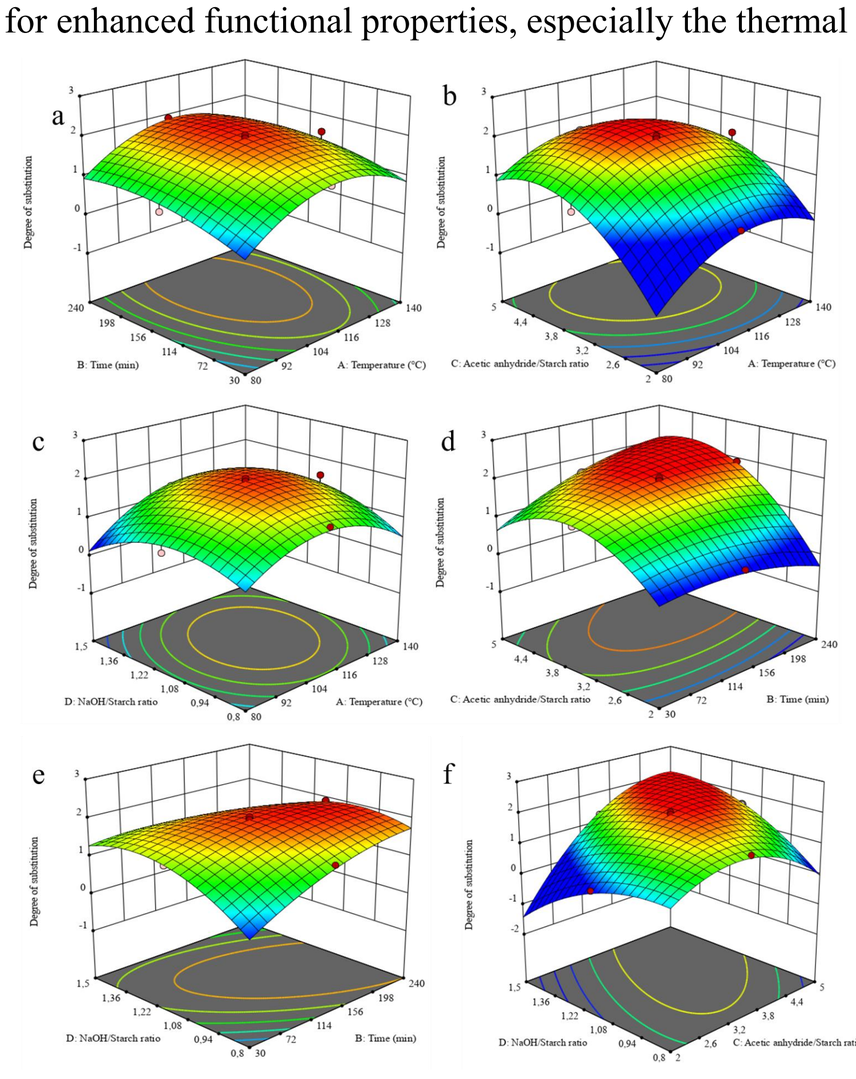

Fig 1 Response surface plots of variables interaction

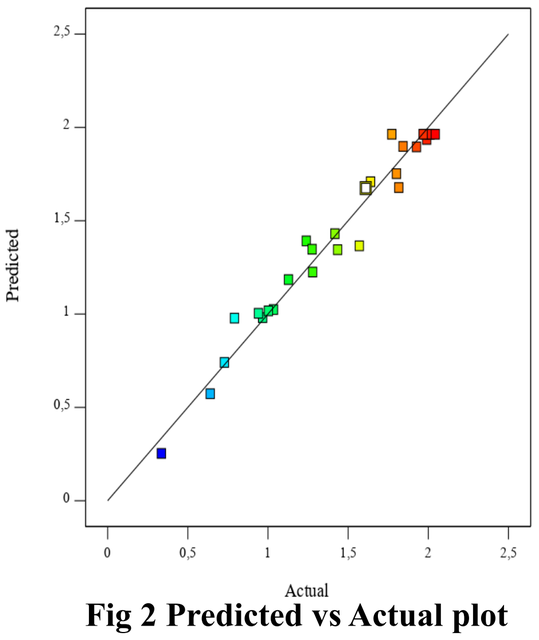

Fig 2 Predicted vs Actual plot

The adequacy of the model generated was validated by carrying out modification reactions under model-predicted conditions, i.e. 112.42°C, 187.5 min, 4.25 NaOH/starch, 1.24 acetic anhydride/starch ratio. The predicted maximal DS of ~2.29 was observed to be proximal with the experimental DS of 2.31. Results show high values of R2 (0.9664) which indicates that ~ 97 % of the total variation can be accounted for by the model.

Results & Discussion

Table 1 CCD design variables & responses

	Real variables				DS	
S/N	Temp °C	Time min	*Acetic A. /Starch	NaOH/ Starch	Predicted	Actual
1	95	82.5	2.75	0.975	0.981	0.967
2	125	82.5	2.75	0.975	1.185	1.128
3	95	187.5	2.75	0.975	1.225	1.279
4	125	187.5	2.75	0.975	1.392	1.239
5	95	82.5	4.25	0.975	1.024	1.035
6	125	82.5	4.25	0.975	1.018	1.003
7	95	187.5	4.25	0.975	1.753	1.802
8	125	187.5	4.25	0.975	1.709	1.640
9	95	82.5	2.75	1.325	0.573	0.640
10	125	82.5	2.75	1.325	1.004	0.941
11	95	187.5	2.75	1.325	*NF	0.731
12	125	187.5	2.75	1.325	0.741	0.729
13	95	82.5	4.25	1.325	1.678	1.816
14	125	82.5	4.25	1.325	1.898	1.843
15	95	187.5	4.25	1.325	1.936	1.990
16	125	187.5	4.25	1.325	*NF	1.642
17	80	135	3.5	1.15	0.978	0.791
18	140	135	3.5	1.15	1.366	1.570
19	110	30	3.5	1.15	1.431	1.418
20	110	240	3.5	1.15	1.896	1.926
21	110	135	2	1.15	0.254	0.335
22	110	135	5	1.15	1.675	1.610
23	110	135	3.5	0.8	1.345	1.434
24	110	135	3.5	1.5	1.348	1.275
25	110	135	3.5	1.15	1.964	1.773
26	110	135	3.5	1.15	1.964	2.012
27	110	135	3.5	1.15	1.964	1.980
28	110	135	3.5	1.15	1.964	2.006
29	110	135	3.5	1.15	1.964	2.044
30	110	135	3.5	1.15	1.964	1.968

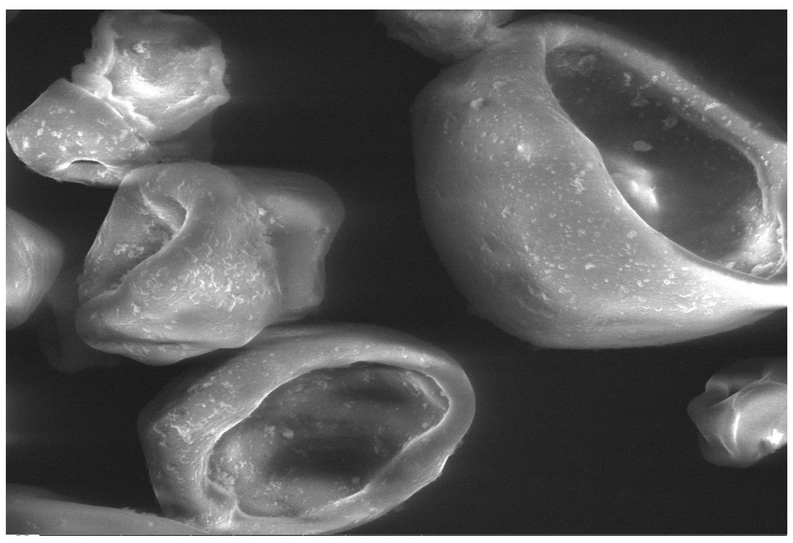

Fig 3 Acetyl-OSA-St (DS 2.01)

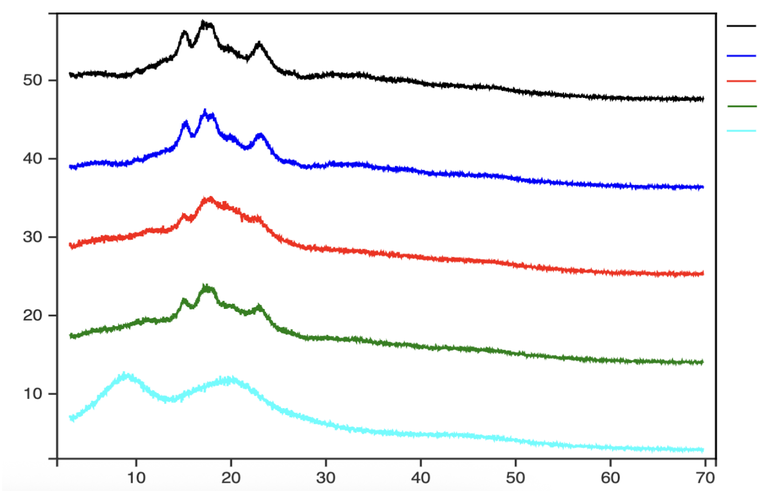

Fig 4 XRD (a) native (b) OSA-St (c) Acetyl-St (DS 0.96) (d) Acetyl-OSA-St (DS ~0.65) (e) Acetyl-OSA-St (DS 2.01)

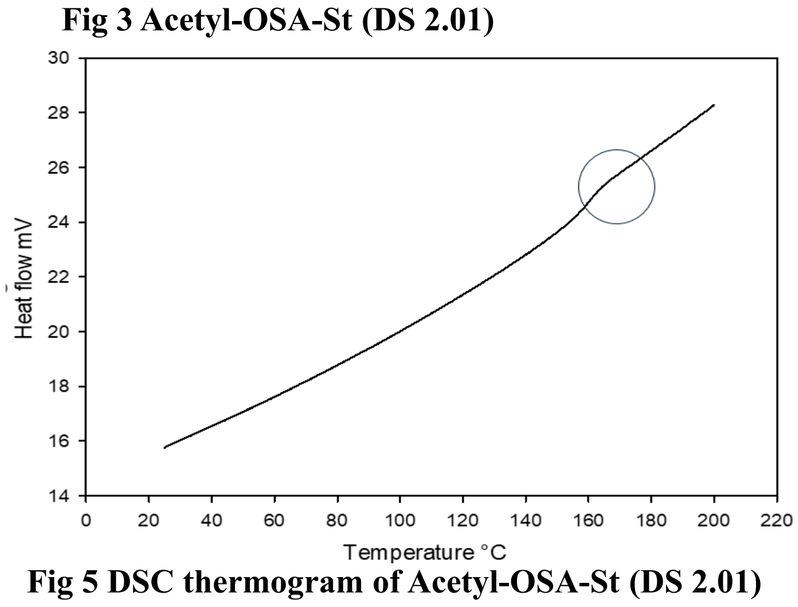

Fig 5 DSC thermogram of Acetyl-OSA-St (DS 2.01)

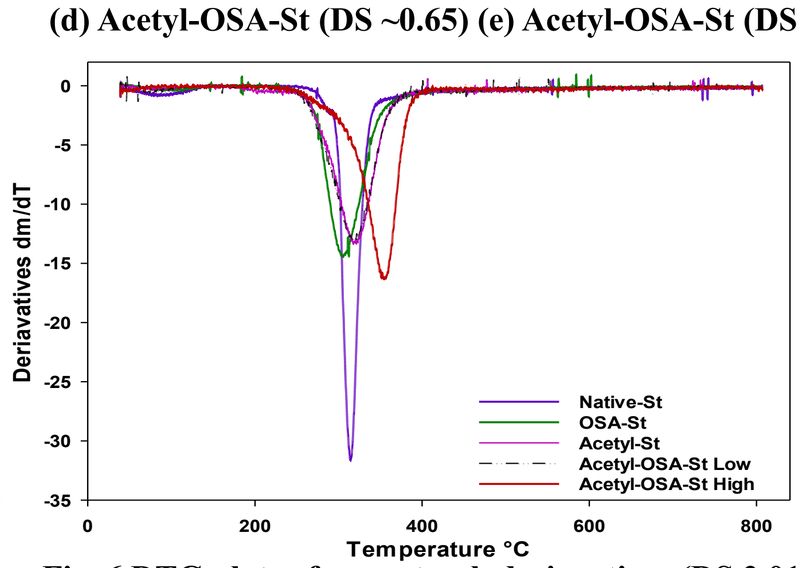

Fig 6 DTG plots of corn starch deriavatives (DS 2.01)

Conclusion

A robust quadratic model was generated for the acetylation of OSA starch from the RSM and regression analysis, hence, a DS of 2.32 was obtained. Double OSA-Acetyl modification at higher DS had the most significant effect on the morphology, crystallinity, and thermal properties of the polymer. XRD of the deriavatives shows a remarkable shift towards amorphous character e.g. a hump at ~18-20° totally replaced the sharp crystalline peaks typical of native starch. Most importantly, the thermal resistance and stability of the native starch was remarkably enhanced by the addition of the OSA and acetyl groups, hence, widening the potential in application involving heat processing such as, biodegradable films, and thermoplastic starch composites

Reference. Si, W. and Zhang, S., 2024. The green manufacturing of thermoplastic starch for low-carbon and sustainable energy applications: a review on its progress. *Green Chem.* 26(3),1194-1222.

Acknowledgement: This project has received funding from the Research Council of Lithuania (LMTLT), agreement No S-PD-24-33.