論 文 の 内 容 の 要 旨

生物材料科学　専攻
平成 28年度博士課程　入学
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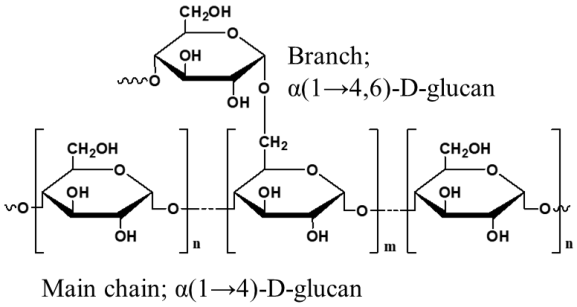
論文題目 Characterization of Dextrin Derivatives by Chemical or Enzymatic Esterification
(化学的または酵素学的エステル化法を用いたデキストリン誘導体の合成と物性評価)

Chapter 1. General Introduction

There has been increasing demand for polysaccharides as a biomass polymer to reduce the carbon dioxide emission. Dextrin is a polysaccharide produced by the partial hydrolysis of starch or glycogen. Its structure consists of an α(1→4) linked main chain with α(1→4,6) linked branches (Scheme 1). A general characteristic of dextrin is that it dissolves well in polar solvents. This allows for its use in the adhesive, paint, cosmetic and biomedical industries. However, because neat dextrin does not exhibit thermoplasticity or hydrophobicity, thus its use in other applications is limited. The limited properties of dextrin can be modified by esterification.



Scheme 1. Molecular structure of dextrin.

Chapter 2. Research Background

Esterification is one of the most popular modification reactions used to obtain thermoplastic and hydrophobic polysaccharides. This reaction can be catalyzed by chemical reagents or enzymes (Figure 2). Chemical esterification is suitable for the production of dextrin derivatives with a high degree of substitution (DS), because both primary and secondary hydroxyl groups are substituted in a non-selective reaction. Another route for the synthesis of dextrin derivatives is enzymatic esterification. This route is not only environmentally benign; it is also highly regioselective, allowing for the synthesis of dextrin esters with controlled structures and functionalities.

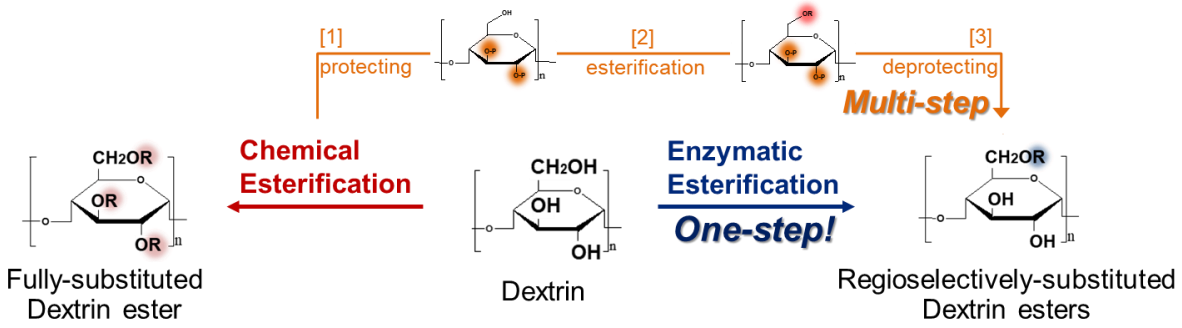
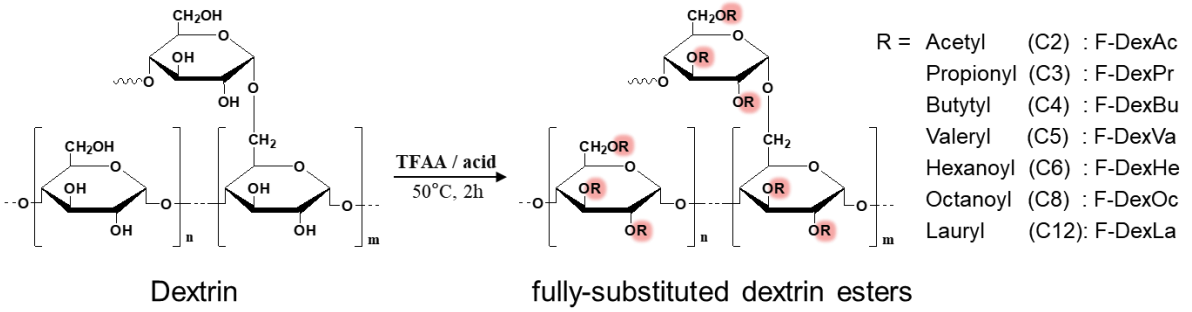


Figure 2. Chemical or enzymatic esterification of dextrin.

Chapter 3. Chemical Esterification; Fully Substituted Dextrin Esters

A series of fully-acylated dextrin esters (DS=3) with varying side-chain lengths (C2-12) were synthesized by heterogeneous esterification using trifluoroacetic anhydride/carboxylic acid (Scheme 2).



Scheme 2. Chemical synthesis of fully-substituted dextrin esters.

The influence of side-chain lengths on structure and properties of dextrin esters were investigated by structural, thermal, mechanical and hydrophobic analysis (Table 1). The thermal stability of dextrin was enhanced by esterification, presenting ca. 40-55 °C higher decomposition temperatures than that of neat-dextrin. The transition temperatures of melting and crystallization were not observed for all dextrin esters because they were amorphous polymers. The glass transition temperature (T_g) was not observed in dextrin but was observed in dextrin esters. As increasing side-chain length, T_gs of dextrin esters decreased ranged from 162.2 ℃ (C2) to 49.2 ℃ (C12). Colorless and transparent dextrin ester films were prepared to measure the film properties. Tensile strength of dextrin ester films tended to decrease with increasing side-chain lengths, whereas the elongation at break increased. And, dextrin ester films showed significantly increased hydrophobicity with a high contact angle (Figure 3).

Table 3-1. Characteristic of dextrin and dextrin esters

Name	M_w $\times 10^{-5}$	M_w/M_n $\times 10^{-5}$	Yield (%)	DS	$T_{d,90\%}$ (℃)	T_g (℃)	δ_m (MPa)	ε_b (%x	E' (MPa)	CA (°)
Dextrin	5.34	5.35	-	-	301	n. d	n. d	n. d	n. d	26.7±5.5
F-DexAc	8.83	4.07	84	3	349	162	n. d	n. d	n. d	71.8±1.6
F-DexPr	9.36	2.49	85	3	344	124	n. d	n. d	n. d	88.3±1.1
F-DexBu	9.73	2.63	83	3	348	78	n. d	n. d	n. d	94.5±0.6
F-DexVa	10.15	3.97	89	3	350	64	n. d	n. d	n. d	95.7±0.5
F-DexHe	11.88	2.15	93	3	355	53	4.5±0.6	34±9	4.5×10^{-5}	97.1±0.5
F-DexOc	11.38	3.28	95	3	352	50	3.5±0.1	70±17	2.1×10^{-5}	99.8±0.5
F-DexLa	12.77	2.18	89	3	340	49	2.2±0.1	78±12	1.0×10^{-5}	103.4±0.5

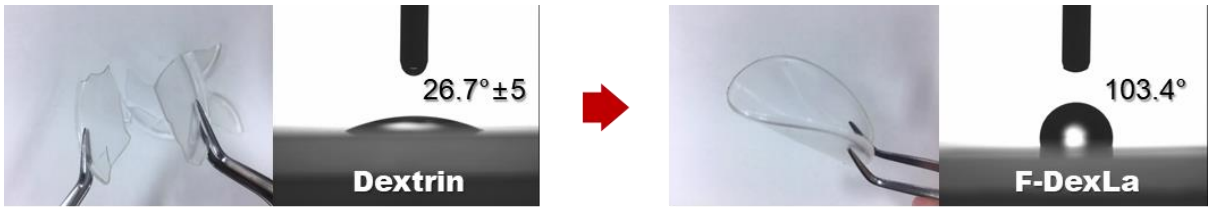
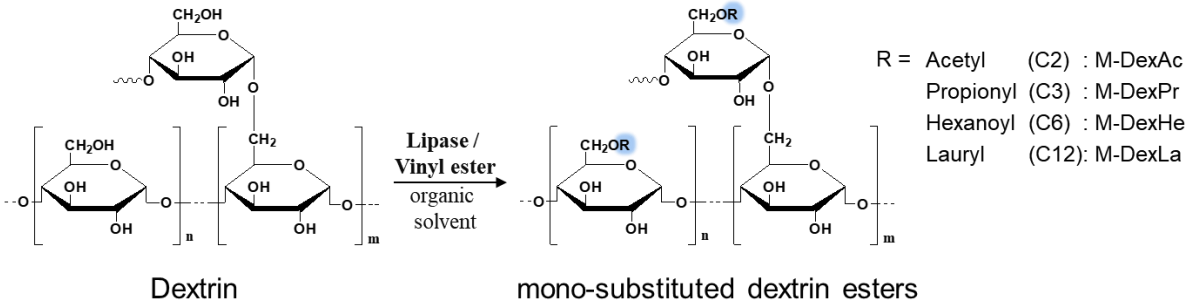


Figure 3. Film properties of dextrin and dextrin laurate.

Chapter 4. Enzymatic Esterification; Regioselectively Substituted Dextrin Esters

Four lipase enzymes were investigated as catalysts in the synthesis of regioselectively mono-substituted dextrin esters from dextrin and vinyl acetate (Scheme 3). An immobilized lipase enzyme (Lipozyme TL IM) exhibited the highest activity. This enzyme showed regioselective substitution of the dextrin at the primary hydroxyl group (C6 position) under optimal conditions (60°C for 24 hours, using a 1:3 molar ratio of glucose unit/vinyl acetate and 2.5 U/mL enzyme dosage in an organic solvent) (Figure 4).



Scheme 3. Enzymatic synthesis of regioselectively mono-substituted dextrin esters.

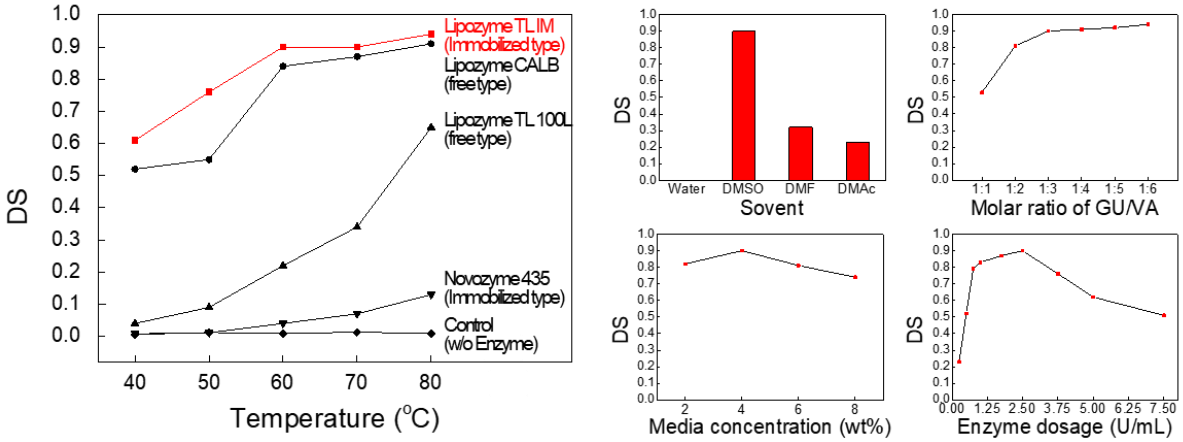


Figure 4. DS values of dextrin acetate obtained by modifying various parameters.

To compare the reactivity of other vinyl esters, mono-substituted dextrin esters (degrees of substitution [DS] ≥ 1) with varying side-chain lengths (C2-12) were synthesized (Figure 4). With increasing side-chain length, the initial catalytic activity of the lipase enzyme decreased, resulting in lower DS values. However, the final DS values of the mono-substituted dextrin esters with longer side-chains were higher than those of the shorter chain analogues, because of an increase in affinity between the substrate and acyl donor.

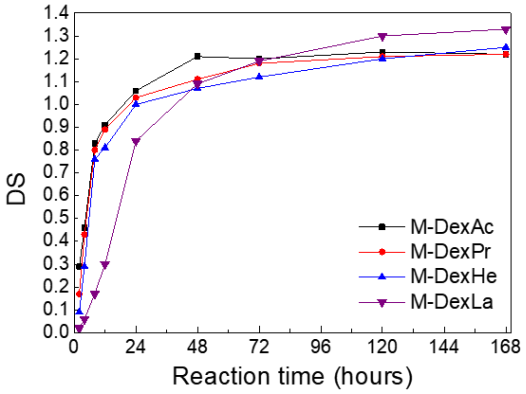
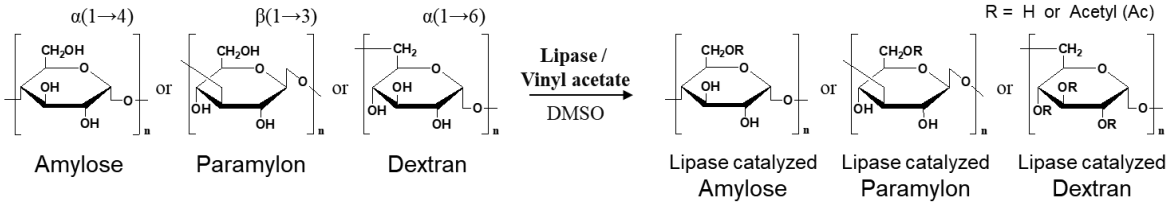


Figure 5. DS of dextrin esters versus reaction time under optimal condition.

Chapter 5. Lipase-catalyzed Polysaccharide Esters

An important property of enzymes is that they exhibit substrate specificity under the conditions required for activity. To investigate the catalytic activity of lipase on polysaccharides, four kinds of lipase as catalysts were used for reaction between three kinds of polysaccharides, amylose (α(1→4) glucan), paramylon (β(1→3) glucan) or dextran (β(1→3) glucan)) with vinyl acetate, respectively (Scheme 4).



Scheme 4. Synthesis of lipase-catalyzed polysaccharide acetate.

Immobilized lipase enzyme (Lipozayme TL IM) showed the most efficient activity, and their activity was in the order of amylose, paramylon and dextrin (Figure 6 and 7). Lipase-catalyzed amylose acetate showed a high catalytic activity with a DS value of 1. Lipase-catalyzed paramylon acetate exhibited lower catalytic activity due to their high viscosity characteristics. Finally, lipase-catalyzed dextran acetate has lowest catalytic activity, indicating that the activity towards C2, C3, C4 positions is less than the C6 position.

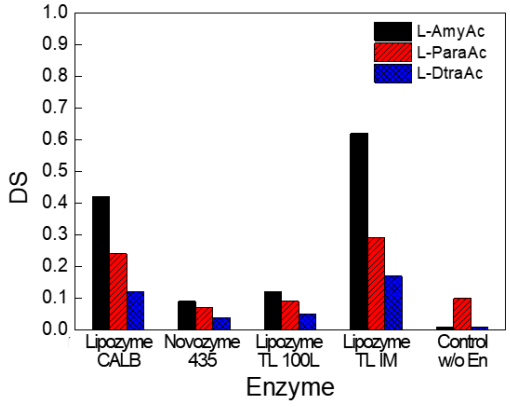


Figure 6. DS of lipase-catalyzed polysaccharide acetate for each type of enzyme.

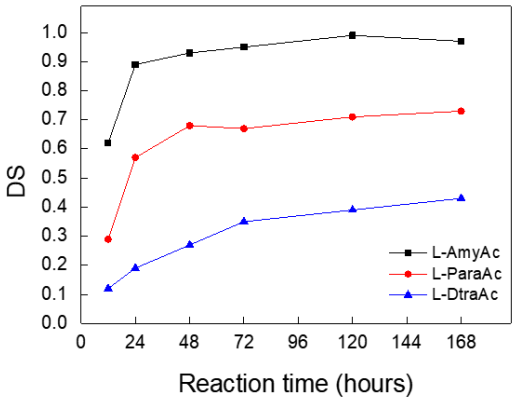


Figure 7. DS of lipase-catalyzed Polysaccharide acetate versus reaction time under optimal condition.

Chapter 6. Summary and Conclusion

In this research, it is confirmed that the functional properties of dextrin can be controlled esterification reaction. In particular, the chemical esterification of dextrin is expected to help resolve the limitations of commercialization of dextrin caused by their low thermoplastic and hydrophobicity. Otherwise, the results of enzymatic esterification demonstrate successful regioselective modification of dextrin using a lipase enzyme as a biocatalyst. Furthermore, lipases enzyme has the potential for catalytic function to other polysaccharides, amylose, paramylon and dextran. This research will contribute to the environmental friendly chemistry in terms of polysaccharide modification.