

Research Article

Reaction Mechanisms Applied to Starch Modification for Biodegradable Plastics: Etherification and Esterification

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Although many studies are being actively conducted to develop biodegradable plastic materials, most of these reports focused more on efficiency or performance improvement than on the reaction mechanism. This paper discussed the reaction mechanism applied to starch modification by etherification and esterification, which are the most studied in the field of biodegradable plastics. In the starch-reforming reaction by etherification, the effects of the reaction temperature, pH, solvent, and by-products on the chemical structure and physical properties of biodegradable plastics were discussed. In esterification, the structure of the substituents and the reaction solvents were examined. As a material that can replace plastics, the aim is to help derive new ideas on the design of reaction condition that can expand the use of starch.

1. Introduction

The mass drilling of petroleum, which began in Titusville, Pennsylvania, in 1859, caused a boom in the research of polymeric materials in the 1900s. As a result, a new material called plastic began to appear in human technological civilization. Plastic refers to the properties or characteristics of a material composed of polymers. Plasticity has the dictionary meaning of “easy to shape and easy to process, etc.” Plastic is a term coined by reflecting this concept in material engineering, and its general process can be explained, as shown in Figure 1 [1]. The addition of a plasticizer that can reduce the attraction among polymer chains can make the polymer properties more flexible. Unlike ceramic materials or metallic materials, polymers can be molded at an appropriate temperature without a plasticizer because of their unique thermal properties, such as glass transition (T_g), crystallization (T_c), melting (T_m), and decomposition (T_d). These materials made without a plasticizer are also included in the category of plastics [2].

Up to date, plastics are being developed as high-performance materials with sufficient physical properties to replace wood, metal, and ceramics, but the developed plastics are not environmentally friendly compared to those traditional materials. They do not degrade easily and remain in nature as microplastics. Therefore, the marine and land environments have been seriously polluted by waste plastics since the mid-20th century, when the amount used increased rapidly. The recycling movement of commodity plastics has been promoted internationally since 1988 to suppress this environmental pollution caused by discarded plastics. Owing to the economic feasibility and convenience of using plastics, however it has not yet reached the level to suppress the increased use of plastics.

Meanwhile, research on biodegradable plastics that can replace commodity plastics has increased rapidly since 2008, as shown in Figure 2 that was searched on the keywords of biodegradability within the plastic category through the Scopus. The published papers on the seriousness of environmental problems caused by plastics began to

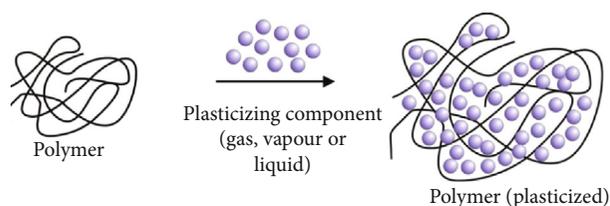


FIGURE 1: Plasticization phenomenon [1].

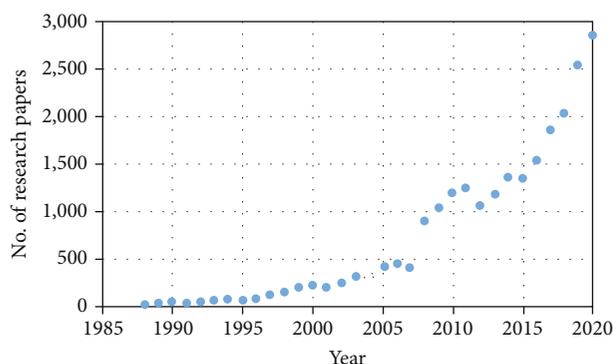


FIGURE 2: Number of research papers related to biodegradable plastics.

attract the international community's attention around this time [3–7].

The chemical structures used most widely as biodegradable plastic materials are β -glucose chain present in cellulose, such as wood and cotton fiber, and α -glucose chain structure in starch. Cellulose, a polymeric material, comprises 40-50% of wood and 90% of cotton fiber and is an environmentally friendly material used widely. On the other hand, the cellulose present in wood has a structure with lignin and hemicellulose intertwined, and β -glucose is linked in a linear structure with *cis*-shaped chains connected by high-density hydrogen bonds. Therefore, β -glucose chain is a polymeric material that is difficult to process [8].

Cellulose structures in wood and fibers were discovered by the French chemist Anselme Payen in 1838. In 1870, John Wesley Hyatt of the United States developed a thermoplastic material called celluloid by applying heat to cellulose. In 1908, the Swiss chemist Jacques Brandenberger developed a chemical treatment process for manufacturing a transparent cellophane sheet by extracting cellulose from wood through treatment with an aqueous NaOH solution and a reaction with CS_2 to make cellulose substituted with xanthate (Scheme 1) [9].

This process was a method that could produce a transparent and excellent cellophane sheet without destroying the basic structure of cellulose, which is still being used in packaging fields, such as food, cosmetics, and gifts. On the other hand, because the synthetic route of phenol resin was reported in 1907 (Scheme 2), plastics with various structures, such as PP, PE, and PVC, have been developed. The interest in biodegradable plastic materials has weakened because of the flow of technological development that places

importance on convenience and economy rather than eco-friendly concepts.

As of 2021, many materials have been studied as biodegradable plastics, including cellulose, starch, poly(lactic acid) (PLA), and poly(butylene adipate-co-terephthalate) (PBAT). In this report, the mechanisms of etherification and esterification, which are the most widely applied reactions in the development of biodegradable plastics for modifying the hydroxyl group of starch, are discussed for novice researchers in this field.

Starch comprises 10 to 35% of amylose, in which 100 to 10,000 α -glucose units are linked spirally, and 65 to 90% of amylopectin, in which 19 to 30 α -glucose units are linked as branched structures (Figure 3(a)). Because the branched amylopectin cannot be formed into a denser structure than helical linear amylose, a higher content of amylopectin results in higher solubility in water [10–12].

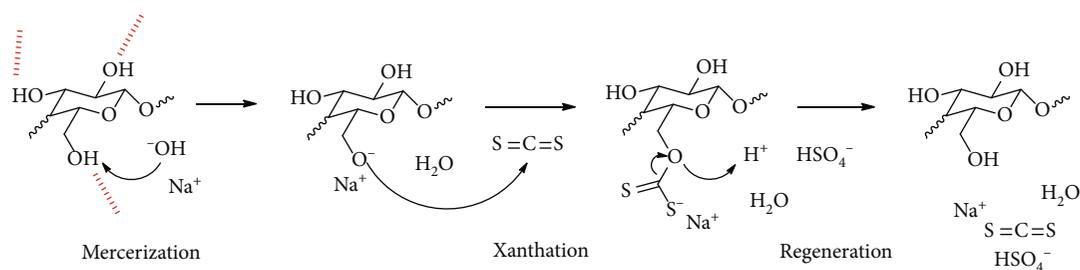
Starch is much easier to materialize into biodegradable plastics than cellulose because the α -1,4-glucosidic bond of starch is weaker than the β -1,4-glucosidic bond of cellulose, and starch has lower crystallinity structurally (Figure 3(b)) and excellent solubility in water. The three hydroxyl groups present in each glucose unit have the greatest influence on the durability and biodegradability of materials manufactured from starch and cellulose. Therefore, the conversion process from starch and cellulose to the materials with improved mechanical properties or durability that can replace commodity plastics is an organic synthesis technology that transforms these hydroxyl groups. The conversion of the hydroxyl group of starch and cellulose proceeds through crosslinking and substitution reactions, but the most converted chemical structure is a reaction mechanism that proceeds through esterification and etherification [13, 14].

2. Etherification of Starch

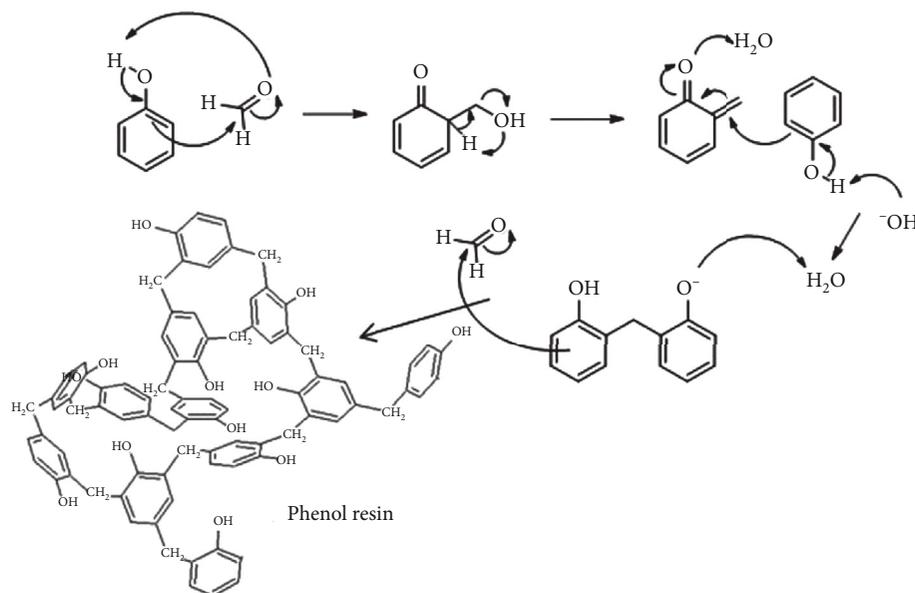
The etherification for the hydroxyl groups of starch can be carried out without difficulty by a nucleophilic substitution reaction between an alkoxide and an alkyl halide developed by Alexander Williamson in 1850 (Scheme 3).

Because the electronegativity of oxygen is higher than that of carbon, ether compounds containing oxygen have higher polarity than chloroform (diethyl ether 1.15 D, chloroform 1.04 D), which is an aprotic polar substance that does not form hydrogen bonds itself. These structural characteristics give ether a lower boiling point and excellent solubility in polar substances than other compounds with a similar molecular weight. Therefore, when the hydroxyl group of starch is converted to an ether structure, the solubility of starch is increased to improve its processability. The improved performance can be carried out in terms of thermal stability and mechanical strength of the modified materials.

Alkoxide, which acts as a nucleophile in Williamson's etherification reaction, can be prepared by a reaction in which alkoxide, a conjugate base of alcohol, and H_2O , a conjugate acid of the OH^- ion, are synthesized by reaction of alcohol with NaOH, a typical acid-base reaction. In this



SCHEME 1



SCHEME 2

reaction, a comparison of the pK_a and pK_b of the reagents involved in the acid-base reaction proceeding in the etherification of starch shows that the reverse reaction can proceed better (Scheme 4). Therefore, some energy must be applied to increase the efficiency of the forward reaction [15].

The etherification for starch reforming can be carried out by nucleophilic substitution with an alkyl halide after forming alkoxide-structured starch under alkaline conditions. To increase the efficiency in this reaction step, it is necessary to maintain favorable reaction conditions for the forward reaction, such as heating of the reactor or the elimination of the generated products, water, and NaCl, during the reaction process (Scheme 5) [16].

The Hamid group published the experimental results on modifying the physical properties of starch, such as thermal behavior, mechanical endurance, and processability, by the etherification of the hydroxyl groups of starch extracted from palm trees with benzyl chloride [17]. In their study, as discussed in Scheme 4, the reaction proceeded with using NaOH at 60°C to increase the conversion rate of hydroxyl groups to methoxy (Scheme 6).

However, what was intensively discussed in Hamid's paper is the change of the physical properties by changing the starch modification process from the commonly used

water-based condition to the ethanol condition. In other words, etherification of the hydroxyl group of starch produced a significantly different result depending on the reaction solvent used to evaluate the size of starch particles, substitution rate, and deformation force. The change in the mechanical properties of starch suggests replacing commodity plastics used in various application fields only by changing the reaction solvent for modifying starch [18]. In this reaction, the solvents capable of forming hydrogen bond, such as ethanol or water, and the polar solvents, such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), may be used as the reaction solvent [19, 20]. The effect of the reaction solvent may be greater in the starch reforming reaction because starch composed of α -1,4-glucose bonds has a lower density of hydrogen bonds than cellulose composed of β -1,4-glucose bonds.

The question remains what causes these changes. As mentioned above, the etherification of starch proceeds with an acid-base reaction followed by a nucleophilic substitution reaction. To understand the flow of the first acid-base reaction in Scheme 6, it is necessary to consider the acidity of substances that may exist in the etherification reaction of starch, such as water, ethanol, and glucose. In this paper, the acidity of hydroxyl groups in the substances was

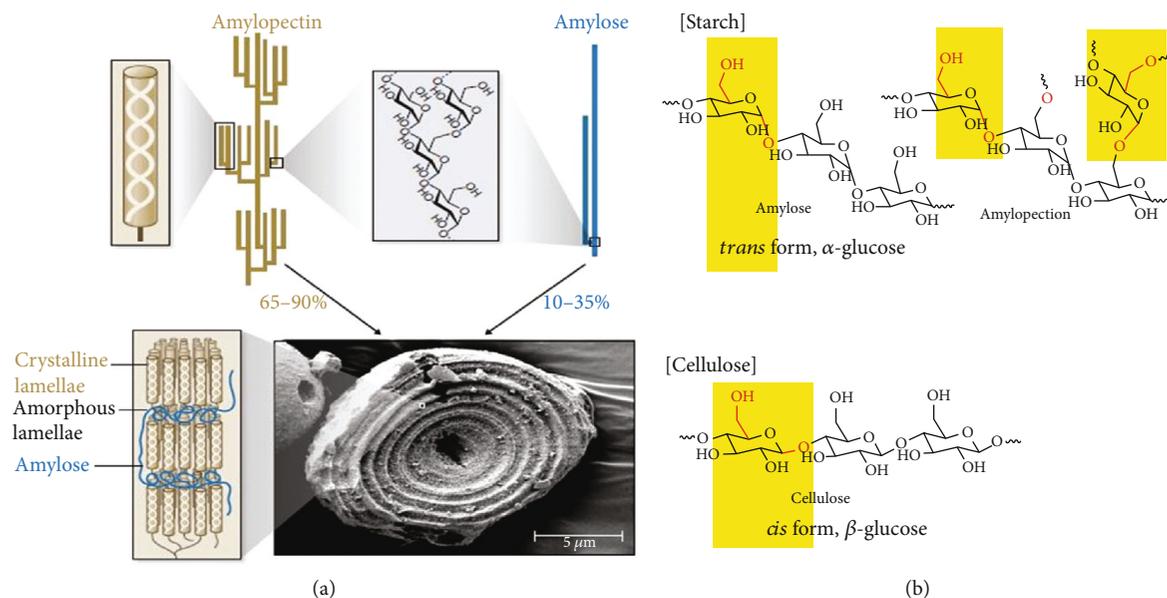
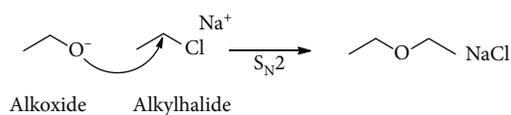


FIGURE 3: Structure of the starch granule (a) [8] and structural difference of starch and cellulose (b).



SCHEME 3: Williamson's etherification.

compared using the ¹H-nuclear magnetic resonance (NMR) data calculated from ChemOffice Suite 20.1. The ¹H-NMR data of the three hydroxyl groups in the glucose unit of starch were compared according to the presence or absence of an ether structure (Figure 4).

By analyzing the electron density of hydrogen atoms between the hydroxyl groups in glucose and cyclohexane, the acidity of the hydroxyl groups in glucose can be compared with that in ethanol indirectly. As shown in ¹H-NMR data of Figure 4, the hydrogen atom of the hydroxyl group in glucose (¹H-NMR-b) was measured at a higher magnetic field than the hydrogen atom of the hydroxyl group in cyclohexane (¹H-NMR-a). This result means that the electron density is higher at the hydrogen atom of the hydroxyl group in glucose, and the adjacent ether structure reduces the acidity of the hydroxyl group. On the other hand, the proton of the hydroxyl group of ethanol was calculated to be present at 4.7 ppm under the same conditions. Because the electron density of the protons of the hydroxyl groups is higher in glucose than in ethanol, the acidity of the substances that may exist in the reactor for the etherification reaction of starch is higher in the order of water > ethanol > hydroxyl group of glucose.

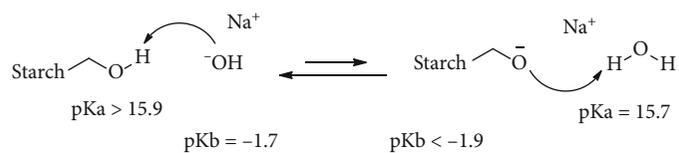
Then, the cause of the difference in the etherification reaction depending on the reaction solvent with such a subtle difference in acidity needs to be determined [21]. First, under experimental conditions in which water is used in excess, the following reaction mechanism may proceed, in which starch is decomposed and converted to glucose, a

monosaccharide (Scheme 7). However, this reaction is easy to proceed under acidic conditions, and it is not easy to proceed under alkaline reaction conditions, as in Scheme 6.

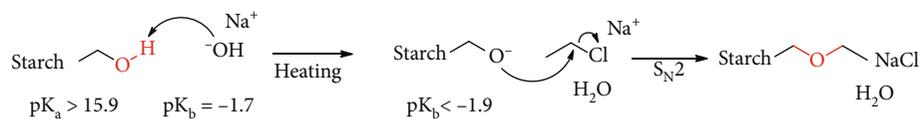
A second possibility to consider is the difference in pK_a of the substances under the reaction conditions. The pK_a of the -OH group differs according to the chemical structure, as shown in Figure 4. The electron density of the -OH group of glucose is higher than that of the compound without an ether structure. Even in this case, the OH⁻ ion of NaOH dissolved in the reaction solvent, water or ethanol, acts as a base, and the reaction proceeds to become alkoxide or water (Scheme 8). A reaction of a substituent, such as benzyl chloride with the generated alkoxide, is the basic reaction of the starch reformation by the nucleophilic substitution.

On the other hand, when water is used as the reaction solvent in this process, the desorption reaction of the substituent by the oxidative decomposition of the ether structure (Scheme 7 or 8) can be actively carried out because the hydration state (H₃O⁺ and OH⁻) may exist in excess compared to the ethanol usage conditions (CH₃CH₂OH₂⁺ and OH⁻). As a result, the substitution rate of the benzyl group may be lowered. However, when ethanol is used as the reaction solvent, the concentration of hydrated ions (H₃O⁺, OH⁻) may be lowered. Hence, the probability of proceeding to the reaction by the mechanism shown in Scheme 6 rather than that in Scheme 7 may increase. A previous study [17] reported that it possible to increase the efficiency of the etherification reaction of starch, as shown in Scheme 6.

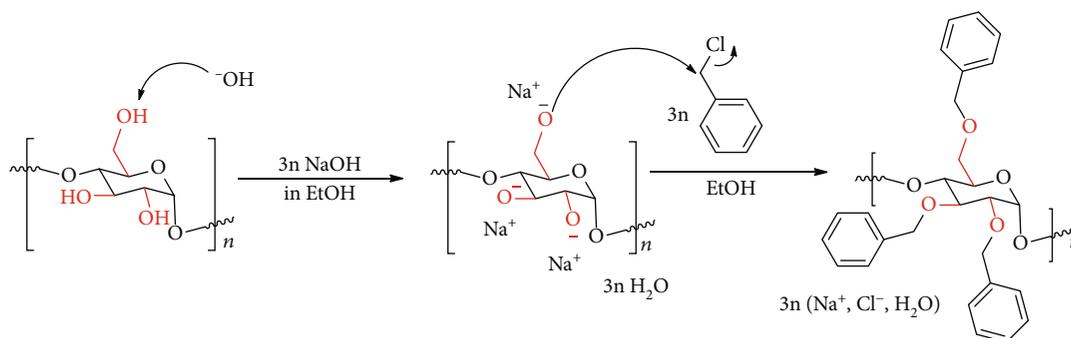
On the other hand, the most important step in the etherification of starch is the nucleophilic substitution reaction between the alkoxide and halide compounds, and this reaction step is most affected by the concentration of the alkoxide. Pieters et al.'s group reported an experimental condition in which the hydroxy groups were substituted by the benzyl groups almost completely by removing the water produced as a by-product in this reaction step [21]. As



SCHEME 4



SCHEME 5



SCHEME 6

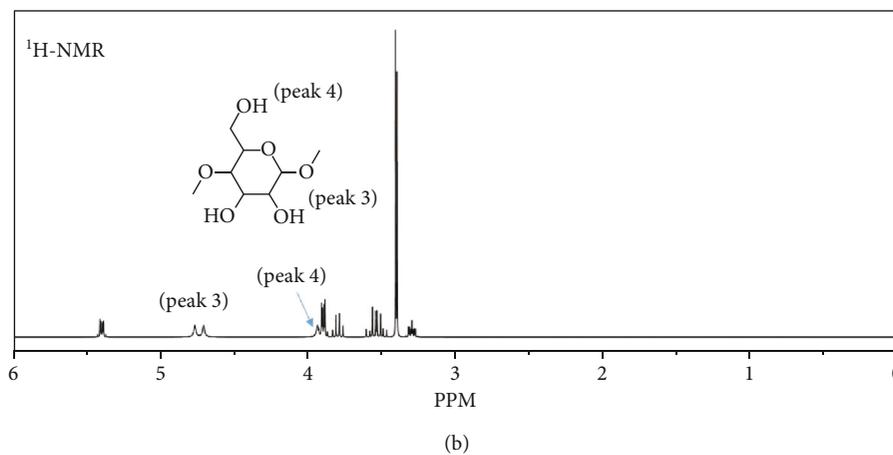
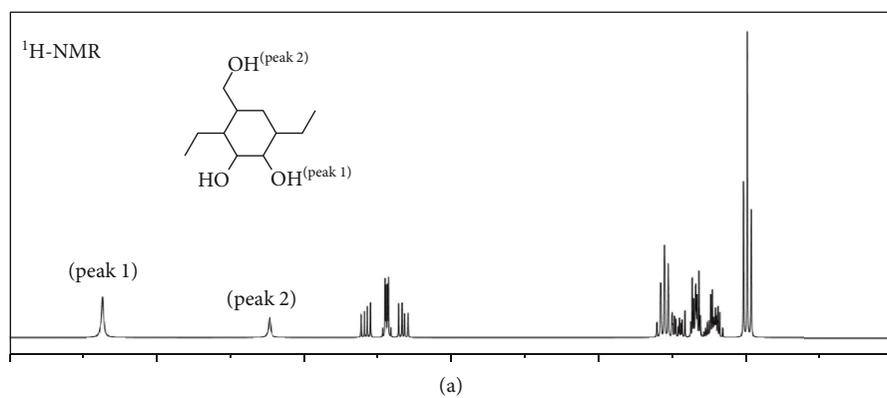
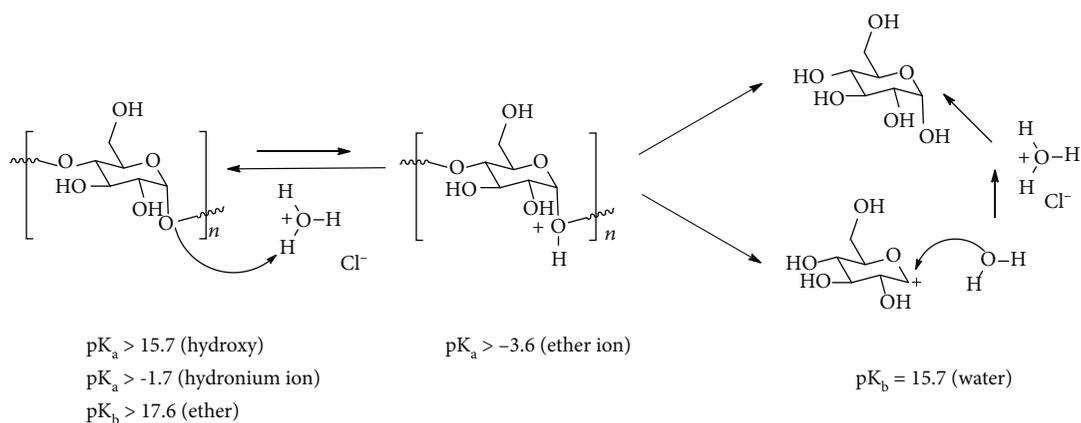
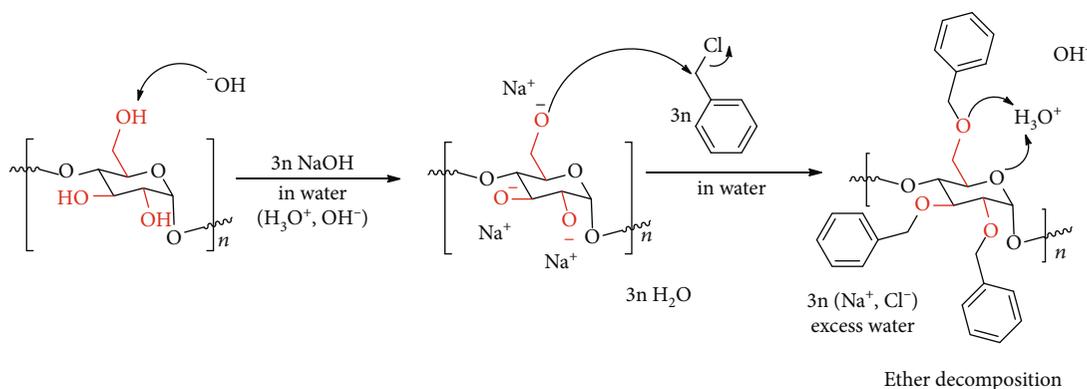


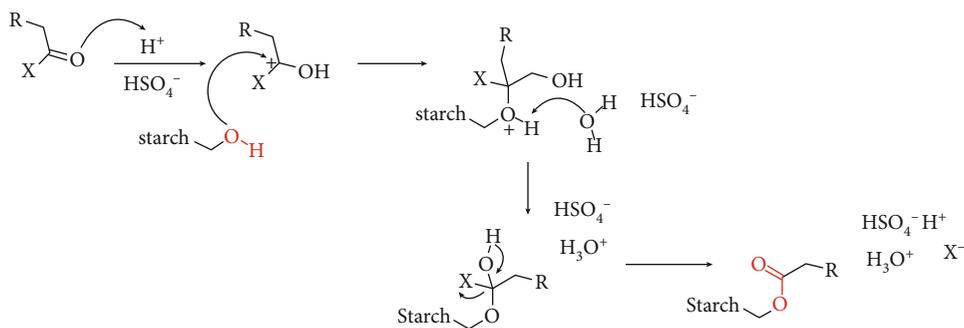
FIGURE 4: Simulated $^1\text{H-NMR}$ data on the protons of the hydroxyl groups of cyclohexane without an ether structure (a) and glucose structure (b).



SCHEME 7



SCHEME 8



SCHEME 9: Fischer's esterification.

described in Scheme 8, these experimental results are interpreted as the effect of suppressing the cause of oxidation of ether by H_3O^+ present in hydration.

Therefore, the reverse reaction can be inhibited if the moisture formed when the hydroxyl group of starch reacts with a OH^- ion is removed, resulting in an increase in the yield for the etherification reaction. This process can be explained by Le Châtelier's law, in that more product can be produced by removing product from the reaction. In addition, a comparison of the concentration of by-products

and the pK_a or pK_b of the substances before and after the reaction can be useful for designing the optimal reaction conditions and improving the product quality and yield [22].

3. Esterification of Starch

The hydroxyl group of starch can be esterified using the Fischer esterification reaction, which is a substitution reaction of a nucleophilic acyl compound with a compound

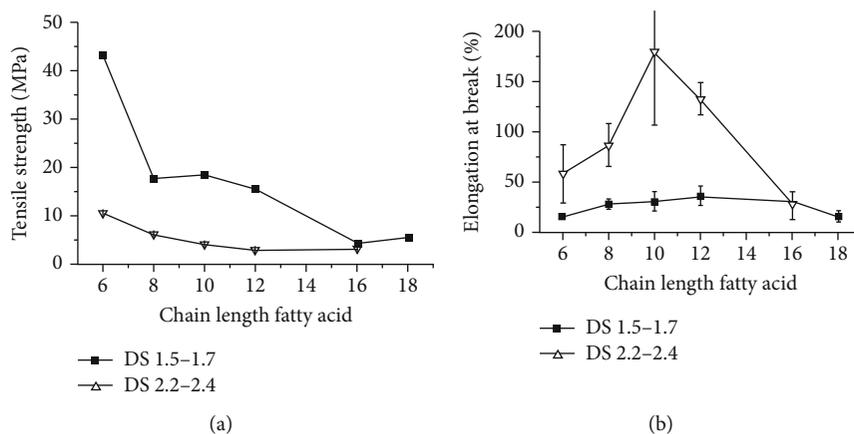
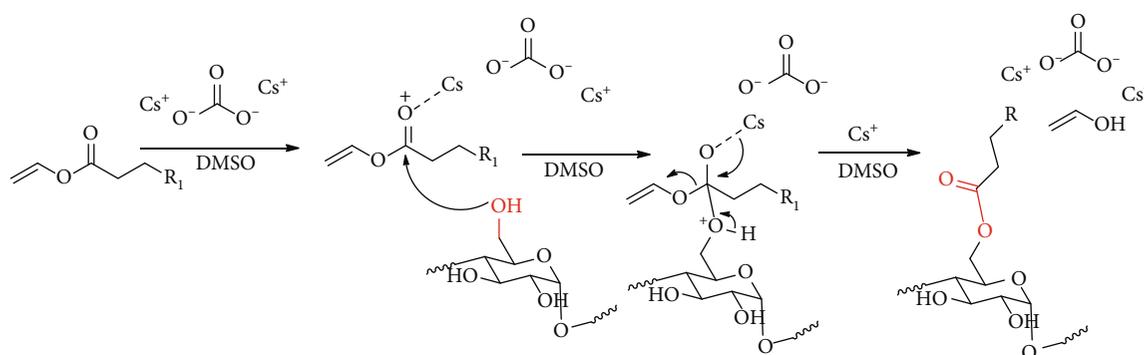
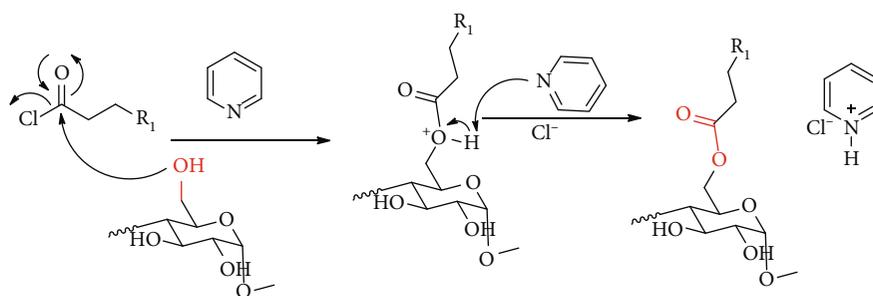


FIGURE 5: Tensile strength (a) and elongation at break (b) depending on the degree of substitution (DS) and type of fatty acid [25].



SCHEME 10



SCHEME 11

containing an acid anhydride, acid chloride, or carboxylic acid structure under an acid catalyst (Scheme 9).

As the hydroxyl group of glucose is esterified by this reaction mechanism, the hydrogen bonding ability of amylose or amylopectin is weakened. This structural change in starch can lower its reactivity with moisture, thereby enhancing its durability [23]. In addition, the basic structure of starch is converted to a thermoplastic material that prevents crosslinking at high temperatures by esterifying the hydroxyl group of the reactive glucose. This is effective when the ester structure is applied to a bioplastic that requires

properties, such as flexibility, elasticity, impact resistance, and chemical resistance [24].

Some studies have reported the production of fatty acid starch esters by reacting 80% amylose-containing starch with vinyl carbonates, such as vinyl laurate ($\text{CH}_3(\text{CH}_2)_{10}\text{COOCH}=\text{CH}_2$) or vinyl stearate ($\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}=\text{CH}_2$). In these reports, the potential for use as a biodegradable packaging material was presented by examining the effects of the starch hydrophobicity, material flexibility at high temperatures, and film properties depending on the length of the alkyl group (Figure 5) [25, 26].

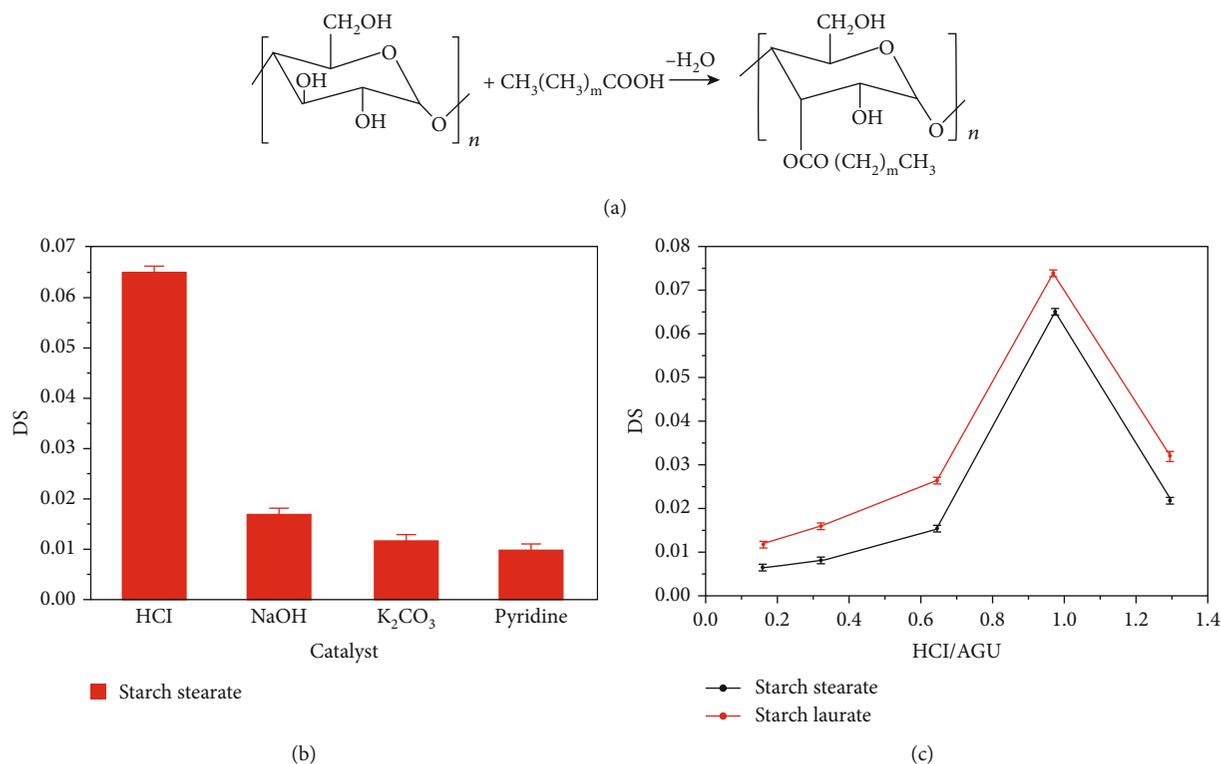


FIGURE 6: Starch esterification by saturated alkyl carboxylic acid (a) and effect of the catalyst on the degree of substitution of starch stearate (b) and HCl dose (c) [29].

The synthesis of fatty acid starch esters in these studies proceeded by a nucleophilic substitution reaction between the electrophilic carbonyl carbon of vinyl carbonate and the hydroxyl group of starch, a nucleophilic functional group, *via* an acid-base reaction between cesium carbonate and vinyl carbonate (Scheme 10). Cesium carbonate was used as a catalyst in many studies related to the esterification of starch because of its higher solubility in polar solvents, such as *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), which can dissolve the reactant starch and carbonate compounds, compared to potassium carbonate or sodium carbonate [27].

A material with enhanced hydrophobicity of starch can be made by introducing a hydrophobic alkyl group through esterification with an acyl halide compound, such as *n*-dodecanoyl chloride. In such a reaction, the use of a basic solvent, such as pyridine, which can remove the acid generated after the reaction, can improve the efficiency of the forward reaction. As shown in Scheme 11, this reaction can proceed smoothly by the basic nitrogen of pyridine, which removes protons of the cationic ether [25].

In the esterification reaction of starch with saturated fatty acids, various acids and bases, such as pyridine, Na₂HPO₄, K₂CO₃, CH₃COONa, potassium silicate, HCl, and NaOH, are used as reaction catalysts [28]. These catalysts weaken the bond strength between the starch chains that are spirally connected by hydrogen bonding and improve the reaction efficiency in the process of inducing a nucleophilic substitution reaction (Fischer's esterification) with the starch hydroxyl group by carbocation formation (Scheme 11).

In the case of a reaction with stearic acid, the substitution rate is higher under acid conditions than under base conditions, as shown in Figure 6. Even under acid conditions, the ratio of the catalyst and glucose monomer, reaction temperature, and reaction time affect the substitution rate of ester groups [29]. On the other hand, the hydrophobicity of starch increases as the length of the alkyl group substituted with the hydroxyl group of starch increases, but many experimental results have shown that the substitution rate is lowered by its steric hindrance [30]. These results mean that it is also necessary to consider the structure of the substituted alkyl carbonyl to synthesize the optimal biodegradable plastic according to the application.

As described above, the hydroxyl group of glucose is a functional group that dominates the physical and chemical properties of starch or cellulose. The physical property of starch and its biodegradability in the presence of moisture can be controlled by substituting the hydroxyl group with ether, ester, or alkyl group. In addition, for plastic materials made from starch or cellulose to replace high-performance plastics, such as PE and PVC, while maintaining biodegradation properties, it is necessary to consider the optimal synthesis conditions through a study of the mechanism of the substitution reaction.

4. Conclusions

The production of biodegradable plastics using starch for developing alternative materials to plastics has attracted considerable attention. This study examined the reaction

factors that can affect the development of biodegradable plastics through starch modification by etherification and esterification. The reaction conditions with high efficiency were suggested after examining the reaction temperature, pH, solvent, and by-products involved in the etherification reaction. Regarding the ester reaction, the structure of the substituent and the reaction solvent affecting the reaction efficiency were examined. Overall, this review would serve as an opportunity to increase the use of starch as a material that can replace commodity plastics for many purposes.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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