

Synthesis and Curing Behaviors of Reactive Cellulose Esters from Renewable Resources

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ABSTRACT: This study deals with synthesis and curing of cellulose esters from renewable resources. Cellulose esters bearing unsaturated groups were prepared from cellulose and fatty acid in LiCl/N,N-dimethylacetamide solution. The subsequent epoxidation produced cellulose esters with oxirane groups in the side chain. The resulting cellulose esters were cured by thermal treatment to give transparent films with gloss surface. FT-IR spectra revealed that reactive groups in the side chain reacted with each other during the reaction to produce crosslinked network structure. The universal hardness and Young's modulus of the crosslinked cellulose esters increased as a function of the number of reactive groups. The crosslinked cellulose esters also exhibited high glass transition and thermal decomposition temperatures. The development of the bio-based material from cellulose and plant oil-based fatty acid would be highly expected to contribute to global sustainability.

KEYWORDS: Renewable resource, Cellulose derivative, Fatty acid, Network polymer.

I. INTRODUCTION

Nowadays, we have confronted a number of environmental problems such as atmosphere pollution and depletion of petroleum resources. The replacement of petroleum-derived plastics and composites by bio-based materials from inexpensive renewable natural sources has the potential to great impact the chemical industries [1-2]. Bio-based starting materials are usually abundant and renewable on a time scale many orders of magnitude smaller than petroleum. Furthermore, they provide various potential properties such as biodegradability, which are often difficult to realize by petrochemical sources.

Cellulose is the most abundant biopolymer on Earth and about 1.5×10^{12} tons of cellulose grow as the main component of plants every year [3]. Cellulose consists of β -D-glucose with various degrees of polymerization. Cellulose from wood, straw, and cotton is widely used in several industries, such as the paper industry, chemical industry, textile industry, and food industry [4-6]. Modification of cellulose has been eagerly investigated for scientific and practical interest. The most successful techniques targeted at improving physical, morphological, and mechanical properties are to grafting onto native forms [7-14]. So far, vinyl polymers and polyesters have been often grafted on the cellulose backbone.

Cellulose esters represent a class of commercially important thermoplastic polymers with excellent fiber- and film-forming characteristics [15-17]. However, cellulose acetate and cellulose propionate require external plasticizers for most molding processes because they possess high softening temperatures. Long acyl chains decrease the softening temperature of cellulose esters, and the lateral aliphatic chain acts as an internal plasticizer of the cellulose ester. These materials have been also identified as potential biodegradable plastics because of the enzymatically labile ester bonding, which is derived from the natural abundance of both cellulose and fatty acids. Several cellulose esters with unsaturated fatty acid were reported [18-19]. The reactive cellulose esters would allow for modification by postreaction such as bromination, oxidation, or graft polymerization with vinyl monomers. Therefore, they are useful as plastics, plastic additives, chromatography supports, cosmetic additives, and slow-release carriers for pharmaceuticals.

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Renewable plant oils have excellent properties which can be utilized for production of valuable polymeric materials such as epoxy resins, alkyds and polyurethanes in addition to their other applications in agriculture and food industries [20-23]. Recently, a green composite was prepared by the curing of epoxidized soybean oil in the presence of porous poly(3-hydroxybutyrate). The porous structure of poly(3-hydroxybutyrate) improved the mechanical properties of the plant oil-based network polymer [24]. Moreover, we have developed crosslinkable polyesters from plant oils. The cross-linkable polyesters were synthesized by lipase-catalyzed polymerization of divinyl sebacate and glycerol in the presence of unsaturated or epoxidized fatty acids under mild reaction condition. The thermal treatment of these polymers produced the crosslinked films, which were subjected to biodegradation in an activated sludge [25-26]. In this study, we synthesized novel cellulose esters bearing reactive groups in the side chain, and the subsequent crosslinking reaction was performed. The resulting cellulose esters consist of renewable resources, cellulose and plant oil-based fatty acids, and were found to be an efficient prepolymer for coating materials.

II. EXPERIMENT

Materials

Cellulose (Whatman CF-11) was purchased from Wako Pure Chemical Industries, Ltd. A thermally-latent cationic catalyst (benzylsulfonium hexafluoroantimonate derivative, commercial name: Sun-Aid SI-60L) were gift from Sanshin Chemical Industry Co. Other reagents and solvents were commercially available and were used without further purifications.

Synthesis of cellulose ester with unsaturated groups (2)

The following was typical procedure for the synthesis of cellulose esters having unsaturated groups. Cellulose (0.32 g) was dissolved in 40 mL of 10 wt% LiCl/N,N-dimethylacetamide (DMAc) solution at 50°C with gentle stirring. Linoleic acid (3.37 g, 12 mmol), p-toluenesulfonyl chloride (2.29 g, 12 mmol) and pyridine (2.85 g, 36 mmol) were added to the solution, and the mixture was stirred at 50°C under argon atmosphere. After 24 h, the reaction mixture was poured into a large amount of methanol. The precipitate was collected by centrifugation, and was dried in vacuo to give 1.48 g of cellulose ester with unsaturated groups (2b) (yield 85 %). ¹H NMR (2b) δ(CDCl₃) δ= 0.9 (t, CH₃), 1.2-1.4 (br, CCH₂C), 1.6 (br, OC(=O)CH₂CH₂C), 2.0 (m, C=CHCH₂C), 2.3 (t, OC(=O)CH₂C), 2.8 (dd, C=CHCH₂CH=C), 3.2-5.2 (br, H of saccharide), 5.3-5.4 (m, CCH=CHC).

The cellulose esters having unsaturated groups from oleic acid and linolenic acid (2a and 2c) were synthesized by similar procedure.

Synthesis of cellulose ester with oxirane groups (3)

The following procedure was typically used in the synthesis of cellulose esters having oxirane groups. Under argon atmosphere, 2b (1.5 g) was dissolved in 20 mL of dichloromethane. To the solution, m-chloroperbenzoic acid (m-CPBA) (2.41 g, 14 mmol) was added, and the mixture was stirred at room temperature. After 48 h, dichloromethane was concentrated under reduced pressure, and then the residue was poured into a large amount of methanol. The precipitate was collected by centrifugation, and was dried in vacuo to give 1.54 g of cellulose ester with oxirane groups (3b) (yield 93 %). ¹H NMR (3b) δ(CDCl₃) δ= 0.9 (t, CH₃), 1.2-1.4 (br, CCH₂CH₂C), 1.5-1.7 (br, OC(=O)CH₂CH₂C and C(O)CHCH₂C), 2.3 (t, OC(=O)CH₂C), 2.9-3.1 (m, CH(O)CH), 3.2-5.2 (br, H of saccharide).

The cellulose esters having oxirane groups from oleic acid and linolenic acid (3a and 3c) were synthesized by similar procedure.

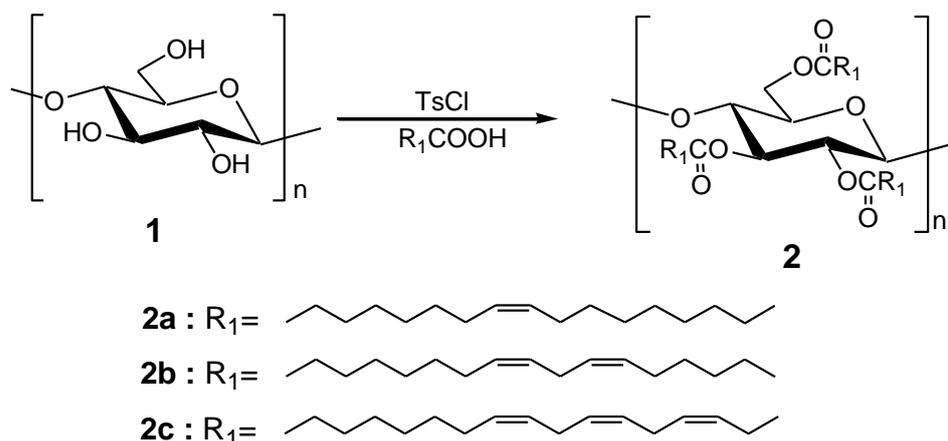
Measurements

¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX400 instrument. Film hardness was evaluated by a Fischerscope H100VS microhardness tester with test force of 40 mN. Fourier-transform infrared spectroscopy (FT-IR) was measured by a Perkin-Elmer Spectrum One. Thermo gravimetric (TG) analysis was performed using a Hitachi High-Tech Science SSC/5200 at a heating rate of 10°C•min⁻¹ under nitrogen. Dynamic viscoelasticity was carried out by using a Hitachi High-Tech Science Exstar 6000 with frequency of 1 Hz at a heating rate of 3°C•min⁻¹.

III. RESULTS & DISCUSSION

Synthesis and curing of cellulose ester having unsaturated groups (2)

Cellulose cannot be manufactured by melt processing technique and casting method in a common solvent, due to the strong hydrogen bonding between intra- and inter-molecules. Cellulose derivatives are usually synthesized by reacting with hydroxyl groups on glucopyranose under heterogeneous conditions. In such cases, cellulose remains suspended in solution, and the reaction proceeds from amorphous regions of the surface. Heterogeneous reaction leads to compositional and structural inhomogeneities. Therefore, many researchers have studied solvents for cellulose, and several solvent systems such as LiCl/DMAc, Ca(SCN)₂/water, LiOH/urea/water, and ionic liquids were reported [27-30]. In this study, we synthesized cellulose esters having reactive groups by homogeneous condition in LiCl/DMAc solution. The solvent system is an appropriate medium for the homogeneous acylation of cellulose having reactive carbonic acid. Scheme 1 shows the synthetic pathway of the acylation for the cellulose. At first, tosylation of cellulose was performed in LiCl/DMAc solution, and subsequently reactive groups were introduced into cellulose by reaction between tosylicellulose and unsaturated fatty acid to produce a cellulose ester with high degree of substitution (DS). DS of the fatty acid, determined by ¹H NMR, were approximately 2.9. The resulting cellulose esters were soluble in common organic solvents like tetrahydrofuran, N,N-dimethylformamide, dimethyl sulfoxide, chloroform, and dichloromethane.



Scheme1

The curing of the cellulose esters having unsaturated groups were performed by following method: at first, the sample was dissolved in chloroform. The solution was cast on a glass plate and the solution was allowed to evaporate the solvent at room temperature. Then, the obtained solid was heated at 150°C for 2h. The curing behavior was monitored by FT-IR and pencil scratch hardness test. Within 2h, 2b and 2c were cured to give transparent films, whereas crosslinking of 2a did not take place due to low numbers of unsaturated groups. These data indicate that 2b and 2c are good crosslinkable cellulose esters and more than two of unsaturated groups in the side chain are required for the hardening. The resulting films exhibited good transparency and gloss surface because the aliphatic chains derived from fatty acid acted as internal plasticizers. The pencil scratch hardness of the films from 2b and 2c were 4H. The obtained films were insoluble in common organic solvents.

Figure 1 shows FT-IR spectra of the film from 2b before and after curing. The cellulose ester having unsaturated groups (2b) had characteristic peaks at 3010 and 723 cm^{-1} , ascribed to C-H stretching and out-of-plane C-H bending of the inner olefin moiety, respectively. After the curing, the former disappeared and the latter became remarkably smaller. On the other hand, a broad peak ascribed to O-H stretching became larger, due to the formation of the hydroxyl-terminated network polymer. These suggest that the crosslinking mechanism is similar to that of oil autoxidation [31].

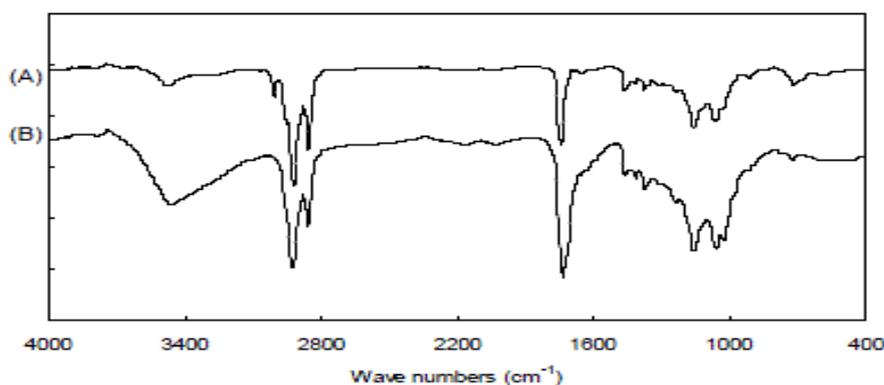


Figure 1: FT-IR spectra of the films from 2b (A) before curing and (B) after cured.

Thermal stability of the resulting films was evaluated by TG analysis under nitrogen. (Figure 2) shows TG traces of the film from 2b before and after curing. Thermal decomposition of the cellulose esters contained two separate degradation steps. The first decomposition, which appeared at lower temperature, resulted from decomposition of the side chain. The second decomposition at higher temperature were derived from the degradation of cellulose backbone. The decomposition of 2b started at 233°C, and temperature at 5% weight loss (Td5) was 293°C. On the other hand, Td5 of the crosslinked film from 2b was higher than that of 2b. This data indicates that the crosslinking reaction improves the thermal stability of the cellulose esters.

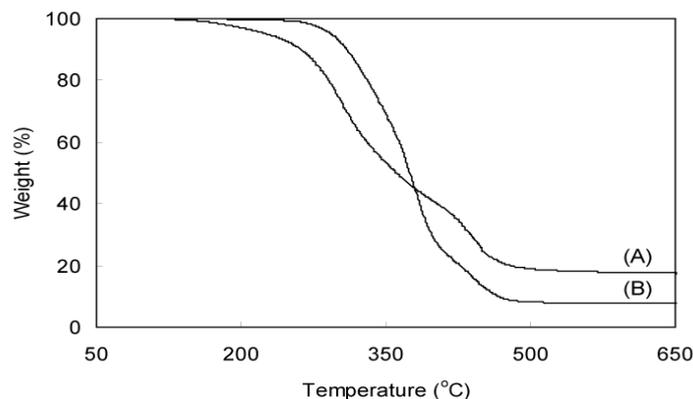


Figure 2: TG traces of the films from 2b: (A) before curing and (B) after cured.

Synthesis and curing of cellulose ester having oxirane groups (3)

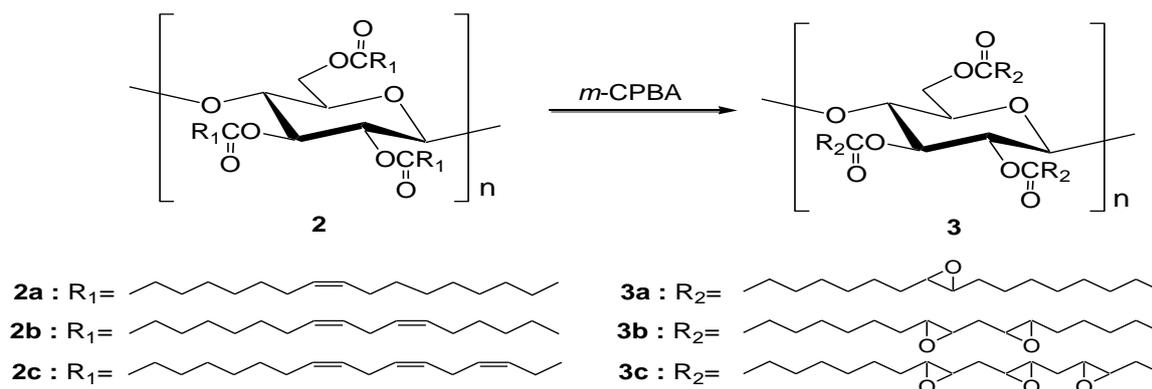
The epoxidation of unsaturated groups in the side chain of cellulose esters was performed. The epoxidation of unsaturated polymer is an important reaction because oxirane groups can be used as reactive intermediates for further reactions such as crosslinking, the attachment of bioactive substances, and the introduction of ionizable groups.

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Epoxy resins are widely used as the basis for coating materials, and have the potential to good chemical resistance, thermal resistance and mechanical properties. In this study, the cellulose esters having oxirane groups were produced in dichloromethane by using *m*-CPBA as an oxidizing agent (Scheme 2). The double bonds in the pendant unsaturated groups were perfectly converted into oxirane groups, as confirmed by ¹H NMR.



Scheme 2

The curing of cellulose ester having oxirane groups was carried out by using thermal-latent cationic catalyst at 150°C for 2h. During the reaction, oxirane groups of cellulose esters reacted with each other, yielding an insoluble network polymer. In FT-IR spectrum of the resulting film, a peak at 830 cm⁻¹, ascribed to C-C antisymmetric stretch of the oxirane groups, was not observed, and a broad peak centered at 3400 cm⁻¹ increased. These data indicate that the oxirane groups are consumed to form a hydroxyl-terminated network polymer. The pencil scratch hardness of 3a, 3b and 3c were 3H, 6H, and over 6H, respectively. The hardness of the films from cellulose esters having oxirane groups (3) was improved, compared with that of the films of cellulose esters having unsaturated groups (2). For quantitative evaluation of the film properties, a micro hardness tester was used (Table 1). The universal hardness and Young's modulus of the films from 3 were also larger than those of the films from 2. These data indicate that the oxirane groups effectively react and the cross linked structure is formed.

Table 1: Film properties of crosslinked cellulose esters

Entry	Cellulose ester	Universal Hardness ^a (N·mm ⁻²)	Young's Modulus ^a (MPa)
1	2a	- ^b	- ^b
2	2b	85	1540
3	2c	127	2330
4	3a	35	520
5	3b	110	1780
6	3c	142	2420

^a Measured by microhardness tester; ^b Not determined.

Dynamic viscoelasticity of crosslinked cellulose esters

In order to investigate the mechanical properties of the resulting films, the temperature dependence of dynamic viscoelasticity was measured. For the film from 2a, the storage modulus fell off slowly in the broad temperature range, and two peaks of loss factor were revealed at 10 and 60°C (Figure 3). The relaxation at higher temperature was accompanied by the most important decrease of storage modulus, and it corresponded to the glass transition of the film. The β transition at lower temperature might be caused by the side chain motion of oleic acid. Lateral aliphatic chains can readily associate with one another, creating local crystalline structures. With increasing temperature, the local aliphatic chains melted and caused a relaxation. On the other hand, a peak and smooth traces of loss factor were observed in the films from 2b and 2c, indicating the homogeneous structure of the resulting films. The glass transition temperature (T_g) of the films from 2b and 2c were higher than that of the film from 2a, and increased with increasing the numbers of unsaturated groups in the side chain. These may be due to the restricted mobility of the aliphatic chain by the crosslinked structure. Above T_g , the storage modulus were almost constant, suggesting that the almost all of unsaturated groups in the side chain were reacted.

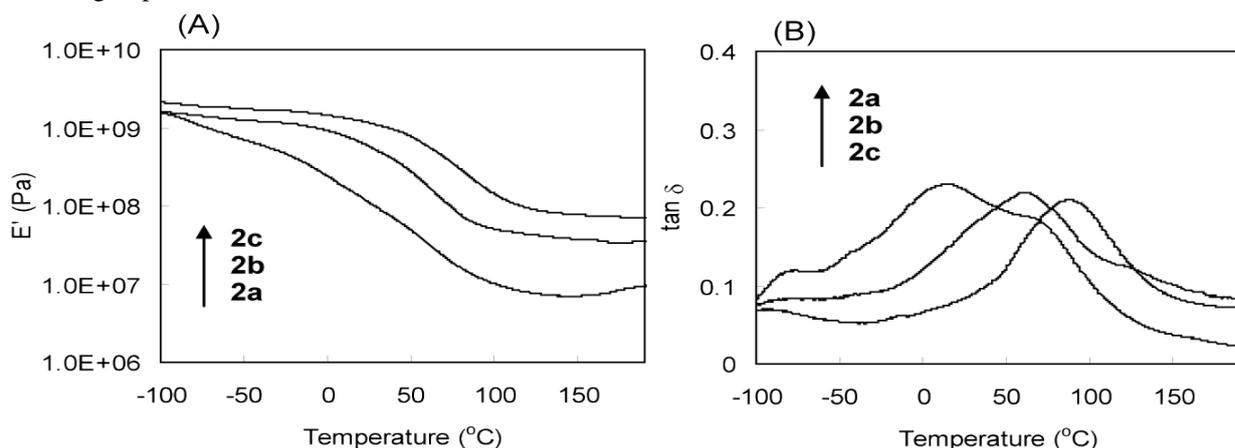


Figure 3: Dynamic viscoelasticity of crosslinked films from 2: (A) storage modulus (E'); (B) loss factor ($\tan \delta$).

In the case of the films from 3, the similar behaviors as the films from 2 were observed (Figure 4). The storage modulus and T_g of the films from 3 were higher than those of the films from 2. Although the storage modulus of the film from 3c also fell off through the glass transition, the value was higher than that of the film of 2c. This is due to the high reactivity of the oxirane groups. Therefore, the film from 3c had high crosslinking density.

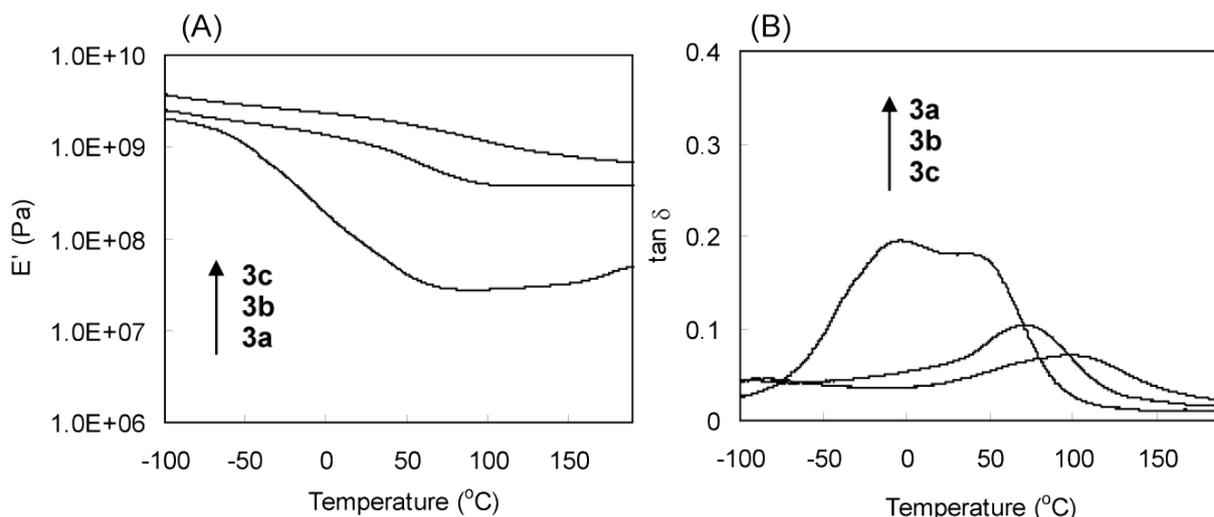


Figure 4: Dynamic viscoelasticity of crosslinked films from 3: (A) storage modulus (E'); (B) loss factor ($\tan \delta$).

IV. CONCLUSION

In this study, cellulose esters bearing reactive groups, unsaturated and oxirane groups, were synthesized, and the crosslinking reaction was carried out. The cellulose esters were hardened by thermal treatment to give transparent films. The resulting films showed excellent coating and mechanical properties. The hardness and the glass transition temperature were dependent on the numbers of reactive groups. Furthermore, the thermal stability was remarkably improved by the crosslinking. Compared with the cellulose ester having unsaturated groups, the crosslinking reaction of the cellulose esters having oxirane groups proceeded effectively due to the high reactivity of oxirane groups, resulting in the bio-based film with high hardness.

Given that the present cellulose esters are derived from renewable resources, biomass content of the resulting film was 100%. Therefore, the present materials should contribute greatly to the reduction of greenhouse gas emissions. This study is expected to provide a novel route of high-performance coating from renewable abundant materials.

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