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The Effect of Water Activation on Chemical Modification of Cellulose and Characterization

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Water activation에 기반한 셀룰로오스의 개질 및 특성

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Abstract Cellulose mixed esters (CME), substituted by various fatty acyl chains, are renewable bio-based polyesters. It has lots of potential due to the biodegradable property. In this study, Alpha cellulose was activated for 2h at 40℃ in deionized water prior to synthesis. Homogeneous esterification of CME was accomplished with water-activated alpha cellulose, various saturated fatty acids and acetic anhydride in lithium chloride/N, N-dimethylacetamide (LiCl/DMAc) medium. CME was obtained after 5 hr at 120℃. The filtrated products were characterized using TGA, FT-IR, 1H-NMR and FE-SEM, and the influence of water activation on the total degree of substitution was investigated.

요 약 다양한 종류의 지방산 아실 체인으로 치환된 Cellulose mixed esters(CME)는 재생 가능한 bio-based 폴리머이다. 셀룰로오스 에스터는 생분해성 고분자로써, 분해되지 않는 석유계 플라스틱을 대체할 미래 고분자 소재이다. 본 연구에서는 개질 실험에 앞서 alpha 셀룰로오스를 40℃의 증류수에 2시간동안 activation하였다. Water-activated 셀룰로오스와, 다양한 불포화 지방산, 무수 아세트산을 120℃의 lithium chloride/N,N-dimethylacetamide (LiCl/DMAc)용매에서 5시간동안 반응시켜 CME를 합성했다. 세척과 감압을 반복한 후, TGA, FT-IR, 1H-NMR과 FE-SEM를 통해 특성을 관찰하였고, water activation이 셀룰로오스의 수산기 치환에 미치는 영향에 대하여 조사하였다.

Key Words : Biodegradable thermoplastic, Cellulose ester, Cellulose mixed ester, Chemical modification of cellulose, Homogeneous esterification of cellulose

1. Introduction

In recent years, the sustainability of plastics has become the most important issuie as the seriousness of environmental pollution has been realized all over the world. Plastics are all made from finite and non-renewable petroleum resources and difficult to dispose[1,2]. Although thermoplastics degrade with hydrolysis, the degradation rate is expected to be decades according to the specific environmental factors such as humidity, pH and temperature[3]. Therefore, many researchers have studied on replacing petroleum-based plastics with bio-based materials.

Cellulose is one of nature's most abundant materials on earth and referred to as "Biomass." It is a renewable carbon resource as well as an alternative material to

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[Table 1] Reagents used in reactions

Reagent	Reagent manufacturer	Purity
n-butyric acid	Daejung Chemical & Material Co., Ltd., Korea	99%
n-caproic acid	Junsei Chemical Co., Japan	98%
n-caprylic acid	Junsei Chemical Co., Japan	98.5%
capric acid	Yakuri Chemical Co., Japan	-
lauric acid	Daejung Chemical & Material Co., Ltd., Korea	99%
N,N-dimethylacetamide(DMAc)	Daejung Chemical & Material Co., Ltd., Korea	99.5%
lithium chloride(LiCl)	Daejung Chemical & Material Co., Ltd., Korea	98%

replace petroleum-based plastics, and derived from two primary sources like cotton linters and wood pulp[4,5]. Cellulose and various cellulose derivatives have been commercialized as fibers, films, filters, and packaging materials. Recentely, cellulose esters, a sort of cellulose derivatives, have been receiving an increasing attention since they have different physical properties depending on the length of substituted chains. Cellulose esters are commonly derived from natural cellulose by acylation with organic acid, anhydrides, or acid chlorides[6,7,8].

In esterification pocess, more than 95% of the α-cellulose content is required[9]. Cellulose can be divided into α-, β- and γ-cellulose. α-Cellulose with higher degree of polymerization than β- and γ-cellulos corrensponds to pure cellulose. α-Cellulose can not be dissolved in a 17.5 % sodium hydroxide solution, while β- and γ-cellulose can be dissolved in a 17.5 % sodium hydroxide solution. β- and γ-Cellulos are tough to filtrate due to their short chains[10]. It's the reason that α-cellulose, which has long cellulose chains, are demanded for esterification of cellulose.

In this paper, the esterification of α-cellulose with an acetic-fatty mixed anhydride generated by the reaction of acetic anhydride and a fatty acid was performed in LiCl/DMAc. The purpose of the research is to study the reactivity of cellulose with several fatty acids and the influence of water activation on synthesis of cellulose esters.

2. Experimental

2.1 Materials

Alpha-cellulose was obtained from Sigma-Aldrich. Reagents used in reactions are shown in Table 1. Alpha-cellulose was dried at 85℃ for 24hr prior to synthesis to remove moisture.

2.2 Activation of cellulose

Dried alpha-cellulose was dispersed in deionized water in order to activate alpha-cellulose. Activation was carried out within a water bath at 50℃ for 2hr.

2.3 Synthesis of CME

Activated alpha-cellulose was dissolved in DMAc at 85℃ under inert atmosphere. LiCl(9% w/w in solution) was added, and a cellulose solution was refluxed with mechanical stirring for 1hr. Fatty acid and acetic anhydride were stirred within a water bath at 85℃ under inert atmosphere, and perchloric acid as catalyst was then added. The molar ratio of fatty acid and acetic anhydride was 1:1. Reactions were allowed to stir at 85℃ for 1hr. The cellulose solution was poured into the mixture of fatty acid, acetic anhydride and perchloric acid. Reactions were carried out in an oil bath at 120℃ for 5hr. The reaction mixture was precipitated with excess ethanol. CME was vaccum filtrated and washed several times with deionized water and ethanol. CME was then vacuum dried to constant weight at 85℃ for at least 36hr. The sample names, based on the number of carbon of fatty acids and water activation, are presented in Table 2.

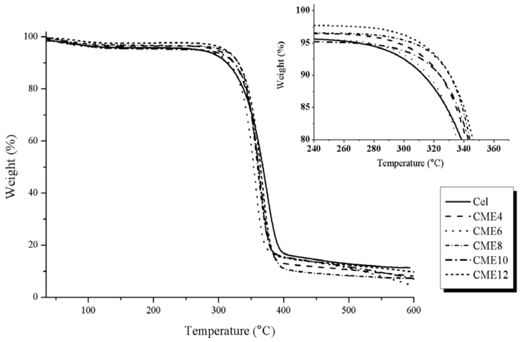
[Table 2] The sample names, based on the number of carbon of fatty acids and water activation

Sample name	Reagent (fatty acid)	Water activation
CME4	n-butyric acid	X
CME6	n-caproic acid	X
CME8	n-caprylic acid	X
CME10	capric acid	X
CME12	lauric acid	X
CME4-W	n-butyric acid	O
CME6-W	n-caproic acid	O
CME8-W	n-caprylic acid	O
CME10-W	capric acid	O
CME12-W	lauric acid	O

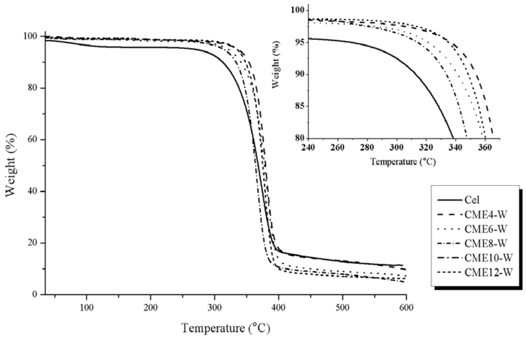
2.4 Characterization

A thermogravimetric analysis (TGA4000, Perkin-Elmer) was conducted from 30℃ to 800℃ at a heating rate of 20K/min. Infrared spectra of the cellulose esters were measured in attenuated transmitted reflectance (ATR) mode on a FT-IR spectrometer (Perkin-Elmer) at a resolution of 4 cm^{-1} in a frequency range from 4000cm^{-1} to 650cm^{-1}. The ^{1}H-NMR spectrum was obtained with a Agilent VNMRS 500 operating at a proton NMR frequency of 500.13 MHz (11.7 T). The spectrum was referenced on residual $CDCl_3$(δ(^{1}H)=7.26ppm). The morphology of the cellulose esters was analyzed by field emission-scanning electron microscopy (FE-SEM), using a JSM-7500F (JEOL Led., Japan).

3. Results and discussion

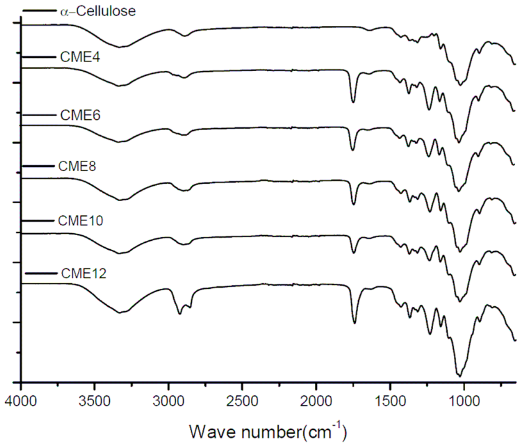


[Fig. 1] TGA thermograms of the CME samples

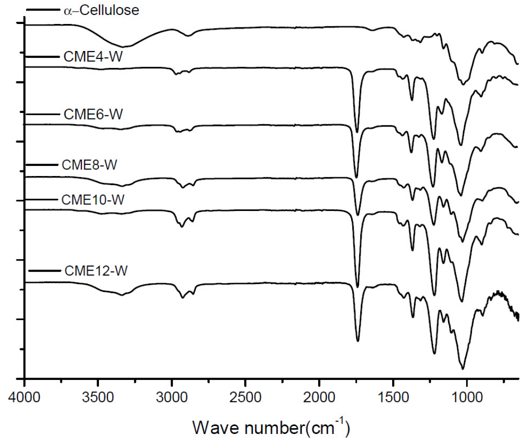


[Fig. 2] TGA thermograms of the CME-W samples

TGA results were investigated to examine whether or not residual reagents are contained. Figure 1 and 2 display TGA thermograms of the CME samples and the CME-W samples. As shown in figure 1 and 2, while the initial decomposition temperature of neat cellulose is above 300℃, the boiling points of all reagents and solvents used are below 300℃. The weight percent was not changed below 300℃. It means that all synthesized mixed cellulose esters don’t have any residual reagents or solvents in them. As a result, the high purity of the mixed cellulose esters was confirmed with the TGA thermograms.



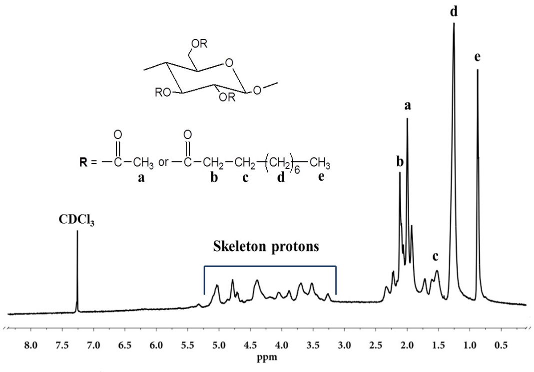
[Fig. 3] FT-IR spectra of the CME samples



[Fig. 4] FT-IR spectra of the CME-W samples

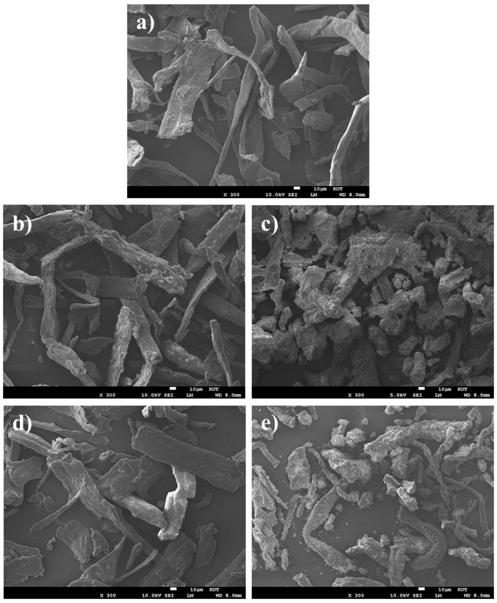
Figure 3 and 4 present FT-IR spectra of the CME samples and the CME-W samples. The bands in the 3200-3600cm^{-1} region are assigned to stretching vibration of hydroxyl group of neat cellulose, and the bands in the 1690-1760cm^{-1} region are assigned to stretching vibration of carbonyl group of cellulose ester[11]. The IR spectra demonstrated the chemical substitution of hydroxyl groups with ester groups. Whereas neat cellulose has no carbonyl groups, cellulose esters have carbonyl groups owing to substituted ester groups. As the TGA results showed that residual solvents or reagents are completely removed, the strong bands in the 1700cm^{-1} region are for the carbonyl groups of synthesized cellulose esters. Chemical substitution led to the the appearance of C=O bands in the 1700cm^{-1} region and the disappearance or decrease in intensity of OH bands in the 3300 cm^{-1} region. Synthesized cellulose mixed esters were confirmed by the IR spectra.

Water activation of cellulose appreciably affected the intensity of the carbonyl and hydroxyl stretching. Significant differences are observed between the CME-W samples and the CME samples. When comparing the CME-W samples with the CME samples, the intensity of the C=O stretching band for the CME-W samples are much stronger than that for the CME samples. On the other hand, the intensity of the OH stretching band for the CME-W samples are much weaker than that for the CME samples. It suggests that water activation trigger the high substitution rate of hydroxyl groups of Cellulose with ester groups and is a very critical factor of the whole experimental process.



[Fig. 5] ^{1}H-NMR spectrum of the CME10-W sample

Figure 5 shows ^{1}H-NMR spectrum of the CME10-W sample. The substituents, which are acetyl groups and fatty groups in cellulose mixed esters were identified by proton NMR spectroscopy[12].



[Fig. 6] FE-SEM micrographs of α -Cellulose and CME a) α -Cellulose, b) CME4, c) CME4-W, d) CME10, e) CME10-W (X300, scale bar=10um)

Figure 6 exhibits FE-SEM micrographs of α-Cellulose and CME. Differences between the surface of the CME samples and CME-W samples explain the effect of water activation. Whereas the surface of Cellulose is clear, that of Cellulose ester is rough. Overall, the rough surfaces are observed in the image of the CME-W samples. However, both the rough and smooth surfaces are shown in the image of the CME samples[13]. As a result, water activation induces effective synthesis of cellulose esters, and the result of the SEM image in accord with the IR spectrum result.

4. Conclusion

The effects of water activation on CME were thoroughly studied with TGA, FT-IR, ^{1}H-NMR, and FE-SEM analyses. The TGA results indicated that residual reagents are not contained to CME. Synthesized cellulose mixed esters were identified by the IR and ^{1}H-NMR spectrum. Water activation promotes an efficient reaction. It has verified by IR spectra and morphological investigations. Intermolecular interaction between hydroxyl groups of cellulose and water can make some space among compact cellulose chains. It is considered that water activated cellulose, consisting of loose cellulose chains, are easier to react than cellulose.

References

[1] N. Lavoine, et al., "Microfibrillated cellulose – Its barrier properties and applications in cellulosic material: A review", Carbohydrate Polymers, vol.90, pp. 735-764, 2012.
DOI: http://dx.doi.org/10.1016/j.carbpol.2012.05.026

[2] E. Gumuskaya, et al., "The effects of various pulping conditions on crystalline structure of cellulose in cotton linters", Polymer Degradation and Stability, vol.81, pp.559-564, 2012.
DOI: http://dx.doi.org/10.1016/S0141-3910(03)00157-5

[3] A.C. Albertsson, et al., "Degradable polyesters as biomaterials", Acta Polymerica, vol.39, pp.95-104, 1988.
DOI: http://dx.doi.org/10.1002/actp.1988.010390118

[4] C. F. Liu, et al., "Structural and thermal characterization of sugarcane bagasse cellulose succinates prepared in ionic liquid", Polymer Degradation and Stability, vol.91, pp.3040-3047, 2006.
DOI: http://dx.doi.org/10.1016/j.polymdegradstab.2006.08.004

[5] K. J. Edgar, et al., "Advances in cellulose ester performance and application", Progress in Polymer science, vol.26, pp.1605-1688, 2001.
DOI: http://dx.doi.org/10.1016/S0079-6700(01)00027-2

[6] J. Peydecastaing, et al., "Bi-acylation of cellulose: determining the relative reactivities of the acetyl and fatty-acyl moieties", Cellulose, vol.18, pp.1015-1021, 2011.
DOI: http://dx.doi.org/10.1007/s10570-011-9528-9

[7] D. L. Morgado, et al., "Thermal Decomposition of Mercerized Linter Cellulose and its Acetates Obtained from a Homogeneous Reaction", Polimerous, vol.21, pp.111-117, 2011.
DOI: http://dx.doi.org/10.1590/S0104-14282011005000025

[8] S. Richardson, et al., "Characterisation of the substituent distribution in starch and cellulose derivatives", Analytica Chimica Acta, vol.497, pp.27-65, 2003.
DOI: http://dx.doi.org/10.1016/j.aca.2003.08.005

[9] S. Park, et al., "Cellulose crystallinity index_ measurement techniques and their impact on interpreting cellulase performance", Biotechnology for Biofuels, vol.3, 2010.
DOI: http://dx/doi.org/10.1186/1754-6834-3-10

[10] Y. Kataoka, et al., "Quantitative analysis for the cellulose Iα crystalline phase in developing wood cell walls", International Journal of Biological Macromolecules, vol.24, pp.37-41, 1998.
DOI: http://dx.doi.org/10.1016/S0141-8130(98)00065-8

[11] M. Akerholm, et al., "Characterization of the crystalline structure of cellulose using static and dynamic FT-IR spectroscopy", Carbohydrate Research, vol.399, pp.569-578, 2003.
DOI: http://dx.doi.org/10.1016/j.carres.2003.11.012

[12] C. Vaca-Garcia, et al., "Cellulose esterification with fatty acids and acetic anhydride in lithium chloride/N,N -dimethylacetamide medium", JAOCS, vol.75, No.2, pp.315-319, 1998.
DOI: http://dx.doi.org/10.1007/s11746-998-0047-2

[13] D. J. Gardner, et al., "Adhesion and Surface Issues in Cellulose and Nanocellulose", Jounal of Adhesion Science and Technology, vol.22, pp.545-567, 2008.
DOI: http://dx.doi.org/10.1163/156856108X295509

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