A study on the synthesis of cellulose acetate from various pulps and application to optical film

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A thesis submitted to the committee of the Graduate School of Changwon National University in partial fulfillment of the requirements for the degree of Master of Engineering

December 2009

Approved by the committee of the Graduate School of Changwon National University in partial fulfillment of the requirements for the degree of Master of Engineering

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2009. 12. 04

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Chapter 1. Introduction

The cellulose, linear glucose polymer, is an abundant resource which is photosynthesized by solar energy in plants [1-2]. The cellulose chain has three hydroxy groups which can be made hydrogen bonds with each other per each unit cell and is the main component of the structural cell wall of all the plants [1]. It had played an important role in many industrial fields like food textile, paint, paper and pharmaceutical industries because of its advantages such as non-toxicity, renewability, biodegradability, modifiability, and the great potential to be used as an excellent materials [2-3].

Although the cellulose has many advantages like these, it can be difficult to be applied to the fields of industry directly because it has an important problem that it is not soluble in common solvents and water. The cellulose is necessary to modify the functional group at the end of chains in other to obtain the soluble products in common solvents. Cellulose triacetate (CTA) is one of the most cellulose derivatives and an important thermoplastic material which has used in our films and membrane industries [4-7]. It is soluble in chloroform but insoluble in more common solvent acetone because all hydroxyl groups in cellulose chain are substituted for acetyl functional groups [8].

CTA film has the properties such as its relatively high moisture regain, significantly low birefringence, excellent dimensional stability, thermal stability and optical isotropy [9, 10]. For these reasons, it has been widely commercialized as photographic film, protective film

for polarizing plate, and optical compensation film for liquid crystal display (LCD) since fifty years [11]. Recently, this material has been investigated as membranes in osmosis and reverse osmosis [12-14], as optical film for the transparent insulation wall heating system [15], and as support for the immobilization of enzymes [16]. CTA film has been also used for the chromatographic separation of enantiomers as a chiral polymeric sorbent [17].

Cotton linter was primarily used to make the CTA optical film because of its high purity, low degree of crystallinity and orientation [17]. However, as its price increases, some economic problems has arisen [18]. Therefore, the new sources are required for replacing the cotton linter. So, many studies have been reported on various raw materials such as sugar cane bagasse [14], wood pulp [4], bamboo pulp [18], recycle paper [7], crop straw [19] corn fiber, rice hull and wheat straw [20]. In this thesis, cotton linter and four wood pulps were used for producing the cellulose acetate (CA).

The aim of this study is to obtain CTA from pulps and cotton linter under various reaction conditions such as temperature, time, and amount of catalyst and reactants and to confirm the optical property of CTA film for the application to the transparent insulation material (TIM).

Chapter 2. Theory

2.1 Acetylation

CTA can be prepared with two acetylation methods shown in Fig. 1. One is the heterogeneous system that the cellulose is reacted with the acetyl functional group of acetic anhydride after dispersing it in acetic acid [7, 14]. The other is the homogeneous system that the cellulose dissolved in the special solvents such as *N*-methylmorpholine-*N*-oxide (NMMO) and dimethylacetamide (DMAc)/ lithium chloride (LiCl) is reacted with the same reactants [21, 22]. The two kinds of CA which is prepared through other acetylation routes make the difference. That is, CA of the homogeneous system is less biodegradable and more crystalline than that of the heterogeneous system [7].

Therefore, when the acetylation was carried out under the homogeneous system, more excellent product was obtained. There are no solvents to dissolve the cellulose effectively, and the homogeneous system has some problems such as the long reaction time and the low reaction yield. For these reasons, the heterogeneous system rather than the homogeneous system was used in other to obtain CA from pulps and cotton linter in this study.

The scheme of cellulose acetylation is shown in Fig. 2. The first step is that acetic anhydride is divided into acetic acid group and acetyl functional group by the catalyst H^+. Next, the divided acetyl functional groups react with cellulose. Finally, CA was obtained by

substituting three proton on the surface of the cellulose for two or three of acetyl functional groups.

The acetylation depends on the accessibility of acetyl functional groups to the surface of cellulose and on the susceptibility of each cellulose crystalline region. Also, the acetylation starts from the amorphous region of cellulose and then, it moves to the crystalline region [23].

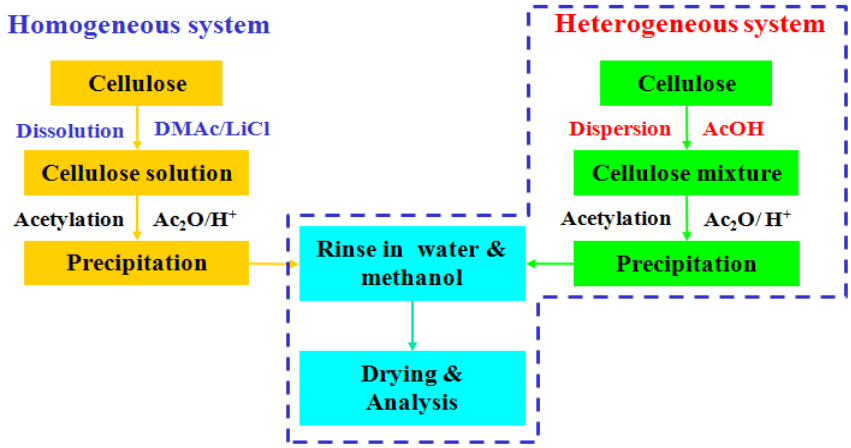


Fig. 1. The whole process of acetylayion in homogeneous and heterogeneous systems.

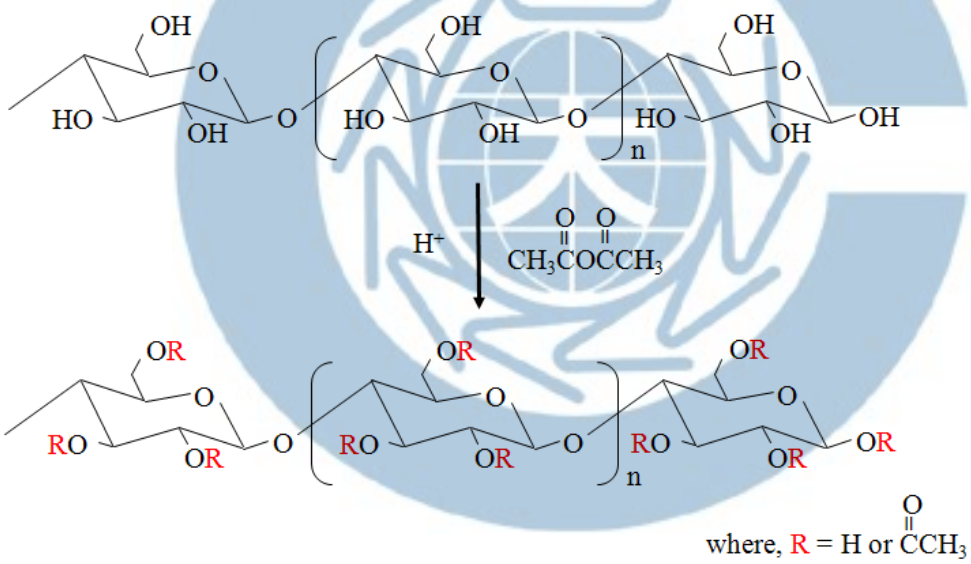


Fig. 2. The scheme of acetylation.

2.2 The DS and solubility

In general studies, after every experiments, the analysis of the product is the most important work to be done. The degree of substitution (DS) can be exactly measured by the titration method and the ^{1}H-NMR analysis. The titration method has a disadvantage that it takes three days to get the DS. Hence, the DS results are easily taken by the simple method to use the various solvents.

The chloroform dissolves CTA which the DS ranges from 2.8 to 3.0, and methylene chloride dissolves CA with the DS from 2.0 to 2.8. Methylene chloride/methanol (9:1) solvent can be applied to CA in the DS range of 2.0 ~ 3.0. Therefore, the DS of products can be predicted with this solvent testing after acetylation. Fig. 3 shows many kinds of solvents to dissolve CA which has various DS values [8].

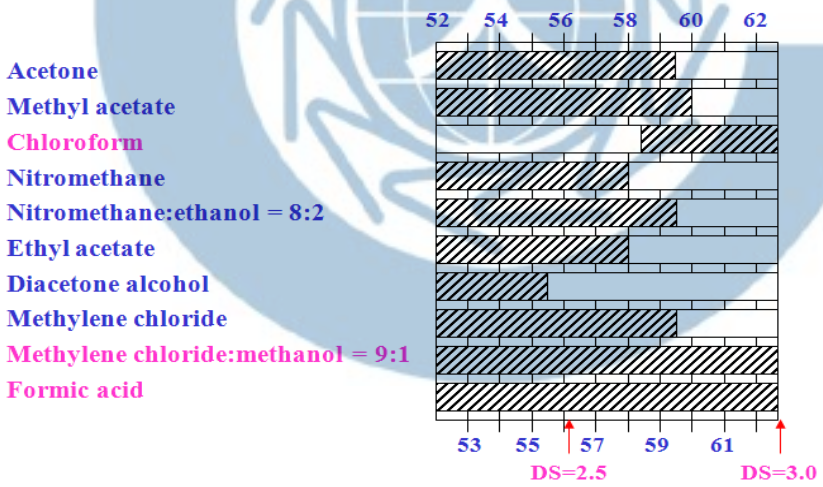


Fig. 3. The various solvents to dissolve CA containing various DS ranges.

2.3 Cotton linter and wood pulp

Cotton plants, an annual shrub, grow in the equatorial regions with tropical and subtropical climate. The various cotton seeds can be obtained according to different conditions and environments. There are four cotton species that are G. hirsutum from Mexico and Central America, G. barbadense from Peru, G. arboretum from India and Pakistan, and G. herbaceum from Southern Africa [24].

The cotton linter which cellulose content is 80% is obtained from the cotton seed in Fig. 4. The lint known as a staple cotton is the long-fiber which the length is 20 ~ 40 mm. On the other hand, the short-fiber, less than 5 mm, around the cotton seed is named as fuzz or linter [25]. The basic differences between cotton linter and cotton lint fibers are shown in Table 1 [24].

The wood pulp is different from cotton linter fiber in the aspect of their chemical compositions. The former has natural composites like hemicellulose and lignin, while the latter has the main cell wall component [26]. Wood pulp is abundant in the countries such as the United States, Canada, Brazil, and Indonesia [27]. However, cotton linter is limited to be got due to climate and location [28]. Therefore, the wood pulp is more cheaper than cotton linter.

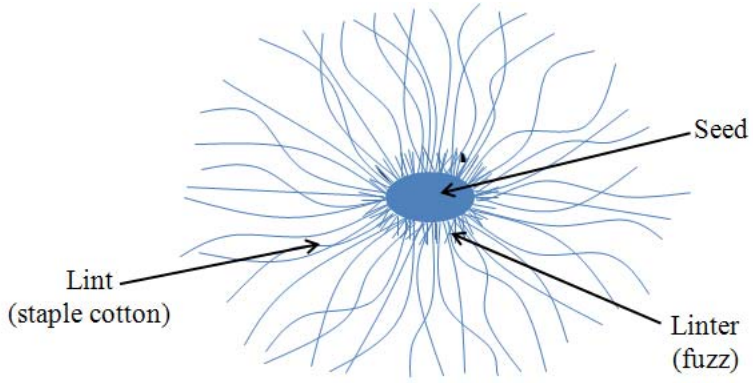


Fig. 4. The cross section of cotton seed.

Table 1. The properties of cotton linter fiber compared to cotton lint fiber

	Cotton linter	Cotton lint
Length (mm)	2 ~ 5	20 ~ 50
Thickness (㎛)	6 ~ 12	2.5 ~ 6
Diameter (㎛)	17 ~ 27	12 ~ 22
Shape	Column	Flat, twisted ribbon with a little curl
Relative reactivity of acetylation	high	low
Whiteness	low	high
Relative crystallinity	low	high

2.4 α-cellulose

After mercerizing the wood pulp with sodium hydroxide, the rest not to be dissolved is α-cellulose. Generally, the α-cellulose content, higher than 95%, is required in acetylation process [26, 28]. This is because the formation of hemicellulose acetate influences on the various properties such as haze, color, viscosity, and poor filterability of CA solution and the degraded short chain celluloses named β-cellulose and γ-cellulose affect the yield of CA [26].

The α-cellulose contains a little of amount of hemicelluloses. β-cellulose with approximately 200 degree of polymerization indicates the degraded cellulose which is produced by the isolation and purification processes. γ-cellulose essentially has about 10 degree of polymerization of hemicelluloses.

2.5 Transparent insulation material

The polycarbonate (PC) and poly(methyl methacrylate) (PMMA) as the transparent insulation polymer are the representative commercial plastics in the TIM industry [29], because the infrared optical properties at approximately 10^4 nm are one of the important factors to select the transparent insulation polymer. In other words, the carbon-oxygen single bond in the polymer is necessary to be used in the field. Likewise, the absorption within the range above should be high, while the high transmittance within the solar spectral range is required [29, 30]. The transparent insulation polymer is necessary to have lives for more than 20 years and the resistance to the heat over 100℃ as well [29].

Fig. 5 illustrates the four types of TIM that has unique patterns of solar transmission and physical behaviour [31, 32]. The absorber-parallel structure (Fig. 5A) is parallel to the black absorber surface. The heat loss can be reduced, but the optical reflection increases. Fig. 5B is related with the absorber-perpendicular structure. The structure makes the incoming beam be transmitted to the absorber. Hence, it has been used in wide application field.

Also, the cavity structure (Fig. 5C) which absorber-parallel structure is mixed with absorber-perpendicular structure can reduce the heat loss without the convection maintaining the transmittance. The last structure (Fig. 5D) containing porous glass fibre or aerogel in the size of 10 ~ 30 nm is characterized by features such as scattering and absorbing the solar energy within the TIM.

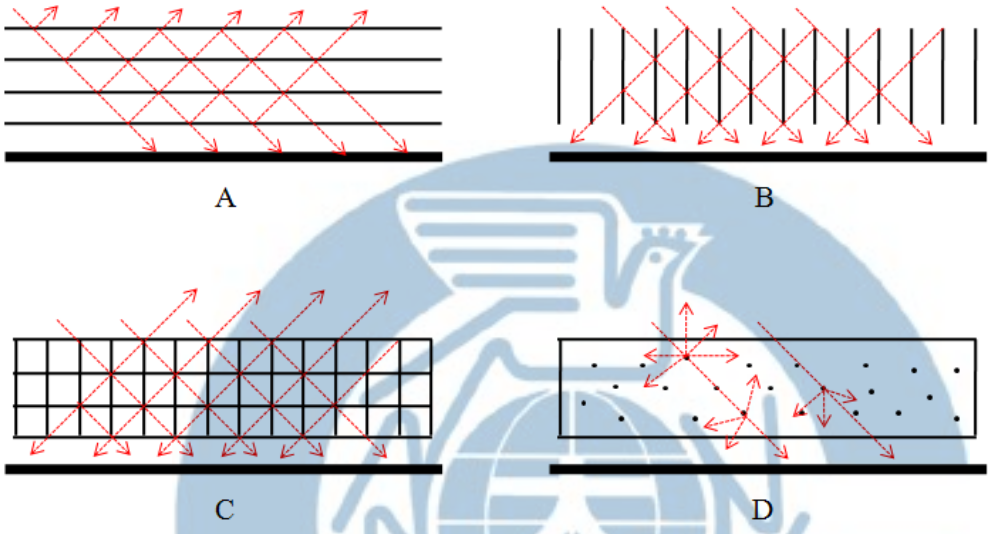


Fig. 5. The classification of transparent insulation materials; (A) absorber-parallel structure, (B) absorber-perpendicular structure, (C) cavity structure, and (D) quasi-homogeneous structure.

Chapter 3. Preparing the cellulose acetate

3.1 Materials

Four kinds of pulps which are V81 (DP = 390, Buckeye), V60 (DP = 354, buckeye), Tembest-LV (DP = 382, Tembeck), and TR922 (DP = 312, Weyerhaeuser) and cotton linter provided from Aekyung Chemical Co., LTD. were used as cellulose source to prepare CA. Acetic acid and acetic anhydrid (1st grade, Daejung chemicals & Metals Co., LTD., Korea), and perchloric acid (1st grade, Junsei, Japan) as catalyst were purchased for acetylation.

After the reaction, acetone, chloroform, methylene chloride, and ethanol (1st grade, Daejung Chemicals & Metals Co., LTD., Korea) were used to measure the solubility of the product and to cast films. DS of CA was measured with sodium hydroxide, sodium carbonate, and hydrochloric acid (1st grade, Daejung Chemicals & Metals Co., LTD., Korea). The cuen solution was prepared with copper hydroxide (1st grade, Junsei Chemical Co., LTD., Japan) and ethylene diamine (1st grade, Yakuri Pure Chemicals Co., LTD., Japan).

Moreover, cellulose acetate (39.8 wt.% acetyl content, Sigma-Aldrich), polycarbonate (303-15, LG-DOW polycarbonate), PMMA (IH830B, LG MMA) were used to confirm the optical property of its films. CTA prepared with V81 pulp was used as well.

3.2 Observance

Fourier Transform Infrared spectrometer (FT-IR 6300, JASCO) was used to analyze the chemical structures of the raw materials and CA. X-ray diffractometer (X-pert MPD PW3040, Philips) was used to confirm the crystal structure and to calculate the relative crystallinity index (RCI). The X-ray spectra were recorded from 2Θ = 5 to 2Θ = 30 with scan size (0.02°) and scan speed (2 sec.).

DS of CA was measured by nuclear magnetic resonance spectrometer (Avance 400, Bruker) and by titration. The transmittance of 1 % CTA solution and CTA film were measured by UV/Vis spectrometer (UV 2100, Shimadzu). The UV/Vis spectra were obtained from 190 nm to 800 nm with scan speed (fast) and slip width (1.0 nm).

The tensile strength and elongation of the various transparent films were measured with 50 mm/min of the velocity at room temperature by Universal Testing Machine (Model 3366, Instron). The thermogravimetric analyzer (TA 5000, TA Instruments) was used to confirm the thermal property of the various films.

3.3 Experimental

3.3.1 Procedure of the heterogeneous acetylation

Pulp was dried in an oven at 105℃ for 2 hours to remove the water and cooled in the desiccator after then. 14 g of dried pulp was weighted and dispersed in 300 g of distilled water at 40℃ for 2 hours in other to activate the pulp. The water in activated pulp was substituted for acetic acid, and it was transferred to a three neck flask containing 200 g of acetic acid and 1.12 g of perchloric acid as a catalyst. At the same time, nitrogen gas was purged into the reactor. 90 g of acetic anhydride that was cooled to prevent the degradation of DP from the heat of reaction was gradually dropped using a dropping funnel. In the end of this reaction, CA was precipitated into a lot of cooled water and washed with distilled water many times to remove an excess of acetic anhydride and acetic acid entirely. After then, it was neutralized with 0.1 N sodium carbonate and re-washed with distilled water and methanol. The final product was dried in vacuum oven at 50℃ for 3 hours. Overall process of the heterogeneous acetylation was shown in Fig. 6.

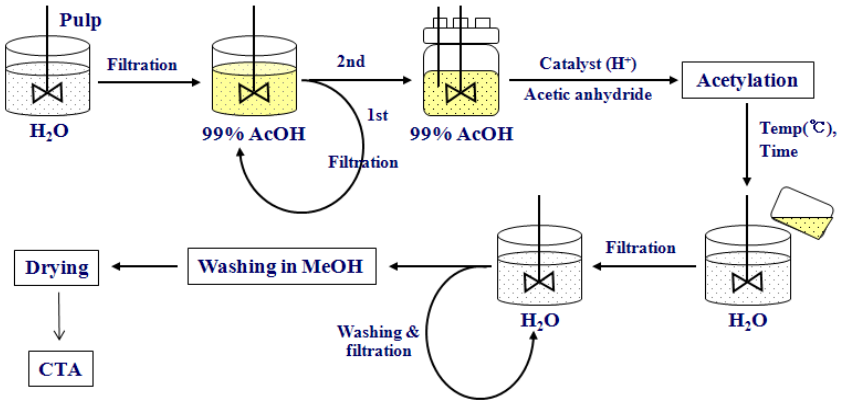


Fig. 6. Overall process of the heterogeneous acetylation.

3.3.2 Casting the various films

Transparent films were prepared on the isolated glass plate like petri-dish at room temperature by the solvent casting method that it is important to control the venting speed and temperature as the kind of solvent. The two kinds of solvents which are methylene chloride : ethanol (80:20) for CTA and cellulose diacetate (CDA) and DCM for polycarbonate (PC) and PMMA bead were used to dissolve the powder and to prepare the films in the thickness of 60 ~ 90 ㎛. 6% solution of each sample was stirred for 2 hours with a magnetic bar to dissolve entirely and it was poured on the isolated glass plate because of its low viscosity. The solvent in the solution was slowly vented at room temperature near 25℃ and the obtained film was dried at 50℃ for 6 hours in a vacuum oven.

3.3.3 Methods for testing

3.3.3.1 The methods of measuring DS

DS of CA was determined with the ASTM D 871 - 96 (Reapproved 2004) standard test method [33]. The sample was grinded by a mortar so that all powder can be passed to a mesh of 500 μm. 1 g of the sample was dried at 105℃ for 2 hours in a convection oven and cooled in a desiccator. The cooled sample was weighted to nearest 0.001 g and transferred to a 250 mL of Erlenmeyer flask. The 40 mL of ethyl alcohol (75%) was added to each sample using a 20 mL of pipette. The flasks were heated at 50℃ for 30 min. After then, 40 mL of 0.5 *N* NaOH solution was added in the flasks, and it was heated at 50℃ for 15 min again. It was allowed to stand at room temperature for 48 hours. At the end of this time, the excess sodium hydroxide (NaOH) in the flask was back titrated with 0.5 *N* hydrochloric acid (HCl) which was standardized with 0.5 N sodium carbonate (Na_2CO_3) with phenolphthalein as the indicator. DS value was calculated as follows:

$$\text{Acetyl } \% = [(D - C)N_a + (A - B)N_b] \times F/W$$

$$DS = (3.86 \times \text{acetyl } \%)/(102.4 - \text{acetyl } \%)$$

where,

A = NaOH solution required for titration of the sample, mL,

B = NaOH solution required for titration of the blank, mL,

C = HCl solution required for titration of the sample, mL,

D = HCl solution required for titration of the blank, mL,

N_a = normality of the NaOH solution,

N_b = normality of the HCl solution,

F = 4.3 for acetyl, and

W = sample weight, g.

3.3.3.2 The methods of measuring DP

① Preparing the cuen solution

The cuen solution can dissolve the pulp. It was prepared to measure the viscosity of pulps. The 48.78 g of copper hydroxide and 433.22 g of distilled water were exactly weighted and poured to the 1000 mL of 3 neck flask that the condenser and dropping funnel were installed. Nitrogen gas was purged into the flask and the solution for 20 minutes to remove air. After then, the 60.2 g of ethylene diamine was slowly dropped using the dropping fennel. The solution was stirred at 25℃ for 15 minutes with 150 rpm. At the end of the reaction, the prepared cuen solution was transferred to a brown bottle and kept in the dark place.

② Measuring DP

DP of the CA was calculated from intrinsic viscosity of it. It was measured with the capillary tube referring to the ASTM D 871 - 96 (Reapproved 2004) standard test methods [33]. The accurate amount

of the sample was dried and weighted in other to take the precise concentration of it. The sample was dissolved in appropriate solvents that is cuen solution for pulp and methylene chloride : ethanol (8 : 2) solution for CA. The Ubbelohde viscometer was used to measure the flow time, and the thermostat was used to control the temperature. The flow time of sample was obtained at 25±0.1℃. The 1 mL of 0.5 M copper-ethylene diamine solution or methylene chloride : ethanol (8 : 2) solution was added three times to obtain the four points with various concentrations. The relative viscosity (η_r) was calculated from the flow times of the sample solution and the solvent. The intrinsic viscosity [η] was calculated from the relative viscosity as follow:

$$\eta_r = \frac{\text{flow time for sample}}{\text{flow time for solvent}}$$

$$[\eta] = \lim_{C=0} (\ln\eta_r / c)$$

where,

c = the concentration of the sample solution.

Also, DP was calculated as follows:

$$DP = K[\eta]^a$$

where,

K and a = value from polymer handbook [34].

3.3.3.3 Solubility

The three solvents which are chloroform, acetone, and methylene chloride : ethanol (8 : 2) were used to test the solubility of CA prepared from various pulps. 0.1 g of CA was dissolved in 9.9 g of each solvent. The solutions were stirred for 24 hours at room temperature. The results were determined with four interpretations which are ◎ : sample is perfectly dissolved, ○ : small amount of insoluble part are remained, △ : a lot of insoluble part is remained, and × : sample is just swelled.

3.3.3.4 Moisture content

The moisture content of the pulp and CA was measured with ASTM D871-96 (Reapproved 2004) standard test method [33]. 5 g of sample was transferred to 100 mL of a beaker and weighted to the nearest 0.0001 g. It was dried in an oven at 105 ± 3℃ for 2 hours. The various values can be changed by the kind of container including the dried sample. Therefore, a desiccator was used to cool the dried sample. The moisture content(%) was calculated as follow:

$$\text{Moisture, \%} = (A/B) \times 100$$

where,

A = weight loss on heating, g, and

B = sample used, g.

3.3.3.5 Relative crystallinity index (RCI)

The X-ray diffraction of pulp powder which is passed through 500 ㎛ sieve was determined by x-ray diffractometer in the range of 2Θ = 5° ~ 2Θ = 40°. The minimum intensity is at 2Θ = 18°, and the maximum intensity is at 2Θ = 22.5°. Using two intensities, RCI was calculated as follow [35]:

$$RCI = [(I_{22.5°} - I_{18°})/I_{22.5°}] \times 100$$

where,

$I_{22.5°}$ = maximum intensity, and

$I_{18°}$ = minimum intensity.

Chapter 4. Results and discussions

4.1 Acetylation of V-81 pulp

V-81 pulp was used to set up the optimal conditions which are temperature, time, and amount of acetic anhydride and acetic acid in acetylation reaction. The products containing the varied DS, DP, and solubility properties were obtained with various conditions under the heterogeneous system. In the acetylation reaction, the activation step is an essential process to increase the accessibility of acetyl group onto the surface of cellulose. Moreover, the cold acetic anhydride with acetic acid plays a very important role in preventing the degradation of DP of CA by the generated heat. Also, the reactor is dipped in ice water during dropping the acetic anhydride.

To begin with, the acetylation was carried out with various amount of acetic anhydride at 40℃ for 60 minutes. The reaction conditions and results were shown in Table 2 and Table 3 respectively. Both DS from and DP increased with the increase of amount of acetic anhydride. CTA which contains 2.8 of DS and 222 of DP was soluble in chloroform and methylene chloride : ethanol (8 : 2) but, insoluble in acetone. Chloroform can only dissolve CTA that DS is more than 2.8 [24]. Therefore, the product containing 2.7 of DS and 180 of DP was soluble in methylene chloride : ethanol (8 : 2). However, it was not soluble in chloroform because the prepared CA occupy a wide range of DS.

In the second place, the acetylation was performed with various

amount of perchloric acid as a catalyst under the same conditions after fixing 90 g of acetic anhydride. This reaction conditions and results were shown in Table 4 and Table 5 respectively. As the mount of perchloric acid increases, DS increased from 2.1 to 3.0 while DP decreased. When 0.56 g of amount of catalyst is used, CA is not soluble in any solvents. Its DS was 2.1 and DP could not be measured due to nonsolubility in methylene chloride : ethanol (8 : 2). Hence, the minimum amount of catalyst was 1.12 g under this conditions.

The third acetylation reaction was carried out with various reaction temperatures for 60 minutes after fixing 90 g of acetic anhydride and 1.12 g of perchloric acid. This reaction conditions and results were shown in Table 6 and Table 7 respectively. Although DS increased with the increase of the reaction temperature, DP decreased. The acetylation reaction should be carried out in low temperature to get the product containing the high DP because the change of temperature is greatly influenced on this reaction more than other reaction conditions. CTA which contains 2.8 of DS and 222 of DP was obtained at 40℃ of the optimal temperature.

Finally, the acetylation at 40℃ was accomplished with various times to get the more excellent product containing the high DP. Table 8 displays the reaction conditions, and Table 9 shows the results of DP, DS, and solubility of product which was prepared for various times. Although the reaction was carried out to increase DP reducing the time, we could not obtain CTA which is soluble in chloroform.

In summary, CTA which contains 2.8 of DS and 222 of DP was

prepared at 40℃ for 60 minutes with 1.12 g of perchloric acid and 90 g of acetic anhydride under the heterogeneous system after dispersing the V81 pulp in acetic acid.

Table 2. The reaction conditions of V81 pulp with various amount of acetic anhydride at 40℃ for 60 min

Sample No.	Time (min)	Temp. (℃)	Cellulose (g)	Acetic acid (g)	Acetic anhydride (g)	Perchloric acid (g)
CA-1	60	40	14	200	30	1.12
CA-2					60	
CA-3					72	
CA-4					90	

Table 3. The properties of CA prepared with various amount of acetic anhydride at 40℃ for 60 min

Sample No.	DS	DP	Solubility		
			$CHCl_3$	DCM:EtOH (8:2)	Acetone
CA-1	1.8	-	×	×	×
CA-2	2.6	176	×	○	×
CA-3	2.7	180	×	◎	×
CA-4	2.8	222	◎	◎	×

Table 4. The reaction conditions of V81 pulp with various amount of perchloric acid at 40℃ for 60 min

Sample No.	Temp. (℃)	Time (min)	Cellulose (g)	Acetic acid (g)	Acetic anhydride (g)	Perchloric acid (g)
CA-5	40	60	14	200	90	0.56
CA-4						1.12
CA-6						2.24
CA-7						4.48

Table 5. The properties of CA prepared with various amount of perchloric acid at 40℃ for 60 min

Sample No.	DS	DP	Solubility		
			$CHCl_3$	DCM:EtOH (8:2)	Acetone
CA-5	2.1	-	×	×	×
CA-4	2.8	222	◎	◎	×
CA-6	3.0	185	◎	◎	×
CA-7	3.0	152	◎	◎	×

Table 6. The reaction conditions of V81 pulp at various temperatures for 60 min

Sample No.	Temp. (℃)	Time (min)	Cellulose (g)	Acetic acid (g)	Acetic anhydride (g)	Perchloric acid (g)
CA-8	30	60	14	200	90	1.12
CA-4	40					
CA-9	50					
CA-10	60					

Table 7. The properties of CA prepared at various temperatures for 60 min

Sample No.	DS	DP	Solubility		
			$CHCl_3$	DCM:EtOH (8:2)	Acetone
CA-8	1.9	-	×	△	×
CA-4	2.8	222	◎	◎	×
CA-9	2.8	178	◎	◎	×
CA-10	2.9	141	◎	◎	×

Table 8. The reaction conditions of V81 pulp for various times at 40℃

Sample No.	Time (min)	Temp. (℃)	Cellulose (g)	Acetic acid (g)	Acetic anhydride (g)	Perchloric acid (g)
CA-11	30	40	14	200	90	1.12
CA-12	40					
CA-13	50					
CA-4	60					
CA-14	70					

Table 9. The properties of CA prepared for various times at 40℃

Sample No.	DS	DP	Solubility		
			$CHCl_3$	DCM:EtOH (8 : 2)	Acetone
CA-11	2.6	284	×	○	×
CA-12	2.6	252	×	○	×
CA-13	2.7	231	×	◎	×
CA-4	2.8	222	◎	◎	×
CA-14	2.8	207	◎	◎	×

4.2 Acetylation with various pulps and cotton linter

Cotton linter and four kinds of pulps were acetylated under the best reaction conditions set up before. In other to confirm the influence of content of α-cellulose in acetylation process, the pulps which contains same XRD pattern of cellulose and similar DP from 312 to 380 were selected. Cotton linter provided from Aekyung Chemcal has 99% content of α-cellulose, and its DP which could be measured due to insolubility in cuen solution was too high to compare with other pulps. Therefore, the reactivity and XRD pattern were just considered. Table 10 shows the specifications of various pulps and cotton linter.

The XRD patters of various pulps and cotton linter are presented in Fig. 7. All pulps has the pattern of celluloseIV_I, but cotton linter is cellulose I type. In general, the native cellulose existing in nature has the pattern of cellulose I. Stating from the native cellulose, cellulose III_I can be obtained with treatment of dry liquid ammonia. The heat treatment of celluloseIII_I leads to celluloseIV_I. Also, these polymorphs can be converted back to original cellulose [36]. Therefore, cotton linter is native cellulose and pulps are prepared from wood with chemical and physical treatments. RCI was also calculated from maximum intensity at 2Θ = 22.5 and minimum intensity at 2Θ = 18 in XRD data values. Cotton linter has 90.81 of the highest RCI and pulps have similar values in the range of 78.73 ~ 83.69.

DP of raw materials was calculated from intrinsic viscosity with K

and a values written in polymer handbook. In Fig. 8, the graphs of reductive and inherent viscosity of pulps are shown. The point of intersection on y-axis denotes the intrinsic viscosity. Actually, when the pulp is dissolved in cuen solution, as time goes by, the viscosity decreased [37]. Hence, it is necessary to measure it as soon as possible for preventing the degradation of DP.

After studying the properties of raw materials, the acetylation was carried out. The reaction results such as DS, DP, and XRD pattern were shown in Table 11. CTA which contain DS above 2.8 were prepared from pulps and cotton linter. The DP results of CTA prepared from V81 and V60 pulps could be only obtained because it was dissolved in DCM:EtOH (8 : 2) solvent. Besides, the yield of acetylation was shown in Fig. 9. The acetylation yield increased with the increase of the content of α-cellulose in pulps. Fig. 10 shows the water content of CTA. It contains low water content than that of raw material.

Even though CTA prepared from Tembest-LV, TR922, and cotton linter have DS above 2.8, it contains insoluble residue in chloroform and DCM : EtOH (8 : 2) solution. The insoluble residue of CTA which is prepared from Tembest-LV and TR922 was mainly formed due to the formation of glucomannan triacetate and xylan diacetate [6]. It is related to low content of α-cellulose in the raw materials. Moreover, CTA prepared from cotton linter has also insoluble residue due to its high crystallinity of the law material. It is necessary to be carried out under the hard conditions such as high temperature, long reaction time, and much more content of reactants for obtaining

soluble product.

Fig. 11 shows the transmittance of 1% CTA solutions, and Table 12 shows the transmittance values in the range of 380 ~ 750 nm. CTA solution of V81 has the highest transmittance in the all ranges, while the solution which contains a lot of insoluble residue has low transmittance relatively. However, the CTA solution prepared from cotton linter has higher transmittance at 380 and 560 nm than that prepared from V60. Therefore, it seems that the content of α-cellulose influenced on the color of CTA solution.

The FT-IR analysis of original pulp and CTA prepared with various raw materials is shown in Fig. 12. The spectrum of CA remarkably shows the peaks at 1750 cm^{-1}, 1370 cm^{-1}, and 1240 cm^{-1} because of the new acetyl functional groups introduced on the surface of pulp. These peaks relate to the C=O stretching, the C-H bending in the methyl of acetyl group, and C-O stretching respectively. Moreover, O-H stretching peak disappeared in the range of 3100 ~ 3700 cm^{-1} also presents the precise evidence of acetylation.

Table 10. The specifications of various pulps and cotton linter

Pulps	V-81	V-60	Tembest-LV	TR922	Cotton linter
CED viscosity (0.5%), cP	7.2	5.0	-	3.5	50
α-cellulose, %	97.0	94.7	87.3	86.0	99.0
S_{10}	3.7	7.3	16.4	15.0	-
S_{18}	1.9	3.7	9.0	-	-
Ash, %	0.06	0.06	-	0.04	-
XRD pattern	CelluloseIV$_I$				Cellulose I
RCI	79.95	83.69	80.91	78.73	90.81
DP	390	354	382	312	-
Water content (%)	6.37	6.30	6.41	5.97	6.70

Table 11. The properties of CTA prepared from the pulps and cotton linter

Pulps		V81	V60	Tembest -LV	TR922	Cotton linter
DS		2.8	2.9	2.8	2.9	2.8
DP		222	191	-	-	-
Solubility	$CHCl_3$	◎	◎	△	△	△
	DCM:EtOH (8 : 2)	◎	◎	○	△	○
XRD pattern		CTA I				

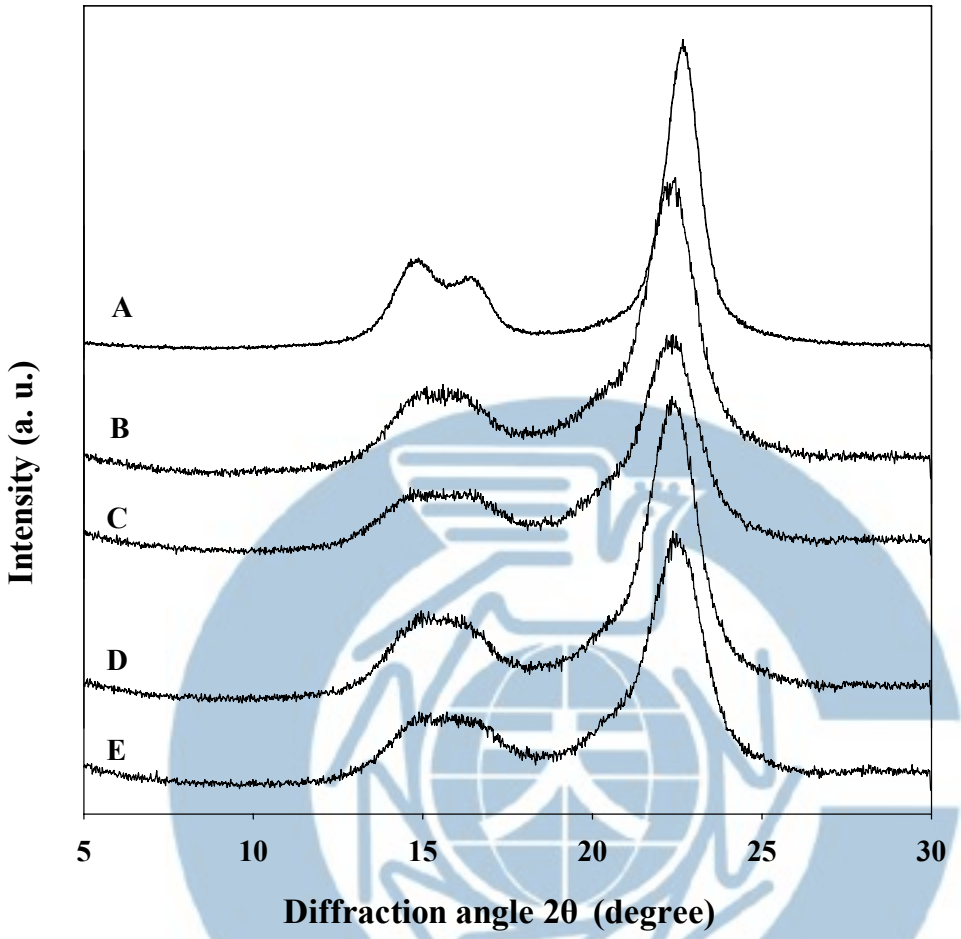


Fig. 7. The x-ray diffractograms of pulps ; (A) V81, (B) V60, (C) Tembest-LV, and (D) TR922.

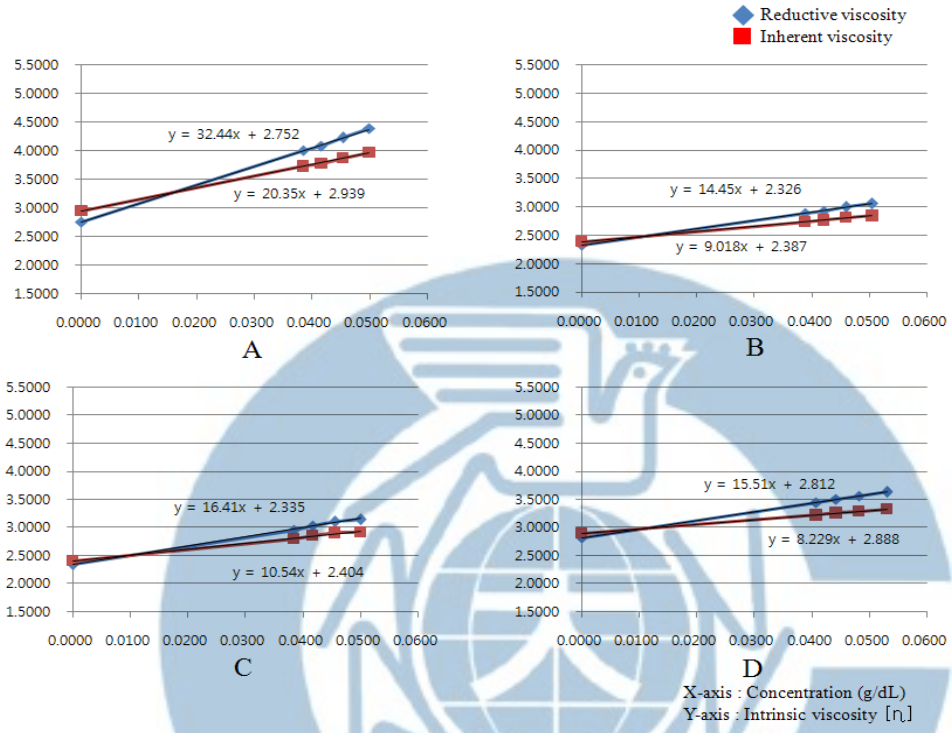


Fig. 8. The graphs of reductive and inherent viscosity of pulps; (A) V81, (B) V60, (C) Tembest-LV, and (D) TR922.

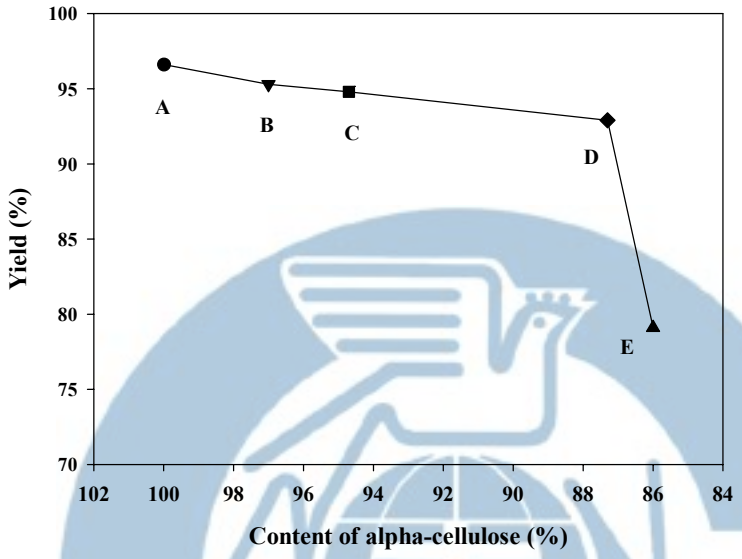


Fig. 9. The acetylation yield of CTA; (A) cotton linter, (B) V81, (C) V60, (D) Tembest-LV, and (E) TR922.

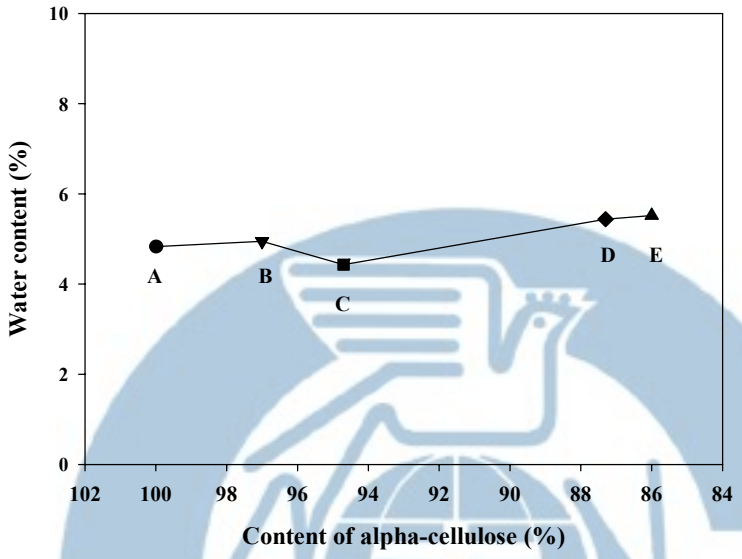


Fig. 10. The water contents of CTA; (A) cotton linter, (B) V81, (C) V60, (D) Tembest-LV, and (E) TR922.

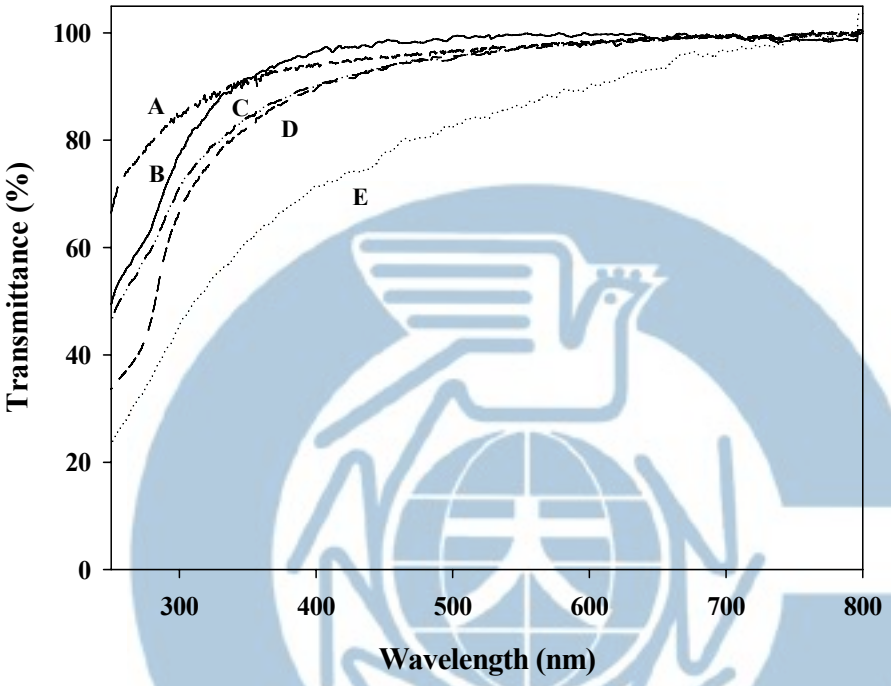


Fig. 11. The transmittance of 1% CTA in DCM:EtOH(8:2); (A) cotton linter, (B) V81, (C) V60, (D) Tembest-LV, and (E) TR922.

Table 12. The transmittance value of 1% CTA solutions at various wavelengths

Wavelength (nm)	Cotton linter	V81	V60	Tembest-LV	TR922
380	93.3	94.9	88.3	87.7	67.6
560	97.7	99.6	97.3	97.7	87.1
750	99.3	99.7	99.6	99.7	99.0

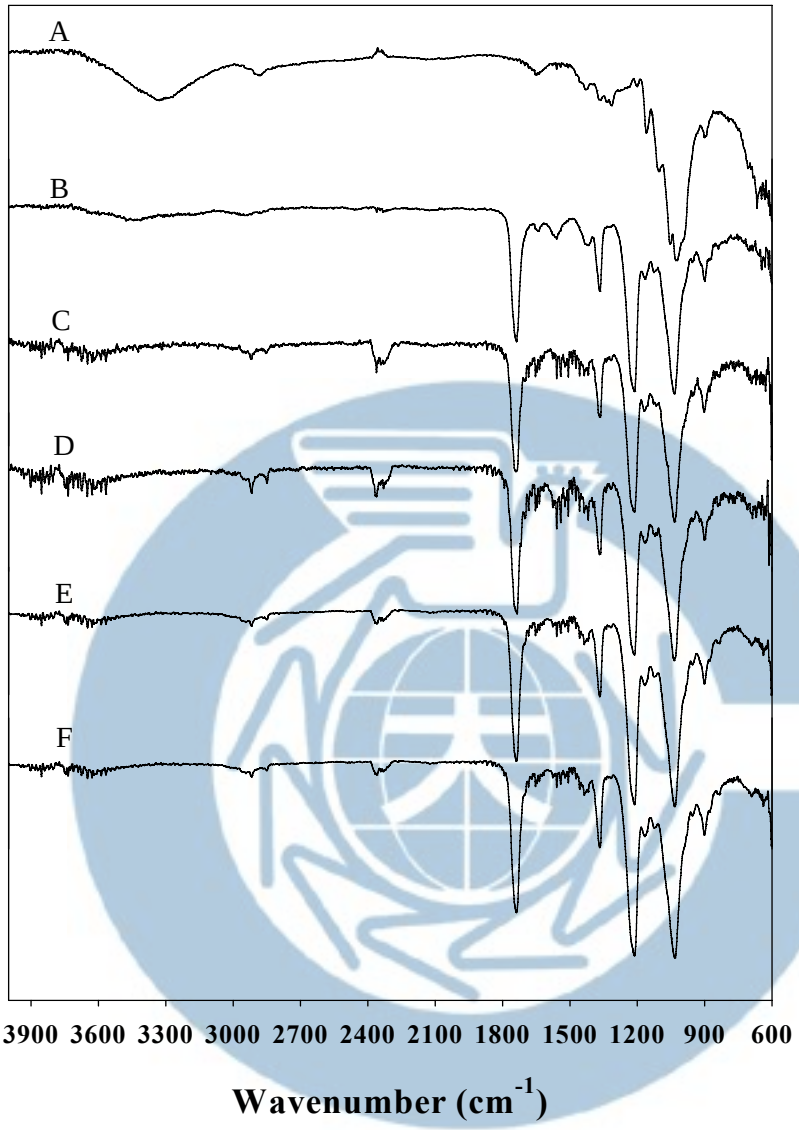


Fig. 12. The FT-IR spectra of CTA; (A) original pulp, (B) cotton linter, (C) V81, (D) V60, (E) Tembest-LV, and (F) TR922.

CTA has two kinds of polymorphs, CTA Ⅰ and CTAⅡ. It depends on the crystal structures of raw materials and the methods of acetylation [38]. Fig. 13 shows the relationship between crystal structures of cellulose and CTA patterns [39]. The two distinct forms, CTA Ⅰ and CTAⅡ, can be obtained by different acetylation processes. CTA Ⅰ is only produced by heterogeneous acetylation with cellulose Ⅰ in which chains are parallel, however, CTAⅡ can be obtained either from heterogeneous acetylation with celluloseⅡ in which chains are antiparallel or from homogeneous acetylation [38-41]. CTA Ⅰ can be also transformed to CTAⅡ with strongly swelling method like mercerization, while CTAⅡ can not be converted back to CTA Ⅰ [42].

In Fig. 14, the XRD patterns of CTA Ⅰ and CTAⅡ are shown [43, 44]. It is easily distinguished with peaks in the 2Θ range of 5 ~ 15°. CTA Ⅰ has only one strong peak around 2Θ = 7°, but CTAⅡ has three peaks between the ranges.

The XRD patterns of CTA prepared from various pulps and cotton linter are shown in Fig. 15. All CTA which has CTA Ⅰ pattern was obtained from cotton linter of cellulose Ⅰ type and pulps of cellulose $Ⅳ_{Ⅰ}$ type under the heterogeneous acetylation. After the reaction, the sharp peaks at 2Θ = 18 and 22.5° of raw material disappeared due to the decrease of crystallinity. The no sharp peaks at 2Θ = 7.5, 17.5, and 22.5° of CTA indicate that crystalline region of raw materials was changed to amorphous region. In other words, this indicates that the space between layers in the crystal facets was increased with the introduction of acetyl group into raw material.

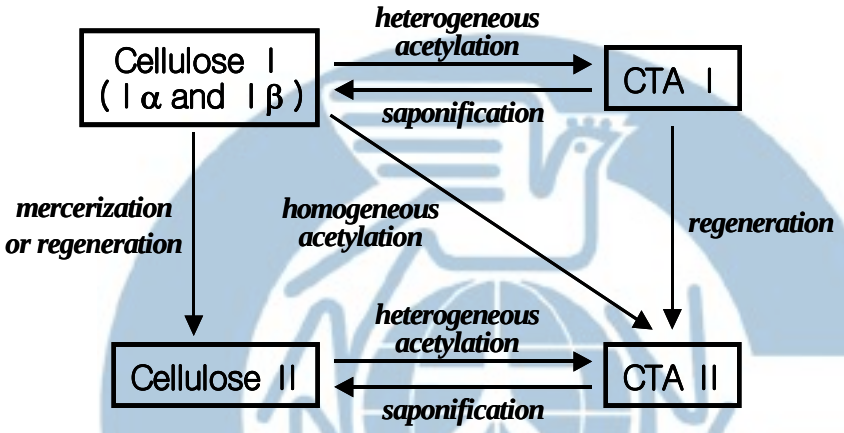


Fig. 13. The relationships between cellulose and CTA polymorphs.

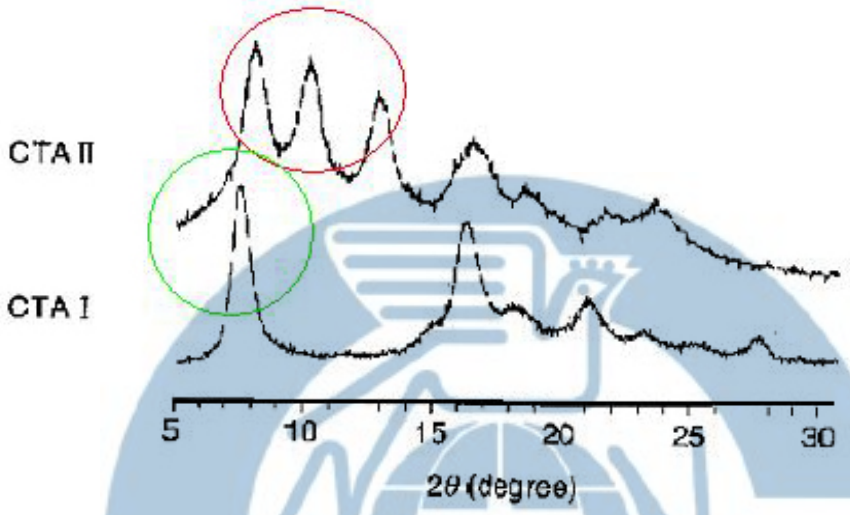


Fig. 14. The x-ray diffractograms of CTA Ⅰ and CTA Ⅱ types.

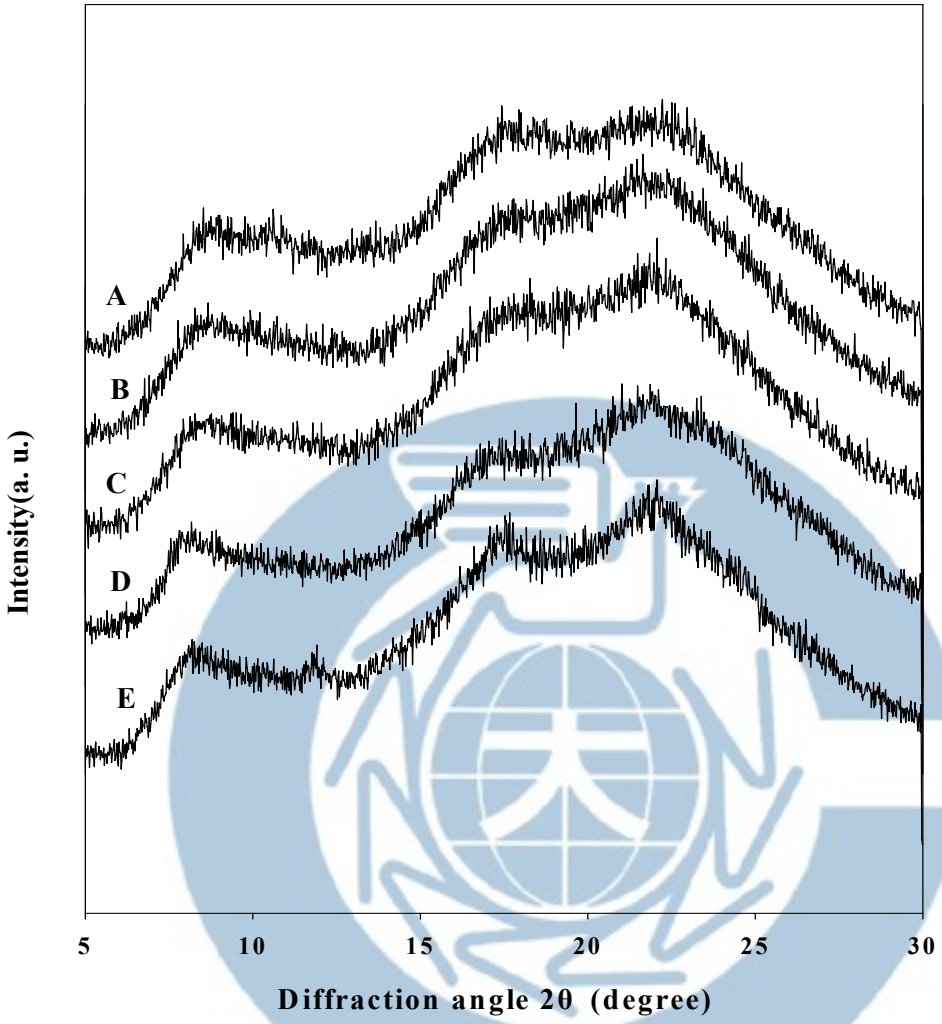


Fig. 15. The x-ray diffractograms of CTA; (A) cotton linter, (B) V81, (C) V60, (D) Tembest-LV, and (E) TR922.

The relationship between ^{1}H-NMR spectrum and CTA structure is shown in Fig. 16 [17, 45]. The six peaks of the protons on the glucose ring appeared in the range of 3.3 ~ 5.2 ppm, and the three peaks of the methyl protons on the acetate group also appeared in the range of 1.7 ~ 2.2 ppm. It plays a very important role in calculating the DS of CTA exactly. The DS can be obtained with the integral values of peaks and the proportional expression below.

3 : DS = 9/16 : [integral value of acetyl H / integral value of total H]

$$DS = \frac{16\times [\text{integral value of acetyl H/integral value of total H}]}{3}$$

The ^{1}H-NMR spectra of CTA prepared from V81 and V60 pulps are shown in Fig. 17. The integral values of proton peaks of CTA are shown in Table 13. The calculated DS with the values support the accuracy of the DS data obtained by titration.

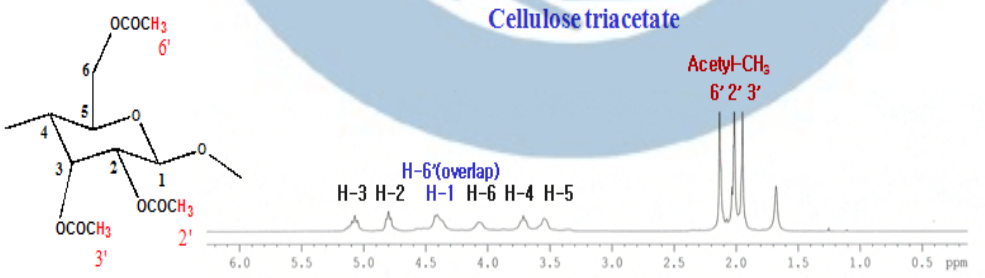
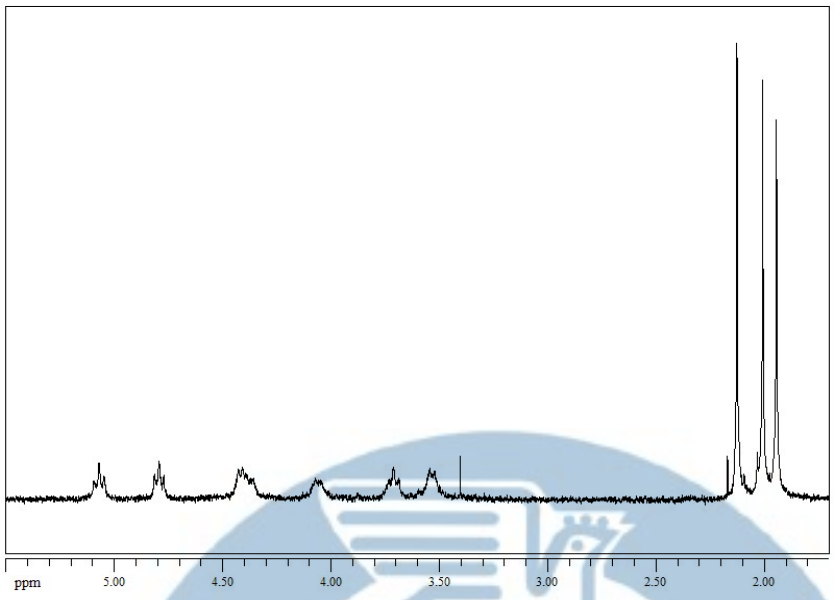
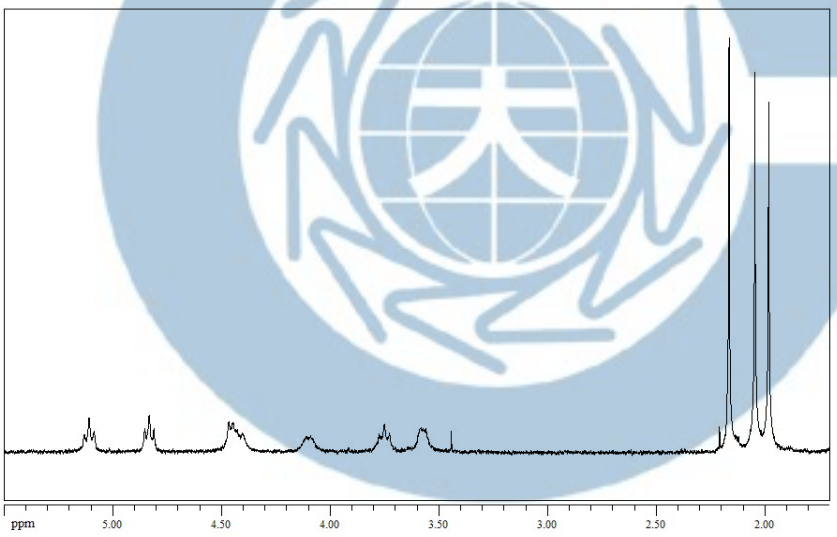


Fig. 16. The general ^{1}H-NMR spectrum of CTA.



(A)



(B)

Fig. 17. The ^{1}H-NMR spectra of CTA; (A) V81, and (B) V60.

Table 13. The integral values of proton peaks of CTA

Peak No.	V81		V60	
	Integrated region (ppm)	Integral value	Integrated region (ppm)	Integral value
1	5.266 ~ 5.057	1.9900	5.250 ~ 5.053	1.2458
2	5.056 ~ 4.623	2.3472	5.053 ~ 4.679	1.3849
3	4.622 ~ 4.252	3.9206	4.606 ~ 4.259	2.5337
4	4.251 ~ 3.928	1.9412	4.258 ~ 3.938	1.3968
5	3.906 ~ 3.678	2.2327	3.901 ~ 3.676	1.4773
6	3.677 ~ 3.395	2.7520	3.676 ~ 3.406	2.0125
7	2.327 ~ 1.774	19.0521	2.312 ~ 1.814	11.6035

4.3 Optical and physical properties of CTA film

The properties of CTA film were optically and physically considered to use as the TIM. It requires the high IR absorption in the range of 1000 ~ 1500 cm^{-1} and the high transmittance in the solar range [46, 47]. Therefore, the four kinds of transparent polymers were used to characterize the optical properties by FT-IR and UV/Vis spectrometers.

The FT-IR spectra and the integral value in the range of 1000 ~ 1500 cm^{-1} of transparent films were shown in Fig. 18 and Table 14 respectively. The integral value between the ranges illustrates the relative mount of IR absorption, and these absorption is mainly related to carbon-oxygen single bonds. The integral value was compensated with the thickness of the films to compare each other. The CTA film has the highest integral value of 72.8. It says that the film can further hold the radiant heat comparing of other films.

Moreover, Fig. 19 shows the UV/Vis spectra of the transparent films. All films has a similar transmittance in the visible ray from 340 to 750 nm. However, the CTA and CDA films have especially the more excellent transmittance in the range from 380 to 400 nm than PC and PMMA films.

The mechanical and thermal properties are also important factors to select the transparent polymer because it should be stood for a long time under the sun light. The S-S curves of four films were shown in Fig. 20. The CTA film have the best tensile strength of 1117.4 kg_f/cm^2 and the PC film have the excellent elongation of 82.3

%. It seems that the PC film can be well stood from external impact more than other films.

The Fig. 21 shows the thermal properties of that films. The curves of CTA, CAD, and PMMA films show similar trends of weight loss between 200 and 400℃. While the loss region of the PC film is from 500 to 600℃. Besides the CTA and CDA films have small weight loss around 100℃ because they contain the water more than the PC and PMMA films. There are no problem to use all transparent films as TIM.

CTA film has not only the excellent optical and physical properties but also some advantages such as economic feasibility and environment-friendliness. Hence, the concern of CTA film will be increased in the many fields of application.

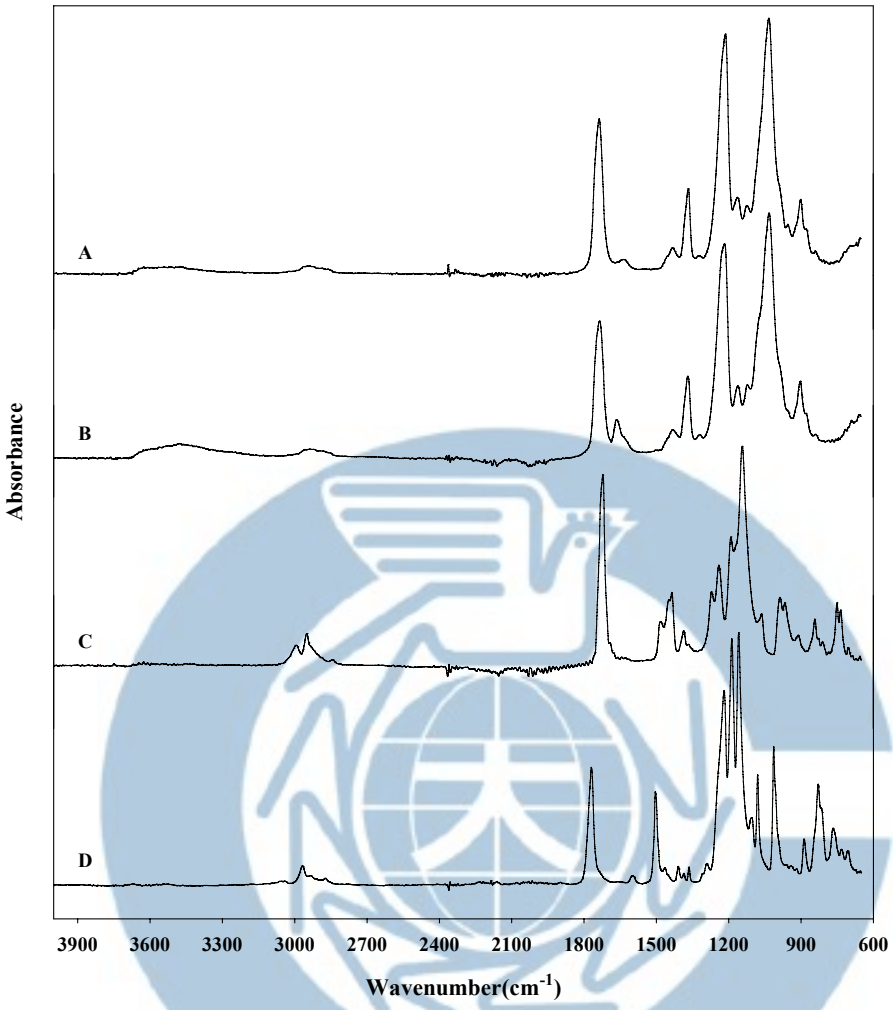


Fig. 18. The FT-IR spectra of various transparent films; (A) CTA, (B) CDA, (C) PMMA, and (D) PC.

Table 14. The integral value of absorbance in the range of 1000 ~ 1500 cm^{-1} of various transparent films

Film No.	Thickness (㎛)	Integral value (1000 ~ 1500 cm^{-1})
CTA	68	72.8
CDA	60	62.3
PC	83	59.2
PMMA	88	41.9

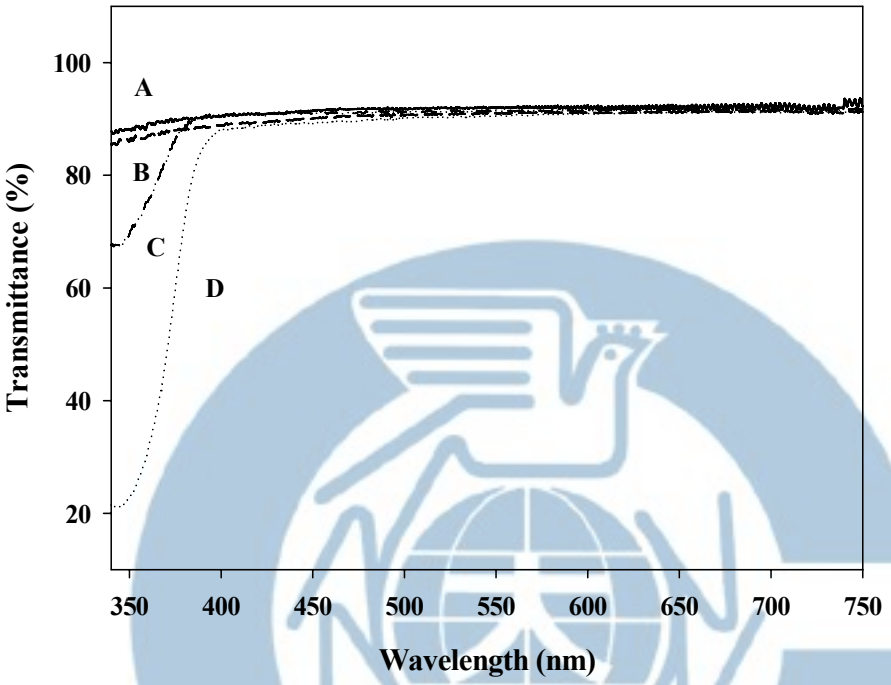


Fig. 19. The UV/Vis spectra of various transparent films; (A) CTA, (B) CDA, (C) PMMA, and (D) PC.

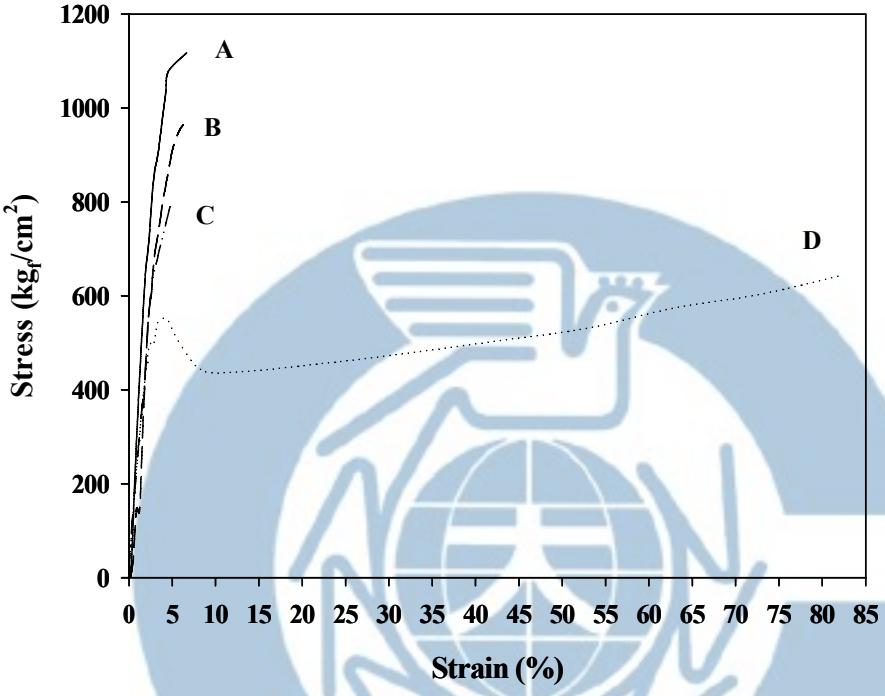


Fig. 20. The S-S curves of various transparent films; (A) CTA, (B) CDA, (C) PMMA, and (D) PC.

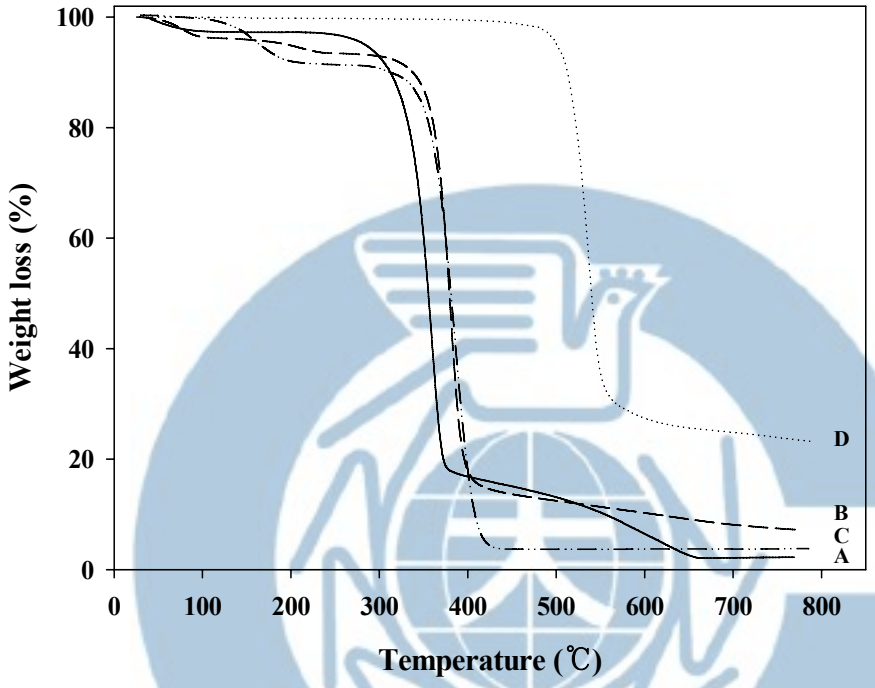


Fig. 21. The TGA curves of various transparent films; (A) CTA, (B) CDA, (C) PMMA, and (D) PC.

Chapter 5. Conclusions

CTA was obtained from pulp under the heterogeneous system, and It was considered that the content of α-cellulose in pulp influenced on acetylation results. Besides, the optical and physical properties of CTA film are as follow.

1. CTA which contains 2.8 of DS and 222 of DP was prepared at 40℃ for 60 min with 1.12 g of perchloric acid and 90 g of acetic anhydride after dispersing the V81 pulp in acetic acid.

2. With the increase of the reaction time, temperature, and amount of catalyst, DS increased, but DP decreased. Moreover, with the increase of amount of acetic anhydride, both DS and DP increased simultaneously.

3. As the content of α-cellulose in pulp increased, the yield of the reaction increased. Even though CTA prepared from Tembest-LV and TR922 have 2.8 of DS above, it contains insoluble residue which was mainly formed due to the formation of glucomannan triacetate and xylan diacetate during the acetylation.

4. After the reaction, the sharp peaks at 2Θ = 18 and 22.5° of pulp disappeared owing to the decrease of its crystallinity. In other words, the space between layers in the crystal facets increased with the introduction of acetyl group into raw material.

5. CTA film has the highest integral value of 72.8 in the range of 1000 ~ 1500 cm^{-1} and especially more excellent transmittance in the range from 380 to 400 nm than PC and PMMA films. It has also the best tensile strength of 1117.4 kg_f/cm^2 and relatively thermal stability.

6. CTA film has not only the excellent optical and physical properties but also some advantages such as economic feasibility and environment-friendliness. Hence, it is possible that alternate the CTA film with expensive PC and PMMA films and the concern of CTA film will be increased in the many fields of application.

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Abstract (국문 요약)

펄프의 종류에 따른 셀룰로오스 아세테이트 합성 및 광학 필름에의 적용 연구

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본 연구의 목적은 α-셀룰로오스 함량이 서로 다른 다양한 펄프로부터 치환도가 2.8, 중합도가 200 이상인 셀룰로오스 트리아세테이트를 합성하기 위한 최적의 아세틸레이션 조건을 얻고 합성된 셀룰로오스 트리아세테이트 필름을 투명단열재에 적용시킬 수 있는 가능성을 검토하는 것이다.

최적의 아세틸레이션 조건을 얻기 위해서 V81 펄프를 사용하여 반응결정요소인 acetic anhydride의 양, 촉매인 perchloric acid의 양, 반응 온도 및 시간에 따라 에스테르화 반응을 실시하였다. Acetic anhydride의 양이 증가함에 따라서 치환도와 중합도는 동시에 증가하는 경향을 나타내었고 촉매 perchloric acid, 반응 온도와 시간이 증가함에 따라서 치환도는 증가하지만 중합도는 감소하는 경향을 나타내었다. 그 결과 1.12 g의 acetic anhydride와 90 g의 perchloric acid를 이용하여 40℃에서 60분 동안 반응시켜 치환도가 2.8이고 중합도가 222인 셀룰로오스 트리아세테이트를 합성하였다.

위의 조건을 사용하여 α-셀룰로오스 함량이 서로 다른 펄프와 카튼린터로부터 셀룰로오스 트리아세테이트를 합성하고 그 특성을 비교해 보았다. 모두 치환도가 2.8 이상이었고, V81과 V60으로부터 합성된 셀룰로오스 트리아세테이트의 DP는 각각 222와 191이었다. 하지만 상대적으로 낮은 α-셀룰로오스 함량을 가지는 Tembest-LV와 TR922로부터 합성된 셀룰로오스

트리아세테이트의 경우, 중합도 측정에 사용되는 DCM:EtOH(8:2) 용매 속에 불용분을 포함하고 있어 DP를 측정할 수 없었다.

1% 셀룰로오스 트리아세테이트 용액의 가시영역에서의 투과도를 보면, α-셀룰로오스 함량이 셀룰로오스 트리아세테이트의 색상과 불용분 함량에 영향을 주는 것으로 나타났고 α-셀룰로오스 함량이 증가함에 따라서 아세틸레이션 수율도 증가하는 경향을 나타내었다. 그리고 적외선 분광분석을 통해 에스테르화반응이 진행되었음을 확인할 수 있었고 X-선 회절장치를 이용하여 합성된 셀룰로오스 트리아세테이트가 CTA I 의 결정구조를 가지는 것을 알 수 있었다.

이 합성된 셀룰로오스 트리아세테이트로부터 투명한 필름을 제조하고 이 필름을 투명 단열재에 적용 가능성을 알아보기 위해 셀룰로오스 다이아세테이트, 폴리카보네이트 그리고 폴리메틸메타아크릴레이트 필름과의 특성을 비교해 보았다. 셀룰로오스 트리아세테이트와 같은 투명 필름을 투명 단열재에 적용하기 위해서는 적외선 영역 1000 ~ 1500 cm^{-1}에서의 흡수능과 가시광선 영역에서의 우수한 투과도가 동시에 요구되고 태양빛에 오랫동안 노출되기 때문에 기계적 열적 특성이 요구된다.

먼저, 적외선 영역에서의 흡수 스펙트럼을 보면 셀룰로오스 트리아세테이트가 72.8로 상대적으로 매우 높은 흡수능을 보였고 가시영역에서도 90% 이상의 우수한 투과도를 나타내었다. 또한, 상대적으로 우수한 기계적 강도와 열적 안정성을 나타내었다. 이와 같이 셀룰로오스 트리아세테이트 필름은 우수한 광학적 기계적 특성뿐만 아니라 경제성과 친환경적인 특성을 가지고 있기 때문에 상대적으로 가격이 비싼 폴리메틸메타아크릴레이트와 폴리카보네이트를 대체 할 수 있을 것으로 판단됩니다.

Acknowledgment (감사의 글)

2005년 겨울 고분자 연구실과의 인연을 시작으로 4년 동안 크고 작은 연구를 수행해 왔습니다. 그 동안의 배움과 노력으로 석사 학위라는 하나의 작은 결실을 맺고자 합니다. 많은 분들의 보살핌과 사랑이 힘이 되었고 스승님의 따뜻한 충고와 가르침이 저를 바른길로 인도해 주었습니다. 받은 것이 너무나 많아서 다 표현 할 수는 없지만 서면을 통해 조금이나마 그 고마움을 전하고자 합니다.

가장 먼저 시골에 홀로 계신 할머니 강량자님께 감사의 말을 전합니다. 철이 없고 민감했던 사춘기 시절의 모든 것을 다 받아 주시고 사랑으로 키워 주셔서 너무 고맙습니다. 그리고 어릴 때 6년과 고등학교 3년 동안 밖에 함께하지 못했지만 언제나 저의 곁에서 믿어주시고 뒷바라지 해 주신 우리 부모님 박종대, 민현숙님 많이 사랑합니다. 대학의 첫 단추를 잘 채우게 도와주고 조언을 아끼지 않았던 큰누나 박미경 양과 매형 김종삼 씨에게도 깊은 감사의 인사를 전합니다. 다시 학교로 돌아온 하나뿐인 형 박상우, 포항에서 딸딸이 엄마, 아빠인 작은 누나 박미진, 작은 매형 이용우씨 모두 모두 사랑합니다.

선생님은 있지만 스승이 없고 학생은 있지만 제자가 없다는 말이 있을 정도로 세월이 변했습니다. 하지만 저에게는 그림자조차 밟을까 조심스럽게 모시는 스승님이 있습니다. 세상을 살아가면서 인간으로서 행해야 할 도리를 먼저 가르치시고 학문적 가치관을 정립시켜 주신 아버지 이 수 교수님 정말 감사합니다. 이 은혜 평생을 함께하면서 조금씩 보답하도록 노력하겠습니다. 그리고 부족한 저에게 용기를 주시고 격려를 아끼지 않으셨던 한종대 교수님, 송주영 교수님, 김종화 교수님, 김병관 교수님, 박근호 교수님 그리고 서용원 교수님께 감사의 인사를 올립니다. 앞으로도 부끄럽지 않은 제자가 되기 위해 꾸준히 노력하는 모습으로 찾아뵙겠습니다.

항상 의지할 수 있는 친구가 있다면 인생을 지혜롭게 살아갈 수 있고 누

구나 친구의 품에서 휴식을 얻고자 합니다. 고분자 연구실에 들어와서 가장 좋았던 것은 앞으로 서로서로 의지하면서 함께 살아갈 수 있는 형님들, 친구들 그리고 동생들을 얻은 것입니다. 처음으로 낚시를 가르쳐주신 진우형, 4년을 동고동락하면서 다투기도 많이 했던 동기 석환이, 어리버리 경용이, 영감 승현이, 핵두 신규, 강작가 나영이, 귀염둥이 지연이, 볼수록 매를 버는 도완이 그리고 마지막으로 어설픈 장기하 혁창이 모두 학위 과정 동안 많이 도와줘서 고맙습니다. 우리는 함께한 시간보다 앞으로 함께 해야 할 시간이 많기 때문에 더욱 소중하고 의미가 있습니다.

이와 같이 사람은 혼자서 살아가는 것이 아닌가봅니다. 저를 도와주고 사랑해주는 사람이 주위에 너무 많은 것 같아 정말 행복합니다. 효빈이 엄마 미선이 누나, 나의 소울메이트 승민이 형, 협박하는 조교샘 희선이, 센스쟁이 정아최, 결과 분석에 많은 도움을 준 공실관 익수형, 바쁜 시간 쪼개서 영어 지도를 해준 전정아, 그리고 이번에 다 함께 졸업하는 상식형, 인욱형, 창훈이 모두 행복하면 좋겠고 오랫동안 서로의 이야기를 나누면서 지냈으면 좋겠습니다.

마지막으로 세상은 넓고 배워야 할 것이 참 많은 것 같습니다. 항상 좋은 말씀으로 저를 감동시켜 주시는 박성호 총장님, 충고와 격려를 아끼시지 않는 정우식 작은아버지와 김재만 국장님, 따뜻한 국밥과 제일 좋아하는 잡채를 챙겨주시는 돼지집 작은 어머니와 이모, 저를 보며 언제나 웃음을 잃지 않으시는 드라시나 이모, 모르는 것은 노트에 적어가면서 이해를 도와주었던 미성폴리머 하홍두 차장님, 과제를 통해 알게 된 대한강관 종윤형 그리고 cotton linter 샘플을 보내 주신 애경화학 정한철 팀장님께 깊은 감사의 인사를 올립니다.

이렇게 따뜻하게 저를 대해 주시고 믿어주셔서 정말 고맙습니다. 가야할 길이 아직 멀지만 더욱 열심히 노력해서 이루고자 하는 꿈을 꼭 이루도록 하겠습니다.

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