



Research Article

THE EFFECTS OF H₂SO₄ CATALYST RATIOS IN PRODUCTION PROCESS ON CELLULOSE ACETATE PROPERTIES

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ABSTRACT

The aim of this study was to determine changes in cellulose acetate properties according to H₂SO₄ catalyst ratios. Cellulose acetate production was carried out at a concentration of 1, 2.5, 5 and 10% H₂SO₄ at 20 °C with traditional acetic acid method. Cellulose acetate samples were investigated FT_IR spectroscopy, x-ray diffraction method and Differential Scanning Calorimeter methods. Free acidity of cellulose acetate was 12.06% for 1% H₂SO₄ catalyst and 10.55% for 10% H₂SO₄ catalyst ratio in process, respectively. Degree of substitution of cellulose acetate was found higher for 10% H₂SO₄ catalyst than those of the other catalyst ratios. The glass-transition temperature (*T_g*) and the decomposition temperature (*T_d*) for 1% H₂SO₄ catalyst in cellulose acetate production were determined 183.5 °C and 329.2 °C, respectively.

Keywords: Cellulose acetate, catalyst, biodegradable polymer, acetic acid.

1. INTRODUCTION

Cellulose is the most abundant organic polymer providing by plants and its other resources but its properties in natural form limits its usage fields. Derivatization of cellulose is one of the most used ways to increase its usage fields by promoting its properties. For this purpose cellulose is reacted with different chemicals including acids, anhydrides or others for producing its ethers and esters or etc.

Cellulose acetate has been used for many applications for about 150 years and it is the most important organic acid ester of cellulose mostly produced from wood. It can be used for production of biodegradable films, membranes, plastic materials, biomedical applications, and raw materials for textile or cigarette filters [1,2]. The amount of acetyl group on main cellulose chain determines its usage fields because it changes its properties directly.

Acetylation of cellulose can be carried out in either homogenous or heterogeneous reaction paths [3]. Heterogeneous acetylation routes are generally preferred because of process economy improvement. The majority of cellulose acetate in industrial scale is produced by heterogeneous route with conventional acetic acid method in which used acetic acid, acetic anhydride

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(esterification reagent) and sulfuric acid (catalysis). In this route, the forming reaction product is solved by acetic acid but cellulose doesn't.

In this paper, the effects of catalysis amount on the properties of cellulose acetate were studied. The chemical characterization and thermal properties of acetylated cellulose were also presented.

2. EXPERIMENTAL

2.1. Raw Materials

Eucalyptus low grade dissolving pulp was provided by Celltech. Other chemicals were purchased from Merck.

2.2. Characterization of Dissolving Pulp

Alpha cellulose content, viscosity, kappa number and alkaline solubility properties of dissolving pulp were determined according to TAPPI standards before starting the activation and acetylation of cellulose.

2.3. Purification of Dissolving Pulp

Dissolving pulp was reacted by %10 of NaOH solution for an hour at 20°C (Cold Caustic Extraction). The mercerized dissolving pulp was washed by fresh water and then the water was removed by filtering equipment with a suction cell. The washing stage was repeated few times until pH value of the filtered water reaching 7.0-8.0. Dissolving pulp was dried until it became air-dried.

2.4. Activation Process

Acetylation of cellulose was carried out in three stages: activation, acetylation and precipitation. Starting with a well-defibrated pulp is necessary for homogenous acetylation. For this purpose, ten grams (10 gr) air-dried pulp was firstly activated by water and then filtered. Secondly, acetic acid was used for activation of pulp. All activation stages occurred under room temperature and constant stirring rate (500 rpm) for ten minute. At the end of every activation stage, the excess solvent (water or acetic acid) was removed by filtering and pressing. The schematic representation of the activation step of cellulose acetate production was given in Figure 1.

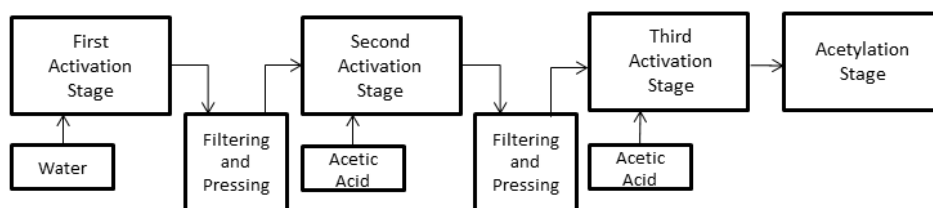


Figure 1. Activation stages of cellulose acetate production

2.5. Acetylation Process

After the completing activation, cellulose was acetylated in a 250 ml sealed beaker with a solution of acetic acid (50 parts), acetic anhydride (6 parts) and sulfuric acid (0.01, 0.025, 0.05 or 0.1 parts). The reaction mixture was gently stirred by a magnetic bar for 3 hours at 20°C.

2.6. Precipitation Process

At the end of the acetylation stage, salty water was used for precipitation of cellulose acetate dissolved in acetic acid – acetic anhydride solution. Salty water was prepared with 5 grams of sodium carbonate added in 5 L tap water. Cellulose acetate dope was poured into the salty water under constant stirring rate (500 rpm) and then precipitated cellulose acetate products were recovered by filtering. The products were washed extensively with water and dried at room temperature without vacuum.

2.7. Analysis of Acetylated Cellulose

2.7.1. Determination of Substitution Degree

Substitution degree of cellulose acetate was determined by Heterogeneous Saponification Method according to ASTM D 871-96. In this method, 0.5 gram cellulose acetate (oven dried) was immersed in 75% ethyl alcohol – water mixture in a sealed 250 ml Erlenmeyer flask and the flask was heated to 50 – 60 °C for 30 minutes in a water bath. At the end of the time, 40 ml of 0.5 N NaOH solution was added into the flask and waited for 15 minutes. After completing waiting time, the flask was removed from the water bath and allowed to stand at room temperature for about 48 or 72 hours depending on acetyl content of cellulose. Afterward, excess NaOH in the flask was titrated with 0.5 HCl solution using phenolphthalein as an indicator and excess about 1 ml of HCl solution was added to the flask. For diffusing NaOH from regenerated cellulose, the flask was stood for overnight at the room temperature. The disappearance of the pink colour indicates the neutralization of the NaOH completed. Calculation of the percentage of combined acetyl or acetic acid was performed by following equation:

$$\text{Acetyl or Acetic acid, \%} = [(D - C) \text{ Na} + (A - B) \text{ Nb}] \times F/W \quad (1)$$

Where;

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

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

Nb: Normality of the NaOH solution,

C: HCl required for titration of the sample, mL,

D: HCl required for titration of the blank, mL,

Na: Normality of the HCl solution,

F: 4.305 for acetyl or 6.005 for acetic acid, and

W: Sample used g.

2.7.2. Determination of Free Acidity Amount

Free acidity amount of cellulose acetate samples were determined according to ASTM D 871-96. In this method 1 gr oven dried cellulose acetate sample was weighed in a sealed beaker and mixed with 30 ml water. The container was allowed to wait for 3 hours and the cellulose acetate suspension was filtered off under vacuum at the end of the waiting period. The filtrate was taken to a vessel and titrated with 0.01N NaOH solution in the presence of phenolphthalein indicator solution.

$$\text{Free Acidity, \%} = [(A - B) \times N \times 0.06 \times 100] / w \quad (2)$$

Where;

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

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

N: Normality of the NaOH solution,

W: Sample used g.

2.7.3. Fourier Transform Infrared Spectroscopy

Synthesized cellulose acetates were grinded in a Wiley mill and prepared for analysing in FTIR Spectroscopy. The test specimens were prepared by the KBr-disk method. FTIR spectra of cellulose acetates were collected on an FTIR ATR spectrophotometer (Perkin Elmer Spectrum 400). In the FT-IR (ATR) analysis, the working range was 4000-500 cm^{-1} with a specified spectral resolution of 4 cm^{-1} .

2.7.4. X-ray diffraction analysis

Dissolving pulp and cellulose acetates were grinded in a Wiley mill and prepared for analysing in XRD. X-ray diffraction analysis was used to investigate the crystallographic nature of dissolving pulp and cellulose acetates by a Rigaku Ultima-IV (Ni-filtered Cu-K α , $k = 0.154$ nm) at 40 kV and 300 mA with a scanning speed of 1° min^{-1} and scanning angle range 5–50. The operating voltage and current were 40 kV and 30 mA, respectively.

2.7.5. Differential Scanning Calorimetry

DSC measurements were performed with a Netzsch Differential Scanning Calorimeter-type 200F3, at a constant N2 flow-rate (30 $\text{ml}\cdot\text{min}^{-1}$), temperature ranging from 20 to 500°C. Heating rate in the DSC was 10°C min^{-1} .

3. RESULTS AND DISCUSSION

Dissolving pulp was characterized according to TAPPI standards mentioned before. Alpha cellulose content, viscosity and kappa number of dissolving pulp were determined as 88.7 %, 478.5 $\text{cm}^3 \text{g}^{-1}$ and 1.0, respectively (Table 1). The pulp with determined properties was categorized as low-grade dissolving pulp. In Table 1, alkaline solubility properties of pulp were also determined and summarized.

Table 1. Properties of dissolving pulp before and after alkaline extraction

	Raw dissolving pulp	After alkaline treatment
Alpha cellulose (%)	88.7	95.7
Viscosity ($\text{cm}^3 \text{g}^{-1}$)	478.5	522.2
Kappa number	1.0	0.97
Alkaline solubility		
R10 (%)	88.5	93.0
S 10 (%)	10.1	4.8
R 18 (%)	92.2	95.4
S 18 (%)	2.9	1.3

The pulps to be used for cellulose acetate production are expected to have low residual amount of residual extractive, hemicellulosic, lignin and free metal ions, a high brightness value

and a homogeneously distributed average degree of polymerisation (viscosity). Dissolving pulps with these characteristics are defined as "acetate-grade" in the industry.

Many researchers tried to improve the quality of pulp from paper-grade to dissolving-grade [4,5,6,7,8,9,10,11,12]. Hot water, enzymes or hot or cold (20 - 40 °C) alkali extraction may be preferred to reduce the amount of residual hemicellulose present in the dissolving pulps [12,13,14,15]. Selectively extraction of hemicellulose from pulp, one of the most preferred way is cold caustic extraction (CCE) [16].

To obtain a high purity cellulose acetate product, the dissolving pulp does not include any impurities, especially hemicelluloses, so; in this study, dissolving pulp was reacted by %10 of NaOH solution for an hour at 20°C. With this one stage-alkaline extraction treatment, the alpha cellulose content of dissolving pulp was promoted from 88.7% to 95.7.

Ibarra et al., 2009 used monocomponent endoglucanase and xylanase enzymes and alkaline treatment for upgrading paper-grade pulps to dissolving pulps in their studies. 9% NaOH, 1 h at room temperature, and 4% consistency was the operation condition in the alkaline treatment. Glucose amounts in eucalypt kraft pulp and sisal soda/AQ pulp were increased from 81.7% to 95.6 and from 81.0% to 94.1, respectively [7].

9% NaOH, room temperature, 1 h and 4% pulp consistency conditions were selected to converting birch, eucalyptus and sisal pulps into dissolving pulps by Koepcke et al. 2010. Glucose amount in birch, eucalyptus and sisal pulps were 73.4%, 78.8 and 81.0, respectively. After alkaline extraction, glucose amounts were determined as 93.0%, 95.9 and 94.1, respectively [5,17].

It has been found that the increase in the amount of catalyst promoted the degree of substitution of cellulose acetate. Degree of substitution of cellulose acetate was found higher for 0.100 part H₂SO₄ catalyst than for the other catalyst amounts. Figure 2 shows the effects of catalyse amounts on substitution degree of cellulose acetate.

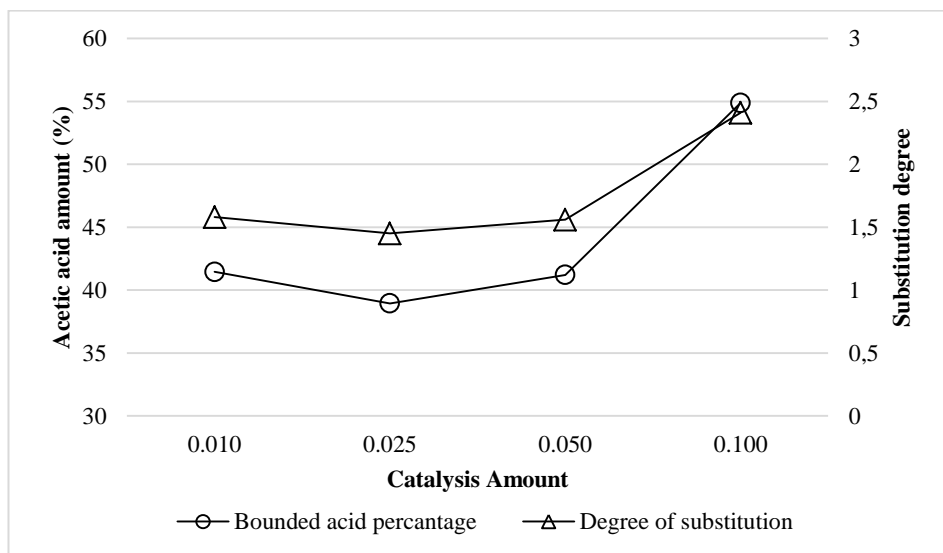


Figure 2. Effects of catalyse amounts on substitution degree of cellulose acetate.

Barkalow et al. (1989), acetylated mechanical wood pulp by acetic acid method in sulfuric acid catalyzed (1.5%, 3.0 and 6.0%). When the amount of catalyst was increased from 1.5% to 6%, the content of bound acetic acid increased from 53.15 to 62.00 [18].

Zhang et al. (2013) studied on acetylation of rice straw (RS) with acetic anhydride catalysed by sulfuric acid and reported that the reaction time was shortened and cellulose acetates with a higher DS was synthesized as the amount of catalyst used increased [19].

Cellulose acetate samples were investigated with FTIR spectroscopy. FTIR spectra of cellulose acetate samples are shown in Figure 3. The ester carbonyl absorption peak at 1734 cm^{-1} verified ester bound. Figure 4 demonstrates that cellulose dissolved during acetylation reactions.

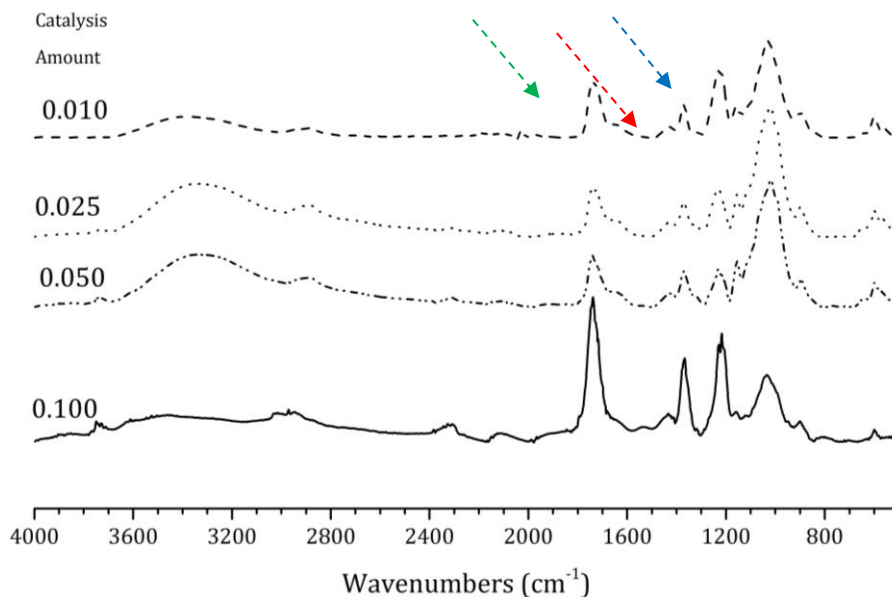


Figure 3. FTIR spectra of cellulose acetates



Figure 4. a. Cellulose in the beginning of acetylation reactions and b. clear acetylation system after completed acetylation reactions.

Free acid amount was enhanced from 12.06 % to 15.63% when the catalyst amount increased. But the further increase of catalyst amount did not help increase free acidity; instead, it diminished free acidity significantly (to 10.55). Changes in free acidity (%) was shown in Figure 5.

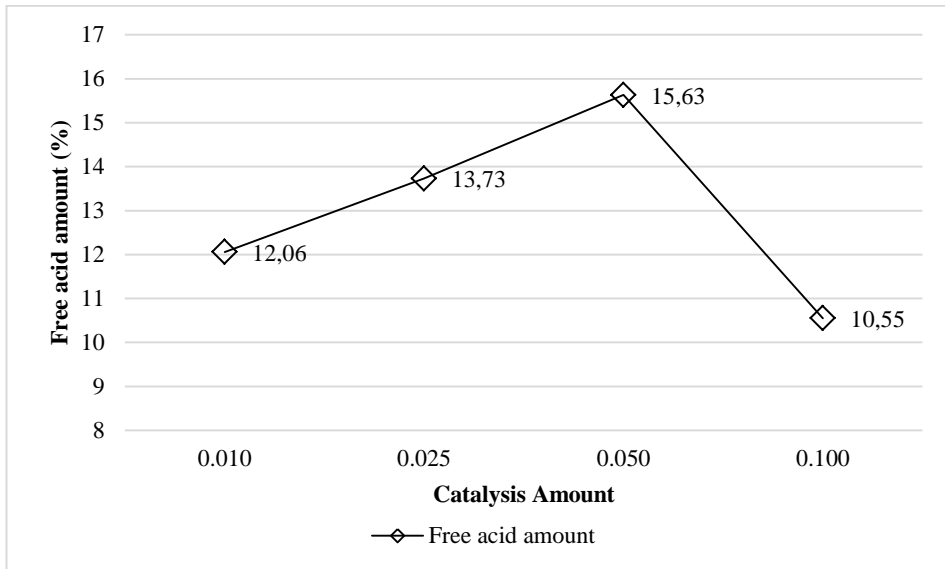


Figure 5. Changing in free acid amount of cellulose acetates sample with catalysis amount

Figure 6 shows X-ray diffraction patterns of cellulose acetate samples and dissolving pulps. When the x-ray diagrams of cellulose acetate samples obtained at 20 ° C by acetic acid method were examined, (101), (10-1) and (002) plane reflections decreased with respect to dissolving pulp used in the production of cellulose acetate.

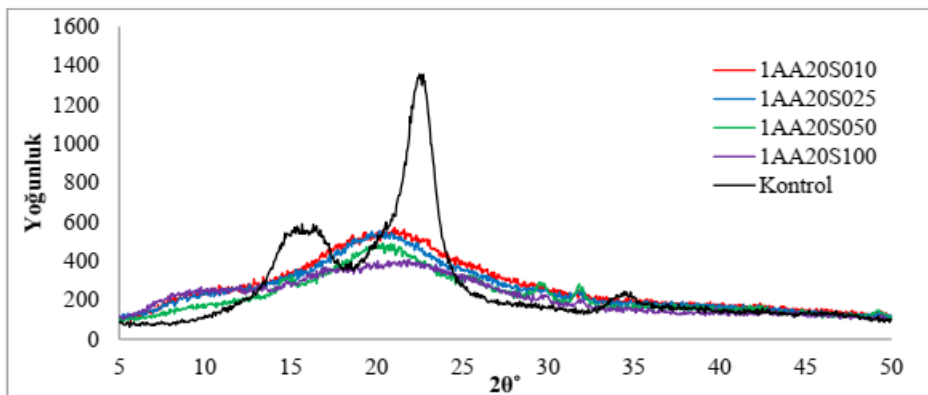


Figure 6. X-ray diffraction patterns of cellulose acetate samples and dissolving pulp (a: 0,010 part catalyst, b: 0,025 part catalyst, c: 0,050 part catalyst, d: 0,100 part catalyst and Kontrol: alkali extracted dissolving pulp).

Figure 7 shows the effect of varying the amount of catalyst on the thermal properties. An endothermic change was observed in the range of 50 - 150°C which means evaporation of water in particles. This was followed by, the first conversion of a polymer in the amorphous structure, glass transition behaviour. The glass-transition temperature (T_g) and the decomposition

temperature (Td) for 0.010 part H₂SO₄ catalyst in cellulose acetate production were determined 183.5 °C and 329.2 °C, respectively. It was observed that increasing the amount of catalyst reduced the glass transition temperature of cellulose acetate first, while it was not effected crucially when the highest amount was reached.

Kamide and Saito (1985) studied the effects of the total substitution degree (SD) and the average molecular weight on glass transition (T_g), melting point (T_m) and thermal degradation (Td) values for cellulose acetate samples with different substitution degrees and different molecular weight distributions. They found that the increase in the substitution degree reduced the glass transition temperature of cellulose acetate [20].

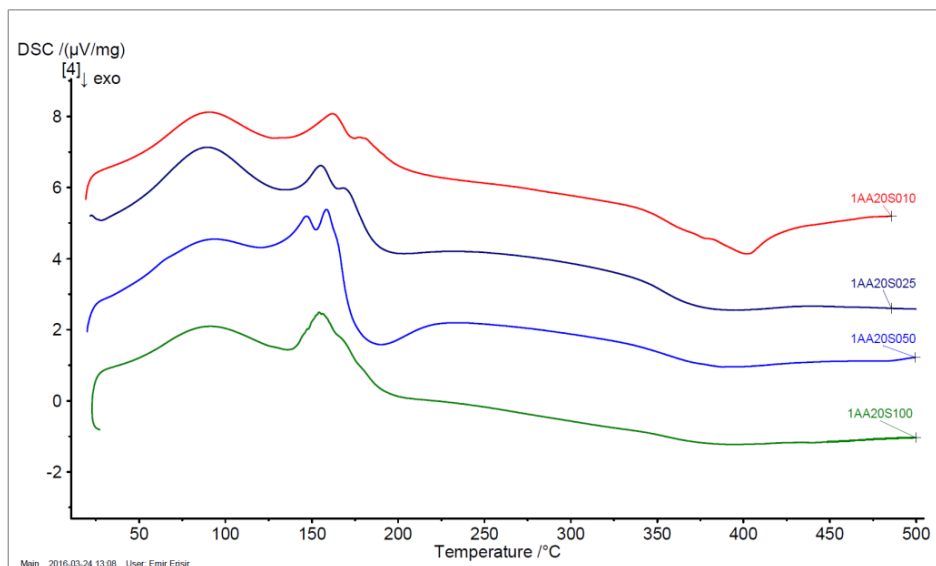


Figure 7. DSC curves of cellulose acetate

4. CONCLUSION

Cellulose acetate was prepared from low grade dissolving pulp purified by cold caustic extraction with conventional acetic acid method using different amounts of sulfuric acid as catalyst in glacial acetic acid at room temperature. XRD and FTIR results showed acetylation reactions were completed successfully. Amount of catalyst affected substitution degree, thermal properties and free acid amount of cellulose acetate.

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