Synthesis and Characterization of Succinic Acid Modified Cellulose

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LIST OF ABBREVIATIONS

^{1}H NMR: Hydrogen Nuclear Magnetic Resonance

^{13}C NMR: Carbon 13 Nuclear Magnetic Resonance

Brij 35: Polyoxyethylene Lauryl Ether

CHN: Carbon, Hydrogen and Nitrogen elemental

CTAB: Cetyl Trimethyl Ammonium Bromide

DMAP: 4-Dimethylaminopyridine

FTIR: Fourier Transform Infra-Red

HPAEC-PAD: High Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection

HPSEC: High Performance Size-Chromatography

HCl: Hydrochloric Acid

KBr: Potassium Bromide

NaOH: Sodium Hydroxide

RI: Refractive Index detection

SEM: Scanning Electron Microscopy

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Synthesis and characterization of succinic acid modified cellulose

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ABSTRACT

Cellulose is an organic component in plant cell which is insoluble in water. In this study, synthesis and modification of cellulose were carried out by dissolved it in aqueous solution. So far, some of the technology has been developed for dissolution of cellulose. There are many of the aqueous solvent can be used to dissolve cellulose before it modified by other functional group. Firstly, facial cottons were undergoes pretreatment process by ultrasonication and maceration to enhance their dissolution in NaOH/thiourea/urea (NTU) solvent system. The cellulose solutions prepared were then gone through modification process. Then, succinic acid was used to modify the cellulose in aqueous solution through esterification reaction by adding sodium hydroxide, NaOH as catalyst. Modification of succinic acid is important to produce water soluble succinic acid modified cellulose and effects of modification process in various synthesis conditions were investigated. Subsequently, nanoprecipitation technique was applied to precipitate succinic acid modified cellulose. Physical and chemical properties of succinic acid modified cellulose were identified and characterized. The functional group of native cellulose and succinic acid modified cellulose were determined by Fourier Transformed Infra-Red Spectroscopy (FTIR). Finally, Scanning Electron Microscopy (SEM) was used to examine the morphology of the native cellulose and succinic acid modified cellulose.

Keywords: cellulose, dissolution, modification, effect, morphology.

ABSTRAK

Selulosa merupakan salah satu komponen organik dalam sel tumbuhan yang didapati tidak larut dalam air. Dalam kajian ini, sintesis dan modifikasi selulosa dijalankan melalui pelarutan dalam larutan akues. Setakat ini, beberapa teknologi telah dibangunkan bagi pemelarutan selulosa. Terdapat banyak jenis akues pelarut yang boleh digunakan untuk melarutkan selulosa sebelumnya dimodifikasi oleh kumpulan berfungsi yang lain. Yang pertamanya, kapas muka mengalami proses prarawatan dengan ultrasonikasi dan maserasi untuk meningkatkan kecekapan pemelarutan dalam NaOH/thiourea/urea (NTU) sistem larutan. Larutan selulosa yang disediakan melalui proses modifikasi. Kemudian, asid suksinik digunakan untuk modifikasi selulosa akues larutan melalui tindak balas pengesteran dengan menambahkan NaOH sebagai pemangkin. Modifikasi bagi asid suksinik amat penting untuk menghasilkan asid suksinik modifikasi selulosa yang berlarut dalam air dan kesan bagi proses modifikasi dalam pelbagai sintesis kondisi telah dikaji. Selain itu, teknik nanopengendapan telah digunakan untuk pemendakkan asid suksinik memodifikasi selulosa. Sifat-sifat fizikal dan kimia bagi asid suksinik modifikasi selulosa telah dikenal pasti dan menandai. Kumpulan berfungsi bagi selulosa asli dan asid suksinik modifikasi selulosa telah dikaji oleh spektroskopi Fourier-Transform Infar-red (FTIR). Akhirnya, mikroskop imbasan elektron (SEM) telah digunakan untuk mengkaji morfologi bagi selulosa asli dan asid suksinik modifikasi selulosa.

Kata kunci: selulosa, pemelarutan, modifikasi, kesan, morfologi.

CHAPTER ONE

INTRODUCTION

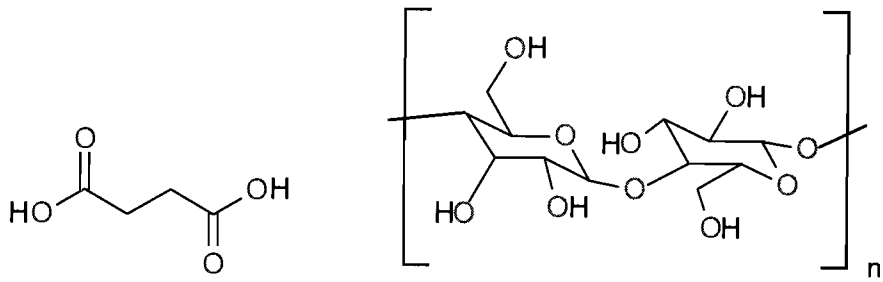
Cellulose is a very stable component in plant due to its formation of intra- and inter- molecular hydrogen bonding. It is insoluble and has a higher thermal stability. The properties of cellulose had been identified by various types of technique. In general, cellulose formed white powder with density about 1.5 g/cm^3. When the temperature reach melting point, it was decomposed and the general molecular formula is $(C_6H_{10}O_6)_n$ (Liu, *et al.,* 2006) with 20 to 30 repeating units. Each of the cellulose has two hydroxyl groups, one is known as reducing end and one is non-reducing end (Ying, 2008).

Succinic acid is a diprotic acid which also known as butanedioic acid (Silberberg, 2009). Normally, it can be found in plant and animal tissues. In human body, it plays an important role in Krebs cycle as an intermediary metabolism. Physical properties of succinic acid includes colorless crystalline solid, soluble in water, slightly dissolved in ethanol, acetone, ether and glycerine. It is insoluble in benzene, carbon tetrachloride, oil ether and so on (Leon *et al.,* 1990). Basically, succinic acid is applied in agriculture, food products, drug and other industrial uses. For example, it acts as flavoring agent for food and beverages, producing some of the heterocyclic compounds such as photographic chemicals, perfumes, intermediate for dyes and plasticizer. It also used in medication as cancer-curing, contraception, and medicines of sedative (Liu *et al.,* 2006).

Then, cellulose was extracted from its lignocelluloses materials, facial cotton, tissue papers or fabric materials. Facial cottons were used as cellulose material and dissolution of facial cotton by using NaOH/thiourea/urea (NTU) solvent system were recently reported by Jin, *et al.* (2007). Modification of cellulose was applied by using various types of chemical reaction. Before modified cellulose, it dissolves by derivatives solvent or non-derivatives solvent. Cellulose can only be soluble in water when it functionalized by other functional group such as dicarboxylic acid. So, succinic acid had been chose for cellulose modification by catalyze it with sodium hydroxide.

Succinic acid has been used to modify cellulose in order to produce a high viscosity aqueous solution (Ambler, 2007). According to the research, a derivative of water soluble cellulose ether had been produced by using succinic acid anhydride. The reaction conditions used were under neutral or acidic condition (Ambler, 2007). The water soluble cellulose ether applied as protective colloids or emulsifiers in suspension polymerization. On the other hand, modifications of succinic acid in produce water soluble cellulose have not been done under basic condition.

The main objective in this study is to prepare water soluble succinic acid modified cellulose. In order to modify cellulose, starting material used was cotton made fabric, facial cotton, cotton wool and paper due to the high contents of cellulose. Before modification, cellulose was dissolved in NaOH/thiourea/urea (NTU) solvent system. After modification, physical and chemical characteristics of succinic acid modified cellulose were characterized by Fourier Transform Infra-Red spectroscopy (FTIR), and Scanning Electron Microscopy (SEM).



Succinic Acid

Cellulose

Figure 1: Molecular structure of succinic acid and cellulose

CHAPTER TWO

LITERATURE REVIEW

Cellulose is a carbohydrate stored in plant cell which is formed by many repeating units of ß (1→4) D-glucose (Nishiyama *et al.*, 2002). It is the most abundant renewable resource in the world. Cellulose is a principle structural of cell wall component in major plants. It characteristics are renewable, non toxic, modifiable, biodegradable and have high potential in excellent industrial material (Liu *et al.*, 2006). There are two types of cellulose which includes modified and unmodified cellulose. Generally, unmodified cellulose is insoluble in water and organic solvents. These properties are based on strong hydrogen bonding between straight chain cellulose molecules. So, solubility of native cellulose can be improved by modified derivatization (Edgar *et al.*, 2001).

There are several ways to modify cellulose and dissolution of cellulose. One of the techniques used for dissolution of cellulose was using NaOH/thiourea/urea (NTU) solvent system. This was the most common way to prepare dissolved cellulose by breaking down strong hydrogen bonding among crystalline cellulose. The advantages of using this solvent system many due to the high efficiency in dissolve cellulose and prepare a more stable spinning solution (Jin and Gu, 2005). Furthermore, NTU solvent system can be easily establish inexpensive and less toxic compare with other dissolution techniques. The optimum dissolution of cellulose in NTU solvent system was by ratio 8:6.5:8. Based on previous studies, heterogeneous reaction is much more difficult to carry out compare to homogenous condition. The main purpose in dissolve of cellulose before modification was to homogenous the cellulose with succinic acid.

Then, dissolution of cellulose with ionic liquids and its application had been done by Zhu (2006). According to Zhu (2006), ionic liquids which are environmental friendly solvent and bio-renewable feed-stocks had been used to determine the application and characterization. Therefore, cellulose extraction methods need to develop as green cellulose methods. This method made full used of cellulose resource and reduced energy and environmental problem. Researchers had proved that the dissolution of cellulose using ionic liquids is a new platform for 'green' cellulose utilization. Besides that, some of the above mentioned cellulose derivatives and it composites have good potential in industrial applications.

Moreover, modification of micro fibrillated cellulose through chemical surface modifications (Stenstad *et al.*, 2007). In that modification various organic and aqueous solvents such as succinic anhydride, glycidyl methacrylate and nitric acid had been used. Succinic acid had been chose to modify cellulose because it will functionalize the hydroxyl group in cellulose. The advantage of using succinic acid is because of the ability to complete recycling the hydrolysis acid in either Purdue or Arkenol approaches (Farone *et al.*, 1998).

Besides that, homogeneous modification of sugarcane bagasse cellulose with succinic anhydride was carried out using ionic liquid in which the ionic liquid will act as reaction medium (Liu *et al.*, 2006). This chemical modification involved temperature control, molar ratio of succinic acid anhydride or anhydroglucose units in cellulose and reaction time. Then, cellulose modification reaction can catalyze by acid or basic condition. For example 4-dimethylaminopyridine (DMAP), supercritical carbon dioxide (CO_2), glacial acetic acid, N,N- carbonyldiimidazole, and sodium hydroxide (Yoshimura *et al.*, 2004; Gaelle *et al.*, 2002; Yin *et al.*, 2006; Sabrine *et al.*, 2009; Sang *et al.*, 2004).

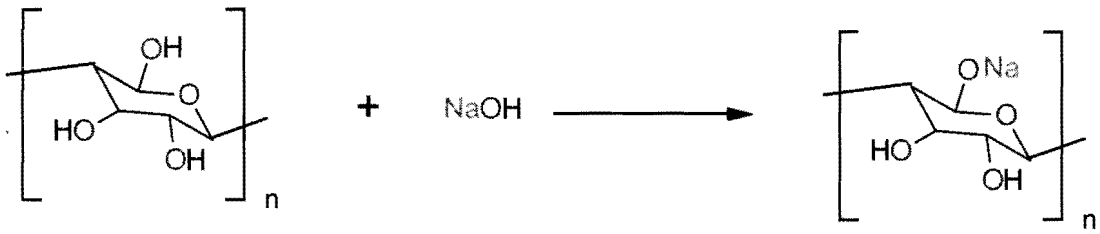


Figure 2: Schematic reaction of cellulose with sodium hydroxide (NaOH)

Nowadays, China have corporation for Institute of Process Engineering with China Academic and Sciences to produce an anti-bacterial fibers using cellulose composite technology. This process clearly takes place in the near future and brings a lot of benefits to human (Wang *et al.*, 2007). In previous study, cellulose can modify by succinic anhydride (SA) to produce novel biodegradable cellulose hydro gels in the presence of 4-dimethylaminopyridine (DMAP) in esterification process (Yoshimura *et al.*, 2004). This gelation is observed during the esterification process, and cellulose hydro gels obtain should not be cross linking. This mean the hydroxyl group of cellulose is partially form diester with SA.

Hydrolysis of sulfuric acid had been done by introduced sulfate groups to nanocrystal surfaces permitting their dispersion in aqueous as well as organic media, including ethanol and N,N-dimethylformamide, in a matter of seconds (Liu *et al.*, 2009). Then, some of the characterization techniques had been used to investigate the result of modification cellulose such as Fourier Transform Infra-Red spectroscopy (FTIR) and Carbon Nuclear Magnetic Resonance spectroscopy (^{13}C NMR). The chemical modification will cause the decreasing of succinylated cellulose (Liu *et al.*, 2009).

Recently, enzymatic treatment was widely used because of the modification is safer and healthier for humans and the environment than other modification methods. Then the advantages of enzymatic treatment are more specific reactions, higher yield, fewer by-products, and less purification requirement. Then, the method use are High Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection HPAEC-PAD, High Performance Size-Chromatography HPSEC with multi angle laser light scattering (MALLS) and Refractive Index RI detection (Hanashiro *et al.,* 1996).

Then, determination of the degree of esterification of cellulose was characterized by Scanning Electron Microscopy SEM, and Fourier Transform Infra-Red spectroscopy (FTIR) (Chatjigakis *et al.,* 1998). Succinic and maleic acid groups could be introduced directly onto the microfibrillated cellulose (MFC) surface as a monolayer by a reaction. Based on previous studies, degree of esterification can be applied by back titration of modified cellulose (Sindhu *et al.,* 2007).

Succinic acid is choosing to modify cellulose and produce cellulose hydro gels. This cellulose hydro gel can be applied in various purposes, such as drug delivery because it is high stability, non-toxic, safe and biodegradable. Cellulose hydro gels can be added on cross linker to produce other compounds such as nanoparticles. These properties bring to environmental friendly and cross linking nanoparticles had been proved that was efficient carrier for therapeutic agents (Xu *et al.*, 2003).

Modification of cellulose treated with sodium hydroxide was chemically analyzed by FTIR (Sang *et al.,* 2004). This instrument used to detect functional group present during modification. There are several factors affecting the solubility of cellulose samples such as reaction temperature, pH medium, time and better dissolution state. Then, medium applied

mostly in acidic condition compare to basic condition. But, study of Sang (2004) treated cellulose using sodium hydroxide to analyze treated cellulose by FTIR.

Succinic acid modified cellulose was produced water soluble cellulose by controlling the molar ratio, temperature, duration, and stirring rate. That water soluble cellulose was produced by varies stirring rate, different condition and characterization of modified cellulose was investigated. The succinic acid modified cellulose can be characterized by using Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red spectroscopy (FTIR). Degree of substitution and solubility test were carried out to distinguish the physical characteristics of succinic acid modified cellulose. Lastly, majority of the study for cellulose had been done in other country such as United State, China, Korea or Japan.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The cellulosic sample used was facial cotton, 50 mm × 60 mm size of each pad which is manufactured by Carefeel Cotton Industries (M) Sdn Bhd. The samples were grinded into smaller particles. Chemicals used were including succinic acid, NaOH, absolute ethanol, hydrochloric acid, urea, and thiourea. These chemicals were purchased from Modern Scientific Sdn. Bhd and Robert Scientific Company Sdn. Bhd.

3.2 Methods

3.2.1 Sample Preparation and Pretreatment

Cellulosic sample such as facial cotton were cut and grinded into powdery form for used. These facial cottons were pretreated by ultrasonication and maceration process. The facial cotton was macerated by using sodium hydroxide solution, (NaOH) 12% w/w for 2 hours. This step was allowing chemical molecules to penetrate through cellulose. Then, 1M of hydrochloric acid, HCl was added and the mixture was soaked for 1hours and 30 minutes, follow by 2% w/w NaOH for 2 hours to remove all the unwanted compounds (Wang *et al.*, 2007). Then, the mixture was sonicated for 15 minutes (Daisuke *et al.*, 2000). Lastly, facial cotton was filtered and rinsed with ultra-pure water and acetone. The pretreated facial cotton was dried in oven at 60 ^{0}C for 24 hours before use.

3.2.2 Dissolution of Pretreated Facial Cotton

Cellulose solution was prepared by dissolution of facial cotton in solvent system. This dissolution was needed for preparing a homogeneous condition to carry out the modification of cellulose with succinic acid. The dissolution of pretreated facial cotton was done by using the aqueous-based solvent system which was NaOH (8% w/w)/thiourea (6.5% w/w)/urea (8% w/w) in ratio (Jin *et al.,* 2007). The solvent was prepared by dissolved NaOH/Urea/Thiourea in ultra-pure water by sonication for 15 minutes. Then, 0.5g of pretreated facial cotton was added into NTU solution. The solution was stirred and mixed well and cooled to -20^{0}C in freezer overnight. Then, the frozen mass was allowed to thaw at room temperature (Ying, 2008). The clear solution formed was cellulose solution without any solid fragments were presence. This solution was stored for modification with succinic acid.

3.2.3 Synthesis of Succinic Acid Modified Cellulose

3.2.3.1 Modification of Cellulose with Succinic Acid

Cellulose solution was modified by succinic acid through esterification reaction in produced water soluble succinic acid modified cellulose. In this reaction, 20 ml of cellulose solution modified with various concentrations of 10 ml of succinic acid by catalyzed with 10 ml of 2M sodium hydroxide, NaOH solution. Cellulose solution which is 20 ml was stirred by adding of 10 ml NaOH for 20 minutes at 80^{o}C in water bath. After the solution form gelatinizes then 10 ml of succinic acid was added for modification by stirred for 6 hours at 80^{o}C in water bath. Then, gelatinizes was kept for further precipitation in produce succinic acid modified cellulose precipitate.

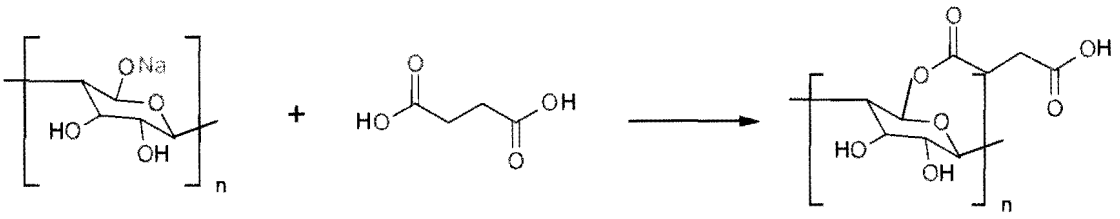


Figure 3: Schematic of succinic acid modified cellulose

3.2.3.2 Effect of Cellulose Modification in Various Conditions

The quantity of pretreated facial cotton to dissolve in NTU solvent system was adjusted proportionately with 0.5g, 0.1g, 0.05g and 0.01g. Then, modifications of cellulose were carried out by each quantity of cellulose in different molar ratio of cellulose with succinic acid by constant other variable such as synthesis duration, stirring rate, temperature and concentration of sodium hydroxide. After that, each of the molar ratios in modification was proceeding to different synthesis duration such as 6 hours, 8 hours, 10 hours and 12 hours. The same procedures were applied for all differences amount of cellulose dissolved in NTU solvent system.

3.2.3.3 Precipitation of Succinic Acid Modified Cellulose

Succinic acid modified cellulose was undergoes nanoprecipitation techniques. Gelatinizes of modified cellulose was added drop by drop into beaker containing absolute ethanol. Then, excess absolute ethanol was added into the beaker drop by drop to precipitate in forming succinic acid modified cellulose precipitate. Then, the solution was centrifuged at 10°C for 15 minutes in 4000 rpm (Zhang *et al.*, 2009). Then, the precipitate was added with ethanol and centrifuged to remove the impurity and unmodified cellulose. This step was repeated for 3 times for purify the precipitate. Finally, the precipitate was dried in oven at 60°C and kept in desiccators.

3.3 Characterization Parameters

3.3.1 Fourier Transform Infra-Red spectroscopy FTIR

FTIR was used to identify the functional group of the samples. The sample of modify cellulose were dried for 5 hours at 100 ^{0}C before analyses (Simoncic *et al.*, 2007). Approximately of 2 mg of sample was mixed with 200 mg of Potassium Bromide KBr. Then, it is pressed under high pressure to form a thick 1-2 mm of a small pellet. The pellet will run through IR radiation and the spectra will be shown through the graph (Sang *et al.*, 2005).

3.3.2 Determination of Degree Substitution

The degree of substitution in cellulose modified succinic acid was determined by titration. The method used was adjusted from Sindhu (2007) and the weight of succinic acid modified cellulose was measured to 0.1g. After that, the sample was dissolved in 5ml of 0.5N sodium hydroxide NaOH and stirred for 30 minutes. Then, excess NaOH was neutralized through back titration method with 0.5N hydrochloric acid HCl. Phenolphthalein was used as indicator to determine the degree of substitution. Degree substitution was calculated by using:

Percentage of succinic modified cellulose (%),

$$\frac{(\text{volume of blank} - \text{volume of sample}) \times \text{normality of acid} \times \text{MW of succinic acid} \times 100}{\text{Sample weight in grams (dry basis)}}$$

Degree of substitution (DS),

$$\frac{\text{Molecular Weight (MW) of cellulose unit} \times \text{percentage of succinic modified cellulose}}{\text{MW of succinic acid} \times 1000 - (\text{MW of succinic acid} - 1) \times \% \text{ of succinic modified cellulose}}$$

3.3.3 Dissolution of Succinic Acid Modified Cellulose

The succinic acid modified cellulose was dissolved in ultra-pure water when the modification of cellulose was done in well. Succinic acid is known as diprotic acid and one side of carboxylic acid was reacted with hydroxyl group of cellulose through esterification. Then, another side of carboxylic group was ionized and dissolved in ultra pure water. The succinic acid modified cellulose precipitate was added with equal volume of ultra-pure water in same mass and the solution was stirred at room temperature. The solubility of succinic acid modified cellulose was determined by the residual mass after centrifugation. These dissolution steps were repeated by different concentration of succinic acid in modifying cellulose.

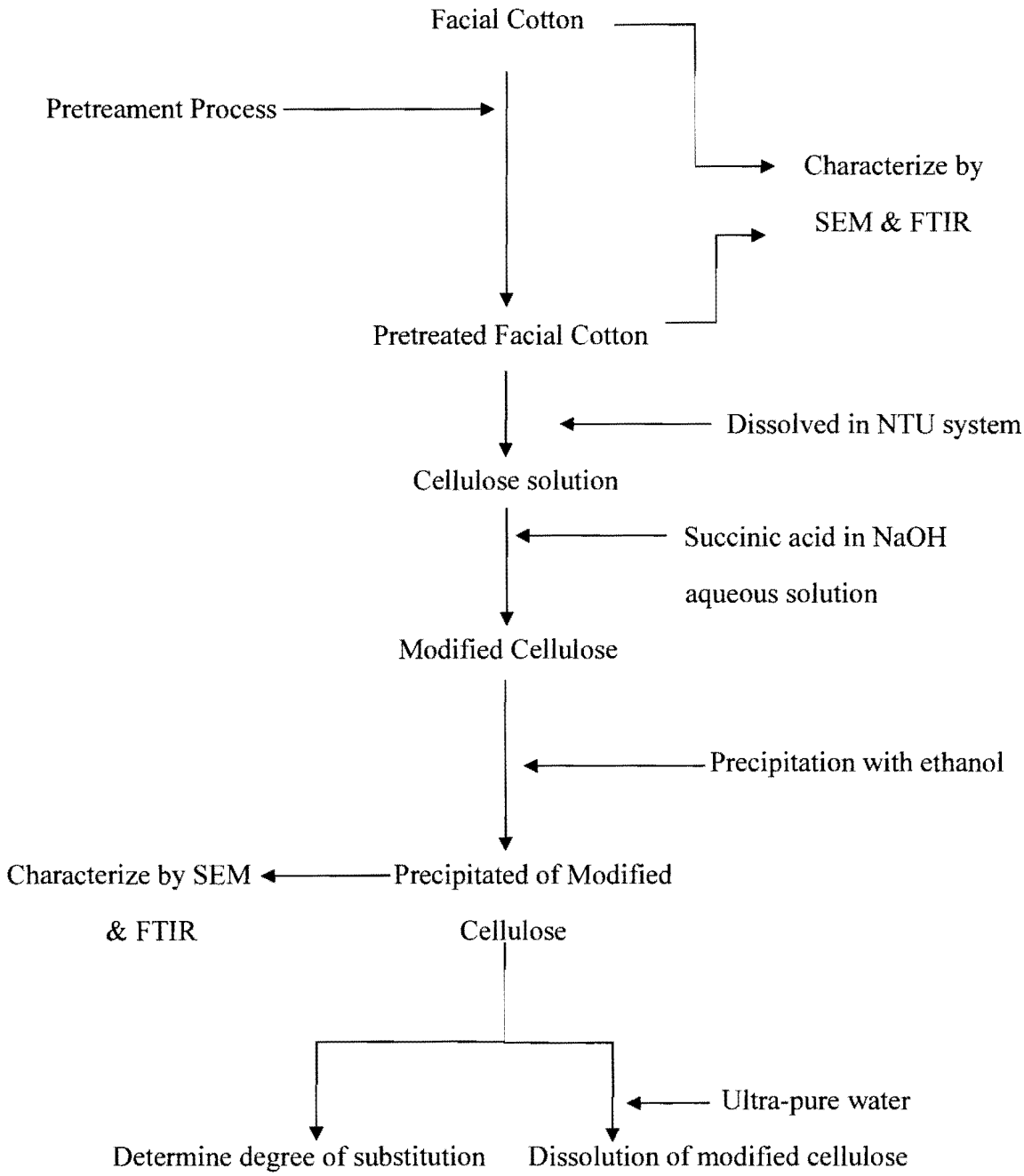
Solubility,

$$\frac{\text{Initial mass of succinic acid modified cellulose (g)} - \text{Residual mass after dry (g)}}{\text{Initial mass of succinic acid modified cellulose (g)}}$$

3.3.4 Scanning Electron Microscopy SEM

SEM was used to study the morphology and size of the samples. Around 1 mg of precipitated was put on an aluminium plate. Then, the surface of the sample was sputter-coated with gold under vacuum before observation through SEM (Duo *et al.*, 2007).

3.4 Summary of Methodology



Flow Chart 1: Synthesis process of succinic acid modified cellulose