

Regeneration of cellulose from cellulosic waste by dissolution in aqueous-based solvent system: cotton fabrics

Kong Mei Chee (21236)

A project submitted in partial fulfillment of the Final Year Project 1 (STF 3013) course

Supervisor: Assoc. Prof. Dr. Pang Suh Cem

Co-supervisor: Dr. Chin Suk Fun

Programme of Resource Chemistry

Department of Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

2011

ACKNOWLEDGEMENT

I granted my wish to thank University Malaysia Sarawak (UNIMAS) for giving me an opportunity to study and doing my final project. This project had given me a chance to be as research and learn how to manipulate the theoretical into practical. I would like to express my sincere gratitude to my supervisor, Dr. Pang Suh Cem and my co-supervisor Dr. Chin Suk Fun for the support and their invaluable guidance during this research study. Their continuous encouragement and support has always been an inspiration and a source of energy for me.

Not forgetting, special thank to my master postgraduate research assistance for giving me advices, some ideas and moral support to finish this project. Besides, I am also thanks to all staffs of Faculty of Resource Science and Technology for allowing me to carry out the experiment and giving permission of using the instrument.

I wish to thank all my fellow friends were always give me a fully support in this research study. Finally, I would like to thank my parents who always give fully support and encouragement during the progress. Other than that, they also give financial support to me for finishing my report.

Table of Contents

Acknowledgement	I
Declaration.....	II
Table of Contents.....	III
List of Tables and Figures.....	V
Abstract	1
1.0 Introduction.....	2
2.0 Literature Review.....	6
2.1 Type pf cellulose materials	6
2.2 Application of celluloses.....	7
2.3 Solvent system fro dissolution and regeneration of celluloses	10
3.0 Material and Method.....	14
3.1 Material.....	14
3.2 Methods.....	14
3.2.1 Preparation and pretreatment of cellulosic material	14
3.2.2 Dissolution of cellulose	15
3.2.3 Regeneration of cellulose	15
3.2.4 Physical characterization	17
3.2.5 Chemical characterization	17
4.0 Result and Discussion	18
4.1 Pretreatment of cellulosic sample.....	18
4.2 Dissolution of cellulose.....	18
4.3 Regeneration of cellulose.....	19
4.3.1 Cross-linker cellulose.....	19
4.4 Yield of regeneration of cellulose.....	21
4.4.1 Non-solvent regeneration	21
4.4.2 Effect of Reaction Temperature	24
4.4.3 Effect of Surfactant: Hexadecyltrimethyl ammonium bromide.....	28
4.4.4 Cross-linking regeneration (STMP)	30
4.4.5 Effects of Rate of precipitation	34

4.5 Physical characterization	37
4.5.1 Raw material and pretreated samples	37
4.5.2 Regeneration of cellulose	38
4.6 Chemical characterization.....	47
4.6.1 Raw material and pretreated samples	47
4.6.2 Regeneration of cellulose.....	50
5.0 Conclusion	60
Reference	61

List of Tables

Table 1: Yield of regenerated cellulose by methanol	21
Table 2: Yield of regenerated cellulose by ethanol	22
Table 3: Yield of regenerated cellulose by isopropanol	22
Table 4: Yield of regenerated cellulose at 30 °C	24
Table 5: Yield of regenerated cellulose at 40 °C	25
Table 6: Yield of regenerated cellulose at 50 °C	26
Table 7: Yield of regenerated cellulose at 60 °C	26
Table 8: Yield of regenerated cellulose at 70 °C	26
Table 9: Yield of regenerated cellulose by 1% surfactant	28
Table 10: Yield of regenerated cellulose by 3% surfactant	29
Table 11: Yield of regenerated cellulose by 5% surfactant	29
Table 12: Yield of regenerated cellulose with STMP at 1:1	31
Table 13: Yield of regenerated cellulose with STMP at 1:2	32
Table 14: Yield of regenerated cellulose with STMP at 1:3	33
Table 15: Yield of regenerated cellulose at 10 drops/min	35
Table 16: Yield of regenerated cellulose at 20 drops/min	35
Table 17: Yield of regenerated cellulose at 30 drops/min	35
Table 18: Characteristic Absorption Peaks of Cellulosic Sample	47
Table 19: Characteristic Absorption Peaks of pretreated cellulose	49
Table 20: Characteristic Absorption Peaks of regenerated cellulose from Whatman CF11 and cotton fabrics	51
Table 21: Characteristic Absorption Peaks of regenerated cellulose by different non-solvent	52
Table 22: Characteristic Absorption Peaks of regenerated cellulose cross-linking to STMP ..	54

Table 23: Characteristic Absorption Peaks of regenerated cellulose at different temperature. 55

Table 24: Characteristic Absorption Peaks of regenerated cellulose by adding surfactant 57

Table 25: Characteristic Absorption Peaks of regenerated cellulose at different rate of precipitate
..... 58

List of Scheme & Figures

Scheme 1: Structure of cellulose.....	2
Scheme 2: Reaction of STMP and cellulose.....	20
Figure 1:Yield of regenerated cellulose by non-solvent.....	23
Figure 2: Yield of regenerated cellulose at different temperature	27
Figure 3: Yield of regenerated cellulose with different concentration of surfactant	30
Figure 4: Yield of regenerated cellulose with STMP by the ratio of 1:1, 1:2, 1:3	34
Figure 5: Yield of regenerated cellulose with STMP by adding ethanol at different rate	36
Figure 6: SEM micrographs of untreated cotton fabrics.....	37
Figure 7: SEM micrographs of pretreated cotton fabrics.....	38
Figure 8: SEM micrographs of regenerated cellulose of cotton fabrics by methanol,ethanol,and isopropanol.....	39
Figure 9: SEM micrographs of regenerated cellulose cross linked to STMP at 1:1, 1:2, and 1:3	41
Figure 10: SEM micrographs of regenerated cellulose cross at 30 °C, 40 °C, 50 °C, 60 °C and 70 °C	43
Figure 11: SEM micrographs of regenerated cellulose by 1%, 3%, 5% CTAB.....	45
Figure 12: SEM micrographs of regenerated cellulose by 10,20 and 30 drops/min.....	46
Figure 13: FTIR spectra of cotton fabrics and Whatman CF 11.....	47
Figure 14: FTIR spectra of pretreated cellulose	49
Figure 15: FTIR spectra of regenerated cellulose from Whatman CF11 and cotton fabrics....	50
Figure 16: FTIR spectra of regenerated cellulose by methanol, ethanol, isopropanol	52
Figure 17: FTIR spectra of regenerated cellulose with the ratio of cotton fabrics to STMP....	53

Figure 18: FTIR spectra of regenerated cellulose from cotton fabrics at different temperature 55

Figure 19: FTIR spectra of regenerated cellulose by adding different concentration surfactant
CTAB 56

Figure 20: FTIR spectra of regenerated cellulose with STMP by different rate of adding ethanol
..... 58

Regeneration of cellulose from cellulosic waste by dissolution in aqueous-based solvent system: cotton fabrics

Kong Mei Chee

Resource Chemistry Programme

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

ABSTRACT

The aim of this study was to identify the optimized condition for dissolution and regeneration cellulose. This study determined the yield, morphology and chemical composition of regenerated cellulose. The handkerchief was used as a cellulosic sample in this experiment. The optimized conditions that have been investigated were non-solvent used to precipitate, usage of cross-linker, temperature variation, usage of surfactant, and rate of precipitate. Before regeneration, there are some important process to carry out, such as pretreatment and dissolution process. After regeneration, the regenerated cellulose can be obtained by centrifuged, washing and drying. The yield of each condition had been concluded in the graph for comparison.

Key words: Cellulose, regeneration, dissolution.

ABSTRAK

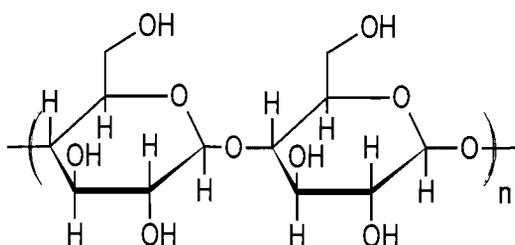
Tujuan kajian ini dijalankan adalah untuk mengenalpasti keadaan optimum untuk perjanaan semula selulosa. Kajian ini dilakukan untuk mengenalpasti kandungan, morfologi dan komposisi kimia dari selulosa yang telah dijana semula. Sapu tangan telah digunakan sebagai sampel selulos dalam kajian ini. Keadaan optimum yang telah diselidiki termasuklah pelarut yang digunakan untuk mengendap, penggunaan 'cross-linker', suhu, surfaktan dan kadar pemendakan. Sebelum regenerasi, ada beberapa process yang penting harus dilaksanakan seperti perlakuan awal dan process pelarutan. Setelah regenerasi, selulosa yang dijana semula dapat diperolehi daripada pengasingan, pencucian dan pengeringan. Keputusan yang terdapat daripada keadaan masing-masing telah menghasilkan kesimpulan dalam graf.

Kata kunci: Selulosa, perjanaan, pelarutan.

1.0 Introduction

Nowadays, it is important for us to take care of the environment from the waste that we had produced. The regeneration of cellulose from the cellulosic waste is a crucial way to reduce our environmental problems.

Cellulose, the most important skeletal component in plants which is the main polysaccharide and the main constituent of cell wall in lignocellulosic plant. Its content depends on the plant species, growing environment, position, growth, and maturity. Generally, cellulose content in lignocellulosic plant is 23-53% on a dry-weight basis, less than that in cotton, which is almost made of pure fibrous cellulose (Chuan & Run, 2007).



Scheme 1: structure of cellulose

Besides, cellulose is based on glucose units having taken the shape of 6-membered rings, called pyranoses or glucopyranises. They are connected by a single oxygen atom between the C1 of the one pyranose ring and the C4 of the next ring. So, cellulose is composed of β -(1 \rightarrow 4)-linked D-glucopyranosyl units with three hydroxyl groups, which can form complex inter- and intramolecular hydrogen bonds (Jin *et al.*, 2007). Changing the shape of cellulose by melt or dissolution is very important for the industrial applications (Sang *et al.*, 2005). There are many materials consist of cellulose, such as coconut husk, 100% cotton fabrics, wood waste, paper, nitrocellulose for explosives, cellulose acetate for films.

Moreover, cellulose is composed of linear chains of covalently linked glucose residues. In the primary cell wall consists one glucose polymer of roughly 6000 glucose units, in the secondary wall is their number increased to 13-16000 units. Cellulose chains form crystalline structures called microfibrils. The microfibrils of each layer are parallel to each other. Their orientation changes from layer to layer (Newton, 1977).

Cellulose chains generally interact with each other through hydrogen bonding and Van der Waals forces to form extensive crystalline regions. Despite the high density of hydroxyl groups in the molecule, cellulose is insoluble in water or in most of solvents and also does not melt until thermal degradation because of intra- and inter-molecular hydrogen bonding present as a formidable barrier against penetration by reagents (Sang *et al.*, 2005). Cellulose may be chemically reacted like any other organic material but the degree of reactivity is usually limited by the accessibility of the reactive sites in the polymer to the reactant of choice. Cellulose may be reacted either homogeneously or heterogeneously. Most commercial chemical reactions on cellulose are carried out heterogeneously (Craver & Carraher, 2000).

Yu *et al* reported that cellulose acts as the framework and cellulose chains are high in orientation in the vascular bundles. In the thickening part of the vessels, cellulose exists in the form of cellulose crystalline lamellae but not cellulose microfibrils. The crystalline lamellae are perpendicular to the tangential direction of rings and tend to clockwise with an angle of about 30-40 °C to the tangential direction of the spiral line in the spiral vessels (Chuan & Run, 2007).

In order to dissolve cellulose, the solvent molecules have to diffuse into cellulose molecules and disrupt the crystallites. Example, $\text{N}_2\text{O}_4/\text{N,N}$ -dimethylformamide, N -methylmorpholine- N -oxide monohydrate and ionic liquid. (Shuai *et al.*, 2010) However, all these solvents are limited to laboratory scale applications due to their volatility, toxicity and high cost.

According to Cai *et al.* (2004), a suitable starting material, type and composition of solvent system, temperature of solvent system should be controlled in order to obtain higher percentage yield of regenerated cellulose with optimized properties. Cellulosic material are found to have a great potential to be utilized as nanomaterials because it is the most abundant resource, easily renewable, and also has special characteristics such as hydrophilicity, chirality, biodegradability, broad chemical modifying capacity and its capability of forming versatile semicrystalline fiber morphologies (Bai, 2006).

Recently, cellulose dissolution in alkaline system has been found as good direct solvents that can fully dissolve low molecular weight cellulose and partially dissolve high molecular weight cellulose. Among the so-called green solvents for cellulose dissolution, ionic liquid (Omar *et al.*, 2007) and NaOH /thiourea/urea aqueous solution (Jin *et al.*, 2007) solvent system were reported as environmental friendly solvent.

Regenerated fibers made from the chemical-induced transformation of natural polymers and basically fall into two categories: protein origin and cellulose origin (Lackman & Michael, 2004). Regenerated fibers of protein origin come from plant protein (such as corn, soy, alginate, and peanut) or from animal protein. Regenerated fibers of cellulose origin are bamboo, rayon, and Lyocell. Lyocell are made of cellulose from tree wood and inner pith and

leaves from bamboo plants using differing fiber manufacturing processes. In the 1890s, fibers used to produce a textile that was then called 'artificial silk' (Lackman & Michael, 2004). This family of regenerated cellulose fibers for textiles and fabrics has also been called reconstructed fibers or natural synthetic fibers.

In this study, the solvent system of NaOH/thiourea/urea aqueous solution was used to dissolve cellulose derived from cotton fabrics and addition of non-solvent for precipitation of cellulose. The focus is to exam the media conditions for regeneration, such as rate of precipitation, temperature of medium, suitable type of medium, effect of surfactant and effect of cross-linking between cellulose and solvent. Optimization of solvent composition is necessary in order to enhance the effectiveness of cellulose precipitation. Cotton-made fabric is used as the starting materials in this study due to their high content of cellulose. During the precipitation of cellulose, cellulose was crosslinked with a non-toxic crosslinker, sodium trimetaphosphates (STMP). The cellulose could be regenerated by other methods with simplified steps and reduced duration of regeneration, such as addition of non-solvent, ethanol. The morphology and size of the regenerated cellulose by the addition of different non-solvent, STMP and surfactant were investigated and compared.

The main objective of this study is to determine the optimal conditions for the regeneration cellulose from cotton fabrics after the dissolve in the NaOH/thiourea/urea solvent system such as its rate of precipitation, temperature and cross-linking. The chemical characteristics of regenerated cellulose were characterized by Fourier Transform Infrared (FTIR) spectroscopy whereas the physical characteristics and morphology of the regenerated cellulose sample were investigated by scanning electron microscope (SEM).

2.0 Literature review

Cellulose was discovered in 1839 by a Frenchman, Anselme Payen, the Professor of Agricultural and Industrial Chemistry (Calvin, 2001). Cellulose is the predominating constituent of plant tissues and as the structural basis of the vegetable world. The highest proportion of cellulose is contained in the cotton hair and its amount around 90%. However, wood and cereal straws contain a lower proportion of cellulose, amounting to 60%. The lignocelluloses are the most important of the compound celluloses and are represented by two well-defined types which are the best fibre and wood or the lignified tissues of perennial stems. (Marsh & Wood, 1942)

2.1 Type of cellulose materials

To reduce the dependence on land and other resources required to produce fibers, current applications of cornhusks is developed in many industries. More than 9 million tons of natural cellulose fibers with a potential sale value of \$19 billion with a value addition of at least \$12 billion can be produced from the cornhusks available every year (Yang, Narendra and Yiqi, 2005). Cornhusk is commonly available with no geographical limitations. Besides, it is cheaper than cotton with the similar structure and properties.

A paper contains 90-99% cellulose fibers which are the primary structural element. After modifications, the hydrogen bond cross-links could be formed between adjacent microfibrils in cellulose structure and it is called hornification of cellulose fibers. The hydrophilic natures of the cellulose within paper structure are very important for good fiber-fiber bonding (Halil & Mustafa, 2008).

Cotton linter, the short fibres remaining on the surface of cotton seed after ginning, is used exclusively for this process. It is a by-product of cotton seed oil mill production. Previously, cotton linter is used and is purified by treating with 3-5% aqueous sodium hydroxide solution at 130-160 °C for 2-6 h, and then is bleached with aqueous sodium hypochloride solution, reduced with sodium sulphite and dehydrated to a water content of 50 wt% . In 2002, Lina Zhang, Dong Ruan and Jinping Zhou found that regenerated cellulose films having various viscosity-average molecular weights ranging from 2.2×10^4 to 8.2×10^4 g/mol were prepared from cotton linters in 6 wt% NaOH/ 4 wt% urea aqueous solution by coagulation with 2 M acetic acid and 2 % H₂SO₄ aqueous solution.

2.2 Application of celluloses

Actually cellulose derivatives have many important commercial applications in the fiber, paper, membrane, polymer and paints industries (Richard *et al*, 2002). It is capable of producing a number of fibrous products with excellent properties whose utility extends into numerous end uses and industries (Lewin, 2007). Cellulose provides fibers for industrial end users requiring strong, tough fibers. In 1855, Switzerland dissolved the nitrated form of cellulose in alcohol and ether and discovered that fibers were formed. These soft strong cellulose nitrate fibers could be collected into fabrics but had a very serious drawback that ultimately prevented their widespread use in textiles.

Cellulose is also used for lamp filaments. Joseph Swan, developer of the first electric lamp and inventor of bromide photographic print paper, has learnt to de-nitrate the cellulose nitrate using ammonium hydrosulphate. He used this cellulose as a better carbon fibre for lamp filaments.

There are some traditional techniques being employed to obtain regenerated cellulose fibers as well as films, for example, viscose technology and cuprammonium process. The viscose process was discovered in 1892 by Cross, Bevan and Beadley and allowed spinning of viscose fibres. In industrial application, the viscose process converted cellulose into sodium cellulose xanthate which was soluble in a caustic solution and produces regenerated cellulose called viscose rayon (Lewin, 2007). Cellulose from wood pulp or cotton linters is treated 17-20% sodium hydroxide (NaOH) at temperature in the range of 18-25 °C, to convert cellulose to alkali cellulose. Then, cellulose is aged under controlled conditions of time and temperature in order to depolymerise the cellulose to the desired degree of polymerization (DP). After that, carbon disulfide (CS₂), in gas or liquid state is added into the solution of alkali-cellulose to react with hydroxyl groups and generate the xanthation reaction (Egal, 2006). Lastly, it is dissolved in dilute sodium hydroxide and forms a viscous solution-viscose. However, viscose technology that is being employed has its disadvantages, as it requires usage of harmful carbon disulfide (Ghittori, 1998).

Cuprammonium technology which generates heavy metal residues that are hard to dispose of is one of those troublesome traditional techniques as well (Fushimi *et al*, 1996). Moreover, the cellulose is converted into artificial silk by the cuprammonium process. Matthias Eduard Schweizer (1857) found that cotton could be dissolved in a solution of copper salts and ammonia and then regenerated in a coagulation bath. Louis Henri Desplaces was extruded the cuprammonium solution of cellulose into water, with dilute sulphuric acid which used to neutralize the ammonia and precipitate the cellulose fibres. Asahi in Japan still used this process to produce artificial silk and medical disposable fabrics which provide a worthwhile income.

Cellulose is essential in serving the pulp and paper industry. In decade, Edward Bevan and Clayton Beadle were discovered that cotton or wood cellulose could be dissolve as cellulose xanthate by viscose treatment with alkali and carbon disulphide (Calvin, 2001). Then, Kamide and co-workers have been applying the steam explosion treatment to dissolving pulp to make it dissolve directly in sodium hydroxide to form alkali cellulose that is allowed to 'age' to give an oxidatively degraded alkali cellulose (Kamide, 1992). To produce paper from cellulose, some investigators used N-methyl-morpholine-n-oxide, NMMO as solvent system. Furthermore, the strength of paper can be increased by adding ammonium chloride or calcium chloride (Calvin, 2001). Other than that, microfibrillated cellulose may have use in the paper industry in order to improve the physical characteristics of paper such as tensile strength and water retention value (APV, 2009). Although the viscose process is still used worldwide to manufacture rayon and other regenerated cellulose products in existing plants, it is unlikely that any industrialized country would permit the construction of a new viscose plant, primarily because of environmental concerns (Craver & Carraher, 2000).

There is a great application of cellulose derivative in the oral drug delivery. Natural polysaccharides have been regarded to prepare nanoparticles for drug delivery. Simultaneously, copolymers of polysaccharides are widely employed to produce biodegradable hydrogel (Chen, 1995). Those are methylcellulose, hydroxypropyl methylcellulose, hydroxypropylcellulose, ethylcellulose and so forth. They are all derived from cellulose by substitution of the hydroxyls. Therefore, their backbone of cellulose is with a repeat anhydroglucose unit (Sakellariou & Rowe, 1995). Because of the anhydroglucose unit in cellulose, chain movements are very restricted and cellulose appears as a highly oriented,

highly crystalline material with a very high glass transition temperature of 250 °C. As a result, cellulose derivatives can be coated into film and then made as drug tablets.

2.3 Solvent system for dissolution and regeneration of celluloses

Among the many aqueous and non-aqueous cellulose solvent systems reported in the past three decades, the N-methyl-morpholine-N-oxide, NMMO/H₂O system is the most powerful in attaining exceedingly high concentration solutions and has been commercialized to produce Tencel or Lyocell fibers in fibre manufacture (Jin, Zha and Gu, 2007). It has been successful for the production of regenerated cellulose textile fibers (Isogai, 1998). In 1969, Dee Lynn Johnson used the cyclic mono(N-methylamine-N-oxide) compounds as a solvent size for strengthening paper by partially dissolving the cellulose fibres (Calvin, 2001). To prepare the solution, cellulose is added into a mixture of aqueous NMMO and n-propyl gallate. The mixture is placed in an airtight vessel. Then, stirred it and heated at 130 °C within 30 min. The NMMO solvent system is of interest because very high concentrations can be attained. However, the NMMO/H₂O system also has disadvantages of requiring high temperature for dissolution and antioxidant to avoid side reactions of solvents, causing degradation of cellulose, and high costs. Thus, it is not suitable for complete replacement of the viscose technology.

N,N-Dimethylacetamide (DMAc) and lithium chloride (LiCl) were discovered by McCormick in dissolving cellulose (Lewin, 2007). This solvent system is reported to be non-degradable and reactive with cellulose. This mixture is refluxed at 165 °C in a nitrogen atmosphere for 20-30 min. Then, the mixture is cooled to ~100 °C and LiCl is added while

stirring at 80 °C for 10-40 min. This complete dissolution can be obtained with concentration up to 15% (w/w) of cellulose.

In order to prevent pollution and waste production and to utilize renewable resources, ionic liquid is used to replace the organic solvent (Richard *et al*, 2002). It has been found that cellulose can be dissolved in ionic liquid without derivatization in high concentrations, around 30 wt% is possible although solutions containing 5wt% cellulose in ionic liquid are more easy to prepare and handle (Richard *et al*, 2002). Ionic liquids containing halide anions have been shown to be strongly hydrogen-bonding. This ability make ionic liquids can be used as non-derivatizing solvents for cellulose.

In 1998, Laszkiewicz reported that the addition of 1% urea in 8.5% NaOH at 5 °C improve the solubility of bacterial cellulose having the higher degree of polymerization (Egal, 2006). Some years later, Zhang's group has successfully developed aqueous NaOH solution systems with either urea or thiourea for cotton linter dissolution. More recently, Zhang and co-workers found that NaOH/urea and NaOH/thiourea aqueous solutions can dissolve cellulose directly and quickly (Zhang *et al*, 2010). Besides, this group of researchers also investigated regenerated cellulose membranes prepared from NaOH/urea or NaOH/thiourea aqueous solutions. Both solvent systems are inexpensive and less toxic and good cellulose fibers can be prepared using simple technology. This simple technology is cheap and environmentally friendly, and can be used to prepare regenerated films and fibers. However, these two solvents containing of high concentration of cellulose are unstable in spinning solution and cannot applied for industrial purposes (Zhang, Ruan, and Gao, 2002). Recently, a better solvent was found, that is NaOH/thiourea/urea aqueous solution that can dissolve cellulose rapidly (Jin *et*

al, 2007). The NaOH/thiourea/urea aqueous solution systems contain higher concentration of cellulose than the two solvent systems before.

Pretreatment process is critical to make sure that the cellulose can dissolve completely in the solvent system. There are many types of pretreatments such as mechanical, alkaline, acidic, thermal, and etc. Mechanical pretreatment is also known as milling which involved the cutting of the lignocellulosic biomass into smaller pieces to reduce the particle size and crystallinity of the cellulosic materials. The reduction in particle size leads to an increase of specific surface. Alkaline pretreatment caused 'peeling' of end groups, alkali hydrolysis and degradation and decomposition of dissolved polysaccharides. Cellulose fibers need to be soaked in NaOH solution for several hours at room temperature to convert native cellulose into alkali-cellulose (Yoo *et al*, 2005).

In addition to yield more cellulose, separation properties of cellulose membrane has improved by changing the solvent in the membrane casting solution. Many efforts have been made. Some researchers modified it by employing different kind of additives or pore-forming agents, such as polyethylene glycol 600 as an additive, polyvinylpyrrolidone as a pore-forming agent (Mulijani *et al*, 2010). Some of them used surfactant to spread and lower the interfacial tension of cellulose molecules, mostly are cationic and anionic surfactants. In this experiment, CTAB is added as cationic surfactant which may increase the hydrophobicity of cellulose surfaces. CTAB is a quaternary ammonium compound which is membrane-active agents having the main target at cytoplasmic membrane in bacteria and causing a loss of their structural organization and integrity. The strong film of CTAB layer may be most interesting within medical applications and the food industry. For example, foreseen advantages may

open for a novel utilization of cellulose-based products. It also aided by the recent advances in nanoresearch and its application (Syverud *et al*, 2009).

3.0 Materials and Methods

3.1 Material

Reagent grade Whatman CF11 fibrous cellulose powder was used in this study. Cotton fabric was used as cellulosic material. Reagent used were including sodium hydroxide (NaOH), thiourea, urea, ethanol absolute, methanol, isopropanol, hydrochloric acid (HCl), hexadecyltrimethyl ammonium bromide (CTAB), sodium trimetaphosphate (STMP).

3.2 Methods

3.2.1 Preparation and Pretreatment of Cellulosic Material

The raw sample of cellulosic materials was cut into small pieces by scissors and grinded into powder-like particle by a grinder. The particles fabric was then underwent the maceration process. The sample was soaked in NaOH (12 % w/v) for 2 hours, enabling chemical molecules to penetrate through the crystalline region. In order to get rid of unwanted impurities and compounds, pretreatment was carried out by the acid treatment with 1M HCl for 1.5 hours, followed by the alkaline treatment with NaOH (2% w/v) for 2 hours. The sample was sonicated for 15 minutes during these two treatments. Then the pretreated cellulose was filtered and washed with ultrapure water.

3.2.2 Dissolution of Cellulose

Dissolution of cellulose was done by the solvent system which reported by Jin *et al.* (2007). The composition of the solvent system was NaOH: thiourea: urea equals to the ratio of 8: 6.5:

8. 1.0g of the cellulosic sample was dispersed in 100ml of solvent with that composition and then sonicated for 10 minutes. After that, the sample was being cooled at 0°C overnight. The cellulose had become frozen solid mass after the overnight cooling and was allowed to thaw at room temperature. As the frozen mass thawed, the residue of cellulosic sample may be filtered and took the clear solution with no suspension for the regeneration processes.

3.2.3 Regeneration of Cellulose

Excess ethanol was added to the cellulosic solution to precipitate the dissolved cellulose. The precipitate as the regenerated cellulose was obtained by centrifugation at 4600 rpm for 5 minutes. The regenerated cellulose was washed with ethanol for 5 times to remove NTU which may remain in the precipitate. The regenerated cellulose was then dried in an oven. The centrifuged bottle and precipitate were weighed and the mass was recorded.

i) Non-solvent Regeneration

Different non-solvents may be employed to regenerate 10ml of dissolved cellulose, which were methanol, ethanol, and isopropanol. Excess non-solvent was added to the cellulose solution in order to precipitate the dissolved cellulose. The precipitate was obtained by centrifugation at 4600 rpm, 10 °C for 5 minutes. The regenerated cellulose was rinsed with alcohol for 5 times in order to get rid NTU. The regenerated cellulose was then dried in an oven. The centrifuged bottle and precipitate were weighed and the mass was recorded.

ii) Cross-linker

Sodium trimetaphosphate (STMP) was used as a cross-linker for crosslinking the dissolved cellulose. The amount of STMP added was based on the molar ratio to 1g cellulosic sample. Ratios of cellulosic samples to STMP are 1:1, 1:2, 1:3. Each ratio may be used to cross-link the dissolved cellulose. After the addition of STMP, the cellulosic solution (pH>7) was sonicated for 15 minutes and then heated it in the water bath at 45 °C for 2 hours. The heating process was accompanied by stirring.

iii) Effects of Reaction Temperature

10ml clear cellulosic solution was used to heat at different temperature which are 30 °C, 40 °C, 50 °C, and 60 °C. Excess ethanol was added in the dissolved cellulose at each temperature. The precipitate as regenerated cellulose was centrifuged, washed by ethanol, dried in the oven and weighed.

iv) Effects of Surfactant

Hexadecyltrimethyl ammonium bromide (CTAB) was used as surfactant. CTAB with 1% w/v, 3% w/v and 5% w/v were added in 10 ml of dissolved cellulose. After the addition of surfactant, the cellulosic solution was regenerated by ethanol, and recovered by centrifugation, washing, drying and weighing. The weight of precipitate is recorded and calculated into percentage.