SYNTHESIS OF CATIONIC CELLULOSE AS POLYMERIC SURFACTANTS

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Abstract

The synthesis of cationic cellulose dissolved in water was conducted at 50^o *for 2 hours continued at temperature 76*^{o}*C for 15 minutes in a glass reactor. The cationic cellulose was synthesized through one-step substitution reaction The chemical composition of cationic cellulose was analyzed by FTIR (Fourier-Transformed Infra-Red). The successful conjugation onto cellulose chain confirmed by* ^{1}*H NMR (Nuclear Magnetic Resonance). Water solubility of cationic cellulose product was measured using UV-Visible spectrophotometer at 600 nm.*

Keywords: *Cationic cellulose, polymeric surfactants, water- soluble polymer,* ^{1}*H NMR, FTIR*

Introduction

Cellulose is a natural polymer which is abundant in nature. Main resource of cellulose is wood. Commonly, composition of cellulose in wood is about 50% and the other major compound is lignin. Cellulose is built by glucose chains which is connected onto β-1,4, glucose having molecular formulation $C_6H_{12}O_6$ (Cowd, 1991 & Kirk, 1993).

Cellulose is a raw material for many products such as paper, film, fiber additive etc. This materials is consist of anhydroglucopyranose connecting each other to form polymer chain. Therefore cellulose can be identified as glucan linear polymer with uniform chain structure (Fengel, 1989). Cellulose is a homopolysaccharide structure of β-D glucopyranose fitted by glycocide (1,4) bond. According to Hardjo et al , each fiber in cellulose is composed from about 3000 glucose molecules with the molecule mass of 500.000 (Hardjo, 1989). In the nature, cellulose is structured in fibril form consisted of several paralel cellulose molecules which connected with hydrogen. The fibrils form crystal structure.

Fengel dan Wegener explained that there are two cellulose crystalline structures, i.e. I-α cellulose and I-β cellulose distinguished by hydrogen bond. In I-α structure of cellulose, one unit triclinate cell containing one cellulose chain, whereas in I-β cellulose one cell monoclinate containing two cellulose chains (Fengel, 1989).

Bacterial cellulose consist of about 60% of cellulose, differ from plant cellulose (e.g hemp and cotton) which is just consist of 30% of I-α cellulose, and the remaining is I-β cellulose. Cellulose have three hydroxyl groups per anhydroglucose residual, so it can be reacted like esterification, etherification, addition, etc (Hardjo, 1989).

Cationic polymer such as cationic cellulose can also be used as a thickening agent besides as a stabilizer. If a certain polymer compound is added into an emulsion system, the system is able to maintain its stability (Schueller, 1999). In this case, polymer material perform as a binding agent between oil phase and water phase. In order to perform as a binding agent attractively, the cationic polymers should be connected with *Hydrophyle Lypophyle Balance* (HLB), which make balance between the water base compound and oil base compound.

Cationic polymer formed by columbic attraction (interaction between charges particles, different charges particle will attract each other and the opposite will reject if it has same charges) on the anion surface.

Generally, cationic polymer is aliphatic polymer that has positive charges in the polymer structure. Cationic surfactant for instance, is cationic polymer that can be applied onto hair and skin because of electrostatic interaction between positive and negative charges. Unlike surfactant, many cationic polymers can form a film with anionic surfactant on hair and skin. This film gives contribution as a softener for hairs and cuticules. Cationic polymers are made by replacing hydroxyl group in fatty alkyl or amine group to form modified natural polymer. When the structure is similar with cationic surfactant in ammonium quaternary form, the polymer has more cationic sides per each molecule and bigger molecular weight.

Cellulose is a natural polymer that can stabilize the system of emulsion. Cationic cellulose derivative containing 2-hydroxypropyltrialkyl ammonium chloride can be used as conditioning agent in hair and skin treatments (Drovetskaya, 2004). The molecular structure of cationic cellulose, which was synthesized in this work, is shown in Figure 1.

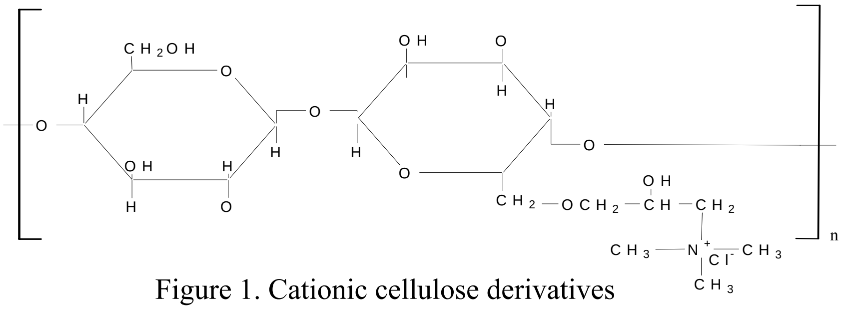

Figure 1. Cationic cellulose derivatives

The aim of this work is to synthesize the cationic cellulose as a polymeric surfactant through one-step substitution reaction. The compounds are prepared by reacting cellulose with 3-chloro-hydroxy-propyltrimethyl ammonium chloride in the presence of a solvent. The chemical composition, atomic bonding C and H with uniquely chemistry movement for each compound were identified using FTIR, and ^{1}H NMR spectra. The water solubility of the obtained cationic cellulose was measured at 25^{o}C by using UV-Visible spectrophotometer at 600 nm.

Materials and Methods

Materials

Cellulose was obtained from PT. Tobako Indah Lestari Pulp (Medan, Indonesia). 3-chloro-hydroxy-propyltrimethyl ammonium chloride (60 wt % soluble in water) was purchased from Aldrich (Singapore). Sodium hydroxide, iso-propanol, and acetic acid were reagent grade.

Glass apparatus, vacuum oven, magnetic stirrer, pipettes, porcelain dish, electric heater, pH-meter, and analytical balance, were used during synthesis of cationic cellulose. Photomicroscope apparatus, FTIR spectrophotometer, NMR spectrophotometer and UV-Visible spectrophotometer were used in order to characterize the obtained products.

Methods

Synthesis of cationic cellulose

Cationic cellulose was synthesized similarly to the previously reported manner (US patent, 1969). 34.3 grams of cellulose dissolved in 480 milliliters of aqueous iso-propanol and 45.4 milliliters of 20 percent sodium hydroxide. The mixture was stirred for 30 minutes at room temperature. To the solution was added 3-chloro-hydroxy-propyltrimethyl ammonium chloride and then the mixture was heated until 50^{o}C temperature for 2 hour continued at temperature 76^{o}C for 15 minutes with vigorous stirring. The molar ratio of 3-chloro-hydroxy-propyltrimethyl ammonium chloride to cellulose was 3:1. The product was washed with acetic acid to neutralize pH. The process was repeated three times, and the product cationic cellulose was dried under vacuum at 45^{o}C for a day.

Characterization of polymers

FTIR spectrum Analysis

Infrared absorption spectra of cellulose and cationic cellulose were studied by FTIR using IR Prestige-21 Shimadzu (Shimadzu Co., Japan). The polymers were mixed with KBr and pressed to a plate for measurement. All of the spectra were measured 16 scans at a resolution of 4 cm^{-1}. A background spectrum containing no sample was substracted from all spectra.

^{1}H NMR spectrum Analysis

The atomic bonding C and H with uniquely chemistry movement for each compound can be seen with ^{1}H NMR spectra. ^{1}H NMR spectra were obtained on a JEOL 500 spectrometer (500 MHz for ^{1}H) on D_2O at 25 °C.

Measurement of Water Solubility of Cationic Cellulose

Series of concentration of the obtained cellulose in aqueous solution were prepared by the addition of cationic cellulose to water such the concentration ranged from 0.2 to 20 g/dL. The transmittance of each solution was measured at 600 nm using a UV-visible spectrophotometer. The materials are considered insoluble when the transmittance of the polymer solution is less than 50% of the transmittance for deionized water.

Result and Discussion

Cationic cellulose was synthesized using 3-chloro-hydroxy-propyltrimethyl ammonium chloride through one-step substitution reaction. The FTIR spectra for cellulose and the synthesized cationic cellulose can be seen in Figures 2 and 3.

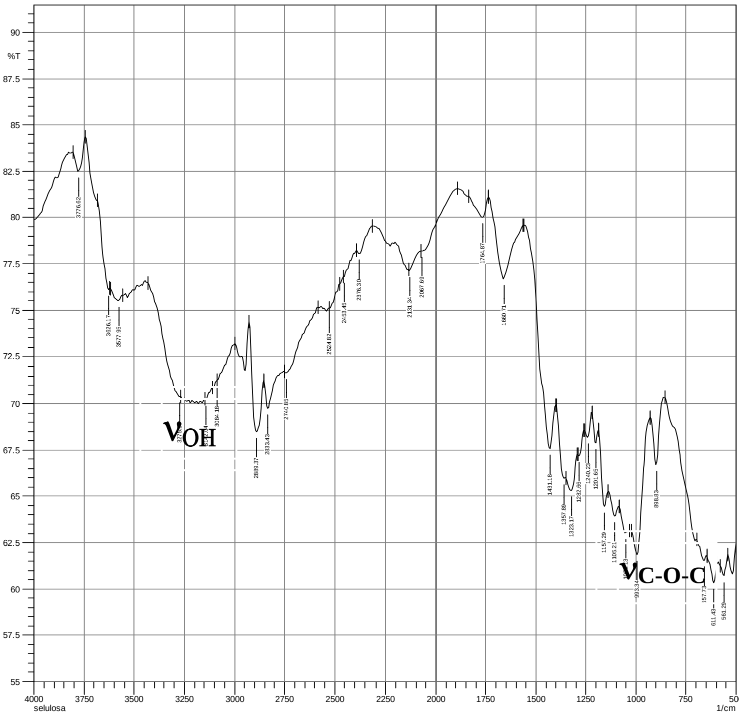

Figure 2. FTIR spectra of cellulose

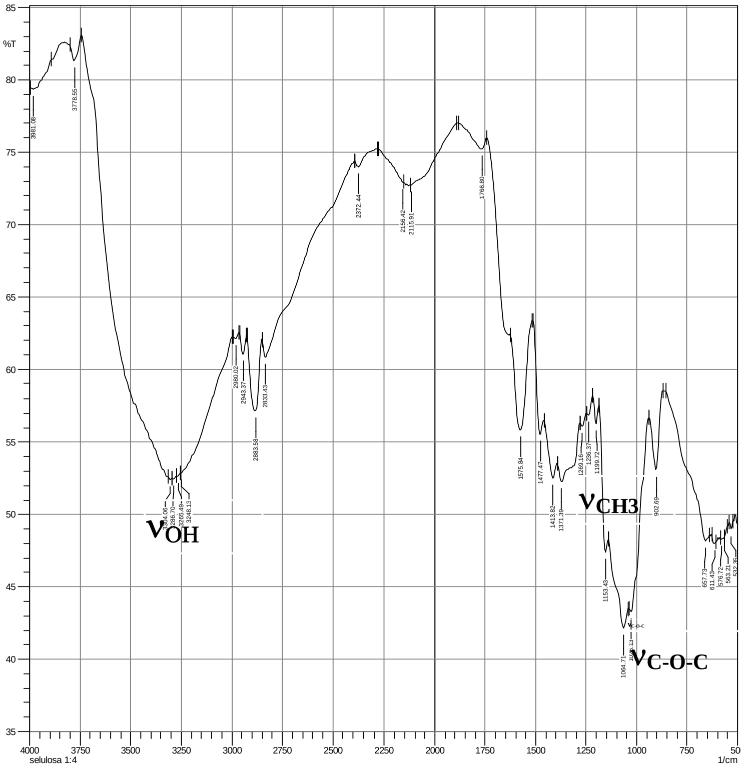

Figure 3. FTIR spectra of cationic cellulose

There are two characteristic peaks of cellulose at 3287 cm^{-1} of *v*(OH), and 1240 cm^{-1} of *v*(C-O-C). The peak represented to the methyl band of 3-chloro-hydroxy-propyltrimethyl ammonium chloride at 1471 cm^{-1} was presented in the spectra for cationic cellulose but not in the spectra for unmodified cellulose. Characteristic peaks of alcohol and second alcohol between 1157 and 1053 cm^{-1} are not changed in cationic cellulose confirming the lack of the introducing the alkyl group at cellulose backbone (Qin, 2002).

Further, to confirm the success of the reaction, ^{1}H NMR analysis of cellulose and cationic cellulose was performed in D_2O solution. The peak position of each functional group in cationic cellulose is shown in Figure 4.

From the obtained NMR spectra, peaks at δ = 3,4-3,5 ppm were attributed to the group of C-3,4,5,6 of the cationic cellulose. Peak at δ = 3.2 ppm represents the $-^{+}N(CH_3)_3$ groups in ammonium side chain of the obtained cationic cellulose.

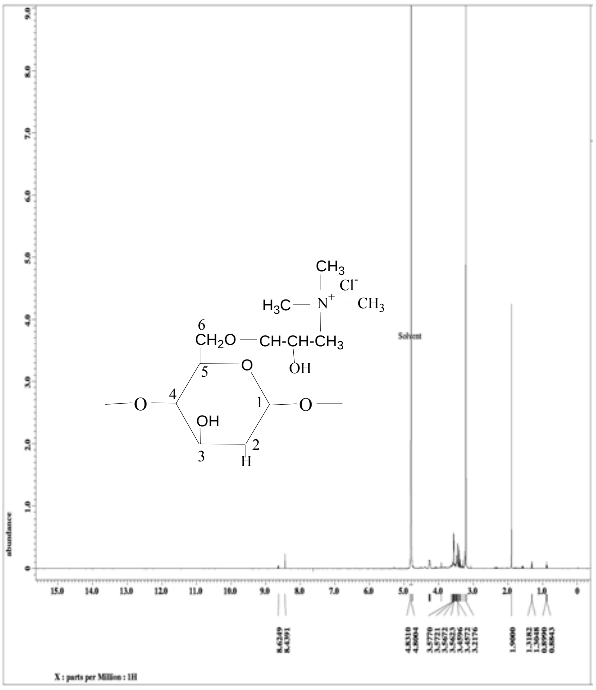

Figure 4. ^{1}H NMR spectra of cationic cellulose

To determine the water solubility of the cationic cellulose, the transmittance of the polymer solutions was measured by UV-visible spectroscopy as a function of the polymer concentration. As shown in Figure 5, the transmittance is dependent on the polymer concentration. With increasing the polymer concentration, the transmittance abruptly decreased. The experimental data were fitted using a polynomial equation, and the curve was extraplotted to 50% transmittance in order to estimate the solubility of the cationic cellulose. The water solubility of the cationic cellulose obtained by the reaction between cellulose and 3-chloro-hydroxy-propyltrimethyl ammonium chloride was 2 g/dL.

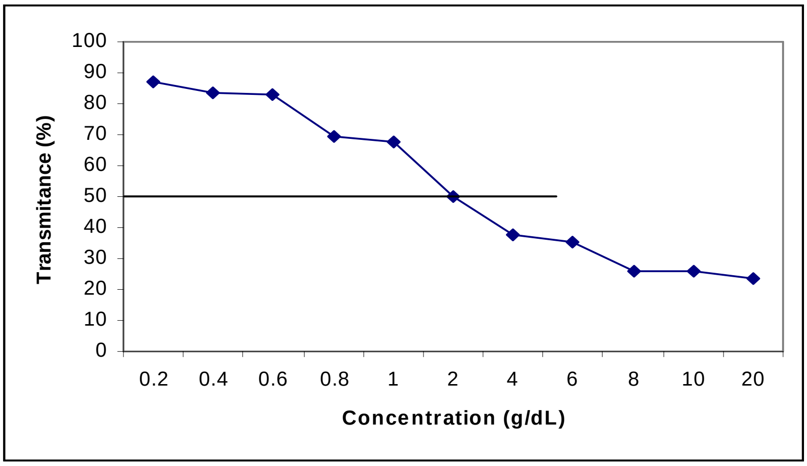

Figure 5. Water solubility of cationic cellulose

Conclusion

A cationic cellulose was synthesized by the substitution reaction of 3-chloro-hydroxy-propyltrimethyl ammonium chloride onto the cellulose chains. The Analyzing of the chemical composition of cationic cellulose was identified by FTIR spectra (Fourier-Transformed Infra-Red) and to confirm the successful conjugation onto cellulose chain was identified by ^{1}H NMR (Nuclear Magnetic Resonance) spectra. Water solubility of the obtained cationic cellulose was 2 g/dL.

Acknowledgments

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