Surface modification and characterization of nano crystalline cellulose

Master of Science Thesis, Chemistry and Bioscience

MENGSHENG WANG

SUPERVISOR: GUNNAR WESTMAN

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Supervisor: Gunnar Westman

Department of Chemical and Biological Engineering

Division of Organic Chemistry

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2011

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Department of Chemical and Biological Engineering

Division of Organic Chemistry

Chalmers University of Technology

SE-412 96 Göteborg

Sweden

ABSTRACT

Nanocrystalline cellulose, NCC, is the highly crystalline material that is formed when cellulose sources such as pulp or cotton is acid hydrolyzed under controlled conditions. A suspension of nanocrystalline cellulose was prepared by sulphuric acid hydrolysis of softwood kraft pulp. Thereafter chemical modifications were done to affect the properties of the NCC. The properties were examined. The chemicals used were Epoxypropyltrimethyl ammonium chloride, EPTMAC, and epoxypropylmethyl morpholinium chloride EPMMC. These chemicals were used to introduce cation charge to the NCC surface. Both EPTMAC as well as EPMMC consist of a reactive epoxy group and a trialkyl ammonium group. The charge of the nano crystalline suspension changed from negative in unmodified suspension to positive in the suspensions treated with cations. AFM showed that the nanocrystals contained their shape after cationization. In the rheological tests showed a different viscosity at the same shear rate, suggesting difference in properties for the suspensions with different cations. HPTMAC-NCC showed a slightly higher thixotropy.   HPTMAC-NCC also showed a lower gelling concentration, which is in agreement with its more pronounced thixotropy. The tetra alkyl ammonium reagents introduce cationic charges to the NCC surface and as a result make the material more hydrophilic. In a complementasry study the NCC was made more hydrophobic by introducing phenoxyacetyl groups on the NCC surface.

A series of phenoxyacetyl celluloses was prepared under slightly different reaction conditions. The reaction conducted in DMAc gave higher DS of the product than the reaction conducted in toluene. The DS was also possible to tune by varying he temperature and molecular ratio of the reagent. All the prepared phenoxyacetyl celluloses had good dispersability in DMAc; however, they were only partially dispersed in CH_2Cl_2 and $CHCl_3$, the dispersability of the particles increased when

increasing the reaction temperature and reagent ratio. From IR spectroscopy it could be concluded that the signals of C=O of the ester were affected by degree of substitution. Mesophases were observed for all of the phenoxyacetyl cellulose with low to medium DS in DMAc and acetone which was identified by the character birefringence.

Keywords: nanocrystalline cellulose, cationisation of cellulose, EPMMC, EPTMAC, , phenoxyacetyl cellulose, DS

ABBREVIATIONS

AFM   Atomic Force Microscopy

EPMMC   Epoxypropyl N-methylmorpholinium Chloride

EPTMAC   Epoxypropyl Trimethylammonium Chloride

NCC   nanocrystalline Cellulose

DS   degree of substitution

IR   infrared spectroscopy

PC   particle charge

DMAC   dimethylacetamide

CONTENTS

7

1. Introduction

Cellulose which is the most abundant polymer found in nature comes from different resources such as grass, wood and reed. The cellulose chains form microfibrils which can be described as thin threads with a length up to several micrometers, The microfibrils consist of amorphous part as well as crystalline domains (NCC). The degree of the crystallinity, ratio between the mass of the crystalline domains and the total mass of the cellulose[1,2] is different from species to species. Algal and tunicate microfibrils are highly crystalline (50%-83%)[3,4,5] whereas the wood microfibrils have lower crystalline. Controlled hydrolysis with acid, (e.g. hydrochloric or sulphuric acid) of the amorphous parts of the cellulose gives a highly crystalline rod-like material called nanocrystallin cellulose, NCC.

NCC has special colloidal and mechanical properties and can form stable suspensions in water. Since it has good stiffness, it can be found in various applications, such as reinforcing filler to increase the strength of thermoplastic materials[6] or for drug delivery[7]. Because of these reasons, the development of the NCC applications is very interesting. In this project the properties of the NCC will be tuned by surface chemical modification. Physical and chemical properties will be characterized and compared from the unmodified NCC. Conclusions will derive from the perspective of structure of the molecules.

EPTMAC and EPMMC were used to cationize NCC surface. The surface charge density was measured by conductometric titration. The shape and dimension of the crystals were characterized by AFM. The rheological properties were examined by measuring the change in viscosity over different shear rates. The gelling concentration

was checked by the gravimetric analysis. The molecular structure was identified by IR.

In part 2 the surface modification was performed by reacting the cellulose OH groups and the phenoxyacetyl chloride under slightly different reaction conditions. Products with different DS were obtained. The dispersability of the products in different solvent was studied. The modified chemical structures were checked by IR. The signals of C=O of the ester were affected by degree of substitution. The mesophases formations in polar and non polar solvent were recorded

2. Research

PART 1

2.1 Objective

Nanocrystalline cellulose (NCC) can be made by controlled acid hydrolysis of the cellulose fibers. It is possible to obtain NCC with a narrow size distribution by the centrifugation technique[8]. The nanocrystalline cellulose obtained has high specific surface area as well as high chemical reactivity as a consequence of a high ratio hydroxyl groups on the surface.

Upon chemical modification of the hydroxyl groups the NCC hydrophilicity is changed and to some extent also the size of NCC. Because cationic polysaccharides, such as starch, have been used in the paper industry for long, in order to increase filler retention and the dry strength of paper, there is an interest in exploring the properties of the cationized nanocellulose derivates. In this work two different cations, EPTMAC and EPMMC were added to NCC suspensions of the same concentration. The products were characterized by IR, AFM, rheological measurements and observation of gel formation in water suspensions.

2.2 Basic information

2.2.1 Cellulose Source

Forest is a big resource on earth. Of the wood composition approximately 40-50% is

cellulose. Wood can be divided into hard wood and soft wood. Hardwood has lower cellulose content compared to softwood (Fig. 1,2) and the cellulose composition of spring wood is lower than the summer wood. The cellulose content of the juvenile wood is lower than the mature wood.

Fig. 1 hardwood


Fig. 2 softwood

2.2.2 Molecule structure of cellulose

Cellulose is a high-molecular weight linear homopolymer which consist of D-glucopyranosyl units linking by 1, 4-β-glycosidic bonds. The hydroxyl group at the C_2 can form hydrogen bonds with the preceding ring oxygen. The hydrogen bonds

prevent the free rotation of the rings and as a consequence form stable chain structure[9]. (Fig. 3) The hydrogen bonding network is one of the reasons to that cellulose is insoluble in common solvents[10].
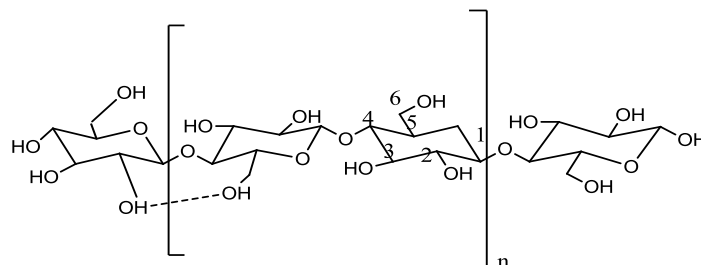

Fig. 3 repeating (1-4)-linked –β-D-glucopyranosyl units

The degree of polymerization (DP) is used to describe the average number of the monomer units in a cellulose chain. DP is dependent upon the origin of the cellulose material.

2.2.3 Fibrillar structure

In the wood, the smallest unit of the fibrillar structure is the elementary fibril, which is aggregated into larger fibrils which are embedded in a matrix of hemicelluloses and lignin. The figure below show how the fiber is composed of fibrils and the microfibrils. (Fig. 4)
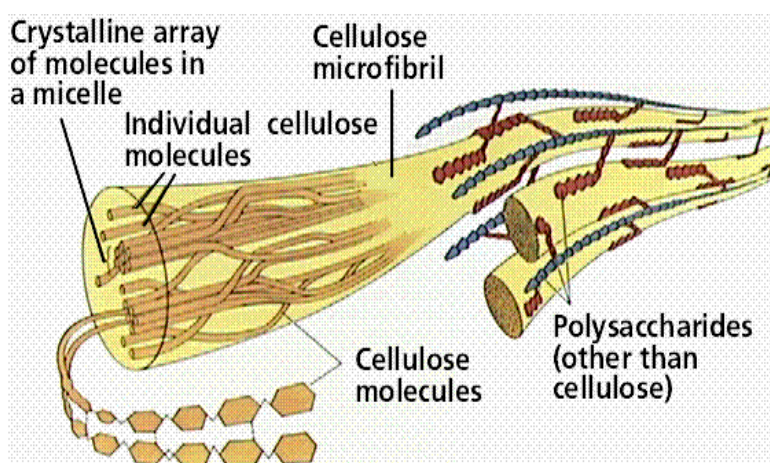
Fig. 4 The hierarchical structure of fibers Purve al., Life:The Science of Biology, 4th Edition

2.2.4 Crystalline structure

The cellulose exists in many different crystalline forms. The cellulose I (Iα, Iβ) and the cellulose II, III, IV, and they can be transformed into each other by chemical and thermal process.

From earlier studies, the crystalline structure has been revealed by ^{13}C NMR spectroscopy and X-ray fiber diffraction analysis. Native cellulose consists of a mixture of two crystalline crystalline forms Iα and Iβ lattice (Fig. 5). Iβ is mainly found in cotton and ramie, in this form two polysaccharide chains are arranged in a monoclinic unit cell. The Iα is predominant in algae and bacteria. The Iα has triclinic unit cell structure. The polysaccharide chain of them are the same although with a hydrogen boding pattern that is different compared to Iβ, the Iα can transfer into the Iβ, however, it is an irreversible process because the Iβ is more stable. The relative ratio of the two forms of lattice is dependent on the origin; as an example, the tunicate only consists of the Iβ.

(a) Iβ   (b) Iα
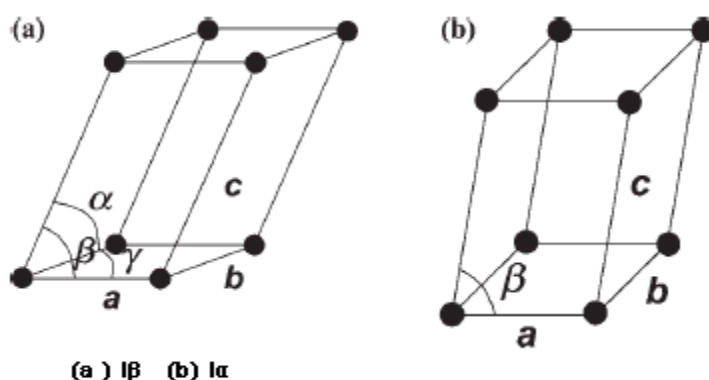
Fig. 5 crystalline forms Iα and Iβ lattice

The dimension of the nano crystsals vary from species to species. The length of nanocrystals from the algae and bacteria[13,14] are up to several micrometers while the length of the wood nanocrystals is shorter[12]. The width of algal cellulose nanocrystals [15,16] is similar to those of cotton whereas the crystallites from wood are smaller.[12,17]

Cellulose	Type length	Cross section
Tunicate	100 nm – several μm	10-20 nm
Bacterial	100 nm - several μm	5-10 nm by 30-50 nm
Algal (Valonia)	>1000 nm	10 to 20 nm
Cotton	200-350 nm	5nm
Wood	100-300 nm	3-5 nm diameter

Table 1 Dimensions of cellulose nanocrystals from various sources

The dimensions and shape of the isolated nanocrystals` are determined not only by the origin but also by the hydrolysis condition (e.g. acid, the reaction time, concentration, and temperature).

The acid will break the cellulose chains, and hydrolyze the glycosidic bonds in the amorphous part and as a result separate the crystallite domains.

2.2.5 Suspension properties

The nanocrystalline cellulose can produce stable colloidal suspensions because of the repulsive electrostatic force between the particles resulting from the sulfuric acid hydrolysis (e.g. sulfate group from the sulfuric acid).

In a dilute system, the NCC particles are randomly oriented; ordered in a isotropic phase[18]. As the concentration increase, (by evaporation), NCC suspensions begin to separate to two layers. The smaller particles are in the isotropic phase on the top and the longer rods are in the anisotropic phase at the bottom.[19] Above the critical

concentration there will be separation into isotropic and anisotropic phase. When the concentration reaches the critical concentration, the anisotropy phase will spontaneously change into chiral-nematic crystalline phase. The stability of the suspension depends on the surface charge density of the particles, the charge distribution and the size of the nanoparticles.

2.2.6 The chemical modification

Two cations, one commercial available, EPTMAC and one produced by the reaction reacting epichlorohydrin with the tertiary amine N-methyl morpholine were used in this project.

Epoxy propyl trimethylammonium chloride, EPTMAC, is commonly used as cationizing agent in the paper and textile Industry. When stored in water it forms a chlorohydrin form that upon reaction with sodium hydroxide forms the epoxide form.
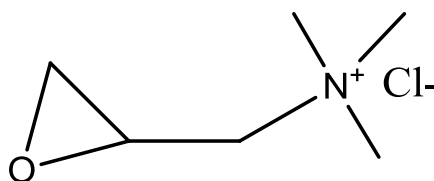
Fig. 6 Structure of EPTMAC
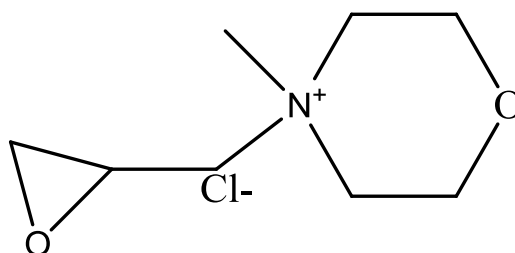
Fig. 7 Structure of EPMMC with chloride

Epoxypropyl N-methylmorpholinium chloride EPMMC (Fig. 7) is also used as cationizing agent.

2.3 The method

This segment will give a profile of the method used during the project. The details can be found in the experimental section.

The first task was to prepare nanocrystalline cellulose (NCC) from a never dried industrially produced softwood kraft pulp. The nanocrystalline cellulose was prepared by hydrolysis with sulfuric acid. Since the epoxy group has a quite similar reactivity towards the accessible hydroxyl groups on the NCC surface and water it is a prerequisite to minimize the amount of water in the reaction. High amounts of water present in the suspension will reduce the possibility for the cations to react with the hydroxyl group on cellulose. To avoid this side reaction the NCC suspension was concentrated to the concentration approximately 5% (w/w).

The following step was cationizing the nanocrystalline cellulose with two different regents, EPTMAC and EPMMC, both of them containing quaternary amines cations. Conjugating cations to the NCC suspensions was performed after the alkalinisation of cellulose with sodium hydroxide.

The dimensions of the product were analyzed by AFM and the charge density of the cationisation suspensions was measured by conductometric titration. Rheology tests were performed in order to study the different fluid behaviors of the two cationized products and reference NCC.
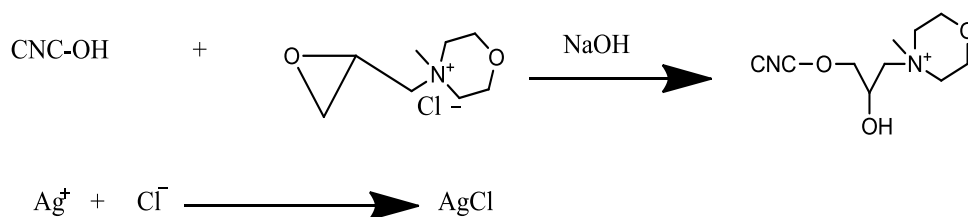
2.4 Result and discussion

2.4.1 Characterization Cationised nanocrystalline cellulose

2.4.1.1 NMM-NCC

The cationized cellulose by EPMMC was with chloride as counter ion on the surface. To determine the degree of cationization the amount of chloride was determined. In the ttitration 1 mol of Ag^+ consumes 1 mol of Cl^- corresponding to one substituted

hydroxyl group on the NCC surface (assuming that all counterions on the ammonium substituents are Cl⁻.

$CNC\text{-}OH$ + [epoxide-morpholinium structure with Cl^-] $\xrightarrow{NaOH}$ [$CNC\text{-}O$ morpholinium structure with OH]

Ag^+ + Cl^- ⟶ $AgCl$

Fig. 8 Conductometric titration NMM-cellulose by AgNO₃

0.01M $AgNO_3$ was added to a pre-determined amount of substituted NCC. $AgNO_3$ was added to that the equivalens point was reached. ; The conductivity trend line was plotted. (Fig. 9)
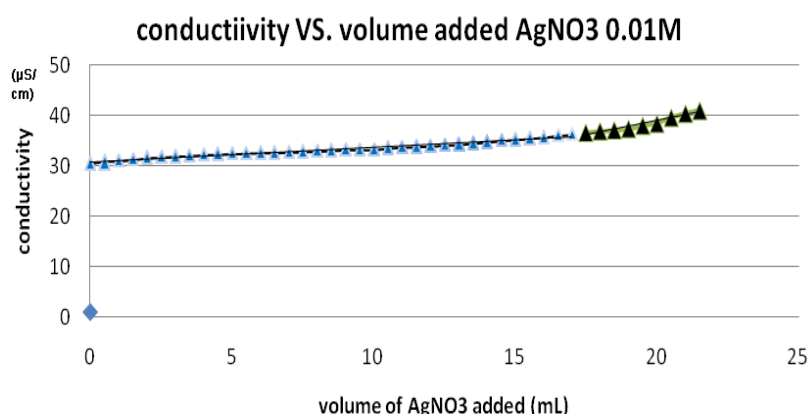
Fig. 9 the conductivity trend line for NMM-NCC

When all Cl⁻ has been consumed by the added $AgNO_3$ solution the number of ions in solution starts to increase which is shown by an increase in conductivity. The result shows that the conductivity was quite stable from the beginning of the $AgNO_3$ addition; this is due to that Cl⁻ is neutralized by reaction with Ag^+. However, since NO_3^- is introduced in equilar amount to the solution, the net charge concentration was not changed until all chloride ions were consumed. The entire molar amount of Cl⁻

which equal to the molar amount of Ag^+ before the equiv. point was exhausted. The equiv. point appeared at 17.133ml The DS of NMM-NCC from titration methods was calculated to 0.44. The calculation is shown in Appendix2.

2.4.1.2 HPTMAC –NCC

The titration method was the same as the method used for the NMM-NCC (Fig. 10)
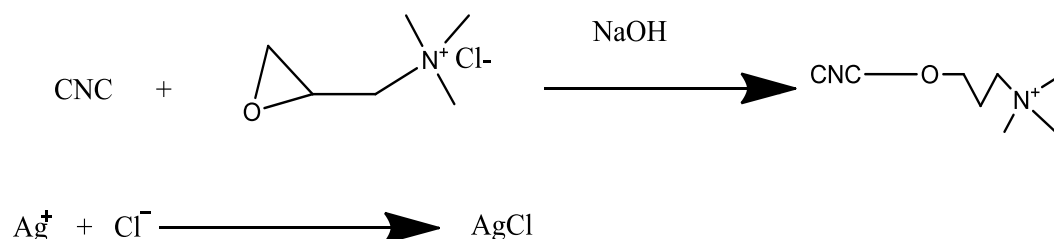
Fig. 10 Conductometric titration HPTMAC-cellulose by AgNO3

Conductivity was recorded (appendix1) and the weight of HPTMAC-NCC suspension was 104.7g (0.3258% w/w) Conductometric titration trend line was plotted. (Fig. 11)

The trend line showed that Cl^- was not on the NCC surface. The possibility was that the Cl^- was replaced by OH^- during the cationisation because of the high alkali content in the HPTMAC-NCC suspensions (0.3258% w/w). During the dialysis after the cationisation, Cl^- was filtered off; therefore the titration could not detect any Cl^-.
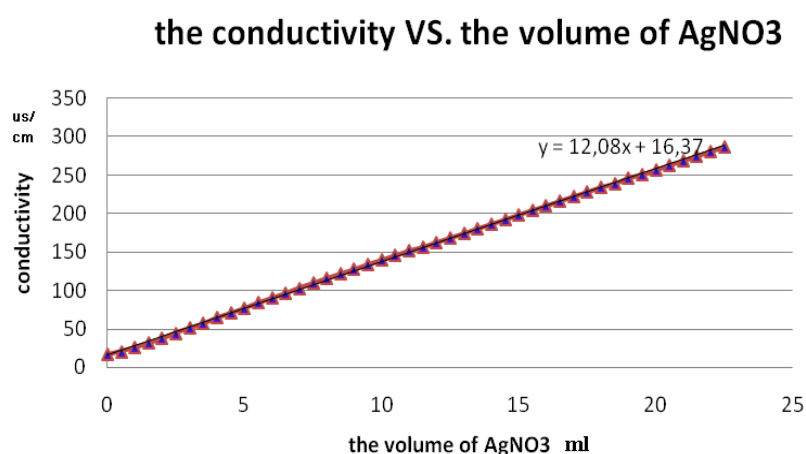
Fig. 11 Conductivity trend line for HPTMAC-NCC

2.4.1.3 Gelling concentration

Gelling concentrations measured for the cationized NCC. (Table 2)

Cationized NCC	Average gelling concentration
NMM-NCC	4.12%
HPTMAC-NCC	2.46%

Table 2 Comparison between NMM-NCC and HPTMAC-NCC

2.4.2 Comparison between unmodified and cationized NCC

2.4.2.1 The surface charge concentration vs. zeta potential

Zeta potential is the electrophoretic mobility of the particle determinated by the size and surface charge of the particles. The significance of zeta potential is that its value can be related to the stability of colloidal system which consisted of the particles.

	DS value	Zeta potential (mv)
Reference NCC	Blank	+0.003
NMM NCC	0.44	+19.6
HPTMAC NCC	No result	+19.9

Table 3 Comparing zeta potential of the unmodified NCC and cationized NCC, there are obvious differences.

The sulfuric acid hydrolysed NCC has negative charge surface. The zeta potential should be negative in theory; however, nanocrystalline cellulose was heated in order to increase the concentration. The sulfate ester groups were hydrolyzed off, resulting in the slightly positive zeta potential. The zeta potentials of the both cationized NCC were positive as expected. The similar zeta potential means that the charge density obtained by two cationizations was similar.

2.4.2.2 Morphology studied by the AFM imaging

The suspension was white and pale yellow after hydrolysis. The ultrasonic treatment after the cationization and dialysis was important in order to disperse the aggregates. Sample from the successful reactions were analyzed with atomic force microscopy which gave the dimensions of the nano crystals.

Figure 12 shows the hydrolyzed NCC in agreement with previous results of Hasani et. al., 2008.
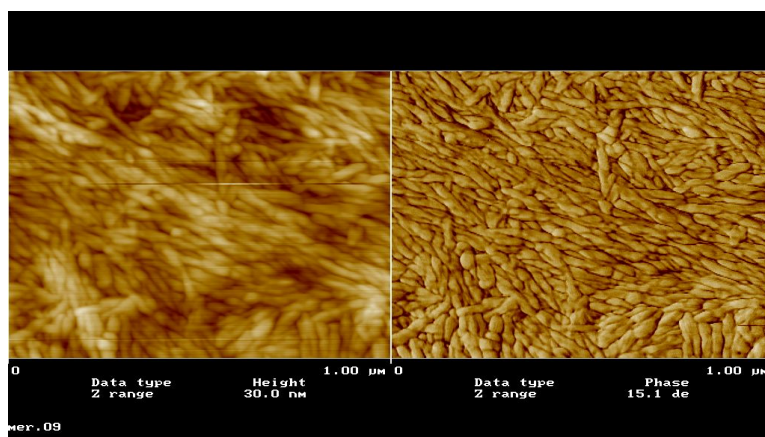
Fig. 12 AFM image of NCC.

The treatment of the NCC with the EPTMAC (Fig. 13) and EPMMC (Fig. 14) did not change crystalline particles formed from the original NCC, the average length was 360nm.
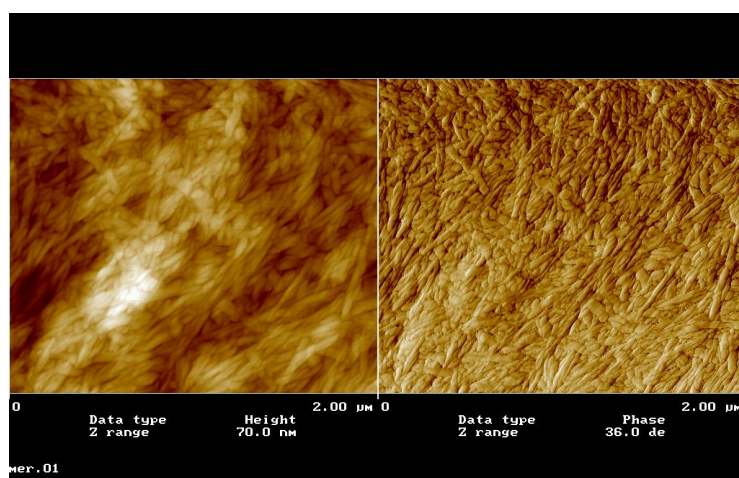
Fig. 13 AFM image for the NMM-NCC

Data type   Height   Data type   Phase
Z range   50.0 nm   Z range   108 de
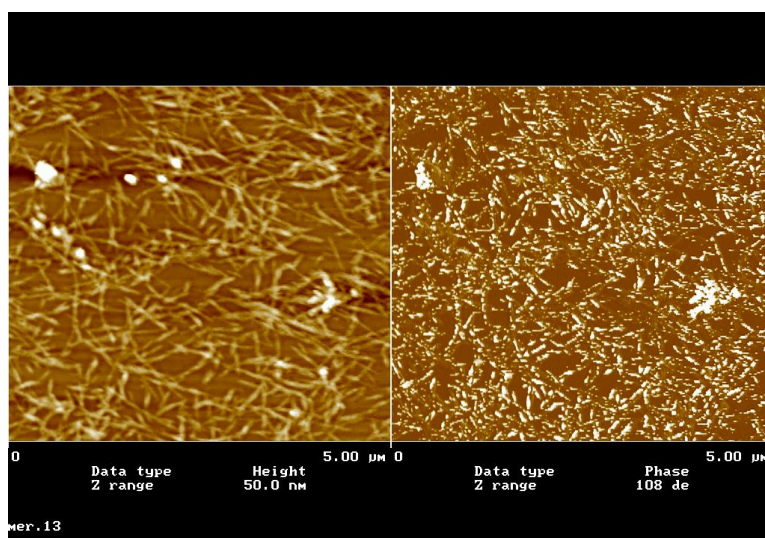
Fig. 14 AFM image of the HPTMAC-NCC

2.4.2.3 Rheology

Oscillatory shear tests were used in detecting the variation of dynamic viscosity as a function of shear rate for NCC (2.1%, W/W), NMM-NCC (2.3%, W/W), HPTMAC-NCC (2.1%, W/W) suspensions in water.

The results of the oscillatory shear tests on NCC, HPTMAC-NCC and NMM-NCC suspensions in water are shown (Fig. 15).

Fig. 15 Oscillatory shear tests on native NCC and HPTMAC-NCC and NMM-NCC suspensions.

NCC before and after modification dispersed well in water. A tendency of thixotropy can be seen. A closed loop was formed. Viscosity is decreased with the increasing shear rate. When the shear rate is decreased again viscosity doesn't increase to the initial level, but retains relatively low values, be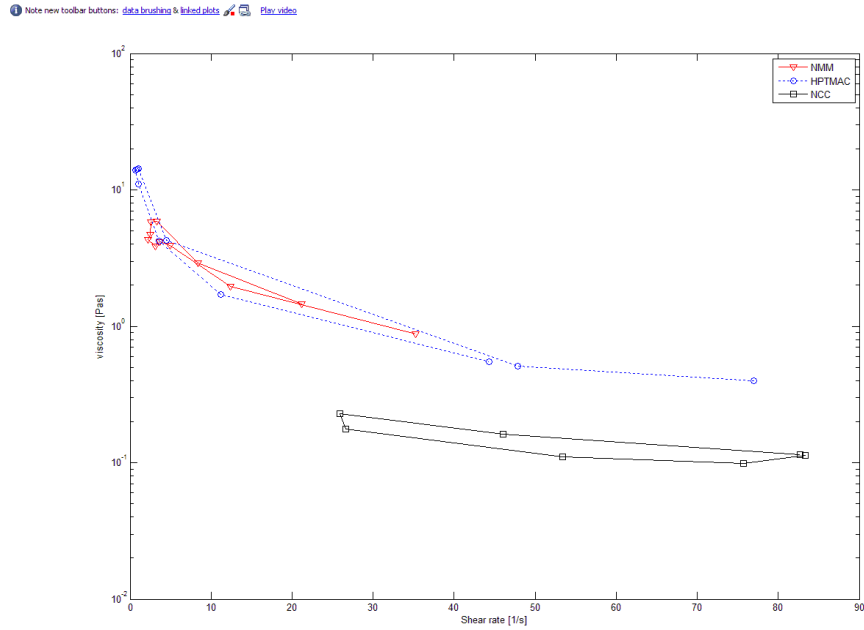cause the gel structure was disrupted during the agitation (increase of the shear rate) and it started to behave as a liquid. After certain time (as the shear rate is continuously decreased) the gel will be re-formed and the viscosity will increase to its initial value.

HPTMAC-NCC showed a slightly higher thixotropy. HPTMAC-NCC also showed a lower gelling conc., which is in agreement with its more pronounced thixotropy.

2.5 Experiment section

2.5.1 Materials

2.5.1.1 Materials

Never-dried, industrially produced, TCF-bleached (peroxide-based sequence) Scandinavian soft kraft pulp (from Södra Cell, Sweden) is used as starting material for the NCC preparation.

Spectrum Spectra/Por regenerated cellulose dialysis membranes, molecular weight filter of 12000-14000 Da were used for dialysis.

2.5.1.2 Chemicals

2, 3-Epoxypropyltrimethylammonium chloride, (EPTMAC) was purchased from Fluka and used as received. N-methylmorpholine and epichlorohydrine were purchased from Aldrich. The sulfuric acid volumetric standard (95%-97%) for hydrolysis was purchased from Sigma. Dilution of the sulfuric acid to 64% (w/w, 360ml distilled water, 349ml sulfuric acid), cooling down for one night.

Sodium hydroxide and silver nitrate for the titrations was purchased from Aldrich. Deionized water (18.2 MU cm, Millipore Milli-Q Purification System) was used without pH adjustments.

2.5.1.3 Apparatus

Atomic force microscope: Digital instrument Ⅲa, with a type G scanner,Micro Masch NSC 15, silicon cantilever; Centrifuge: Heareus; Conductmetric Analyser:EcoScan from Euten instruments; Vibracell sonicator: VC 505 CiAB; Rheometer: Bohlin VOR Millennium Rheometer

2.5.2 Methods

2.5.2.1 Pulp treatment

The pulp was dried for two days in a fume hood at ambient condition; the dry pulp was cut into pieces, and milled to pass through 20-mesh screen.

2.5.2.2 Sulfuric acid hydrolysis

Suspensions of cellulose nanocrystals were prepared as follows: 40g pulp was treated

with 700ml of sulfuric acid (64% w/w). The reaction was performed at 45℃ for 45 min with constant stirring. Immediately following hydrolysis, the suspensions were diluted to 10-fold with distilled water to stop the reaction while cooling in ice bath to avoid overheating.

2.5.2.3 Centrifugation

The suspensions were then centrifuged at 4000rmp for 10 min to concentrate the nanocrystalline cellulose. The excess acid and water was removed. The resultant precipitate was washed once with water, and recentrifuged. Supernatant was removed.

2.5.2.4 Dialysis

Diluting the re-concentrated nanocrystalline cellulose to 5-fold, the filled dialysis membrane was placed in distilled water for 7 days. The water was changed twice a day till the neutral pH was achieved and remained constant.

2.5.2.5 Evaporation

The suspensions from all the membrane were combined and evaporated at reduced pressure to concentrate the nanocrystalline cellulose. The concentration of the cellulose after evaporation was determined as follows: Several ml of sample in a vial were weighted and stored in an oven for the whole night. The remaining solid part was weighted. The ratio of the weight before and after the heating is the concentration, w/w, of the nanocrystalline cellulose prepared.

$$\text{The concentration of the NCC suspensions} = \frac{\text{the weigt of the solid sample of the NCC after heating in the oven}}{\text{the totla weight of the sample includingthe water beore heating}}$$

The suspensions were evaporated at the reduced pressure until the concentration was about 6% w/w.

2.5.2.6 Sonication

To obtain colloidal and homogenous cellulose suspensions, the suspensions were sonicated for 5*7 min with the intensity of 60% output while cooling in ice bath to avoid overheating.

2.5.2.7 Cationisation of NCC

Alkalinisation of the suspension: The concentrated suspension was alkalinized with 5% NaOH with the ratio of 1M OH group equivalent to 1.5M NaOH for 15 min at room temperature with stirring.

Cationisation (Fig. 16, Fig. 17): EPTMAC or EPMMC (1.5 equiv/cellulose hydroxyl group) was added into suspensions, which were alkalinized by NaOH treatment and the mixture was stirred for 5 hours at 50 ℃. After 5 hours, the reaction was quenched by water and diluted to 5-fold and dialyzed against distilled water for 5 days. The water was changed once a day until the conductivity of the dialyzed water was constant. Suspensions were sonicated and concentrated by reduced pressure evaporation in the room temperature.
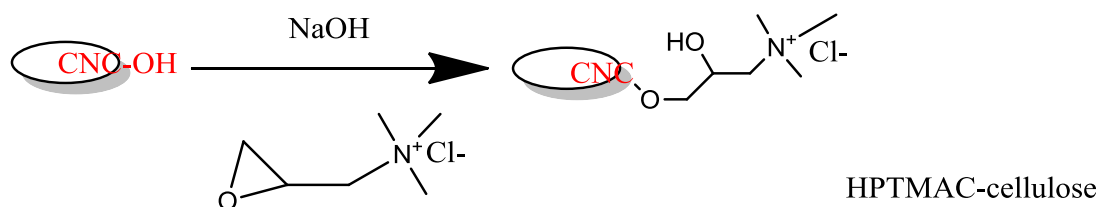
Fig. 16 Cationisation with EPTMAC
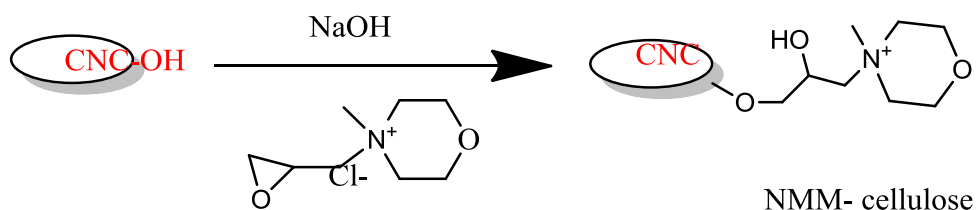
Fig. 17 N-(2, 3-Epoxypropyl)-N-methylmorpholinium chloride reacted with cellulose formed a white cellulose derivative - NMM-cellulose

2.5.2.8 Conductometric titration analysis

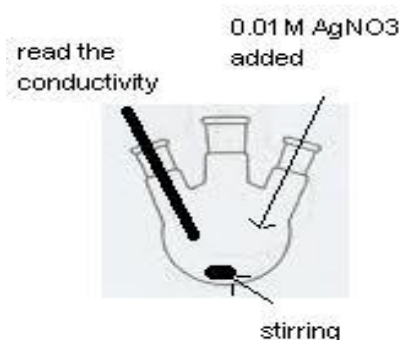Conductometric titration was used to quantify the amount of cations on the surface assuming that all of them coordinate to chloride counterions on the surface of the nanocrystalline cellulose.

The suspensions of modified NCC were titrated with 0.01M AgNO$_3$, (Keep the prepared AgNO$_3$ solution in the dark). Every 30 seconds approximately 300μl of the AgNO$_3$ was added, and the conductivity was measured. (Fig. 18).

Fig. 18 Conductometric titration measuring the charge density of NCC

Atomic force micro spectroscopy

A sample of the suspension was diluted to 10^{-5}ml and added to a mica plate. The AFM analysis was performed at Polymer Technology, Chalmers.

2.5.2.9 Gravimetric anaysis

In order to obtain the gelling concentration of the NCC suspension, gravimetric analysis was performed. Forms were made of the slide glass; two to three measurements were made for each sample. First the form was weighted and 1ml suspension was added and the mass was weighted again and noted, the form was place in an oven at 105 ℃, for a couple of hours to evaporate the water, the form was weighted again and the mass of particles could be determined by subtraction the original mass of the foil.

2.5.2.10 Rheology test

The suspensions were evaporated to a concentration of 2% (w/w), approximately 1.5 ml of suspension was applied to the horizontal plate on the viscometer and viscosity was read for shear from 5.58 to 233 $\gamma°/s^{-1}$ for each sample.

PART 2

2.2 Objective

Cellulose and many of its derivatives form liquid crystalline phases in solutions and melts, because of the chirality of the cellulose backbone, cellulosic liquid crystalline phases form chiral nematic structures. A series of phenoxyacetyl celluloses prepared under slightly different reaction conditions was synthesized. The dispersability of the products with varied DS in DMAc and CH_2Cl_2, $CHCl_3$, toluene, acetone was studied and discussed. The modified chemical structures were analyzed by IR. The signals of C=O of the ester were affected by degree of substitution. The mesophases formations in polar and non polar solvent were recorded.

2.3 Basic information

Liquid crystalline materials generally have several common characteristics. These have a rod-like molecular structure, rigidness and are strong dipoles or contain easily polarizable substituent.

The distinguishing characteristic of liquid crystalline state is the tendency of the molecules to point along a common axis, named the director. This is by comparison to molecules liquid phase, which is not in well-organized order. While in the solid state, the molecules are highly order, however, have little translational freedom. The characteristic orientation order of the liquid crystal state is between the solid and liquid phases. (Fig. 19)

Solid   Liquid Crystal   Liquid
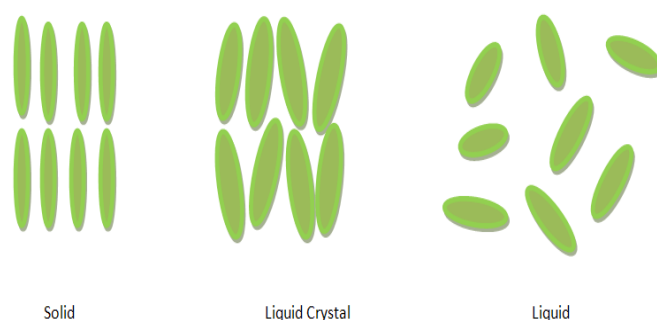
Fig. 19 Alignment of the molecules in different phases.

It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions while an isotropic liquid has no orientational order. Liquid crystals are not as ordered as a solid, yet have some degree of alignment. Their properties are found between solid and liquid.

Nanocrystalline cellulose is the cellulose crystalline domains obtained with sulphuric acid. An investigation reveals that NCC is randomly oriented in the dilute solution, while a nematic liquid crystalline alignment appears when the NCC concentration increases. Nematic phase is an arrangement in which the rod-shaped particles align with their axes in parallel lines. (Fig. 20)
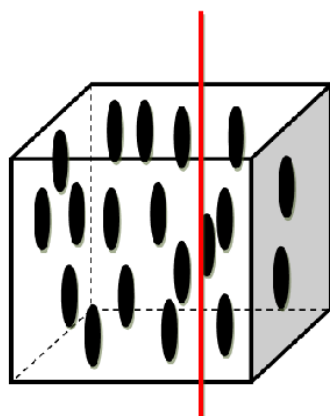
Fig. 20 molecules alignment in a nematic phase

When the suspension reaches a critical concentration of the NCC, it forms chiral

nematic liquid crystal. This means that the rod-shaped particles arrange in different layers. With long axis aligned in the same direction in each layer and with a certain angle twist between the layers.(Fig. 21)
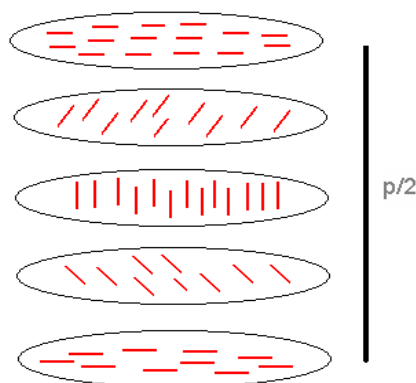
Fig. 21 The chiral nematic phase

The spontaneous helical self-assembly are often observed in naturally occurring materials containing cellulose[20,21,22]. Helical structure packing is assumed to be induced by the asymmetry. Revol and Marchessault supposed the twist in the NCCs itself due to the negative charges from ionized sulfate groups on the surface of NCCs give rise to the helical twist. For this reason suspensions of uncharged NCCs generated from HCl, do not has the chiral nematic order. Recent studies showed that the surface modification[23] and polymer grafting[24] do not prevent formation of chiral nematic phases Cellulose derivatives form an interesting range of polymer liquid crystals. Many of these derivatives form liquid crystals in suitable solvents. Anistropic solutions of cellulose acetate (Fig. 22) and triacetates in trifluoroacetic acid are attractive cellulose derivative. optical properties[25.26], the refractive index[27], phase boundaries[28], nuclear magnetic resonance spectroscopy[29,30] and different scanning calorimetry[27] have been reported for a variety of cellulose derivates with liquid crystals properties.
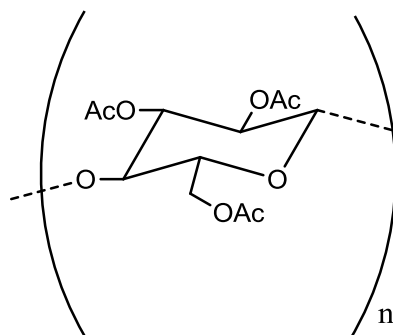
Fig. 22 Triacetates cellulose

The liquid crystalline mesophase formed by another cellulose derivative hydroxypropylcellulose (HPC) (Fig. 23) in water is stable and easy to handle. HPC displayed iridescent color that changed with concentration and viewing angle[31]
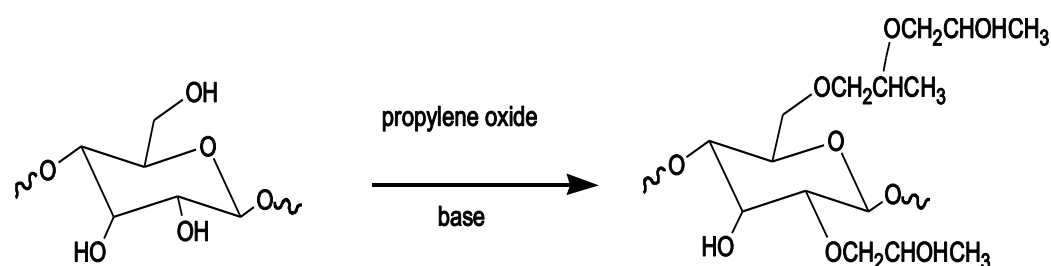
Fig. 23 Hydroxypropyl cellulose (HPC)

The cellulose ester, phenylacetoxy cellulose has been shown to form both thermotropic and lyothopic mesophase and to readily regenerate into cellulose. I report the synthesis and mesophase properties of a similar structure which is phenoxyacetyl NCC, the solubility and structure modification, and the birefringence of the products from different reaction conditions are reported. This phenoxyacetyl NCC gave stable suspensions as expected and the crystalline suspensions in DMAc and acetone showed birefringence.

2.4 Result and discussion
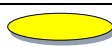
2.4.1 Phenoxyacetate nanocrystalline cellulose synthesis

Phenoxyacetate-NCC was prepared by reacting nanocrystalline cellulose with chloroacetyl chloride in DMSO, and then the product continually reacted with phenol using NaOH as the catalyst in the same solvent. The strategy was practiced both at room temperature and at 60 ℃ without destroying the cellulose crystalline structure. Unfortunately the products obtained did not show any phenol ether or benzene signals in infrared spectroscopy.

The reason was supposed to be that phenol with a bulk molecular structure difficultly reached the surface of the nano crystalline particles whose hydroxyl groups were highly substituted by the acetyl chloride.

The synthesis method was changed by employing a one-step reaction of phenoxyacetyl chloride with nanocrystalline cellulose instead. Pyridine was utilized as the catalyst and acid scavenger to neutralize the HCl generated. DMAc and toluene were used as reaction media.

Nanocrystallince cellulose was more dispersed in DMAc than in toluene. With different reagent ratio the reactions were conducted under heterogeneous conditions. in the more polar solvent (DMAc) and the less polar solvent (toluene) by slight heating and no heating. The products showed different color and state (Table 4)

Reaction			Product	
Solvent	Ration (1OH glucose unit/phenoxyacetyl)	Temperature °C	Color	State
DMAc	1:2	room		Powder
DMAc	1:2	55		Block
DMAc	1:3	Room		Powder
Dmac	1:3	55		Block ,sticky
Tolene	1:0.5	55		Block
Tolene	1:3	55		Block

Table 4 different color and state of the products

The reactions were conducted in tolene systems, since none of these solvents can dissolve cellulose. The color of the product ranged from white (Low DS) to lightly yellow (high DS). The high temperature and high regent ratio improved the yield and yellow coulor(High DS) products were always obtained. DMAc reaction system yielded higher degree of substitution in shorter reaction time partly because NCC suspension in DMAc is stable and the one in toulese is not. Furthermore, DMAc is better in activating cellulose surface than toluene, which is the reason cellulose is more reactive in this solvent.

2.4.2 Dispersability

The dispersability was checked as followed 10 mg product was dispersed in 1ml solvent selected in room temperature; the solubility was recorded (Table 5)

sample	solvent			CH$_2$Cl$_2$	CHCl$_3$	EtOH	Aceton	DMAc	Iso-propanol
1	DMAc	no heating	1vs2	↓ ○ 0	↓ ○ 0	↓ ○ 0	↓ ○ 0	↓ ≡ 3	↓ ○ 0
2	DMAc	no heating	1vs3	↓ ● 0	↑● 0	↓ ● 0	↓ ● 0	↓ ≡ 4	↓ ● 0
3	DMAc	heating	1vs2	≡ 4	↑≡ 3	↓ ○ 0	↓ ≡ 3	* 5	↓ ○ 0
4	DMAc	heating	1vs3	* 5	≡ 4	↓ ○ 0	* 5	* 6	↓ ○ 0
5	Toluene	heating	1vs0.5	↓ 2	↓ ≡ 2	↓ ○ 0	↓ 2	↓ ≡ 3	↓ ○ 0
6	Toluene	heating	1vs3	↓ 3	↓ ≡ 3	↓ ○ 0	↓ 3	↓ 4	↓ ○ 0

Table 5 the solubility of the products from different conditions in selected solvent
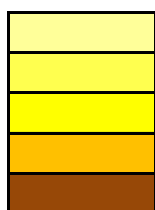
Solvent color

**Small swollen particle○ Big swollen particle● Insoluble particle precipitate ↓
Insoluble particle float ↑ Homogeneous suspension≡ Solution ＊**

Very soluble 6, Free soluble 5, Soluble 4, sparingly soluble 3, slightly soluble 2, Very slightly soluble 1, Insoluble 0

The dispersability was greatly affected by the DS by replacing the hydroxyls with phenoxyacetyl groups. Heating at 55℃, reagent ratio with 1OH equiv. / 3 phenoxyacetyl chlorides in DMAc resulted in higher DS products, which had good dispersability appearing as clear solutions, less insoluble part or smaller swollen particles.

Phenoxyacetyl cellulose with different DS had the best dispersability in DMAc; it was difficult to disperse in alcohol and iso-propanol.

2.4.5 Infrared spectroscopy
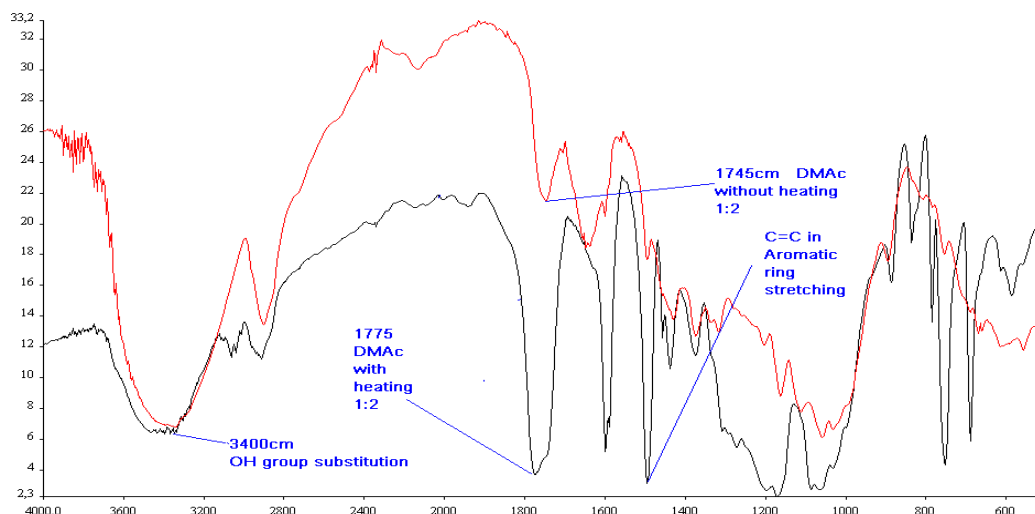
Fig. 25 IR spectroscopy of phenoxyacetyl-NCC from polar solvent

An FTIR spectrum of phenoxyacetate nanocrystalline cellulose was measured with a Perkin-Elmer 16Pc FTIR spectrophotometer as KBr pellets.

The IR spectroscopy showed a decrease in the absorbance around 3400cm-1, indicating the cellulose OH group substitution.

Comparing with the non-modified nano crystalline cellulose, a strong absorption appeared at 1745cm-1 (without heating the reaction, phenoxyacetyl chloride equiv. to 2 OH groups, DMAc) or 1775cm-1 (with heating the reaction, phenoxyacetyl chloride equiv. to 2 OH groups, DMAc). These peaks were indicative for the carbonyl functionality of esters. The reason for the different absorptions was supposed to be the effect of the intra molecular hydrogen bonding between the hydrogen of hydroxyl group at position 2 and the C-O of the ester at position 6 and the inter molecular hydrogen bonding between the hydrogen of the hydroxyl group at position 3 and the C-O of the ester at position 6 (Fig. 26). It might also be affected by substituting different positions in cellulose under different reaction conditions. For the high DS

products, more OH groups at position 2 or 3 were substituted. The effect of the hydrogen boding was weakened. The signal of the C=O will appear at the 1775 cm-1 with the less hydrogen boding existing.

In addition the absorption at the 1449cm-1 is indicative of aromatic C=C stretching associated with the phenoxyacetyl substituent.
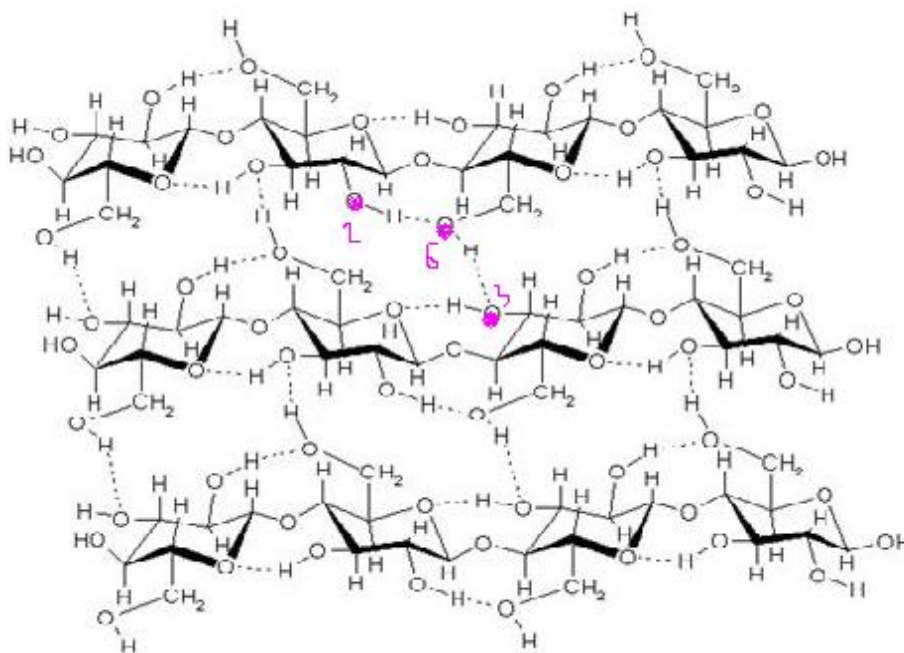
Fig. 26 Inter molecular and intra molecular hydrogen bonding in cellulose.

2.4.6 Mesophase formation in solution

High dispersability of rigid nano crystalline cellulose particles in a certain solvent does not guarantee the formation of the liquid crystalline state. Mesophase formation is a delicate balance of crystalline particles-solvent interactions. If the particles are too soluble mesophase formation will not occur, rather forming a gel at a higher concentration. Therefore the formation of the mesophases is strongly influenced by the degree of substitution and the distribution of substituent, and solvent used.

1g products from different reaction conditions (with different DS) were dispersed in

10 ml DMAc, acetone or toluene and sonicated with 60% output for 3 mins. Mesophase formation was determined by the appearance of birefringence. Solutions that did not exhibit birefringence were considered isotropic. The texture of the solutions was observed at room temperature.

Phenoxyacetyl cellulose	DMAc	Acetone	Toluene
DMAc 1:2 heating	Mesophase	mesophase	Isotropic
DMAc 1:2 noheating	Mesophase	mesophase	Isotropic
DMAc 1:3 heating	Isotropic	Isotropic	Isotropic
DMAc 1:3 noheating	mesophase	mesophase	Isotropic
Toluene 1:3 heating	Mesophase	mesophase	Isotropic
Toluene1:0.5 heating	Mesophase	mesophase	Isotropic

Ratio: 1 OH equiv. /phenoxyacetyl chloride

Table 6 the effect of solvent and products on mesophase formation was recorded

The products with the high degree of substitution from the reaction condition (DMAc 1:3 heating) did not display the character birefringence of liquid crystal cellulose because of the good dispersity in DMAc. Unfortunately the product with different DS almost precipitated in toluene and as a consequence did not form mesophase either. (Fig. 27)

Fig. 27 Birefringence of Phenoxyacetyl cellulose suspension in DMAc (DMAc 1:2 heating)

Other medium DS value products showed the obvious characteristic birefringence for liquid crystalline cellulose in DMAc and acetone.

The effect of solvent and DS for the mesophase forming needed further investigation.

2.5 Experiment section

2.5.1 Materials

Chemicals were used as obtained from manufacturer. The never-dried, industrially produced, TCF-bleached (peroxide-based sequence) Scandinavian softwood Kraft pulp, from Södra Cell, Sweden. Phenoxyacetyl choride was purchased from Fluka and used as received. Deionized water (18.2 MΩ cm,Millipore Milli-Q Purification System)was used without pH adjustment, pyridine and DMAc were obtained from Aldrich.

Sulfuric acid volumetric standard (95%-97%) for hydrolysis was purchased from

Sigma.

2.5.2 Method

The cellulose phenoxyacetate was synthesis by the reaction of cellulose with the phenoxyacetyl chloride using pyridine as the catalyst. (Fig. 24)
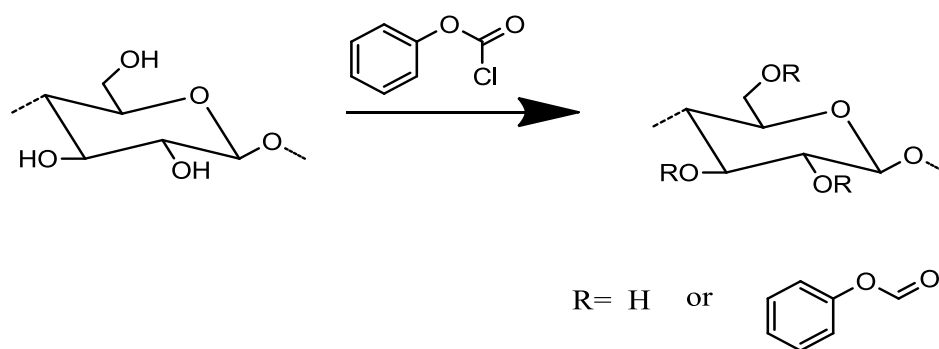
Fig. 24 cellulose phenoxyacetate synthesis

In a typical reaction, 1g powder of the nanocrystalline cellulose was dispered in 20ml dry DMAc or toluene and then sonicated for 30 seconds at the 60% output. , Pyridine (1 equiv. /1OH) was added and the solution was heated to 70 ℃ with the constant stirring for 30 min. The phenoxyacetyl chloride was added dropwise to the cellulose solution in three equal portions at 0, 1, 2h with different molar ratio (OH/ phenoxyacetyl) and solvent. (1:2 in DMAc; 1:3 in DMAc 1:0.5 in toluene, 1:3 in toluene) The reaction was stirred at 70 ℃ for 11h. After 11 h the reaction was allowed to cool to room temperature by quenching in water. The product was dialyzed against distilled water for 7 days, filtered and washed with the methanol /water (50/50, v/v), and dried under vacuum at room temperature. The reactions with the same reagent ratio in DMAc were repeated without heating with a longer reaction time (over night).

3. Conclusion

The main conclusion is that it is possible to change the property of the nanocrystalline cellulose by cationization and reactions with acetyl chloride.

The AFM pictures show cellulose particles with the expected rod-like shape, cationization process did not change the shape to confirm that the cationisation reaction does not affect the oeral structure of thetystals. The particles charges of suspensions treated with cations are positive, implying a successful cationization. To say anything about the degree of the substitution, conductometrric titration measurement gave the result approxietly 0.4Cationization increase the thixotropy compared the unmodified NCC. The differences also appeared between the suspensions treated with cations in gelling concentration and rheology under the similar DS. HPTMAC-NCC showed a lower gelling conc., which is in agreement with its more pronounced thixotropy.

In part two, the phenoloxyacetyl cellulose was synthesized under different condition, the result shows that the products has higher DS (deeper color) under the higher reaction ration and temperature in the same reaction solvent. The DMAc is more activated solvent for the nano crystalline cellulose. For all the products, the DMAc is the best dispersity solvent at the same concentration. And the

For the high DS products, more OH groups at position 2 or 3 were substituted. The effect of the hydrogen boding was weakened. The signal of the C=O in IR shift to the left. The product with higher DS value did not show any character birefringence as identification of the mesophase formation, because good dispensability. Unfortunately

the entire product almost precipitated in toluene and as a consequence did not form mesophase either. Otherwise the medium DS value products showed the character birefringence in DMAc and acetone because the good interaction between the product and the solvent.

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APPENDIX 1

Conductometric titration data for the NMM-NCC

conductivity	Correction	corr. Conductivity
us/cm	Factor	us/cm
30.5	1	30.5
30.9	1.04864339	32.40308075
31	1.010809642	31.33509891
31.2	1.016214463	31.70589125
31.6	1.021619284	32.28316939
31.7	1.027024106	32.55666414
31.9	1.032428927	32.93448276
32	1.037833748	33.21067993
32.2	1.043238569	33.59228192
32.3	1.04864339	33.87118149
32.4	1.054048211	34.15116204
32.5	1.059453032	34.43222354
32.6	1.064857853	34.71436601

32.6	1.070262674	34.89056318
32.7	1.075667495	35.1743271
32.8	1.081072317	35.45917198
32.9	1.086477138	35.74509783
33	1.091881959	36.03210464
33.2	1.09728678	36.42992109
33.2	1.102691601	36.60936115
33.2	1.108096422	36.78880121
33.5	1.113501243	37.30229164
33.7	1.118906064	37.70713436
33.8	1.124310885	38.00170792
33.9	1.129715706	38.29736245
34.1	1.135120528	38.70760999
34.2	1.140525349	39.00596692
34.5	1.14593017	39.53459086
34.7	1.151334991	39.95132418
35	1.156739812	40.48589342
35.2	1.162144633	40.90749108

35.4	1.167549454	41.33125068
35.7	1.172954275	41.87446763
36	1.178359096	42.42092747
36.2	1.183763917	42.85225381
36.6	1.189168739	43.52357583
36.9	1.19457356	44.07976435
37.1	1.199978381	44.51919792
37.4	1.205383202	45.08133175
38	1.210788023	46.00994487
38.4	1.216192844	46.70180521
39.6	1.221597665	48.37526754
40.4	1.227002486	49.57090044
41	1.232407307	50.5286996

The conductometric titration data of HPTMAC-NCC

AgNO3 added ml	conductivity us/cm	correction factor	corr. Conductivity us/cm

0	16.3	1	16.3
0.5	20	1.004776	20.09551098
1	25.1	1.009551	25.33973257
1.5	30.8	1.014327	31.24126074
2	37.3	1.019102	38.01251194
2.5	43.3	1.023878	44.3339064
3	49.8	1.028653	51.2269341
3.5	55.7	1.033429	57.56198663
4	61.9	1.038204	64.26485196
4.5	67.6	1.04298	70.50544413
5	73.3	1.047755	76.80047755
5.5	79.5	1.052531	83.67621777
6	85.1	1.057307	89.97679083
6.5	90.9	1.062082	96.54326648
7	96.4	1.066858	102.8450812
7.5	101.9	1.071633	109.1994269
8	107.2	1.076409	115.391022
8.5	112.1	1.081184	121.2007641

9	117.5	1.08596	127.6002865
9.5	122.3	1.090735	133.3969436
10	127.2	1.095511	139.3489971
10.5	132.1	1.100287	145.347851
11	137	1.105062	151.3935053
11.5	140.5	1.109838	155.9321872
12	145.5	1.114613	162.1762178
12.5	150.5	1.119389	168.4680038
13	155.1	1.124164	174.3578797
13.5	160	1.12894	180.6303725
14	164.2	1.133715	186.1560649
14.5	169	1.138491	192.4049666
15	173.1	1.143266	197.8994269
15.5	177.5	1.148042	203.7774594
16	181.7	1.152818	209.4669532
16.5	186.3	1.157593	215.6595989
17	190.5	1.162369	221.4312321
17.5	195.4	1.167144	228.0599809

18	199.8	1.17192	234.1495702
18.5	203	1.176695	238.86915
19	208	1.181471	245.7459408
19.5	211	1.186246	250.2979943
20	216	1.191022	257.260745
20.5	220	1.195798	263.0754537
21	224	1.200573	268.9283668
21.5	228	1.205349	274.8194842
22	232	1.210124	280.7488061
22.5	236	1.2149	286.7163324

APPENDIX 2

conductiivity VS. volume added AgNO3 0.01M
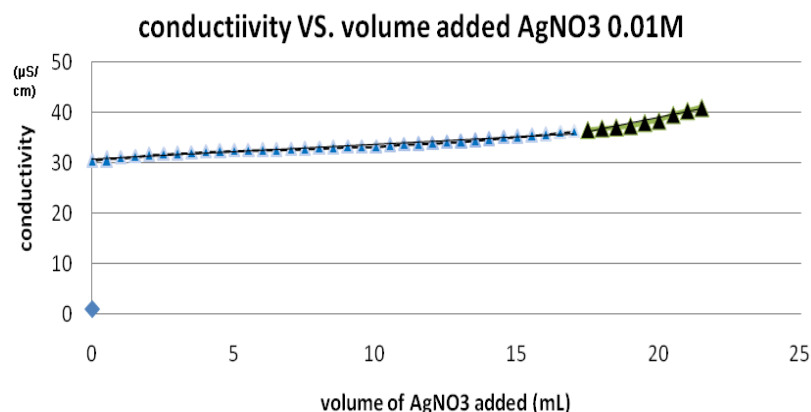
Caculation of DS for the titrition method as   DS= mol cationsed NCC / mol NCC

DS=mol substitued Cl-] / mol NCC

The trend line of blue was expressed as $Y = 0.2871X + 30.759$

The trend line of green was expressed as $Y = 1.1367X + 16.213$

The volume of $AgNO_3$ added when all the Cl^{-1} was consumed equal to the equiv. point, (Fig. 13) 17.133ml.

Conductivity showed that all the chloride in the suspensions were utilized, The chloride amount was equivalent with the amount of the Ag^+ in $AgNO_3$ added   before the equiv. point 17.133ml

$[Ag+] = 0.01M$ mol Ag^+ = mol Cl^- =17.133*0.01 *10^{-3}= 0.1713*10-3
M NCC= M suspension.*conc suspension
M NCC =92.51g *0.67%=0.63g
Mol NCC= 0.63g /162 (molecular weight of AGU) =3.9 mmol
DS is 0.44.