# IMPROVING THE YIELD OF TRIMETHYLSILYL CELLULOSE BY ACTIVATION OF CELLULOSE WITH ETHYLENEDIAMINE

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Trimethylsilyl cellulose (TMSC), an important precursor of regenerated cellulose, is difficult to obtain since cellulose is difficult to react with hexamethyldisilazane (HMDS) due to its low solubility in common solvents. Therefore it is necessary to activate cellulose prior to the reaction. In this investigation, alkali and ethylenediamine (EDA) were used for cellulose activation prior to TMSC production and their effects were evaluated by TMSC yields. Initially, cellulose was pretreated by either alkali or EDA, and then activated cellulose was dissolved in LiCl/DMAc solution. At last, HMDS reacted with the prepared homogenous cellulose to produce TMSC. The results showed that the yield of TMSC obtained from cellulose activated by alkali and EDA was 50.1% and 86.7%, respectively. It means cellulose pretreated by EDA improves the yield of TMSC by up to 36.6%, comparing with that treated by NaOH under the same reaction conditions. XRD results unveiled that the allomorph transformation and the associated crystallinity reduction of cellulose when treated by EDA may contribute to the easy dissolution of cellulose and improved yield of TMSC.

*Keywords*: cellulose, trimethylsilyl cellulose, ethylenediamine

## INTRODUCTION

Trimethylsilyl cellulose (TMSC) has been extensively studied recently due to its potential to regenerate cellulose simply by treatment with acids to produce cellulose fibers, particles or films.[1-6] TMSC can be obtained from the reaction of cellulose with silylating agents, such as chlorotrimethylsilane,[7] hexamethyldisilazane[8,9] and N,N-dibutylamino-trimethylsilane[7] in the media of LiCl/DMAc,[9] liquid ammonia[7,10,11] or ionic liquids.[8,9] Hexamethyldisilazane is the most often used silylation agent, since one molecule of hexamethyldisilazane can react with two hydroxyl groups over the cellulose chain and release one molecule of $NH_3$, theoretically. Cellulose, especially micro-crystalline cellulose (MCC), connected by a large extent of intramolecular and intermolecular hydrogen bonds, is therefore difficult to dissolve in normal solvents. The lack of solubility of cellulose makes it difficult to react, which results in the need for cellulose activation

of prior to reaction. In order to activate crystalline cellulose, McCormick *et al*. dispersed MCC in methanol repeatedly and then in DMAc solution for several times to ensure that it can be dissolved in the LiCl/DMAc solution completely.[9] This procedure is not only time-consuming, but wastes a lot of solvents. Ammonia is known to activate cellulose, forming an ammonia–cellulose complex by interaction in the cellulose crystal lattice and replacing the OH···O hydrogen bonds by OH···N.[7,10,11] However, this method has to be conducted in pressured autoclaves with sophisticated pressure control. Ethylenediamine (EDA) is a promising alternative of liquid ammonia, since it is in the liquid state at atmospheric pressure. When cellulose is treated with EDA, it forms a "cellulose–EDA complex", a similar principle with that in liquid ammonia. The structure and characteristics of cellulose–EDA complexes have been investigated

by Wada *et al*.[12] Wang *et al*. found that EDA pretreated pulp, even with high lignin content, can be dissolved in LiCl/DMSO system without milling.[13] This indicates that EDA can activate the cellulose to dissolve in solutions. Since NaOH is an excellent swelling and mercerization agent for cellulose, 18% NaOH solution was used by Song *et al*.[14] to pretreat cellulose to make it dissolve in LiCl/DMAc solution.

In this investigation, EDA was introduced for cellulose activation to produce TMSC and its effect was compared with that of NaOH. The results showed that EDA pretreatment can improve the yield of TMSC by up to 36.6%, compared to the treatment by NaOH under the same reaction conditions.

## EXPERIMENTAL
### Materials

Microcrystalline cellulose (DP = 215~240) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Lithium chloride (analytically pure) was purchased from Xilong Chemical Co., Ltd (Guangdong, China). Dimethylacetamide (DMAc, chemically pure) was provided by Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Hexamethyldisilazane (HMDS) was purchased from Shanghai Darui Fine Chemical Co., Ltd (Shanghai, China). HMDS was stored in a cool and dry place. Other chemicals, such as ethylenediamine (EDA), tetrahydrofuran (THF, analytically pure) and methanol (analytically pure) were all obtained from Nanjing Everbright Chemical Reagent Co., Ltd (Jiangsu, China). All chemicals were used as received without further purification. All solutions were prepared using distilled/deionized water, which was treated with a Milli-Q system (Millipore Corporation, US).

### Methods
#### Activation of cellulose

In this investigation, ethylenediamine (EDA) was employed for the activation of cellulose. NaOH pretreatment was also used for the same purpose. The methods for the activation of cellulose were as follows.

The procedure of cellulose activation by NaOH: cellulose (2 g) was first swelled in 200 mL 17.5% (w/v) sodium hydroxide solution at 0 °C for 3 h and then washed alternately with distilled water and ethanol for several times. The obtained cellulose was suspended in DMAc at 25 °C for 5 h to further swell and increase its accessibility and reactivity.

The procedure of cellulose activation by EDA: cellulose (2 g) was put into a triangular beaker and then 100 mL EDA was poured in. The suspension was stirred continually at room temperature overnight. Activated cellulose was then separated from EDA using a funnel and the cellulose portion was freeze-dried.

#### Dissolving cellulose in LiCl/DMAc

DMAc (100 mL) was added into a 250 mL flask and the flask was heated in an oil bath. Lithium chloride (8 g, anhydrous) was added into the flask when the temperature was raised to 80 °C. Then the suspension was kept under continuous stirring with a magnetic stirrer. Minutes later, lithium chloride dissolved in DMAc completely. 1 g of accurately weighed activated cellulose was put into the flask under continuous stirring. And then, the temperature was raised to 130 °C for 5 minutes and then decreased to 80 °C and maintained for 3 hours under stirring. At last, the temperature was cooled down to ambient temperature, until cellulose dissolved completely. Transparent cellulose solutions were obtained for the cellulose samples activated by both NaOH and EDA.

#### Synthesis of TMSC and its purification

Dissolved cellulose was transferred to a 250 mL three-necked RB flask equipped with a water condenser. The vessel was continuously purged with nitrogen gas. At 80 °C, hexamethyldisilazane (HMDS) (10.5 mL) was added dropwise to the system with continuous stirring. After 1 h reaction, the container was cooled in an ice water bath for half an hour. The precipitated product was filtered and THF (50 mL) was added to the filtered precipitate and left overnight.

TMSC is soluble in THF. The THF solution was filtered to remove the insoluble part. The filtrate was poured into 300 mL methanol solution and a cloudy solution was observed immediately, since TMSC crystallized in methanol and precipitated again. Then, the above steps were repeated twice to purify the product of TMSC. Finally, the purified product was dried in a vacuum oven at 60 °C.

#### Characterizations by FTIR, XRD and EDX

FTIR spectra were obtained with a Nicolet 210 spectrometer. The sample for FTIR analysis were all dispersed in KBr.

Wide-angle X-ray diffraction (WAXD) was measured with an X-ray diffractometer DX-2000 (Dandong, China). The diffracted intensity of CuKα radiation (k = 0.1542 nm; 40 kV, and 40 mA) was measured in a 2θ range between 10° and 40° for MCC without any treatment, MCC activated by NaOH and MCC activated by EDA at a speed of $0.05°·s^{-1}$.

Energy-dispersive X-ray spectroscopy (EDX) was carried on a JOEL JSM-7600F (Japan) to determine the elemental composition of the resultant samples. Field-emission scanning electron microscopy (FESEM) was performed under a primary energy of 10 keV, with a distance of ca. 7 mm and an aperture size of 60 μm. The specimens were examined directly without coating.

## RESULTS AND DISCUSSION
### Effects of activation method on TMSC yield

Since cellulose can hardly dissolve directly in solutions even under high temperature, the pretreatment of cellulose prior to reaction is a prerequisite for cellulose dissolution. The primary structure of cellulose allows extensive interactions between its chains, resulting in a highly crystalline supramolecular structure (crystallinity is usually over 60-70%).[15-18] In order to make available additional surfaces or to alter crystal structure, cellulose is usually treated by various physical or chemical methods. This process is called activation. It weakens the intermolecular forces of cellulose and therefore it makes the cellulose after activation dissolve in the LiCl/DMAc solvent system easier.[14]

In this investigation, to facilitate MCC's dissolution in the solution of LiCl/DMAc, EDA and alkali were employed for cellulose activation. Eventually, the yields of TMSC obtained through activation by NaOH and EDA were 50.1% and 86.73%, respectively. It indicates that MCC activated by different chemicals has different impacts on the dissolution and reactivity of cellulose.

The X-ray diffractograms of samples of initial MCC, MCC activated by NaOH and MCC activated by EDA are presented in Fig. 1. In this graph, the XRD patterns of MCC, MCC activated by NaOH, and MCC activated by EDA are quite different. MCC without any treatment exhibits characteristic XRD pattern of cellulose I with a pronounced peak at $2\theta = 22°$ and two small peaks at 14° and 15.8°. MCC processed with NaOH has pronounced bimodal peaks at 20.3° and 21.6°, a shoulder at 12.3°, which is a typical XRD pattern for cellulose II.[19] While MCC treated with EDA has a pronounced peak at 22.5° and a broad shoulder at 16.8°, which is a featured XRD pattern for cellulose III. It provides evidence that the crystalline structure of cellulose is transformed to other allomorphs, for example Cellulose II for MCC activated by NaOH and Cellulose III for MCC activated by EDA during the activation process. The crystalline structure transformation may have facilitated the dissolution of cellulose into LiCl/DMAc solution.
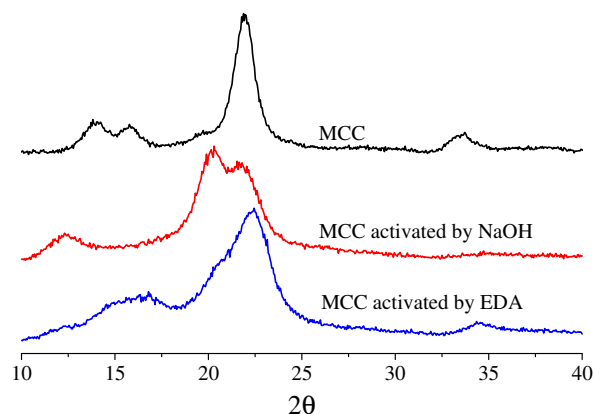


Figure 1: X-ray diffractograms of microcrystalline cellulose (MCC), MCC activated by NaOH, and MCC activated by EDA

In addition to the transformation of the supermolecular structure, the crystallinity of cellulose treated by alkali and EDA changed to some extent as well. The crystallinity of MCC, MCC activated by NaOH and by EDA checked by XRD was 0.85, 0.59 and 0.66, respectively, after Segal's procedures.[20] It indicates that the crystallinity reduced to some extent in the course of the supermolecular structure transformation, especially for cellulose activated by NaOH. However, the sample of MCC activated by EDA was much easier to dissolve in LiCl/DMAc, even though it had a little higher crystallinity than that activated by NaOH. It hints that allomorph conversion may be the intrinsic contributor that alters the solubility of cellulose. This is consistent with Zhiguo Wang's observation[13] in wood dissolution. This can also account for why the yield of TMSC originated from EDA activated MCC was higher than that from MCC activated by NaOH due to better dissolution, which facilitated the homogenous reaction of cellulose with HMDS.

**Degree of substitution (DS) of TMSC checked by EDX and products' FT-IR characterization**

The elements of TMSC compounds obtained with different activation methods were analyzed using SEM-EDX data. A typical EDX spectrum of TMSC from MCC activated by NaOH and EDA is shown in Fig. 2, and the elemental composition of two TMSC samples based on atomic percentage was given in Table 1. The elemental composition was averaged by at least three scanning spots.

The DS value of TMSC was determined by Si content and O content in the samples, and calculated according to the following equation:

$$DS = 5 \times Si\% \div O\% \qquad (1)$$

where Si% and O% are represented in atomic percent. The constant of 5 originates from the five oxygen elements in one anhydroglucose unit.

Table 1
Elemental analysis of TMSC from MCC activated by EDA and NaOH

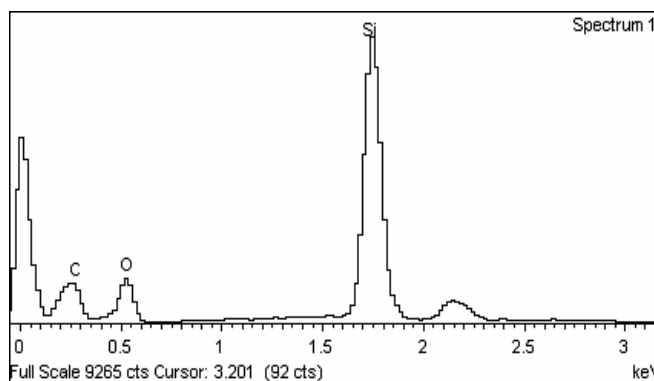| Element (Atomic %) | TMSC-EDA | TMSC-NaOH |
|---|---|---|
| C | 55.41 | 56.07 |
| O | 33.38 | 34.08 |
| Si | 10.21 | 9.49 |
| Totals | 100.00 | 100.00 |



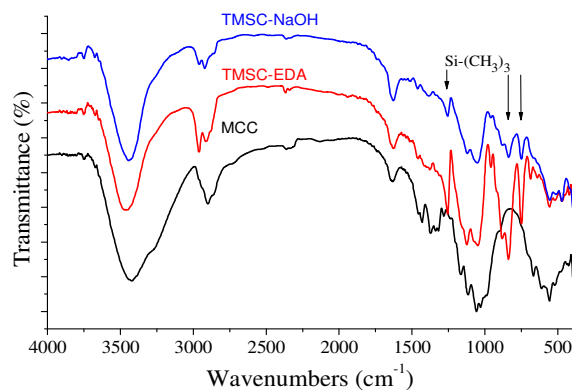Figure 2: Typical EDX spectrum of TMSC



Figure 3: FTIR spectra of microcrystalline cellulose (MCC), TMSC obtained from EDA activated cellulose

(TMSC-EDA) and TMSC obtained from NaOH activated cellulose (TMSC-NaOH)

According to Eq. 1, the average DS of TMSC obtained from MCC activated by NaOH and EDA was 1.39 and 1.53, respectively. Apparently, DS of TMSC from cellulose activated by EDA is slightly higher than that for TMSC from cellulose activated by NaOH. This also evidences that the solubility of MCC differs by different activation means.

The FTIR spectra of MCC, TMSC-EDA and TMSC-NaOH are presented in Fig. 3. Compared with the spectrum of MCC, three distinct bands at *ca.* 750 cm$^{-1}$, 840 cm$^{-1}$ and 1255 cm$^{-1}$ were observed for both samples of TMSC-EDA and TMSC-NaOH, as the arrows point in Fig. 3. It indicates the presence of (Si-(CH$_3$)$_3$) in the samples. The intensity of these three peaks is quite different between the spectrum of TMSC from NaOH activated MCC and those of TMSC from EDA activated MCC due to different degrees of substitution.

**CONCLUSION**

Cellulose pretreated by EDA can get a higher yield of TMSC than that pretreated by NaOH. EDX data demonstrated that the degree of substitution of TMSC obtained from EDA activated cellulose is higher than that of TMSC from NaOH activated cellulose too. XRD results suggest that the supermolecular structure conversion and the crystallinity reduction of cellulose when treated with EDA or alkali contribute to the dissolution of cellulose in LiCl/DMAc solution and, as a consequence, facilitate the reaction with HMDS, and the allomorph conversion to cellulose III is preferable to cellulose dissolution.

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