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Structural Changes and Activation of Cellulose by Caustic Soda Solution with Urea

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Summary: Investigations on the activation of cellulose by mixed solutions of caustic soda and urea are reported. The structural effects of those solutions on various dissolving pulps are studied by ^{13}C-CP/MAS-NMR spectroscopy. In a series of steeping lyes, the concentration of NaOH was varied in a range from 0% to 8% and the urea-concentration in a range from 15% to 40% at ambient temperature and –25 °C.
Using solely the single NaOH or urea solutions in the concentration ranges given above, no or only minor structural changes were found. In contrast to that, the cellulose I structure was partially or completely destroyed by using the bicomponent solution with urea added to caustic soda. The structural effect of the bicomponent solutions is comparable with the effect of solely caustic soda solutions of approx. 10% to 18% NaOH. However, the ^{13}C-CP/MAS-NMR-spectra from the bicomponent pretreated samples indicate a structure different from the usual ordered structures of sodium cellulose I or II, namely a special urea-NaOH-cellulose complex. The results show that for cellulose activation the NaOH concentration of the caustic soda can be remarkably reduced by adding urea. The improved activating effect of an optimized caustic soda solution with added urea was proved to be useful for the synthesis of cellulose carbamate.

Keywords: activation; cellulose; NMR; structure; urea

Introduction

The reactivity and thus processability of cellulose materials depends on the fiber morphology and its regularity, its porosity, the degree of crystalline order, and the inter-fibrillary bonds. Activation of cellulose usually means a treatment of pulp, linters or other cellulose raw materials with the aim to increase the accessibility and the reactivity of cellulose for subsequent reactions by structural changes on the various structural levels. Thereby a higher degree of substitution and/or a more homogeneous substituent distribution, a higher reaction rate and thus a higher yield and better product properties are achieved.[1] Swelling agents which improve the accessibility of pores, penetrate the highly ordered regions, and split bonds between chains and fibrils are most frequently used for cellulose activation.

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Caustic soda is favoured for cellulose activation from the very beginning of industrial scale processing. The treatment of cellulose with caustic soda reduces the degree of supermolecular order and/or changes the cellulose modification depending on the NaOH concentration. [2, 3, 4] The thus-formed alkali cellulose represents an activated form of cellulose and is applied as the reactive initial stage in many derivatization routes.

This article reports on the structural changing and activating effects of caustic soda solution with urea as an additional component on different dissolving pulps. The structural changes were detected by high-resolution ^{13}C solid state NMR spectroscopy (CP/MAS) by investigating the as-treated wet samples. The activating effect of urea containing caustic soda solution on pulp with regard to a subsequent derivatization was investigated for the example of the reaction to cellulose carbamate. The activation of cellulose, as described here, entails largely a substitution of NaOH by urea with additional economical and ecological benefits.

Experimental

Various dissolving pulps (Buckeye VFC, Borregaard SVS, Modo MCD Plus) were treated with lyes in the range of concentration from 0% to 8% NaOH and 15% to 40% urea. The cellulose was steeped in an excess of solution for about 1 hour at room temperature. Another treatment at –25°C was about 12 hours.

There are several well known routes to synthesize cellulose carbamate.[5] We used mainly a slurry process according to the CarbaCell®-technology [6] of the Zimmer AG which has been further improved and simplified.[7] It is characteristic for the process that an optimized amount of urea containing caustic soda solution is added to cellulose which is suspended in xylene as an inert medium. Subsequently the suspension was heated to run the reaction to carbamate.

The ^{13}C NMR spectra were recorded using a Varian UNITY 400 NMR spectrometer at a frequency of 100.58 MHz. High-resolution solid-state spectra were obtained with the cross-polarization/magic angle spinning (CP/MAS) method at spinning frequencies of 5-6 kHz. The radiofrequency field strength for cross-polarization and decoupling was 50-70 kHz, the contact time 1-2 ms and the repetition time of the experiments 3 s.

For the ^{13}C-CP/MAS NMR measurements the samples wetted with lye were mechanically squeezed. About 0,1 cm^3 of the activated cellulose were filled into a sample rotor. Depending on the sample and the specific goal the measuring time ranged from 1 to 15 h.

Results and Discussion

The Basic Effect: Synergy of NaOH and Urea

The NMR-spectra of Figure 1 demonstrate the effects of treatments with solely 30 % urea, solely 7% NaOH, and of the treatment with a mixed NaOH and urea solution in comparison with a sample simply wetted in water.

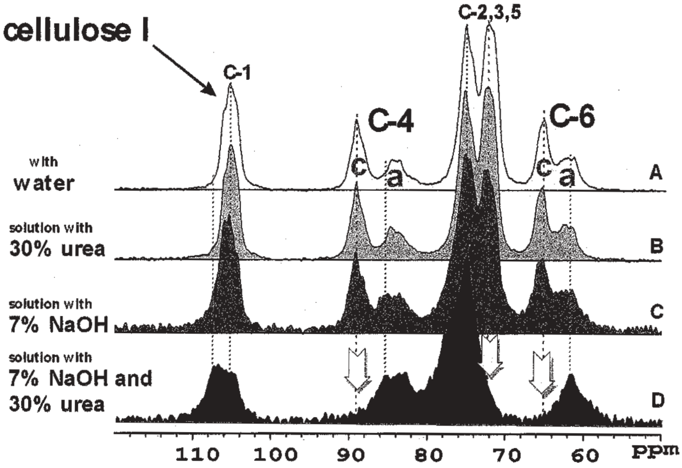

Figure 1. ^{13}C-CP/MAS NMR spectra of the humid samples of Borregaard-pulp after treatments with different solutions.

Generally, the various physical and chemical modifications of cellulose (cellulose I to IV, sodium celluloses, cellulose derivatives) result in spectra with different line positions due to the different electronic environments of the ^{13}C nuclei of the anhydro-glucose units.[8] Ordered and random chain segments also result in different line positions. In particular, the lines of C-4 and C-6 split into crystalline (c) and amorphous (a) line components. If the randomly ordered cellulose structure prevails, all lines of the spectrum become very wide due to a broad distribution of chemical shifts. Based on this, the spectra of Figure1 can be interpreted as follows: As compared to an air dried dissolving pulp (not shown here), the pulp wetted with water (spectrum A) reflects a rather highly ordered state of cellulose I. If water is replaced by a solution with 30% urea (spectrum B), only a negligibly small change takes place. Due to the treatment with 7 % NaOH solution, a slight reduction of the degree of order can be observed (spectrum C). This is indicated by the lower spectral resolution of the line group C-2,3,5 and the decreased intensity at approx. 72 ppm. Thus, the single component treatments do not change the cellulose I basic structure and result in a slight reduction of order, at the most. In contrast to the single component treatments, a solution with both the solutes (7% NaOH and 30% urea) completely changes the modification of cellulose I as clearly seen from spectrum D. In particular, the crystalline C-4 and C-6 line components (see arrows) of cellulose I disappeared and a new structure was formed comparable to the structure of alkali cellulose according to ref.[4].

Influence of Urea and NaOH Concentrations

The effects of reduction of order and lattice conversion as indicated in Figure 1 were investigated by NMR spectra of samples treated with bicomponent solutions with varying NaOH and urea concentrations. In Figure 2 two groups of spectra are filed: The upper group (A-D) consists of spectra originating from dissolving pulp samples each treated with a solution containing constant 6 % NaOH and an addional urea content increasing up to 40%. The spectra in the lower part of Figure 2 (E-G) result from a series of samples treated with constant 30% urea in the solution and a varying NaOH content from 4 % to 8%.

It is very clearly shown by the upper series A-D that the negligible structural effect of 6% NaOH (A) is modified by the addition of 20 % urea (line broadening of spectrum B), and further amplified by 25% and 40 % urea as indicated by the completely changed spectra C, D. The addition of small quantities of NaOH to a 30 % urea solution may cause a considerable broadening of some or all lines, depending on the pulp-type used. This indicates a reduction of the degree of order. With a further increase of the NaOH concentration the process of reducing the degree of order continues. Above 5 % NaOH in the urea solution the Borregard pulp already starts to dissolve partially. This is reflected in the ^{13}C solid-state NMR spectra C, F by a dramatically decreased signal-to-noise ratio due to the reduced proportion of cellulose with solid state properties. The addition of urea to low concentrated NaOH solutions at appropriate temperatures can result in a dissolution of cellulose as already shown in refs. [9, 10]. The spectrum F resembles the spectrum of amorphous cellulose. If the NaOH concentration is increased over 6 %, or if the urea

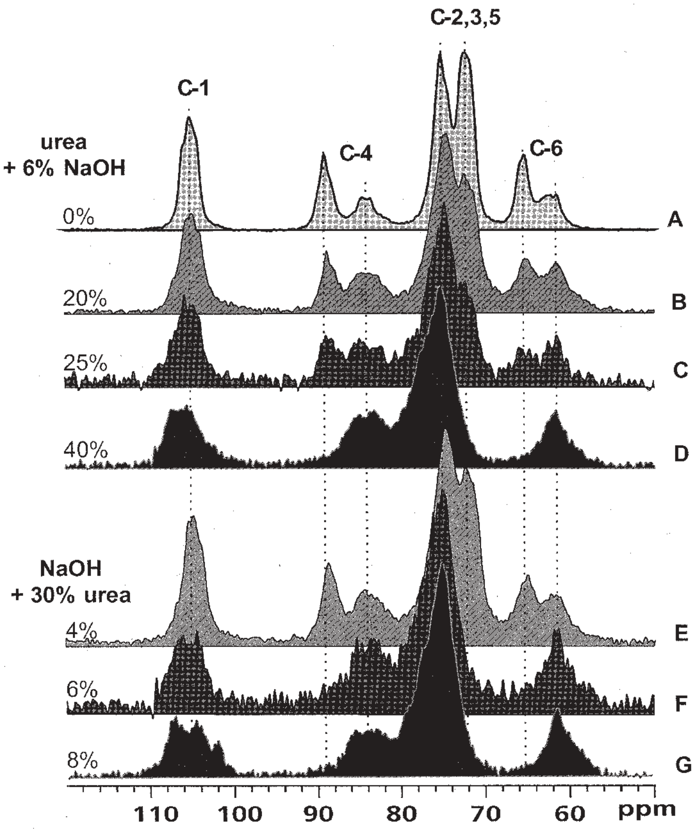

Figure 2. ^{13}C-CP/MAS NMR spectra of wet samples of dissolving pulp (Borregaard) treated with various solutions of NaOH and urea; upper series (6% NaOH each): A= 6 % NaOH, B= 6% NaOH + 20 % urea, C= 6% NaOH + 25 % urea, D= 6 % NaOH + 40 % urea; lower series (30 % urea each): E= 4 % NaOH + 30 % urea, F= 6 % NaOH + 30 % urea, G= 8 % NaOH + 30 % urea.

concentration is increased (e.g. from 30% to 40%) while the NaOH concentration is kept constant, a material has been formed which shows no tendency of dissolution. From the resulting NMR spectra (D, G) the formation of a complex comparable to the structure of alkali cellulose can be deduced.

Generally, from the results of Figure 2 we concluded that both an increase of the NaOH concentration and an increase of the urea concentration lead to a very similar final structural state. The NMR spectra (D, G) indicate the formation of a cellulose/NaOH/urea complex.

Effect of a Reduced Lye Temperature

It is well known that the temperature plays an important role in the cellulose I – sodium cellulose transformations. So, we performed additional investigations of the cellulose-alkali-urea system at a temperature of – 25 °C. Figure 3a shows the NMR spectra of a series of samples treated solely with water and alkali (0 %, 7 %, 14 % NaOH) at room temperature (A-C) and at –25 °C (D-F). Figure 3b shows the spectra from samples treated with bicomponent solutions of 7 % NaOH and 5 % and 30 % urea at room temperature and at –25°C as well (spectra a-d).

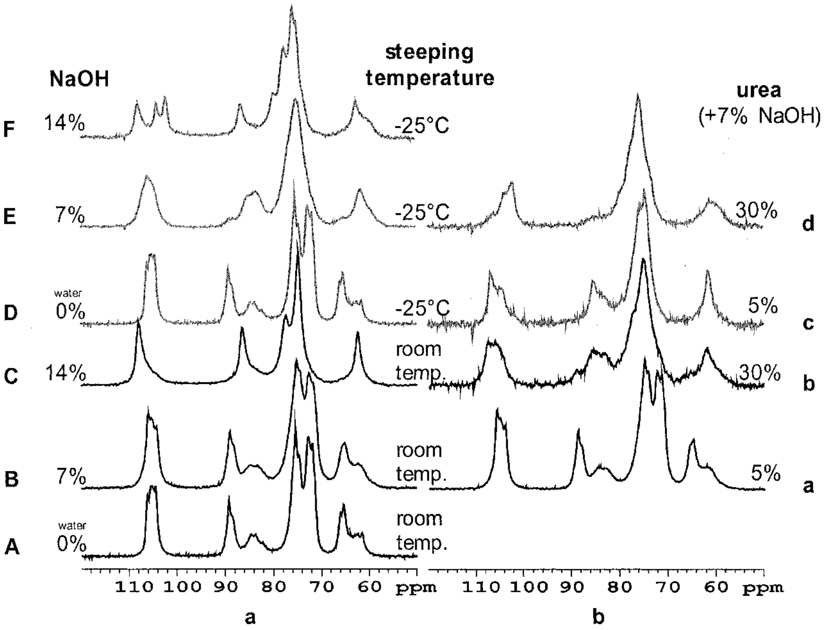

Figure 3. Effect of treatment temperature on the formation of sodium cellulose or NaOH/urea cellulose modifications (room temperature and –25°C); 3a: steeping lye without urea; 3b: steeping lye with urea (NaOH concentration: 7%).

Regarding the NaOH treatments at room temperature, with increasing NaOH concentration we found only a sligth effect at 7 % NaOH (comp. A and B), however a complete lattice transformation from cellulose I to sodium cellulose I at 14 % NaOH (C). At the decreased temperature of –25 °C the 0 % NaOH sample D does not differ from the sample A wetted at room temperature. However, at low temperature already 7 % NaOH (spectrum E) results in a lattice transformation of cellulose I. 14 % NaOH at –25 °C leads to a mixture of sodium cellulose I and sodium cellulose II as indicated by the spectrum F. Thus, a decrease of temperature acts similar to an increase in NaOH concentration.

Figure 3b shows the effect of the bicomponent solutions (7 % NaOH each, 5% and 30% urea) at room temperature and at –25 °C (spectra a-d). At room temperature, there is no significant effect by a treatment with 7 % NaOH and 5 % urea (spectrum a). With a solution of 7 % NaOH and 30 % urea the cellulose I lattice is nearly destroyed and a sodium cellulose I -like structure was formed. With the decreased temperature the lattice transformation already occurs at 7% NaOH/5 % urea. The low-temperature treatment with the 7 % NaOH/30% urea bicomponent solution results in a structure similar to sodium cellulose II (spectrum d). Thus, both the decrease of the temperature and the addition of urea act similar to an increase of the NaOH concentration of the steeping lye at room temperature.

Influence of Chemical Pulp Structure

The treatment of cellulose with caustic soda of an appropriate concentration is reducing the degree of supermolecular order and is changing the cellulose crystal structure. Depending on the supermolecular order, cellulose materials like e.g. dissolving pulps from the various raw materials or cotton linters can be activated to a different extent by the same concentration of the caustic soda. On the other hand, the degree of structural changes of the cellulose raw material after a specific alkali treatment can be considered as a measure for the reactivity of the pulp.

With the help of ^{13}C-CP/MAS-NMR spectroscopic analyses we found that an aqueous solution from 30% urea and only 4% NaOH results in a reduction of the degree of order and a partial transformation of the cellulose crystalline modification. The degree of structural conversion sensitively depends on the origin or the pre-treatment of the cellulose material. In Figure 4 three examples are presented. The NMR spectra of untreated samples (gray lines) and the samples treated with an excess of solution are superposed. Comparing the intensities of the lines for C-2,3,5 and the narrow line for C-6 it can be concluded that the urea containing caustic soda solution causes only minimum structural transformations for Buckeye-pulp. The pulp from Borregard and Modo Plus in contrast are changed considerably and to varying degrees. Thus, Buckeye VFC has the greatest resistance to this kind of activation and Modo MCD Plus can be activated to the highest degree for the following derivatizations. Urea containing caustic soda solution thus differentiates cellulose materials better than caustic soda solution.

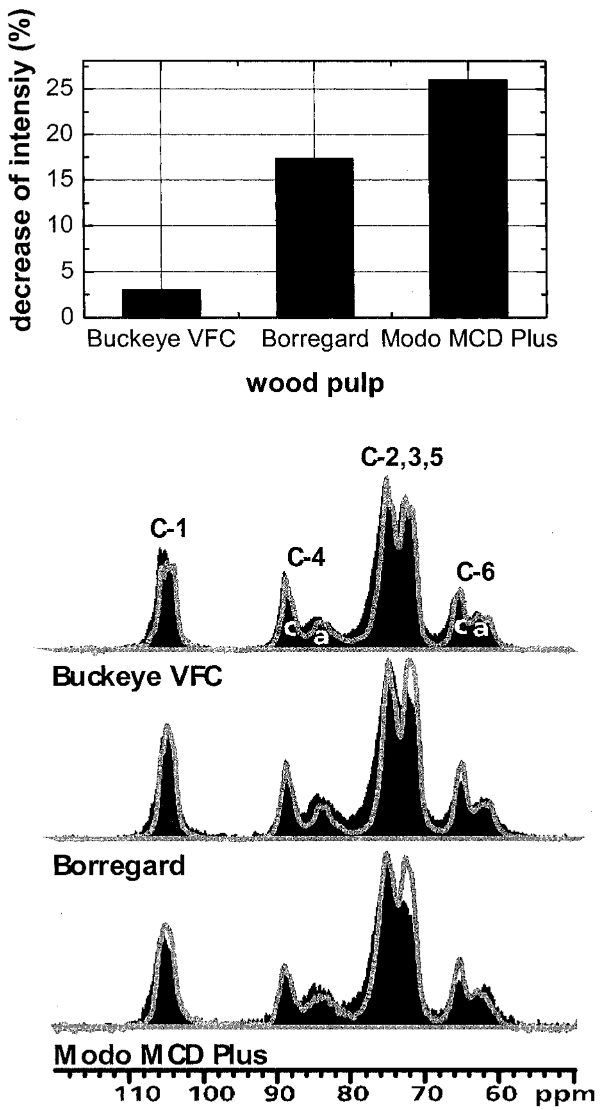

Figure 4. Effect of cellulose structure on the degree of transformation of cellulose I; bottom: ^{13}C-CP/MAS NMR spectra of activated pulps (dark area, 4% NaOH and 30% urea); top: percentage reduction of the height of the right flank of the line group C-2,3,5) as a measure of activation.

Influence of the Liquid-to-Solid Ratio

The slurry process is very suitable for cellulose derivatization on an industrial scale. To optimize this process the dosage of the activation reagent must be minimized, among others. Adding of too little amounts of urea containing caustic soda solution to cellulose can result in an inhomogeneous distribution of lye in the cellulose material and to an insufficient activation which is disadvantageous.

Thus, we examined these conditions by measuring the ^{13}C-CP/MAS-NMR spectra after varying loadings of the cellulose samples with lye (7% NaOH+30% urea). Two samples with a loading of 500 g and 800 g solution per mol cellulose were compared to the spectra of samples loaded solely with water and with a surplus of solution, i.e. with the spectra of cellulose and the cellulose complex, respectively (Figure 5).

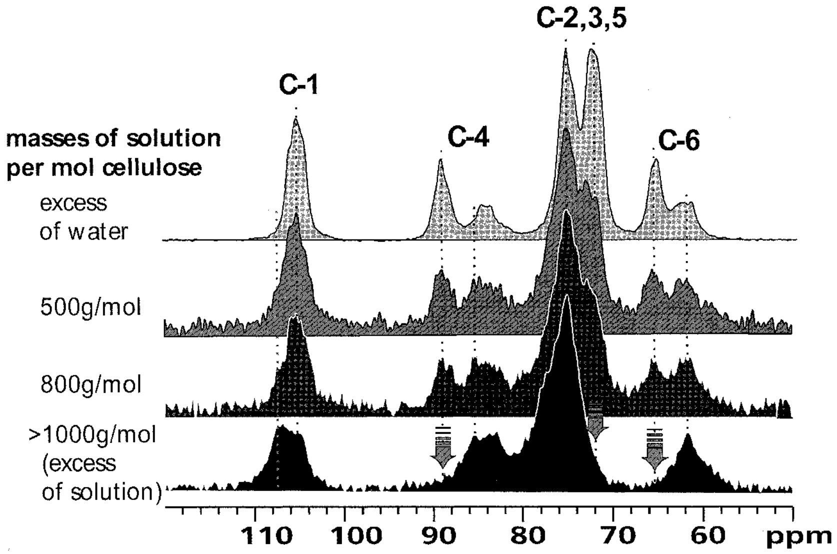

Figure 5. ^{13}C-CP/MAS NMR spectra: activation of Borregard-pulp with an urea containing caustic soda solution (7% NaOH /30% urea) by varying liquid-to solid ratio.

Although the sample with 800g solution per mol cellulose seems to be homogeneously wetted after a visual evaluation, considerable parts of cellulose I can still be detected in the spectra. These are just transformed after loading with about 1050g solution per mol cellulose. Thus, the homogenous wetting of cellulose does not indicate sufficiently the completeness of activation, but NMR spectra show which amount of solution is necessary.

Regeneration Effects

If the pulps which were treated with urea containing caustic soda solution are washed with water (regenerated), these samples present NMR spectra which can be identified as a mixture of cellulose I and cellulose II-type or just cellulose II-type. The cellulose II amount in the regenerated samples increases with a decreasing cellulose I amount in the activated samples (see Figure 2).

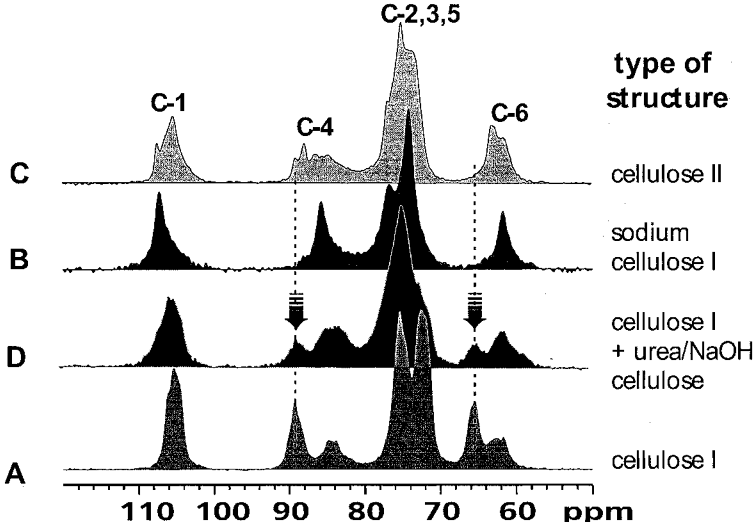

Figure 6. Varying regeneration of sodium cellulose I by ^{13}C-CP/MAS-NMR spectra; A= starting cellulose I; B= treatment with 18% NaOH; C= sample B washed with water; D= sample B washed with urea solution.

A further method to receive one of the NaOH/urea cellulose structures, as shown in Figure 2, is to apply a two-step treatment. First, sodium cellulose I is produced. In the second step, the treatment with concentrated urea solution (e.g. 40%) allows the formation of NaOH/urea cellulose structure. This can be considered as a regeneration of alkali cellulose with urea solution. The spectra in Figure 6 show that a mixture of cellulose structures with clearly discernable parts of cellulose I (see arrows) are formed thereby from alkali cellulose. The appropriate spectrum in Fig. 6 is comparable with the spectrum (C) in Figure 2 from a sample treated with a solution of 25% urea and 6% NaOH. This means that cellulose I can be reconverted from alkali cellulose by a treatment with concentrated urea solution. This is another evidence of the earlier found possible reconversion of cellulose I from sodium cellulose.[11]

Influence of Activation on the Cellulose Carbamate Formation

There are several routes for synthesizing cellulose carbamate.[5, 6, 7] As a rather simple way, the pulp can be steeped in urea solution or in NaOH-containing urea solution and the

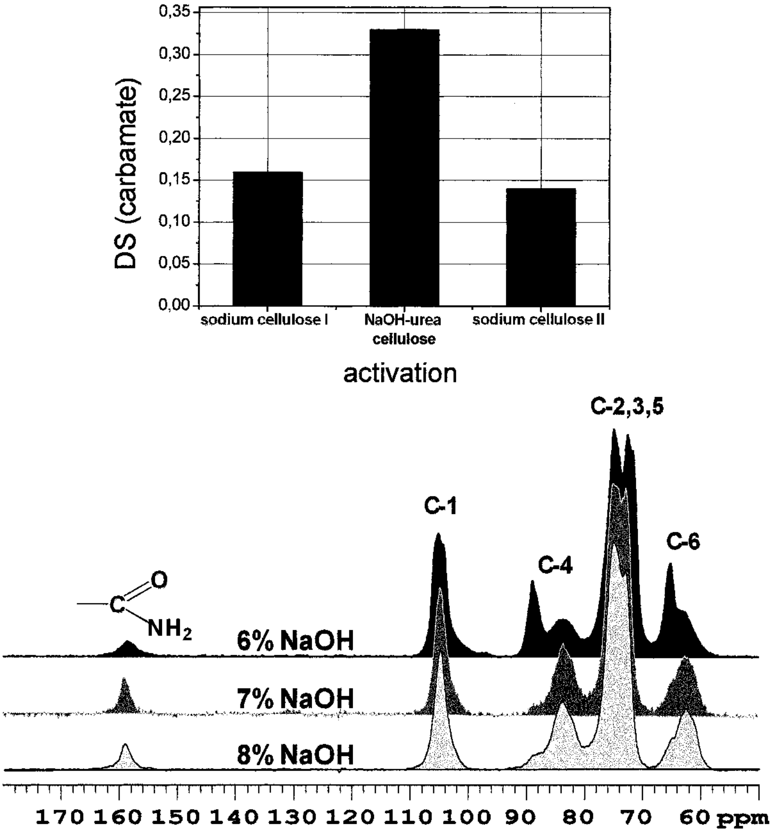

Figure 7. Stronger activating effect of urea containing caustic soda solution for cellulose carbamate synthesis; above: dependence of the DS on cellulose aktivation; left column: lye with 18% NaOH (sodium cellulose I), center column: lye with 7% NaOH and 30% urea, right column: sodium cellulose I washed with methanol (sodium cellulose II); below: dependence of the DS on the NaOH concentration of the lye with 30% urea each.

mixture can be heated after separating the excessive solution. During heating of non-activated pulp which has been immersed in pure urea solution, cellulose carbamate is formed in significant amounts only at temperatures above the urea melting point of 132.7°C. In contrast to that, the reaction temperature can be reduced below 130°C if activated cellulose is used which can be formed by a pre-treatment with alkali-containing urea solution. Cellulose carbamate produced at temperatures between about 100°C and 130°C allows a better dispersion in water and also the dissolution in diluted NaOH is improved as well as the properties (filterability) of spinning solutions. The improvement of the filter value is probably due to the homogeneous substituent distribution.

The activating effect of a treatment with urea containing caustic soda was examined for the synthesis of cellulose carbamate. As the starting materials we used Borregaard pulp with the different activation versions: i) treatment with 18 % NaOH (sodium cellulose I), ii) treatment with 18 % NaOH and washed with methanol (sodium cellulose II), and iii) treatment with 7 % NaOH + 30 % urea (sodium/urea cellulose). Urea was added separately in case i) and ii) wheras in the case iii) the urea is included in the activation treatment. In Figure 7 (top) the degrees of substitution (DS) are presented which were received after the reaction with urea.

As to be seen from Fig. 7, the combined NaOH/urea pre-treatment results in a by far superior DS as compared with the single NaOH-pretreatments.

With regard to the combined NaOH/urea pre-treatment, we investigated the influence of the NaOH concentration (30 % urea) on the formation of cellulose carbamate. Below in Figure 7 the NMR spectra reflect the DS of the carbamate in dependence on the activating NaOH concentration (compare the line intensity at 160 ppm). The maximum DS was achieved at 7% NaOH. Remarkably, at a NaOH concentration above 6 % the residual cellulose I portion disappeared, indicating the formation of a homogeneous cellulose carbamate derivative.

Conclusions

By means of ^{13}C-CP/MAS-NMR spectroscopy it was shown that urea containing caustic soda solution has a considerably stronger effect on the cellulose structure than pure caustic soda solution. Generally, the treatment of cellulose with the bicomponent solution results in a decreased degree of order and/or the transformation of cellulose I into another crystalline cellulose polymorph. Pulps with different reactivities can be distinguished much better by the bicomponent lyes than by pure caustic sodas. Additionally to the concentration of the two solution components NaOH and urea the treatment temperature plays an important role.

The ^{13}C-CP/MAS NMR spectrum of the samples treated with urea containing lye is similar, but not identical to the spectra of the sodium celluloses I or II. That indicates a specific urea-NaOH-cellulose complex. This complex is also formed by treating sodium cellulose I with concentrated urea solution. Moreover, cellulose I is partially regenerated from the starting alkali cellulose.

For the synthesis of cellulose carbamate, the urea containing caustic soda solution has an activating effect on the cellulose and improves the product properties. A further advantage of urea containing caustic soda solution is that the NaOH content of the activating lye can be reduced significantly.

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