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Studies on the Thermostability of Modified Lyocell Dopes

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Summary: Modification of Lyocell dopes with special additives enables the creation of new innovative materials. Additives with functional groups and active surfaces may initiate complex chemical reactions in cellulose/*N*-methylmorpholine-*N*-oxide monohydrate (NMMO) solutions. The effect of carboxylic groups on the thermostability was investigated by incorporating of sugar acids, acidic ion exchange resins (IER) and superabsorbing polymers (SAP) into the solutions. Whereas the sugar acids show strict correlations between the carboxyl group content in solution and onset temperature, viscosity reduction, coloration and by-product formation, the additives show an induction time, which finally leads to accelerated degradation reactions. The cellulose/NMMO solutions were additionally characterized by means of UV/VIS spectroscopy.

Keywords: additives; cellulose; ion exchangers; Lyocell fibers; *N*-methylmorpholine-*N*-oxide

Introduction

Manufacture of fibers by direct dissolution of cellulose in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) is established in the last decade as the well-known Lyocell process.[1-3] The benefits of being a physical process without chemical derivatization of the polysaccharide and the nearly complete recovering of the solvent emphasise this technology as an alternative to conventional processes of cellulose fiber making. Although further technical improvements and economic and environmental friendly advantages appear, a wide acceptance of Lyocell products for common textiles is coming slowly.[4] The advantages of the Lyocell technology are increasingly used outside the textile sector creating new innovative materials. The physical dissolving process of cellulose and the high loading capacity of the solution enable novel opportunities for incorporating soluble blend components or even insoluble substances with particle sizes in micron and submicron ranges as recently reviewed.[5] Cellulosic fibers with additional functional

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properties are applied not only for textiles but also for a wide variety of special products. It is important that the amount of the additives exceeds the concentration of cellulose many times. Furthermore, additives are involved and compacted into the cellulose structure very strongly as the regeneration/crystallisation of the cellulose during the recovering process leads to a shrinkage. By keeping moderate textile-physical properties, incorporation of ion exchange resins, superabsorbing polymers, charcoal, carbon black, ceramics, etc., give functional products as follows: filter for heavy metals,[6] water absorbing articles,[7] adsorber for organic compounds[8] or conductive materials.[9]

Although the dissolution of cellulose in NMMO and the fiber spinning are entirely physical processes, chemical alterations may appear under industrial conditions involving both discoloration and degradation reactions of NMMO and cellulose. These reactions result in lowering the recovery rate of the solvent and in decreasing product performance. Under certain conditions, even exothermicities, so-called thermal runaway reactions may appear, which may end up in deflagrations.[10-13]

By inserting substances with functional groups or surface-active materials into the cellulose/NMMO solutions, an additional deterioration of the thermal stability may be expected. Rosenau et al.[14] reported about *Polonovski* type processes initiated by acidic ion exchange resins, which decompose NMMO to the intermediate *N*-(methylene)morpholinium cation and, finally, to morpholine and formaldehyde. The evidence of autocatalytic reactions by UV/VIS spectroscopy and thermal analysis by own measurements confirmed this fact.[15] In general, substantially describing of the thermostability of modified Lyocell dopes is hitherto not achieved.

This paper focuses on degradation processes of modified cellulose/NMMO solutions.

Experimental

Materials

Chemicals were obtained from Merck, Darmstadt, Germany and were of the highest purity available. *N*-methylmorpholine-*N*-oxide (BASF, Ludwigshafen, Germany) was used as 50 % (v/v) aqueous solution. The cellulose, a bleached beech sulfite pulp is characterized by the following data: α-cellulose 90.6%, degree of polymerisation (DP) 495, carboxyl groups 6.9 µmol/g, carbonyl groups 48.3 µmol/g, moisture 7.5%. Caustic soda and propyl gallate (both Merck, Darmstadt, Germany) were applied as stabilizers. Modification was provided with the following additives: acidic cationic exchange resin (IER) based on polyacrylic acid (Rohm & Haas, Frankfurt/M., Germany), super absorbing polymer (SAP) based on polyacrylic acid (Degussa Krefeld, Stockhausen, Germany), Al_2O_3 (Sasol, Hamburg, Germany), TiO_2 and $BaFe_2O_4$ (laboratory samples), carbon black (Degussa, Frankfurt/M., Germany) and activated charcoal (A.U.G. Döberitz, Germany).

Preparation of Cellulose Solutions

227 g of 50% (v/v) aqueous NMMO and 13.9 g of cellulose were weighed in a laboratory reactor. Stabilized solutions were prepared by addition of 0.06% propyl gallate and 0.04% NaOH with respect to the cellulose content. Modification was carried out by admixture of the above mentioned additives with varying concentrations specified in the text. After stirring the mixture for 15 min at room temperature the reactor was connected to a rotary evaporator working at 30 mbar and the temperature of the reactor was raised up to 90°C gradually. A solution was obtained after stirring for 240 min, and was immediately subjected to the measurements.

Reaction Calorimetry

Thermal investigations were realized with the Systag calorimeter RADEX (mini-autoclave).[15] Approximately 2 g of the cellulose/NMMO solution were used in the steel vessel (design pressure: 100 bar) equipped with bursting disk and an internal temperature sensor. The vessel is kept by a temperature controlled steel/aluminium jacket. Ensuring a defined thermal resistance of the airspace between jacket and vessel, the temperatures of sample and jacket are measured continuously. For dynamic measurements (screening), the vessel was heated with a heating rate of 0.75 K/min from room temperature up to 300°C followed by holding at this temperature for 1 h. The onset temperature (T_{on}) was determined by plotting the deviation of pressure with respect to time (dp/dt) against the temperature.

Rheological Analysis

The zero shear viscosity was determined with the HAAKE rheostress RS 100 with TC 500 temperature control unit at a temperature of 85°C. For investigating the viscosity reduction measurements of cellulose/NMMO solutions were conducted immediately after production of the solution and after tempering at 90°C for 6 h.

DP of cellulose and cellulose/NMMO solutions was measured by the Cuoxam method. DP degradation is defined as the ratio of original DP and DP immediately after preparing the solution by subsequent precipitation, drying, and measuring in Cuoxam.

UV/VIS Spectrometry with Temperature Programming Cuvette

A Shimadzu UV-2401 spectrometer with a special designed cuvette[15] was used for monitoring of the time dependent changes in cellulose solutions. Extinction-time graphs were recorded with a wavelength of 400 nm at a temperature of 120°C.

Coloration

Aqueous extracts of cellulose/NMMO solutions were used for measuring the coloration with a Shimadzu UV-2401 spectrometer. 10 g of the cellulose/NMMO solution was mixed with 30 ml of pure water and left for 48 h. The extinction of the filtrated extracts was measured at a wavelength of 470 nm.

HPLC

A DIONEX HPLC system with diode array detector UV 340 was used for the determination of morpholine and *N*-methylmorpholine. Aliquots of distillates collected in the rotary evaporator during the preparation of cellulose/NMMO solutions were subjected to measurements. The following parameters were adjusted: injection volume 100 µl, Nucleogel RP100 - 8/150 column (Macherey-Nagel), eluant methanol/water (0,05 M sodium metaborate tetrahydrate), flow rate 1 ml/min, temperature 35°C, wavelength 200 nm.

Results and Discussion

Additives have to fulfil various requirements with regard to the Lyocell process especially with regard to the aqueous conditions and the chemical structure and properties of *N*-methylmorpholine-*N*-oxide (NMMO). They have to show a high chemical resistance against water and NMMO, compatibility to cellulose, a less solubility in water, and a particle size below 20 µm. These requirements have consequences concerning the product performance and affect the safety of the process. As any additive possesses special properties, e.g., pH value, functional group (-COOH, -NH_2), structure (polymeric, sterical hindrance), particle size, surface, etc., the desired product design is limited. Furthermore, to reach an efficient effect higher amounts of the additive have to be incorporated. Thus, reactivity and concentration of the additives enhance the complexity of reactions in cellulose/NMMO solutions, which might occur. Reactions arise from the thermal instability and reactivity of the solvent NMMO, its reactions with cellulose and redox reactions initiated by heavy metals.[13] Additives with functional groups or reactive surfaces may influence the reaction mechanisms and may even cause subsequent reactions. In Table 1 the decrease of the onset temperature (T_{on}) as the beginning of a first thermal activity is summarized for a solution of cellulose in NMMO in the presence of various additives of different amounts.

Table 1. Comparison of onset temperatures (T_{on}) obtained from dynamic mini-autoclave measurements for modified cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions (9% cellulose).

Additive		T_{on} [°C]
Type	Amount [%][a]	
-	0	146
NaOH, propyl gallate[b]	0	160
Aluminium oxide	33.3	153
Titanium oxide	100	155
Bariumhexaferrite	500	132
Acidic ion exchange resin	95	148
Superabsorbing polymer	50	150
Carbon black	100	144
Activated charcoal	95	131

[a] With respect to cellulose, [b] Usually applied stabilizing mixture[16]

Within this study, especially the effects of additives containing carboxyl groups are demonstrated, i.e., acidic ion exchange resin (IER) and superabsorbing polymer (SAP) were investigated. Even unmodified cellulose/NMMO solutions exhibit an increase of carboxyl groups at temperatures above 85°C as previously reported.[17] Own measurements carried out with different types of cellulose concerning the carboxyl groups showed although minimal but measurable effects (Figure 1) for the degradation by monitoring change in the degree of polymerisation (DP).

Whereas the concentration of carboxyl groups of the cellulose is in the region of µmol/g only (see Figure 1), IER or SAP possess mmol carboxyl groups per g. In agreement with the request of filling the fiber with high levels of these resins in order to get desired properties, sugar acids were added into the cellulose/NMMO solutions in order to gain an understanding of reactions caused by the carboxyl groups containing additives. Gluconic and glucuronic acids may be generated in such solutions by degradation reactions.[14,18] As shown in Figures 2-4, increasing amounts of sugar acids and hence increasing amounts of carboxyl groups result in decreasing the thermal stability. The decrease of the T_{on} is accompanied by the reduction of viscosity and by an increase of coloration of the solution indicating the formation of chromophoric compounds.

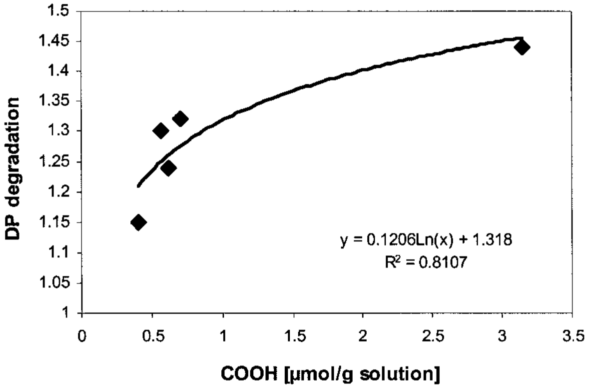


Figure 1. Relationship between carboxyl group content of different cellulose types dissolved in *N*-methylmorpholine-*N*-oxide monohydrate and the degree of polymerisation (DP) of the regenerated cellulose (DP degradation is defined as the ratio of DP of original cellulose and of the regenerated polymer).

In contrast, IER and SAP do not show negative influence on the cellulose/NMMO solution. No decrease of the T_{on} appears. It is interesting to note that the IER leads to a viscosity reduction, however, only by addition of comparable low amount (Figure 3).

Carboxyl groups (-COOH) may protonate the N-O bond in NMMO. By activating this bond, NMMO enters in reactions as reported by Rosenau.[13,14] Radical deoxygenation and *Polonovski* reactions are the main types (Scheme 1). The produced species *N*-methylmorpholiniumyl radical (**1**) and *N*-(methylene)morpholinium cation (**2**) are very labile and highly reactive intermediates, which enter into subsequent reactions, possibly autocatalytic reactions.[19-21]

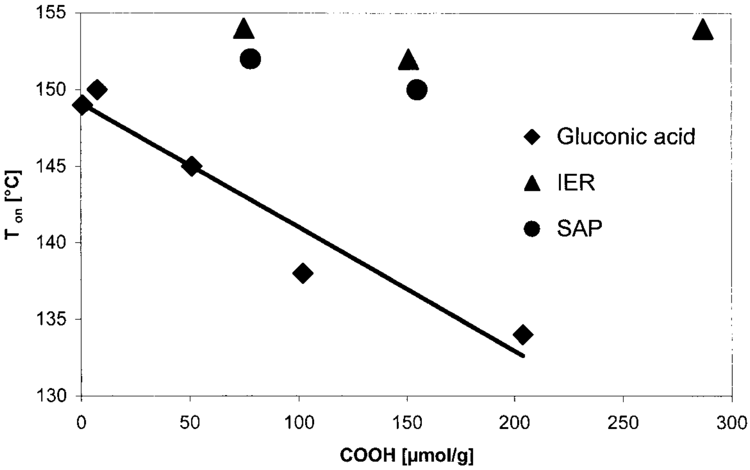


Figure 2. Relationships between carboxyl group content in solution and onset temperature (T_{on}) of cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions in the presence of gluconic acid, acidic ion exchange resin (IER) and a superabsorbing polymer (SAP).

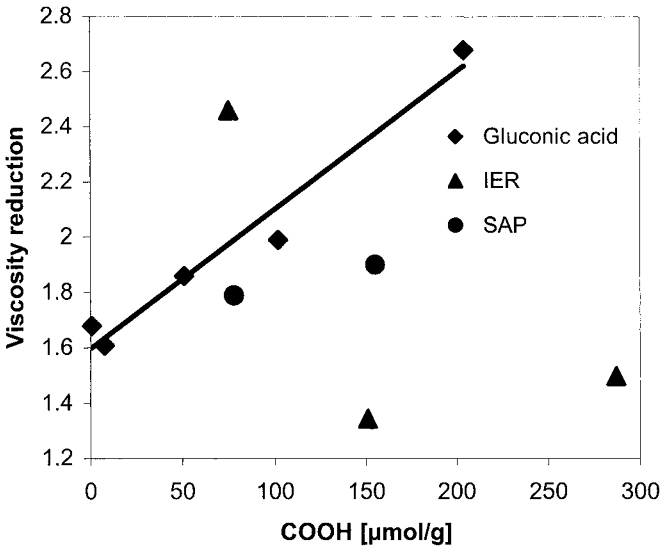


Figure 3. Relationships between carboxyl group content and viscosity reduction (before and after treatment at 90°C for 6 h) of cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions in the presence of gluconic acid, acidic ion exchange resin (IER) and superabsorbing polymer (SAP).

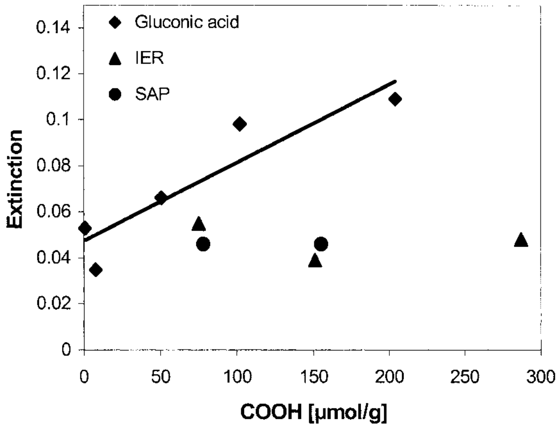
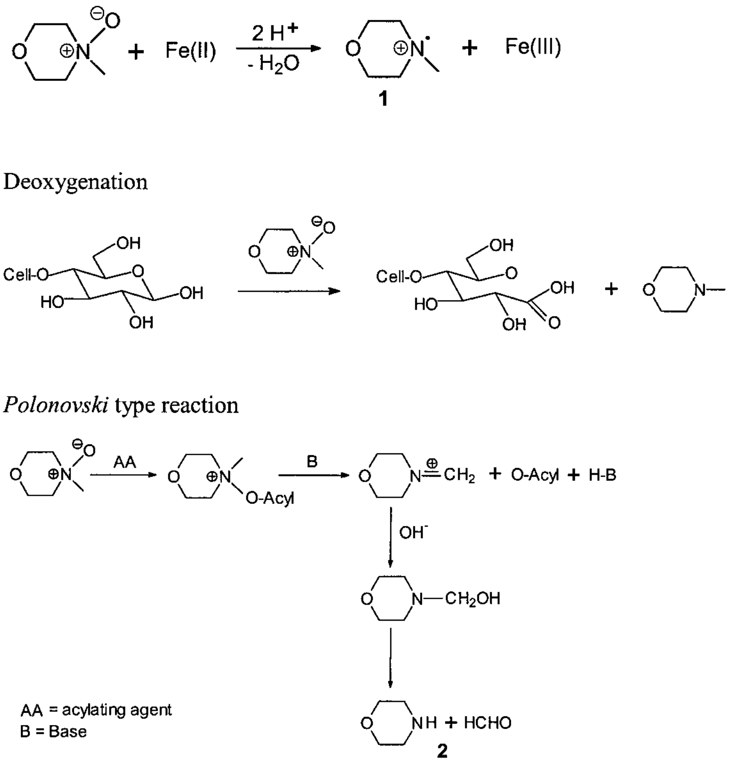


Figure 4. Relationships between carboxyl group content in solution and coloration of cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions in the presence of acidic ion exchange resin (IER) and superabsorbing polymer (SAP).

Measurements of the degradation products morpholine (M) and *N*-methylmorpholine (NMM) in distillates exhibit a change of the ratio with increasing amount of the acid (Figure 5). It is obvious that NMM exceeds the concentration of M suggesting a preference of deoxygenation over *Polonovski* processes. Decreasing concentration of formaldehyde supports this assumption.

Although the examined IER and SAP contain carboxyl groups in a similar range, a completely other behaviour is found as depicted in Figures 2-5. Without exception the values of the solutions modified with IER and SAP differ from those with sugar acids independent of the amount of carboxyl groups. Higher degrees of filling of the additive enhance the viscosity. Thus, this parameter is inapplicable for characterising degradation processes. Onset temperature and coloration do not show changes. The values of NMM of IER increase moderately to a lower content. To explain these facts the structures of the used IER and SAP have to be considered. Both are branched polymers embedded in the entangled structure of the cellulose. The carboxyl groups are sterically hindered and their reaction with NMMO is possibly inhibited. Furthermore, cellulose and IER/SAP may act as a scavenger of intermediates, e.g., *N*-(methylene)morpholinium cation. It seems to be a stabilizing effect depending on time. This inhibition is more illustrative using UV/VIS spectroscopy (Figure 6).



Radical reaction

Deoxygenation

Polonovski type reaction

AA = acylating agent
B = Base

Scheme 1. Reactions in the cellulose/*N*-methylmorpholine-*N*-oxide monohydrate system adapted from Rosenau et al.[13]

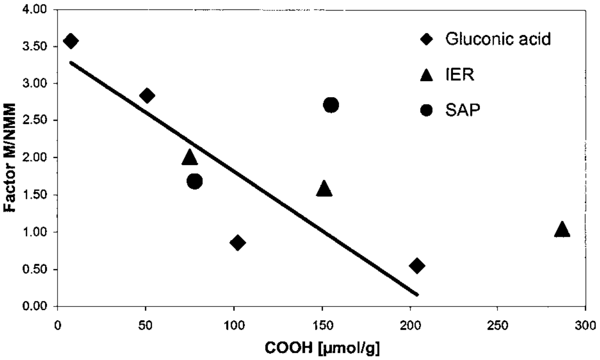


Figure 5. Relationships between carboxyl group content in solution and ratio of morpholine/*N*-methylmorpholine generation (M/NMM) in distillates of cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions added with gluconic acid, acidic ion exchange resin (IER), and superabsorbing polymer (SAP).

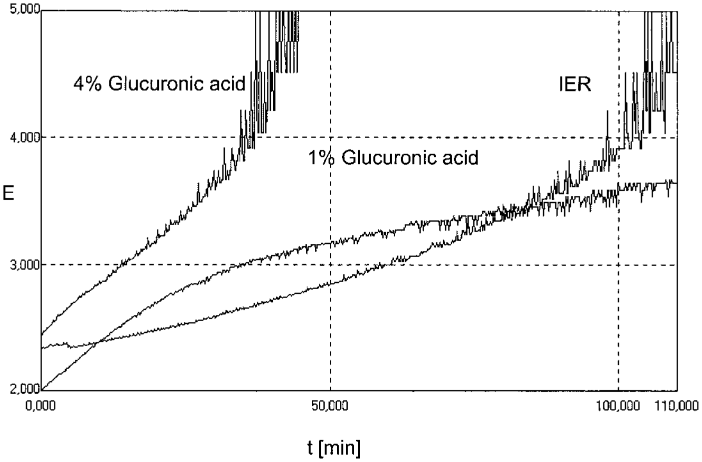


Figure 6. Relationships between heating time and extinction of a 9% cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solution in the presence of glucuronic acid respectively acidic ion exchange resin (IER), determined at λ=400 nm and 120°C.

Whereas the extinction of the system in the presence of 1% glucuronic acid increase gradually, the solution with 4% glucuronic acid shows an exponentially course even after 35 min. Obviously, the amount of carboxyl groups is high enough that the formation of chromophores proceeds very fast. In contrast, extinction of the IER modified system exhibits a slope after an induction period of approximately 100 min. Noteworthy, during this period the extinction is even below the value of the solution containing 1% glucuronic acid indicating the temporary stabilizing behaviour of the IER. Later, the concentration of intermediates is enhanced accelerating the reaction rate. As described by Wendler et al.[15] such an autocatalytic reaction mechanism clarifies the potential of vigorous exothemicities.

Conclusions

The effect of carboxylic groups on the thermostability of cellulose/NMMO solutions was investigated. Sugar acids, acidic ion exchange resins and superabsorbing polymers were incorporated into the solutions. Whereas the sugar acids show strictly correlations between the carboxyl group content in solution and onset temperature, viscosity reduction, coloration and *N*-methylmorpholine formation, the polymeric additives exhibit completely other behaviour. UV/VIS measurements reveal inhibited reactions, which lead finally to the accelerated, dangerous degradation reactions.

To create new products, stabilization of modified cellulose/NMMO solutions is necessary and a challenge for further studies.

Acknowledgement

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