Macromol. Symp. 2008, 262, 72–84 DOI: 10.1002/masy.200850208

Studies on the Stabilization of Modified Lyocell Solutions

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Summary: Additives with functional properties makes the Lyocell process a versatile tool for the creation of new innovative materials beyond the textile sector. Occupying functional groups or active surfaces the additives emphasize the suitability of Lyocell fibers, but simultaneously enhance the complexity of chemical reactions in cellulose/*N*-methylmorpholine-*N*-oxide (NMMO) solutions, respectively. Concerning to the concentration acidic ion exchange resins, activated charcoals, carbon black etc. shift the start of decomposition to lower temperatures, decrease the viscosity, enhance the formation of amines as the main degradation products or cause autocatalytic reactions.

New routes in stabilization of modified Lyocell solutions applying a polymeric stabilizer system are described. Using calorimetric, UV/VIS, ESR and HPLC analysis the degradation processes and thermal stability of modified Lyocell solutions compared to the unstabilized were studied. Moreover, as kinetic investigations show a distinguished behavior for modified solutions autocatalytic reactions can be suppressed by the stabilizing system. ESR kinetic study of radicals reveals that formation and recombination rates of radical reactions depend on cellulose concentration in Lyocell solutions and additional ingredients.

Keywords: additives; cellulose; ESR; lyocell fibers; *N*-methylmorpholine-*N*-oxide; stabilizers

Introduction

Lyocell process[1–3] exhibits an environmentally friendly alternative compared to conventional fiber-making processes. Dissolution of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) is accompanied by chemical alterations under industrial conditions involving both discoloration and degradation reactions of NMMO and cellulose resulting 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. NMMO as very labile compound and strong oxidant is favored to react with cellulose and heavy metals leading to the main degradation products *N*-methylmorpholine, morpholine, carbon dioxide and water[4] and very unstable intermediates such as *N*-methylmorpholiniumyl radical and *N*-(methylene)morpholinium cation.[5]

The industrial up-scaling of the Lyocell technology was accompanied by increased efforts to stabilize cellulose/NMMO solutions. Combination of alkaline and antioxidant stabilization (NaOH, PG) is generally accepted as the most efficient mode, however, concerning to cellulose/NMMO

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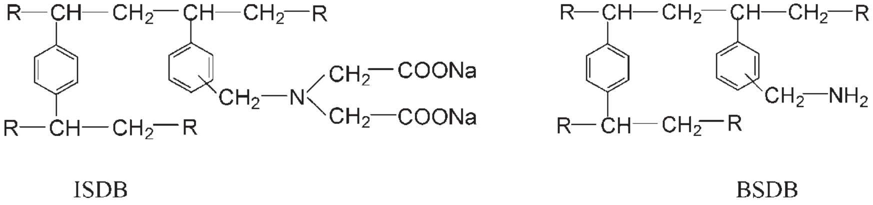


Scheme 1.
Newly established stabilizer system for modified cellulose/*N*-methylmorpholine-*N*-oxide solutions.

solutions without any additive. Substances with functional groups or surface-active materials cause degradation processes additionally.[6,7] In a preliminary study[8] a novel polymeric stabilizer system consisting of iminodiacetic acid sodium salt (ISDB) and benzyl amine (BSDB) each covalently bound to a styrene/divinyl benzene copolymer were studied (Scheme 1). Calorimetric, spectroscopic, rheological and HPLC analysis were performed to describe the thermal stability of modified Lyocell solutions compared to unstabilized solution and to that with conventional NaOH/propyl gallate (PG) stabilizer. This work is devoted to the application of further matrices and will expand the knowledge about the effects of the new stabilizer system, especially kinetic approaches.

Experimental Part

Reagents

Chemicals were obtained from Merck, Darmstadt, Germany and were of the highest purity available. *N*-Methylmorpholine-*N*-oxide (NMMO; BASF, Ludwigshafen, Germany) was used as 50% (v/v) aqueous solution. The cellulose used was a bleached spruce sulfite pulp characterized by the following data: content of α- cellulose = 90.6%, degree of polymerisation (DP) = 495, carboxyl groups = 6.9 μmol/g, carbonyl groups = 48.3 μmol/g, moisture = 7.5%. Benzyl amine, morpholine, *N*-methylmorpholine, *N*-formylmorpholine, formaldehyde, polyethylene imine (Lupasol WF, BASF, Ludwigshafen, Germany), vinylpyrrolidone/vinylimidazole copolymer (Luvitec VPI55K72W, BASF Ludwigshafen, Germany), 1,2-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine (Irganox MD 1024, Ciba, Basel, Switzerland), $Ba(OH)_2$, butylated hydroxytoluene (BHT), NaOH, NH_2OH, propyl gallate (PG), iminodiacetic acid sodium salt covalently bound to a styrene/divinyl benzene copolymer - TP207 (abbr. ISDB, Bayer AG, Leverkusen, Germany) and benzyl amine covalently bound to a styrene/divinyl benzene copolymer - VPOC1065 (abbr. BSDB, Bayer AG, Leverkusen, Germany) were applied as stabilizers. Modification was provided with an weak acidic, strong acidic and strong basic ionic exchange resin (Rohm & Haas, Frankfurt/M., Germany), super absorbing polymer (Degussa Krefeld, Stockhausen, Germany), aluminium oxide, aluminium/silicon oxide (Siralox, Sasol, Germany), titanium oxide, yttrium oxide, zinc oxide, zeolite (Südchemie AG, Germany), lead zircon titanate, barium hexaferrite, nano-silver (Bio-Gate, Bremen, Germany), graphite (Graphitbergbau Kaiserbarg, Austria), paraffin (Rubitherm, Berlin, Germany), quaternized vinylpyrrolidone/dimethylaminoethylmethacrylate copolymer (PVP/MA, ISP, Köln, Germany) activated carbon (Precolith, A.U.G. Döberitz, Germany and three laboratory samples) and carbon black (Degussa, Frankfurt/M., Germany).

Preparation of Cellulose Solutions

227 g of NMMO as 50% (v/v) aqueous solution and 13.9 g of cellulose were weighed in a laboratory reactor. Stabilization and modification was carried out by

admixture of the above stated additives/modifiers with varying concentrations specified in the text. After stirring the mixture for 15 min at room temperature the reactor was connected to a Rotavapor (appr. 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).[9] 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 sensor device for temperature determination. Dynamic measurements (screening) were provided by heating the vessel with a heating rate of 0.75 K/min from room temperature up to 300 °C followed by holding this temperature for 1 h. First thermal activity of the solution indicated as the onset temperature (T_{on}) was determined by plotting the deviation of pressure with respect to time (dp/dt) versus temperature. For the isoperibolic long time mode the surrounding temperature was kept at 140 °C for 24 h. Temperature and the deviation of pressure with respect to time (dp/dt) were investigated.

UV/VIS Spectrometry with Temperature Programming Cuvette

A Shimadzu UV-2401 spectrometer with a special designed cuvette[9] was used for monitoring of the time dependent changes in cellulose solutions. Extinction-time graphs were recorded with a wave length of 400 nm and at a temperature of 120 °C.

High Performance Liquid Chromatography (HPLC)

A DIONEX HPLC system with diode array detector UV 340 was used for the determination of aldehydes and amines.[7]

Aldehydes: 30 ml of pure water was added to 10 g of a cellulose/NMMO solution and left for 48 h. 5 ml of the filtrated extract was mixed with 4 ml acetonitrile and 0.5 ml 2,4-dinitrophenylhydrazine solution and filled up to 10 ml with pure water. After 1 h the measurements were carried out by the following conditions: injection volume 20 μl, Eurospher C18 RP100-5/150 × 4 column (Knauer), eluent acetonitrile/water; 60 min, 60% acetonitrile, isocratic; flow rate 1 ml/min, temperature 25 °C, wave length 350 nm.

Amines: Aliquots of distillates collected in the Rotavapor during the preparation of cellulose/NMMO solutions were subjected to measurements. After filtration (0.45 μm) the distillates were measured with the following parameters: injection volume 100 μl, Nucleogel RP100 - 8/150 column (Macherey-Nagel), eluent methanol/water (0,05m sodium(meta)borate tetrahydrate), flow rate 1 ml/min, temperature 35 °C, wave length 200 nm.

Electron Spin Resonance Spectroscopy (ESR)

ESR experiments were carried out using BRUKER X-band ESR spectrometer ELEX-SYS E500 with resonators Bruker 4104 OR and 4102 ST. Photolysis was performed with appr. 15 ns pulses from a LAMBDA PHYSIK excimer laser COMPEX 205 operated at $\lambda = 248$ nm employing a repetition frequency of 10 Hz and maximum pulse output energy up to 300 mJ. To prevent samples from destruction during experiments maximum density energy at the sample above 10 mJ/cm^2 were used. Experiments were performed at a temperature of 77 K using liquid and cool gas nitrogen.

Results and Discussion

Stabilization of Modified Cellulose/NMMO Solutions – General Aspects

A wide variety of additives is applied attaining modified fibers with special functions. By keeping satisfactory textile-physical properties the incorporation of ion exchange resins, super absorbing polymers, charcoal, carbon black, ceramics etc.

gives functional products as follows: filter for heavy metals, water absorption articles, adsorber for organic compounds or conductive materials.[6–8] Neutral adsorbers, especially activated charcoal, are used to remove contaminations from liquids and gases. Based on a cellulose matrix, a new class of materials with tailored adsorption characteristics are produced. Moreover, the addition of conductive carbon black exhibits fibers with a conductivity behavior across a wide electrical resistance range by keeping satisfactory textile-physical properties. Interesting applications in form of electrical shielding materials for use in sensitive production areas as well as heatable textiles are opened.

However, each additive possesses distinctive properties such as pH value, functional groups (–COOH, –NH_2), structure, surface, pore size, particle size, etc. that may lead to potential interaction with the main components of the spinning solution (Figure 1). Because the efficiency of an additive depends on its volume filling ability when embedded into fibres, it is often indispensable to load higher amounts. Thus it becomes obvious that chemical and physical properties of an additive influence the thermal stability. Even the solvent *N*-methylmorpholine-*N*-oxide monohydrate (NMMO, **1)** as a potentially reactive compound and strong oxidant,[10] reacts with cellulose and readily undergoes redox reactions with heavy metals initiating radical and heterolytical subsequent reactions.[5,11,12] Consequently, by-products, e.g. *N*-methylmorpholine (NMM, **2**), morpholine (M, **3**), formaldehyde (**4**)[4,13] and unstable intermediates such as aminiumyl radical (*N*-methylmorpholiniumyl, **5**),[14] and carbonium-iminium cation (*N*-methylenemorpholinium cation, **6**)[15] have already been found to occur.

NMMO/cellulose segregation occurs as soon as the hydrogen bond system, which is considered as being responsible for cellulose solubility, is deteriorated.[16] Local enrichment of NMMO and generated boundary surfaces of crystallized cellulose represent potential sites for subsequent reactions. Especially high amounts of additives are able to disrupt hydrogen bonds by changing the polarity of the cellulose/NMMO system. In Figure 1 the factors influencing the thermal stability are summarized.

Apart from the impacts of the additives some remarks has to be included concerning the solvent NMMO and cellulose. The

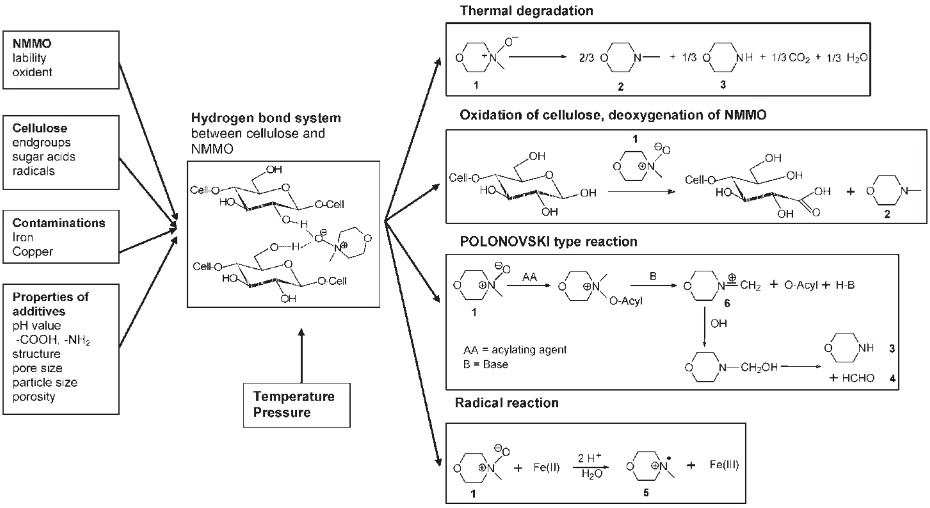


Figure 1.

Main actions and degradation reactions in the system cellulose/*N*-methylmorpholine-*N*-oxide (NMMO) adapted from Taeger et al.[4] and Rosenau et al.[5]

propensity of NMMO to decompose by low thermal stress and without co-reagents is a crucial issue amplifying even during long time exposure at higher temperatures. By-products formed interfere into the reaction scenery leading to generation of chromophoric substances and non-condensable gaseous products. Thereby reactions including the N–O bond outside the ring as well as via ring degradation were described in literature[5] and own findings will be discussed later. Moreover, cellulose is quite far away from an inert material. Considering the reactive end groups, DP, impurities etc. concentration and nature of cellulose influence the complexity of reactions in cellulose/NMMO solutions. Degradation reactions are enhanced by the presence of cellulose. Already 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 to the carboxyl group amount showed albeit minimal but measurable effects respectively for the DP degradation.[6] In case of carbonyl groups higher reactivity has to be ascertained compared to carboxyl groups.[18]

Beside the kind of cellulose also its concentration displays an affecting parameter. Higher cellulose concentrations in the solution means more reactive end groups and so, higher concentrations of degradation products were measured. Chromatographic methods yield further details about degradation products and reactions mechanisms. Morpholine (M), *N*-methylmorpholine (NNM), *N*-formylmorpholine and formaldehyde are the main products resulting from reactions of the N–O bond.[4,5] The activation of the most labile structure in the molecule occurs by protonation, complex formation with metals or *O*-alkylation. The cleavage of the NMMO ring structure as a consequence leads to resonance-stabilized nitroxyl radicals and stable ring degradation products. Acetaldehyde, 2-methylaminoethanol, 2-

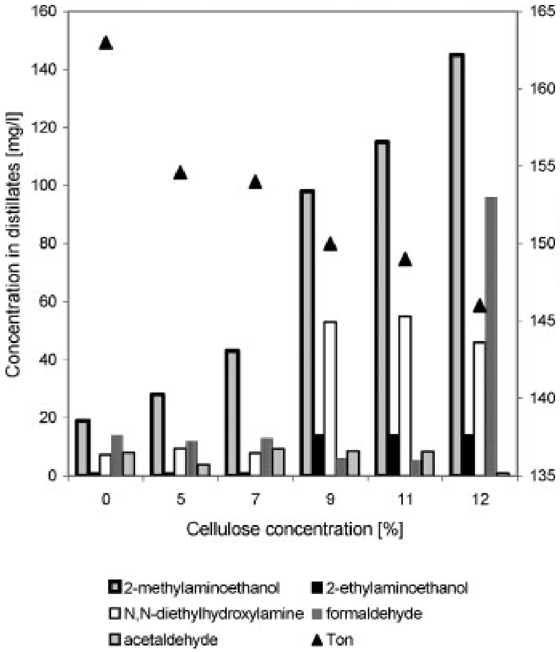


Figure 2.
Ring degradation products and the corresponding onset temperature (T_{on}) of cellulose/NMMO solutions with varying cellulose concentration.

ethylaminoethanol and *N,N*-diethylhydroxylamine were detected by HPLC and attributed to cleavage products. In all solutions as well as NMMO (50% (v/v) aqueous solution) degradation products are detected with the highest concentrations measured for M and NMM compared to the remaining compounds (appr. factor 10). Thus, deoxygenation of NMMO and *Polonovski* type reactions are the main reaction mechanisms.[5,19] Figure 2 displays the individual fingerprints of ring degradation products for solutions with different cellulose concentrations and the corresponding onset temperature.

In order to prevent segregation and degradation of cellulose and NMMO, a stabilizer has to adjust the pH value, to scavenge by-products and to complex heavy metals.[20] According to these requirements different bases, amines, complexing agents and phenolic oxidants were employed for our investigations under real time conditions as depicted in Table 1. As continuation of ref.[8] the number of stabilizers has been exceeded, especially by amines and a morpholine/formaldehyde system.[21] The measurements of the onset temperature (T_{on}) were taken as indicator for thermal stability. Commonly used stabilizers like propyl gallate, irganox, a phenolic hydrazine stabilizer in plastics processing[22] or the morpholine/HCHO system show high T_{on} for unmodified solutions but fail to work for solutions modified with a reactive charcoal or ion exchange resins, respectively. Therefore the above mentioned demands on stabilizers have at least to be extended by the term – weakening of surface reactions. Additives such as activated charcoal or carbon black may have an effect as heterogeneous catalysts.

Novel Stabilizing System

Own investigations using functional ion exchange resins revealed higher T_{on} indicating stabilization effects. The combination of iminodiacetic acid sodium salt (ISDB) and benzyl amine (BSDB) each covalently bound to a styrene/divinyl benzene copolymer exhibit favorable stabiliz-

Table 1.
Comparison of onset temperatures obtained from dynamic mini-autoclave measurements for 9% cellulose/*N*-methylmorpholine-*N*-oxide solutions stabilized with different stabilizers.

Stabilizer Type	Amount of stabilizer [%]	T_{on} [°C]
None	–	146
NaOH	0.04	149
NaOH, propyl gallate	0.04; 0.06	155
NaOH, NH_2OH, propyl gallate	0.04; 0.1; 0.06	160
Benzyl amine	5	149
Morpholine	0.1	153
N-Methylmorpholine	0.33	150
N-Formylmorpholine	0.42	149
Morpholine, HCHO	0.32; 0.1	160
Polyethylene imine	5	153
Luvitec	5	149
Irganox	5	156
$Ba(OH)_2$	0.14	152
BHT	0.1	150
ISDB/BSDB	0.21; 0.21	152
NaOH, propyl gallate[a]	0.04; 0.06	131
Irganox[a]	5	135
Morpholine, HCHO[b]	0.32; 0.1	140

[a] 9% cellulose/*N*-methylmorpholine-*N*-oxide solution modified with activated charcoal (95% with respect to cellulose).

[b] 9% cellulose/*N*-methylmorpholine-*N*-oxide solution modified with weak acidic cation exchange resin (95% with respect to cellulose).

ing properties concerning to cellulose/NMMO solutions modified with carboxyl group containing and surface-active additives.[23] To estimate the effects of the polymeric stabilizing system the chelating ionogenic groups of ISDB in combination with the amine reaction potential of BSDB have to be taken into account. The iminodiacetic acid group forms coordination bonds between its donor atom nitrogen and metals. On the other hand the partly sodium ion neutralized carboxylic groups act as a buffer keeping constant pH values and, thus the hydrogen bond system between cellulose and NMMO is maintained. Benzylamine of BSDB as a primary amine is able to bind carbon dioxide, acids and aldehydes.[24] Additionally, BSDB may deactivate highly reactive intermediates, e.g. the aminiumyl radical, by scavenging these compounds within the polymeric skeleton.

Calorimetric, spectroscopic and rheological measurements were used to describe the stabilization effects of ISDB/BSDB on modified solutions compared to solutions without stabilizers and the ''state-of-the-art'' stabilizer NaOH/PG as described in ref.[8] In that study ion exchange resins (IER), superabsorbing polymers (SAP), activated charcoals (Acc) and carbon black (Cb) were included to emphasize the efficiency of ISDB/BSDB. Investigations were continued with further additives, e.g. inorganic oxides, graphite, polymeric compounds, nano-scaled silver and paraffin. Table 2 summarizes an extract of the investigated additives. Since it is not possible to present here detailed examinations only the onset temperature (T_{on}) were used to evaluate thermal stability when the new stabilizer system is applied.

Generally, a shift of T_{on} to higher values were registered on an average increase of 4.5 °C in a range from 0 to 8 °C. As expected, inactive oxides and titanate give only minimal impact on T_{on}. However, stabilization of aluminium/silicon oxide mixture possessing surface acidic groups (pH 5) succeeded only by additional pH

Table 2.
Comparison of onset temperatures obtained from dynamic mini-autoclave measurements for modified cellulose/NMMO solutions (9% cellulose) without and with ISDB/BSDB stabilizer system.

Additive		T_{on} [°C]	
Type	Amount of additive [%][a]	Without stabilizer	With stabilizer
–	0	146	152
Aluminium oxide	33.3	150	153
Aluminium/silicon oxide	75	147	153
Titanium oxide	100	155	155
Yttrium oxide	15	152	154
Zinc oxide	50	158	160
Zeolite	50	144	150
Lead zircon titanate	50	158	158
Barium hexaferrite	500	132	137
Nano-silver	0.05	148	155
Graphite	100	143	147
Paraffin	70	153	160
PVP/MA copolymer	20	147	151
Weak acidic cation exchange resin	95	148	156
Strong acidic, gel type cation exchange resin	100	150	154
Strong basic anion exchange resin	100	157	160
Superabsorbing polymer (polyacrylic acid)	50	151	157
Carbon black	100	144	149
Activated charcoal, strong reactive	95	131	134
Activated charcoal, strong reactive	50	137	141
Activated charcoal, reactive	50	140	144
Activated charcoal, medium reactive	50	147	152
Activated charcoal, weakly reactive	50	149	156

[a] with respect to cellulose.

value adjustment (at least pH 11). The same is valid for barium hexaferrite but temperatures above 138 °C were not achievable. Here, special features have to be applied as described later.

Incorporation of acidic groups concerns also to IER and SAP each with higher amounts (mmol/g) of –COOH groups. The acidic groups may protonate the N–O bond in NMMO. Activation of oxygen causes subsequent cleavage of the bond by *POLONOVSKI* type reactions.[19] These processes generate carbonium-iminium cations (**6**) as very labile and highly reactive intermediates, which enter into further reactions, possibly autocatalytic reactions.[9,25,26] Beside an enhancement of T_{on} isoperibolic measurements revealed that it takes more than 10 h until the maximum pressure value is reached for the spinning solution containing ISDB/BSDB stabilizers in comparison to the unstabilized and the conventionally stabilized solution, whose maximum pressure values appear after 6 and 8 h. ISDB/BSDB reduces the generation of gaseous degradation products indicating a higher thermostability. The extinction-time curves of the unstabilized and the NaOH/PG stabilized solution increase exponentially after an induction period of less than 200 min caused by rapid formation of chromophores (Figure 3). In opposite to that the solution stabilized with ISDB/BSDB shows only a moderate slope of the extinction over the entire period of observation time (400 min). No exothermicity was found to occur.

Compared to Lyocell solutions modified with carboxyl group containing additives activated charcoal (Acc) or carbon black (Cb) place extraordinary demands on an effective stabilization. Porosity, pore size and pore distribution determine the reactivity of surface-active materials. Contaminations, e.g. heavy metals like iron or copper, are physically bonded to their porous systems. Moreover, the particle size, especially when nano-scaled particles are applied, influence the thermostability.[7]

Only the use of a weakly reactive activated charcoal and carbon black connected with the polymeric stabilizing system lead to sufficiently stabile spinning solutions. ISDB/BSDB stabilized solution shows a higher value for T_{on} and a moderate rise of the isoperibolic curve (dp/dt) compared to the unstabilized solution. On closer examination the difference to the NaOH/PG stabilized solution is only small. The combination of NaOH/PG and the benzylamine containing BSDB stabilizer exhibits in this special case an alternative variation,

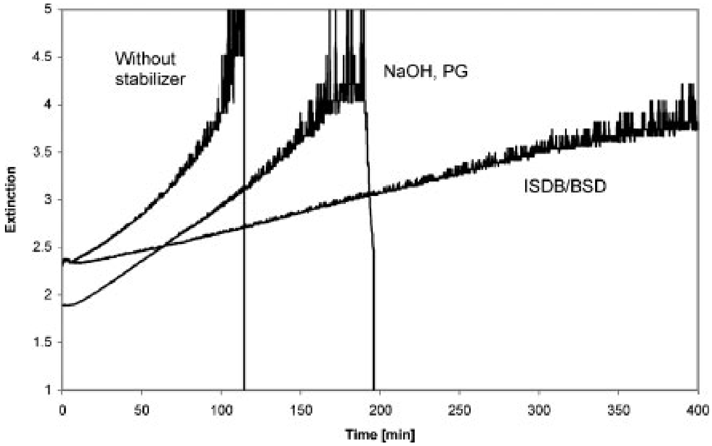


Figure 3.
Relationships between heating time of a 9% cellulose/*N*-methylmorpholine-*N*-oxide solution added with an weakly acidic ion exchange resin (95% with respect to cellulose) stabilized with different substances and extinction determined at λ 400 nm and at 120 °C.

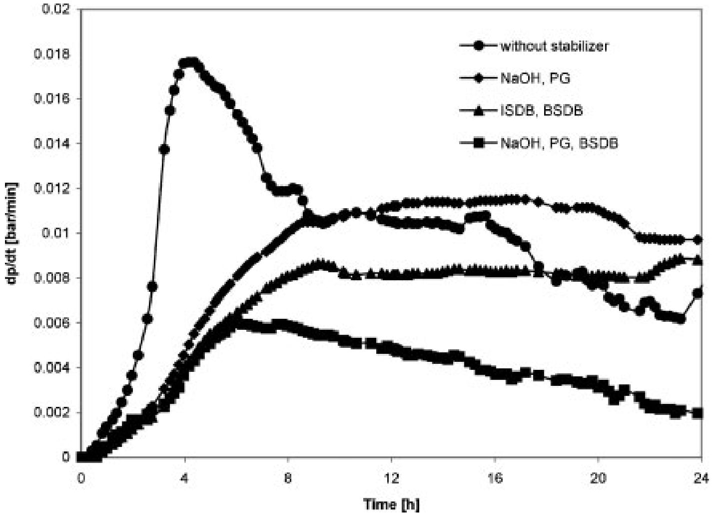


Figure 4.
Relationships between heating time and dp/dt values of 9% cellulose/*N*-methylmorpholine-*N*-oxide solutions filled with activated charcoal (50% with respect to cellulose) and stabilized with different substances at 140 °C.

probably a synergistic effect between both stabilizers (Figure 4).

Stabilization of solutions with enhanced reactive charcoals (Acc III and Acc IV) and barium hexaferrite, special technological features must be applied, for instance the insertion of charcoal into the cellulose/NMMO solution by dynamic mixing as well as short transportation paths and times of freshly prepared solutions.[27]

Nanoscaled carbon black and silver particles show with regard to the applied amounts moderate reduction of Ton with 144 and 148 °C, respectively. However, isoperibolic measurements reveal a completely different behavior as depicted in

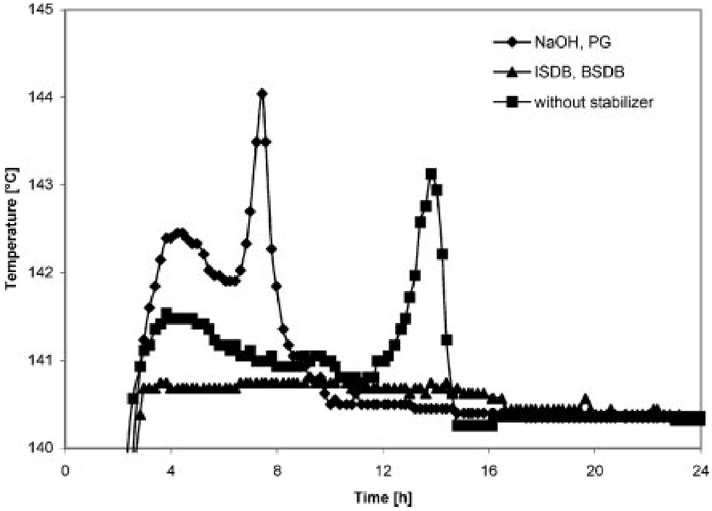


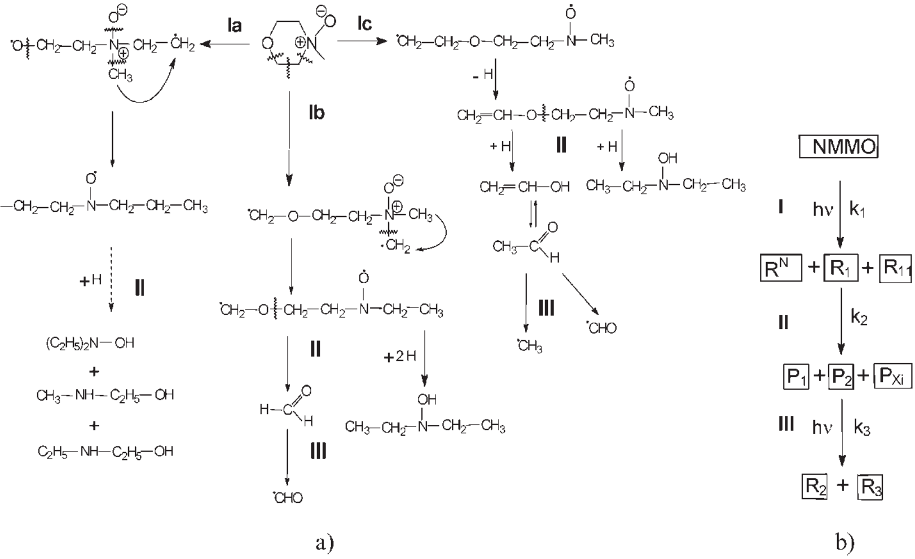
Figure 5.
Relationships between heating time and temperature of 9% cellulose/*N*-methylmorpholine-*N*-oxide solutions filled with carbon black (95% with respect to cellulose), stabilized with different substances at 140 °C.

Figure 5 for solutions modified with carbon black. It is obvious, that particles below 50 nm influence the catalytic efficiency. The temperature maxima of the unstabilized solution appear after 12 h proving the occurrence of autocatalytic reactions.[9] Whereas the solution stabilized with NaOH/PG shows maxima after approx. 4 and 8 h, no temperature maximum is detectable with regard to the ISDB/BSDB stabilized solution. The catalytic effect is reduced. In the case of nanoscaled silver particles both stabilized solutions show a reduced pressure slope maximum after approx. 5 h, however, no second maximum but with a slight advantage for the NaOH/PG stabilizer.[28]

Kinetics of Radicals Accumulation

Detailed ESR spectroscopy analysis of degradation processes in cellulose/NMMO solutions as well as a description of kinetics concerning several radical type formations under UV flash photolysis at 77 K have been carried out in a preliminary study.[29,30] Here, only some important parts of that study are included to emphasize the performance of the ISDB/BSDB system.

In view of the comparative kinetic analysis the radical accumulation (formation/degradation) processes depend on additional ingredients in cellulose/NMMO solutions and hence, its analysis may be a fruitful preliminary step studying degradation processes. Although the experimental conditions of the present study are not close to the Lyocell technology, the results obtained under/after highly extensive light irradiation may be useful to understand the origin of complete radical reaction mechanisms in these compounds. According to the spectroscopic results a probable photochemical reaction pathway of radical formation and degradation (Scheme 2) under high quantum energy irradiation (UV excimer laser flash photolysis) at 77 K for NMMO is suggested.[29] Nitroxyl type radicals R-NO•-R′ (R^N) and oxymethylene species $^{\bullet}O\text{–}CH_2\sim$ (R_1) and $^{\bullet}CH_2\text{–}O\sim$ (R_{11}) at the first step (I) were detected under irradiation as a result of ring degradation



Scheme 2.
a) Suggested reaction pathway, b) kinetic steps. (Konkin A., Wendler F., Roth H.-K., Schrödner M., Bauer, R.-U., Meister F., Heinze T., Aganov A. and Garipov R. "Electron spin resonance study of radicals generated in cellulose/N-methylmorpholine-N-oxide solutions after flash photolysis at 77 K." Magn. Reson. Chem. 2006; 44: 594-605. Copyright 2006 John Wiley & Sons, Ltd)

by a first order reaction pathway (Scheme 2). Proposed NMMO ring degradation mechanism includes three variants (Ia, Ib, Ic) of $R^N \sim R_{1,11}$ diradical types. The second step (II) as a second order reaction is invisible for ESR because the products are not radicals, however, they have to be potential precursors of further radical formations by step (III) under the continued laser illumination and were studied by high performance liquid chromatography (HPLC). Further on, methyl $^\bullet CH_3$ (R_2) and formyl $^\bullet CHO$ (R_3) radicals are formed at the third step (III). The radical spectra double integral (DI), which is directly proportional to the amount of radicals, were recorded at different times after irradiation for both radical groups (R^N, R_1, R_{11}) and (R_2, R_3) respectively, demonstrating the opportunity to study the photo-induced radical reactions quantitatively. Main problems of the spectra analysis are connected with separation of the complicated overlapped radical spectra in order to determine the DI of the spectral lines correctly. Therefore, all ESR spectra were simulated as well as fitted in some cases and discussed in detail in ref.[29]

The processes of radical generation (R^N, R_1 and R_{11}) follow a first order reaction pathway with rate constant k_1 (and k_{11} for cellulose radical product formation). According to Scheme 2b, the process of radical pair formation from pure NMMO and pure cellulose with k_1 and k_{11} rate constants, respectively, is described usually by differential Equations (1)

$$\begin{aligned} \frac{dR^{(Bi)}}{dt} &= (M_0 - R^{(Bi)})k_1 \\ \frac{dR^{(Ce)}}{dt} &= (C_0 - R^{(Ce)})k_{11} \end{aligned} \qquad (1)$$

where $R^{(Bi)}$ is the summarized DI of radicals R^N, R_1, R_{11} as well as $R^{(Ce)}$ analogous to cellulose radicals, M_0 and C_0 are initial concentrations of NMMO and/or anhydro glucose units, respectively which take part in the degradation reaction. Formation of the neutral molecular product P_D at the second step proceeds as a second order reaction generally and, as supposed mainly depends on $R^{(Bi)}$ and $H^\bullet$ radical formation at the first step. Kinetics of P_D can be described by the following differential equation

$$\frac{dP_D}{dt} = k_2[R^{(Bi)} - P_D][R_H^{(Ce)} - P_D] \qquad (2)$$

where $R_H^{(Ce)}$ are the radical cellulose products including $H^\bullet$ radicals and k_2 is the second order rate constant of product formation kinetic processes. With supposing of the formation of secondary radicals R_2 and R_3 from P_D under UV illumination at the first order reaction with rate constant k_3, the differential equation of their kinetics can be written in the same way as (1) as follows

$$\frac{dR_{2,3}}{dt} = (P_D - R_{2,3})k_3 \qquad (3)$$

Solutions of Equations (1)–(3) result in DI time dependent ESR spectra of NMMO and different modified cellulose/NMMO

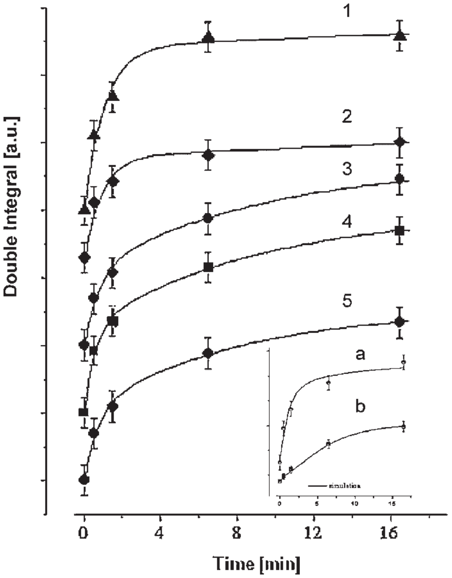


Figure 6.

Radical product accumulation kinetics. Experimental and fitted DI time dependence of recorded ESR spectra of NMMO and different cellulose/NMMO solutions: **1** NMMO, **2** 9% cellulose stabilized with ISDB/BSDB, **3** 9% cellulose stabilized with NaOH/PG, **4** 12% cellulose, **5** 9% cellulose added with Fe(II); insert: DI time dependence of: (**a**) $\sum R^N, R_1, R_{11}$ and (**b**) $R_{2,3}$ for sample **4**.

Table 3.
Calculated parameters.

	k_1 [min^{-1}]	k_{11} [min^{-1}]	k_2 [min^{-1}]
NMMO	0.96	0.63	0.015
9% cellulose stabilized with ISDB/BSDB	1.07	0.76	0.045
9% cellulose stabilized with NaOH/PG	0.81	0.73	0.13
12% cellulose	0.95	0.65	0.17
9% cellulose added with Fe(II)	0.84	0.54	0.19

solutions as shown in Figure 6 with calculated parameters k_1, k_{11} and k_2 in Table 3. To show the significant difference in radical accumulation kinetics of preliminary diradicals R^N, R_1, R_{11} and secondary radicals R_2, R_3 the insert in Figure 6 show for sample 4 (12% cellulose) the kinetic curves of their DI‘s separately. This result was the main reason for the supposition of the product formation step. It is remarkably that experimental kinetic curves of both types of radical spectra DI‘s time dependence are well described by approx. the same kinetic parameters, although of there essential difference.

As it was pointed before, the product formation processes at the second step are more complicated concerning the approach of the study. Possibly another steps are included and hence, the rate constant k_2 (some effective summarized constant) may depend not only on diffusion and activation properties of reagents but also on cellulose (or cellulose radical) concentration. Consequently, it was registered in ref.[29] that the increase of cellulose concentration initiates and accelerates product formation processes (increase of k_2). These results refers excellently to the above stated correlation of the onset temperature with higher amounts of cellulose. With regard to Fe(II) on the reaction rates some insignificant enhancement of k_2 was registered compared the other solutions in all experimental series. These preliminary results correlates with literature.[5,11,12] where the action of Fe(II) on NMMO generating radicals is established unambiguously.

In case of NMMO and the solution with ISDB/BSDB the magnitude of k_2 was several times less than in the another samples. This is remarkable and was expected because that stabilizer system operates as a quenching radical agent.

In principle, ESR spectra were only registered after UV illumination at low temperature (close to liquid nitrogen) in order to stabilize radicals formed under irradiation for longer time periods. Very recently investigations revealed that the obtained alkylnitroxyl type radicals $\sim CH_2–NO^\bullet–CH_3$ and $\sim CH_2–NO^\bullet–CH_2\sim$ are stable at temperatures of the industrial Lyocell process (~370 K).[31]

Conclusion

Cellulose/*N*-methylmorpholine-*N*-oxide solutions filled with carboxyl group containing or surface-active additives can be efficiently stabilized with a novel polymeric stabilizer system consisting of iminodiacetic acid sodium salt (ISDB) and benzyl amine (BSDB) covalently bound to a styrene/divinyl benzene copolymer. By complexing metal ions, adjusting the pH value and scavenging of reactive species, the thermal stability is enhanced compared to the unstabilized solution and to that with conventional NaOH/PG stabilizer. Additionally, segregation processes of cellulose and NMMO, autocatalytic reactions and surface catalyzed reactions are suppressed. Radical formation and deformation rates are minimized by ISDB/BSDB.

Applying ISDB/BSDB to solutions modified with surface-active additives distinctive improvements of the thermal stability is received for a weakly reactive charcoal, carbon black and nano-silver. Solutions added with highly reactive charcoals can be managed by means of special technological features and will be a subject for further studies.

The described stabilizing system is a basic tool for manufacturing of cellulosic fibers with additional functional properties. Only an efficient and safe process management enables applications not only for textiles but also for a wide variety of very special products.

Acknowledgements: Financial support by the German Federal Ministry for Education and Research (BMBF) under contract No. 94/02 is gratefully acknowledged.

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