Trace Element Status of Activated Charcoals and Carbon Black: Influence on Thermal Stability of Modified Lyocell Solutions

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ABSTRACT: The influence of surface-active additives on the thermal stability of cellulose/N-methylmorpholine-N-oxide monohydrate solutions were investigated. The application of a dynamic mixing tool incorporating the additive directly before the forming module enhances the thermal stability. Thermal stabilization by means of a polymeric stabilizer system and adjusting the pH value by sodium hydroxide increased the storage life-time for the additive suspension as revealed by calorimetric isoperibolic step measurements. Further investigations concerned the analysis of the trace element status of the additives. Analytical results for 16 elements have been obtained by inductively coupled plasma optical emission spectrometry (ICP OES) after microwave-assisted acidic digestion, and seven elements, Cr, Cu, Fe, Mn, Mo, Ni, and V have been determined using direct solid sampling high-resolution continuum source graphite furnace AAS (SS-HR-CS GF AAS) as a reference method. Partial least squares regression between measured and calculated temperatures for beginning exothermicity (T_{on}) has been used to investigate the prediction capability of the investigated techniques. Whereas the ICP OES measurement gives only an acceptable correlation employing all 16 metals plus Fe(II), results obtained by SS-HR-CS GF AAS exhibit a correlation coefficient of 0.99. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3408–3418, 2010

Key words: calorimetry; cellulose; N-methylmorpholine-N-oxide; mixing; thermal properties

INTRODUCTION

Direct dissolution of cellulose in N-methylmorpholine-N-oxide monohydrate (NMMO) was established as the well-known Lyocell process in the last decade.[1–3] Compared to conventional fiber-making processes, cellulose is dissolved without chemical derivatization, and the solvent can be recovered almost completely. Using the Lyocell technology beyond the textile sector, new fields are opened up for generating 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 the micrometer and submicrometer ranges.[4] Accompanied by an only moderate deterioration of the textile-physical properties the incorporation of ion exchange resins, super absorbing polymers, charcoal, carbon black, ceramics etc. results in functional products such as filters for heavy metals, water absorption articles, adsorbers for organic compounds or conductive materials.[5,6] Neutral adsorbers, especially activated charcoal, are used to remove contaminations from liquids and gases. Moreover, the addition of conductive carbon black produces fibers with a conductivity behavior across a wide electrical resistance range by keeping satisfactory textile-physical properties. Interesting applications in the form of electrical shielding materials for use in sensitive production areas and as heatable textiles are opened.

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, lowering the recovery rate of the solvent and decreasing product performance. Under certain conditions, even exothermicities, so-called thermal runaway reactions might occur, which could end up in deflagrations. The solvent NMMO is thermally instable and reactive, particularly in the presence of heavy metals.[7–9] Furthermore, higher amounts of additives have to be

incorporated to reach an efficient effect. Thus, reactivity and concentration of the additives enhance the complexity of reactions in cellulose/NMMO solutions.[10,11] Most additives decrease the onset temperature (T_{on}), which is defined as the beginning of exothermicity and has to serve as a reference for the evaluation. In general, T_{on} is measured precisely by means of reaction calorimetry, but this is very time-consuming and only possible after having prepared the solution.[10] Nevertheless, the thermal stability is to be characterized by other variables, apart from T_{on}.

Precise evaluation of additive properties such as surface topology and metal content is therefore a must for the choice of the proper materials. Usually the determination of metallic elements in additives is carried out after acid digestion or extraction using atomic absorption spectrometry (AAS) or inductively coupled plasma optical emission spectrometry (ICP OES). However, activated charcoal and carbon black samples are particularly difficult to bring into solution, requiring long and complex procedures. The direct analysis of solid samples has a number of advantages over solution analysis, particularly in cases where the samples are difficult to digest, such as: (i) a significantly reduced risk of contamination and loss of analyte; (ii) an increased sensitivity, as samples are not diluted; (iii) the use of expensive and/or hazardous reagents is not required, resulting in both economic and environmental benefits; (iv) results are obtained more rapidly.[12,13]

The industrial up-scaling of the Lyocell technology was accompanied by increased efforts to stabilize cellulose/NMMO solutions. A mass-related accumulation of the reaction mixture in the course of production increases the risk of exothermicities, so-called thermal runaway reactions with an erratic temperature and pressure rise. Both chemical stabilization and special technological features may prevent exothermicities or deflagrations.[2] A promising approach is the incorporation of the reactive additive directly before the forming module using dynamic mixing tool.[14] The spinnable molding mass with the incorporated functional material is formed by two different mass streams, produced, stabilized and stored separately. The first material stream comprises a solution of cellulose in NMMO, the second is a mixture of NMMO, particular additive and water.

The aim of this work was firstly, to investigate the opportunities of incorporation of activated charcoals and carbon black (soot) of different reactivity into the Lyocell solution by a dynamic mixing step. Secondly, the heavy metal status of activated charcoals and carbon black had to be investigated. Besides microwave-assisted digestion, followed by ICP OES determination, the feasibility of direct determination of metals in solid samples using SS-HR-CS GF has been studied. The results of both techniques have been compared for their ability to predict the onset temperatures (T_{on}) of modified cellulose/NMMO solutions.

EXPERIMENTAL

Materials

All reagents were at least of analytical grade. Hydrogen peroxide, 30% (v/v) and nitric acid, 65% (v/v) were purchased from Merck (Darmstadt, Germany). De-ionized water from a Milli-Q system (Millipore, Bedford, MA) with a resistivity of 18 MΩ cm has been used throughout. For ICP OES analysis following calibration standards (Merck, Darmstadt, Germany) has been applied: ICP multielement standard IV (Al, Pb, Cd, Ca, Cr, Co, Cu, Fe, K, Mg, Mn, Na, Ni, V, Zn) and Mo ICP standard. Stock standard solutions containing 1000 mg L^{-1} each of Cu, Mn, Mo, Ni, and V for AAS measurement have been prepared by dissolution of high-purity Cu, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$, $(NH_4)_2MoO_4$, Ni, and NH_4VO_3, respectively (SPEX, Edison, NJ). For Fe and Cr stock standard solutions (1000 mg L^{-1}) from Merck have been used. Calibration solutions have been prepared by appropriate dilution of the stock standard solutions with 0.5% v/v HNO_3.

The cellulose used was a bleached spruce sulfite pulp characterized by the following data: content of α-cellulose = 90.6%, degree of polymerization (DP) = 495, carboxyl groups = 6.9 μmol/g, carbonyl groups = 48.3 μmol/g, moisture = 7.5%. NaOH, propyl gallate (PG), iminodiacetic acid sodium salt covalently bound to a styrene/divinyl benzene copolymer—TP207 (Bayer AG, Leverkusen, Germany) and benzyl amine covalently bound to a styrene/divinyl benzene copolymer—VPOC1065 (Bayer AG, Leverkusen, Germany) were applied as stabilizers.[15,16] Modification was provided with the following activated charcoals and carbon black samples (additives): two samples of carbon black (CB) from Degussa (Frankfurt/M., Germany), and seven activated charcoals (A1 – A7) from A.U.G. (Döberitz, Germany), Blücher GmbH (Erkrath, Germany), Kureha GmbH (Düsseldorf, Germany), Pica (Levallois, France) and three laboratory samples. All samples were ground to a particle size of ≤20 μm.

Preparation of cellulose solutions

Spinning solution

1510 g of NMMO as 50% (v/v) aqueous solution and 129 g of cellulose were weighed in a laboratory reactor. Stabilization was carried out with 0.04% NaOH and 0.06% PG, modification by admixture of the above stated additives with varying

TABLE I
Comparison of Onset Temperatures (T_{on}) Obtained from Dynamic Reaction Calorimetry Measurements for 9% Cellulose/N-methylmorpholine-N-Oxide Solutions Modified with Activated Charcoals (A) and Carbon Black (CB)

Additive	Amount	T_{on}
Type	[%][a]	[°C]
–	0	146
NaOH, propyl gallate[b]	0.04; 0.06	160
CB1	4.5	144
CB2	4.5	146
A1	4.5	147
A2	4.5	144
A3	4.5	140
A4	4.5	139
A5	4.5	134
A6	4.5	141
A7	4.5	137
A7	8.55	128

[a] With respect to the solution.
[b] Usually applied stabilizing mixture.[15]

concentrations as denoted in Table I. After stirring the mixture for 15 min at room temperature the reactor was connected to a Rotavapor (~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.

Suspension

When using a dynamic mixing process described in detail in Ref. 14, the additive suspension was extra produced immediately before blending. 752 g of activated charcoal (A7) and 1453 g aqueous NMMO, 50% (v/v), were weighed in a laboratory reactor. Stabilization was provided with the above denoted polymeric compounds TP207/VPOC1065 each 21.5 g. After stirring the dispersion for 15 min at room temperature the reactor was connected to a Rotavapor (~30 mbar) and the temperature of the reactor was raised up to 60°C gradually. The completed suspension (S1) was obtained after stirring for 240 min, and also given to the measurements. Further suspensions were produced analogous to S1 with the following modifications: S2 was stabilized with double mass of stabilizers, S3 was warmed up only up to 40°C, S4 was stabilized additionally with 5% (v/v) NaOH, S5 was further heated for 24 h at 60°C without stirring. During dynamic mixing step, the suspension was continuously blended with a nonmodified dope of about 12% cellulose in NMMO monohydrate (ca. 83%) immediately at a constant pressure of 40 mbar and at 95°C before entering the mixing chamber. The cellulose/NMMO solution was stabilized with 0.06% PG and 0.04% NaOH.

Reaction calorimetry

Thermal investigations were realized with the SYSTAG reaction calorimeter RADEX (mini-autoclave) as described in Ref. 10. 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. The vessel is kept by a temperature controlled steel/aluminum 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 this temperature for 1 h dwell time. The onset temperature (T_{on}) was determined by plotting the deviation of pressure with respect to time (dp/dt) against the temperature and registering the temperature at the threshold value of 0.0002 bar/s.

In the isoperibolic step mode the sample was heated at a defined surrounding temperature (heating rate 10 K/min), held for 12 h at this temperature followed by increasing the temperature by 10°C, and another dwell time of 12 h. Pressure measurements were achieved at the temperatures: 110, 120, 130, 140, and 150°C for cellulose solutions and 50, 60, 70, 80, 90, and 100°C for suspensions, respectively.

ICP OES

The ICP OES analyzes were carried out using an OPTIMA 2000 DV ICP optical emission spectrometer (Perkin Elmer, Shelton, CT). Instrumental parameters used for ICP OES analysis were outlined in Ref. 17. Argon with a purity of 99.996% (Air Liquide, Saalfeld, Germany) has been used as plasma gas.

SS-HR-CS GF AAS

A prototype high-resolution continuum source atomic absorption spectrometer, built at ISAS, Berlin, has been used for AAS measurements of Cr, Cu, Fe, Mn, Mo, Ni, and V. The equipment is based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany) as described previously, e.g., by Heitmann et al.,[18] Welz et al.,[19] and Lepri et al.[17] Solid samples were weighed directly onto the SS platforms using an M2P microbalance (Sartorius, Göttingen, Germany, accuracy 0.001 mg) and inserted into the graphite tube using a preadjusted pair of tweezers, which is part of the SSA 5 manual solid sampling accessory (Analytik Jena). Aqueous standards were injected manually onto the SS platform using micropipettes with disposable tips. Argon (99.996%, White Martins, São Paulo, Brazil) was used as purge and

protective gas throughout. The graphite furnace temperature program and the operating parameters for the determination of seven elements in activated charcoal and carbon black samples are presented in Ref. 17.

UV/VIS spectrometry

A UV/vis spectrophotometer (UV-1202, Shimadzu) has been used to determine the Fe(II) absorbance at 510 nm.

Microwave-assisted acid digestion

Sample solutions for ICP OES analysis have been prepared using microwave-assisted acid digestion. A 0.1-g sample mass was weighed into a quartz vessel, 2.5 mL of hydrogen peroxide were added and the mixture was allowed to stand for a dwell time of 24 h. Afterwards 2.5 mL of concentrated nitric acid was added, the vessel sealed and placed into the rotor of the microwave oven (MIKROWAVE, Perkin–Elmer, Shelton, CT). Six vessels were used in each run using the temperature program described in Ref. 17. After treatment, the clear solutions were diluted to 25 mL with distilled, deionized water and used directly for measurement. In the case of residual particles the solution has been filtered before measurement.

Determination of Fe(II)

For the determination of Fe(II) 1 g of sample has been heated under reflux with 18 mL of 36% (v/v) HCl for 2 h and afterwards diluted to 100 mL with water. 25 mL of the extraction solution was mixed with 2.5 mL NH_4CH_3COO and 1 mL phenanthrolinium chloride. The absorbance of the resulting colored solution was measured at 510 nm by UV-vis photometry.

Multivariate data analysis (MVA)

Cluster analysis, principal components analysis (PCA) and partial-least-squares regression (PLS) were used for analysis.[20,21] All data were auto-scaled before the multivariate modeling. Calculations were carried out with STATISTICA[22] and UNSCRAMBLER[23] software.

RESULTS AND DISCUSSION

### Thermal stability of modified Lyocell solutions

Activated charcoal incorporated in cellulose fibers is accessible by the Lyocell technique. Thereby the charcoal particles have to be suspended in the Lyocell spinning solution, and then fibers may be pro-
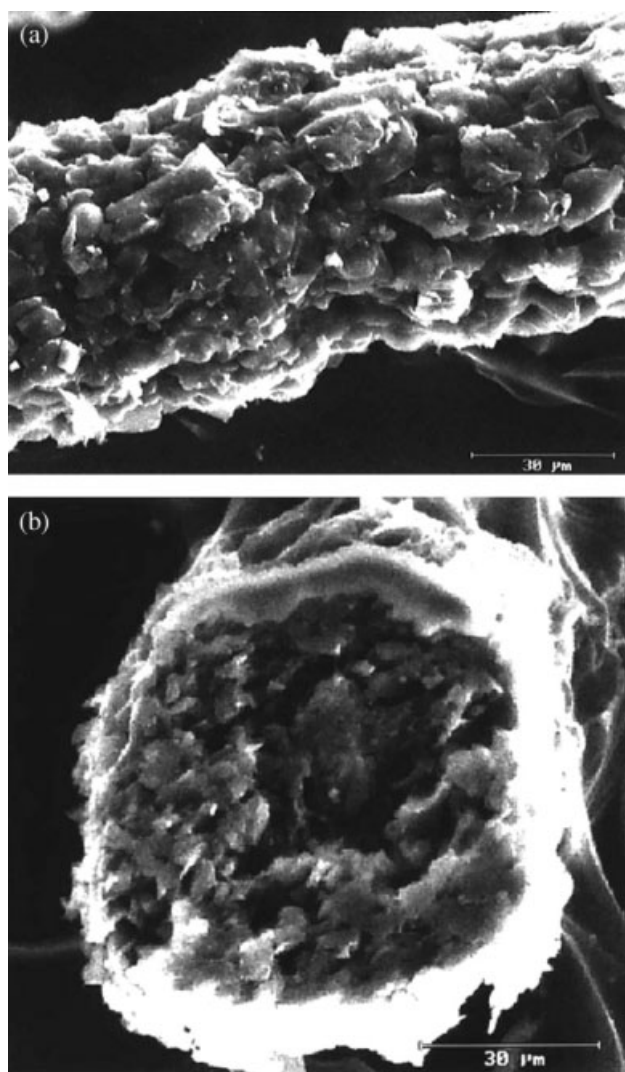
Figure 1 Scanning electron image of 100% activated charcoal incorporated in Lyocell fibers, 2000×.

duced from the solution by passing it through a nozzle into a water bath. By that way a blend of charcoal and cellulose is formed, whereas the charcoal particles are kept together by the surrounding cellulose matrix. The shape of a modified Lyocell fiber is depicted in Figure 1. The fiber has a rough and irregular exterior. On its surface particles of less than 10 µm diameter can be observed, that are nonabrasively embedded in the cellulose matrix. In this way the surface is enlarged and an extraction of organic compounds from vapor may be easier than with a fiber with a smooth surface.

Additives have to fulfill various requirements with regard to the Lyocell process, especially the aqueous conditions and the chemical structure and properties of NMMO. They have to show a high chemical resistance against water and NMMO, compatibility to cellulose, less solubility in water and a particle size below 20 µm. These requirements have
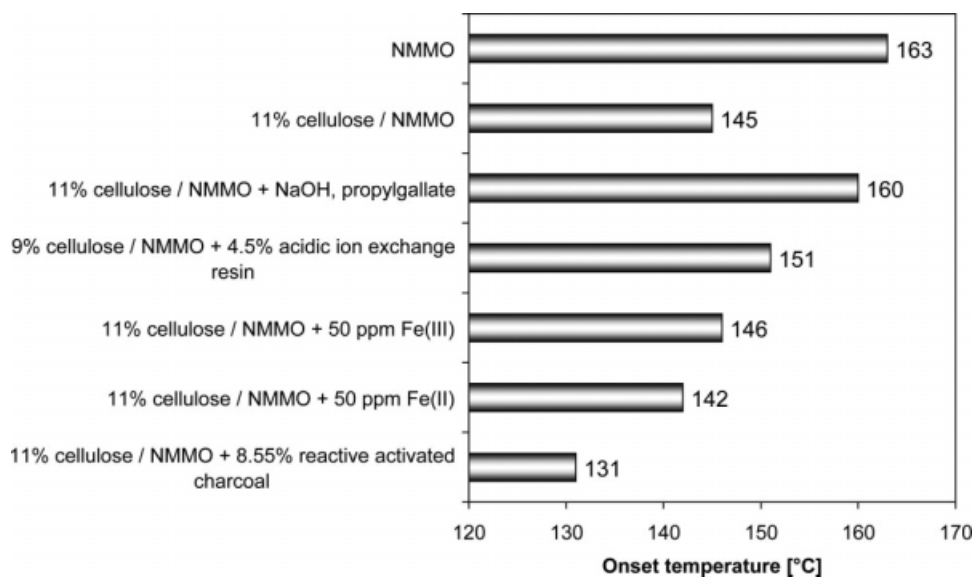
Figure 2 Comparison of onset temperatures obtained from dynamic reaction calorimetry measurements for NMMO and different modified cellulose/NMMO solutions.

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 obtain an efficient affect, 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. These reactions arise from the thermal instability and reactivity of the solvent NMMO, its reactions with cellulose and redox reactions of heavy metals.[8] Additives with functional groups or reactive surfaces influence the reaction mechanisms, change their directions or cause subsequent reactions. Figure 2 shows for NMMO and cellulose/NMMO solutions with different additives the decrease of the onset temperature (T_{on}) as the beginning of a first thermal activity.

To differentiate the effect of surface-active additives more precisely, investigations with different samples of activated charcoals (A) and carbon black (CB) were proceeded. Table I shows T_{on} for cellulose/NMMO solutions modified with different additives distinguishing in reactivity, adsorption capacity and concentration. It is obvious that reactivity and amount of the additive shift the start of decomposition to lower temperatures compared to unmodified cellulose/NMMO solutions. The solution filled with 8.55% A7 reaches a T_{on} of 128°C. T_{on} is enhanced by NaOH and PG being a commercialized stabilization system employed in the Lyocell process.[15] However, stabilization of modified solutions, especially with surface-active additives is a crucial issue, which is

partly solved for coals of lower reactivity as reported in earlier studies.[24] Stabilization of solutions with enhanced reactive charcoals (A6 and A7), special technological features must be applied as described later.

Stabilization of modified solutions

To evaluate the effect of activated charcoals and carbon black on the thermostability further calorimetric measurements were proceeded. Isoperibolic step experiments by means of the reaction calorimeter demonstrate the temporal behavior of the sample surrounded by a constant temperature but without shearing. Under technical conditions dead times may occur due to intermediate storage and transport. Therefore, it is necessary to test the thermal stability of cellulose solutions and suspensions at constant temperatures over long time periods. The formation of gaseous degradation products is attained by registering the pressure gradient at different temperature steps.

Figure 3 illustrates the isoperibolic pressure graphs of NMMO and 9% cellulose in NMMO as well as a 9% cellulose/NMMO solution modified with a reactive activated charcoal (A7) at different temperatures. Up to 120°C the unmodified solution and NMMO tend to a moderate pressure rise. A distinctive differentiation can be registered at 130°C and more enhanced at 140°C. Noteworthy, the pressure curve of NMMO lies clearly below that of the cellulose/NMMO solution. Even at 150°C a very intensive peak is detectable exceeding that of cellulose solution. As expected, NMMO shows an accelerated decomposition by cellulose. Quite far away from
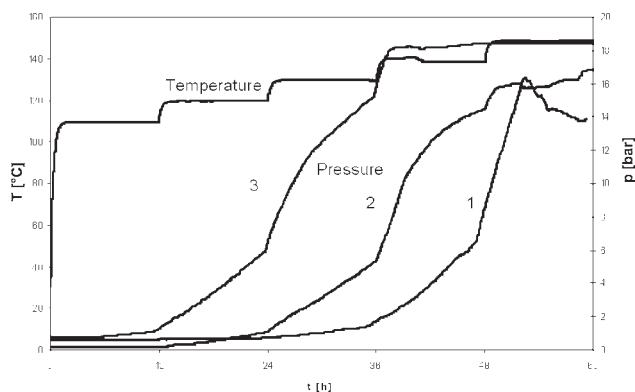
Figure 3 Changes in isoperibolic pressure of cellulose/NMMO and NMMO at different temperatures. Each temperature period was set to 12 h. (1) NMMO, (2) 9% cellulose in NMMO, (3) 9% cellulose in NMMO modified with an reactive activated charcoal.

that behavior concerns to the solution modified with charcoal showing amplified degradation processes. Even at 120°C a pressure rise is detected which is fortified at the change from 120 to 130°C. It has to be pointed out that also the application of stabilizers for the charcoal modified solution has no effect on the pressure slope. Neither the NaOH/PG system nor the recently studied polymeric system succeeded in the case of strongly reactive charcoals.[15,24]

From the above drawn conclusion for stabilizing charcoal modified Lyocell solutions, the insertion of charcoal into the cellulose/NMMO solution by dynamic mixing as well as short transportation paths and times of freshly prepared solutions are favorized.[14,25] Here, the spinnable molding mass with the incorporated functional materials is formed by two different mass streams, produced, stabilized and stored separately and firstly mixed directly before the forming module, for example, the spinning bar. The first material stream comprises a solution of cellulose in NMMO, the second is a mixture of NMMO, particular additives and water. The aim is to avoid the risk of a heat build-up in the spinning solution, production of cellulose molded bodies with adequately high DP and excellent functional properties and to restrict the decomposition of NMMO. The interactions between cellulose and additive are also to be restricted and a storage life for the additive suspension guaranteed.

Investigations have been carried out concerning the long time storage of the additive suspensions. As explained in the experimental part all suspensions were stirred in the reactor under vacuum up to a temperature of 60°C over 240 min and then directly subjected to the calorimetric isoperibolic measurements. The polymeric stabilizer system containing chelating iminodiacetic acid and benzyl amine bound to styrene-divinylbenzene-copolymer were used in all trials. Table II gives an overview of the maximum pressures and maximum pressure rises of the five suspensions and Figure 4 shows the pressure curves, respectively. Suspension S1 shows already after 24 h at temperature change from 60 to 70°C a remarkable pressure rise reinforced from 80°C and reaching the maximum at 90°C. So does suspension S2 stabilized with double mass of stabilizers even though with a lower rise. Also suspension S3, which was warmed up only up to 40°C, possesses a similar curve shape, however, below the curves of S1 and S2. In opposite to that, suspension S4 stabilized additionally with 5% NaOH shows not before reaching 90°C a diminished pressure rise, which is immediately attenuated. This behavior expresses minor degradation of NMMO, reactions between reactive sites of activated charcoal are depressed. By further storage of that suspension over 24 h before measurement (S5) pressure rise is moderately enhanced but at very low scale (less 2 bar). Fibers produced by using suspension S4 gave advantageous adsorption properties coupled with high adsorption capacities of organic solvents.

TABLE II
Maximum Pressure Slopes (dp/dt) and Maximum Pressures (p_{max}) of Suspension S1–S5 of Isoperibolic Measurements at 50, 60, 70, 80, 90, and 100°C, Each Stored for 12 h

Temperature	Suspension 1		Suspension 2		Suspension 3		Suspension 4		Suspension 5	
[°C]	dp/dt	p_{max}	dp/dt	p_{max}	dp/dt	p_{max}	dp/dt	p_{max}	dp/dt	p_{max}
50	0	0.61	0	0.67	0.0046	0.61	0.0060	0.55	0.0001	0.55
60	0.0061	0.79	0.0061	0.79	0.0051	0.61	0.0060	0.55	0	0.55
70	0.0073	1.89	0.0063	1.40	0.0061	1.04	0.0061	0.61	0.0061	0.55
80	0.0149	5.92	0.0115	4.33	0.0089	2.99	0.0064	0.79	0.0069	1.22
90	0.0214	8.42	0.0184	6.25	0.015	3.91	0.0082	1.04	0.0093	1.59
100	0.0211	9.22	0.0170	7.21	0.0161	3.91	0.0085	0.85	0.0071	1.42

p in [bar], dp/dt in [bar/min].
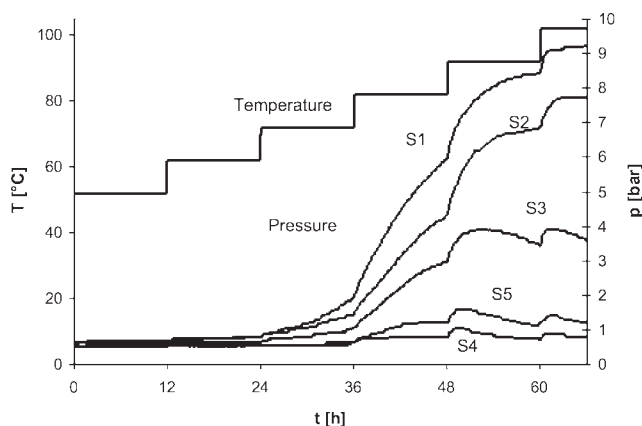
Figure 4 Changes in isoperibolic pressure of suspensions (S1–S5) from a reactive activated charcoal at different temperatures. Each temperature period was set to 12 h.

Trace element determination in coals and carbon black

Impurities in additives can severely attract reactions in cellulose/NMMO system resulting in a lower thermostability; namely, metals and halogens are embedded in meso- and micropores of activated charcoals and carbon black. Depending on their concentration (alkali and alkaline-earth metals) and valence state (heavy metals) they might interfere with the hydrogen bond system of cellulose and NMMO, shifting the pH level or initiating redox or radical reactions.

The ICP OES analysis of the coal and carbon black samples has been carried out after a microwave-assisted digestion using HNO_3 and H_2O_2, which could be considered the method of choice.[17] In this

work the proposed method has been modified, expanding the dwell time of H_2O_2 with the coals to 24 h. Addition of HNO_3 after that long period simplifies the access to the reaction sites, resulting in complete digestion for most samples. Each sample has been digested several times and the clear and colorless solutions were used for the measurements. Microwave-assisted digestion of the investigated coals has been successful without using HF mainly because they were originating of plant materials; lower alumina and silica contents promote complete or almost complete digestion.

Table III shows a survey of wavelengths, concentration ranges, quantification limits and relative standard deviations (RSD) for 16 elements in activated charcoal and carbon black samples measured by ICP OES after microwave-assisted digestion. Fe(II), determined by photometry, has been brought in as well because it is known to be an initiator of radical reactions.[7,26] The concentrations of the various elements are very differently distributed with higher amounts of Na, K, Ca, Mg and Fe and traces of the other elements. Ni and V could be determined in one carbon sample only with a concentration of 307 mg kg^{-1} and 653 mg kg^{-1}, respectively. Noteworthy, the proportion of Fe(II) is about 50–90% of total iron.

The limits of quantification (LOQ) of the ICP OES measurement (Table III) were calculated by calibration curve method according to the German standard DIN 32645. Except for nonspecific interferences there have been only slight spectral coincidences with the analytical lines. As an example, the copper line at 327.393 nm is affected by sodium (327.422 nm); however, the resolution of the spectrometer

TABLE III
Survey of Element Concentrations, Wavelengths, Quantification Limits (LOQ) and Relative Standard Deviation (RSD) in Activated Charcoal and Carbon Black Samples Measured by ICP OES After Microwave-Assisted Digestion and Photometry (Fe[II]), Respectively

| Element	Wavelength/nm	LOQ/mg kg^{-1}	Concentration range/mg kg^{-1}	RSD/%	n
Al	396.153	12	21 – 402	6 – 25	5
Pb	220.353	4	4 – 13	7 – 10	3
Cd	228.802	0.4	0.5 – 1.1	2 – 31	5
Ca	317.933	5	42 – 562	4 – 6	5
Cr	267.716	1	1 – 106	2 – 20	6
Co	228.616	2	2.5 – 3	5 – 23	3
Cu	327.393	1	1 – 18	5 – 10	6
Fe	238.204	2	14 – 684	1 – 10	6
Fe(II)	510	2.5	28 – 657	10 – 15	4
K	766.490	25	16 – 9813	3 – 10	5
Mg	285.213	5	8 – 319	3 – 8	5
Mn	257.610	0,5	0,5 – 10	3 – 8	6
Mo	202.030	2	2 – 12	19	6
Na	589.592	25	147 – 896	2 – 7	5
Ni	231.604	2	2 – 307	1 – 17	5
V	292.464	1	1 – 653	10	6
Zn	206.200	2	2 – 14	9 – 25	5
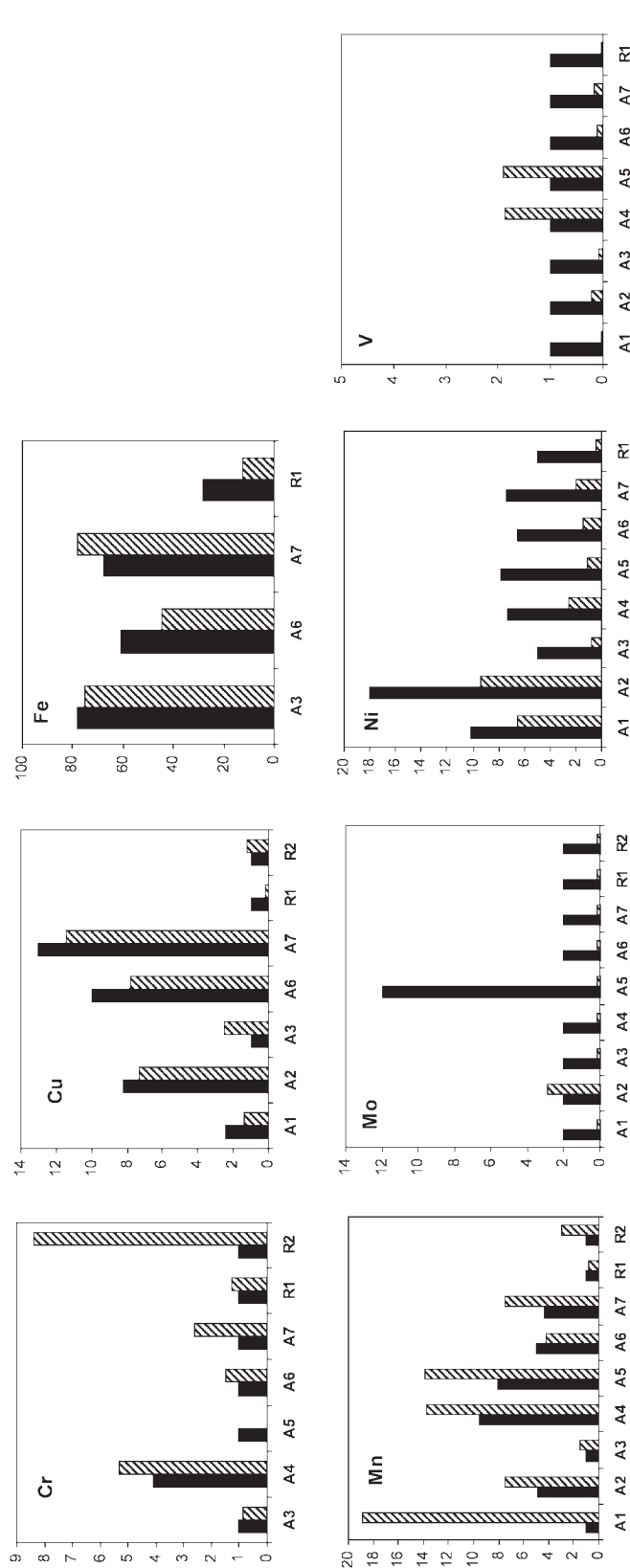
Figure 5 Results (mg kg^{-1}) obtained for the analysis of activated charcoal and carbon black samples using ICP-OES (■) and SS-HR-CS GF AAS (▨).

and the reading of only two or three pixels in the middle of the analyte line guarantee an accurate measurement.

The elements Cr, Cu, Fe, Mn, Mo, Ni, and V have also been determined using direct solid sampling high-resolution continuum source graphite furnace AAS (SS-HR-CS GF AAS) as a reference method. The GF AAS technique is well suited for trace and ultra trace analysis, particularly when direct SS is used, as no sample dilution is involved. Hence, the determination of iron is a challenge, firstly because of its ubiquitous character in the environment (blank values), and secondly, as it is often present not as a trace element, but at relatively high concentration, especially in coals. For this reason suitable iron lines had to be searched for, the sensitivity of which is appropriate for the iron concentration. Fortunately iron has more than 600 absorption lines that are all available for analytical purposes in HR-CS AAS due to the use of a high-intensity continuum radiation source.[19] Measurements have been carried out simultaneously at two secondary lines at 344.099 nm and 344.388 nm, which are both within the spectral range covered by the array detector, increasing even more the dynamic range for the iron determination. Consequently, two calibration curves for Fe were established both with blank and six calibration standards. While wavelength 344.099 nm covers the concentration range of 0.1–0.8 mg L^{-1} with a linear relationship $A_{int} = 0.01889$ m $+ 0.0008$ ($R = 0.9995$), wavelength 344.388 nm spans the concentration range 0.4–2.5 mg L^{-1} with $A_{int} = 0.00511$ m $+ 0.0064$ ($R = 0.9992$), respectively.

In Figure 5 the results of AAS are compared with those obtained by ICP OES after microwave-assisted acid digestion. The AAS values are the average of five measurements (confidence interval at the 95% level); typical RSD data of the ICP OES analysis are given in Table III. As mentioned earlier SS-HR-CS GF AAS is a technique for trace and ultra trace determinations; consequently, not all samples could be measured with this technique due to excessively high analyte concentration, especially in the case of Fe. On the other hand, quite a number of samples could not be measured with ICP OES as the concentrations were below the LOQ of this technique (Mo, Ni, V). Nevertheless, there have been a sufficiently large number of samples that could be analyzed with both techniques, particularly in cases where less sensitive lines have been used for HR-CS GF AAS, making possible a comparison of the results.

The RSD figures of both methods are between 1 and 25%, depending on the concentration level and with throughout higher values for ICP OES measurements, except for high analyte concentrations. As expected the LOD of SS-HR-CS GF AAS are far lower than those of ICP OES. Even Mo and V could
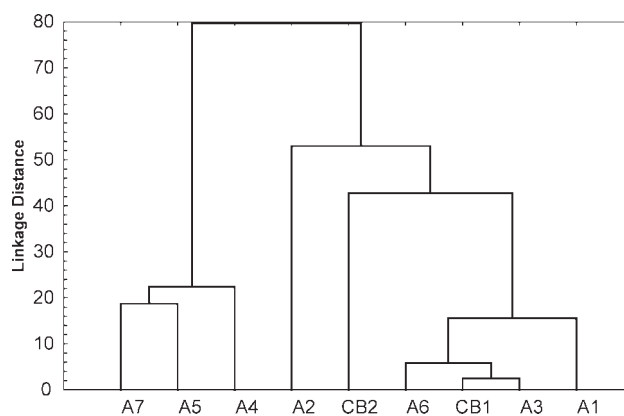
Figure 6 Dendrogram of clustering for activated charcoals and carbon blacks based on 16 elements determined by ICP OES and Fe(II); WARDs method, squared Euclidian distances.

be determined much more accurately and with higher sensitivity as described in detail in Ref. 17.

Prediction capability of T_{on}

For further comparison of both methods the correlation between heavy metal status and onset temperatures (T_{on}) of cellulose/NMMO solutions modified with the activated charcoals and carbon black ought to be considered. Regarding a statistical interpretation partial least squares regression (PLS) between measured values for T_{on} and those calculated from metal concentrations has been found to be a useful tool.[27] T_{on} is a very convincing variable to investigate the beginning of exothermicity and has to be served as a reference for the evaluation. Hierarchical agglomeratic cluster analysis (CA) and principal component analysis (PCA) have been applied before the data were treated with PLS to evaluate the data structure and to discover classes among the samples. Figure 6 shows the dendrogram of clusters of seven activated charcoals and two carbon black samples calculated for the 16 parameters obtained by ICP OES plus the Fe(II) obtained by photometry. It has been found that Euclidean distance and Ward's linkage was the best combination using CA. Two main clusters are apparent: (i) coals A4, A5, A7; and, (ii) coals A1, A2, A3, A6 and carbon blacks CB1 and CB2. Interestingly, the main clusters correlate well with the onset temperature (T_{on}) of those solutions modified by the additives. Coal sample A1 with T_{on} 147°C appears in the dendrogram with the highest distance to solutions added with coal A7 (T_{on} 137°C) and A5 (T_{on} 134°C). Thus, there is a relation between T_{on} of the solution and the metal status. The element concentration possesses a data structure and is representative for a calibration. PCA revealed that Fe, Fe(II) and K deliver the highest variance and,

	T_{on} (measured)	T_{on} (calculated)
	[°C]	[°C]
A1	147.0	146.0
A2	144.0	143.0
A3	140.0	139.3
A4	139.0	139.8
A5	134.0	134.0
A6	141.0	139.9
A7	137.0	136.7
CB1	144.0	144.0
CB2	146.0	145.8

consequently, the most information concerning thermostability.

The results of PLS regression for calculation of T_{on} using ICP OES showed that this technique only gives an acceptable correlation of $R = 0.7714$ with an error of prediction of 2.66% employing 16 metals and Fe(II). With only seven variables (the elements that have also been determined by AAS), the correlation coefficient has only been $R = 0.416$ with an error of prediction of 3.67%. The results obtained by SS-HR-CS GF AAS with 7 variables (Cr, Cu, Fe, Mn, Mo, Ni, V), in contrast, exhibit a correlation coefficient of $R = 0.99$, and an error of prediction of only 0.68%. A comparison of the T_{on} values predicted by the metal determinations of SS-HR-CS GF AAS and the values obtained from dynamic reaction calorimetric measurements is shown in Table IV for all the investigated samples. It is evident that Fe belongs to the significant variables with the highest variance and, consequently, the most information concerning the thermostability.

CONCLUSIONS

Cellulose/NMMO solutions filled with surface-active additives have been investigated. This report concerns a continuation of stabilization studies concerning the handling of solutions modified with higher reactive activated charcoals. The application of a dynamic mixing tool to incorporate an additive suspension directly before the forming module reduces the risk of exothermicities. Beside this technological feature, the stabilization by means of a polymeric stabilizer system containing chelating iminodiacetic acid and benzyl amine bound to styrene-divinylbenzene-copolymer and sodium hydroxide increased the storage life-time for suspensions of reactive activated charcoals in NMMO. Thermal long-time behavior of that suspensions has been investigated by isoperibolic step measurements. Reduced

pressure rise indicated minor degradation of NMMO, interactions between cellulose and additive are also to be restricted and a storage life for the additive suspension guaranteed.

Further investigations concerned the precise evaluation of the additives. Properties such as metal content is of utmost importance for the application of coals for the Lyocell process. Heavy metal impurities can severely attract reactions in the cellulose/NMMO system leading to a lower thermostability. Different additives, especially activated charcoals decrease the onset temperature (T_{on}) as the beginning of a first thermal activity. Activated charcoal and carbon black samples have been analyzed for 16 elements by means of ICP OES after microwave-assisted acid digestion and Fe(II) by spectrophotometry. For comparison Cr, Cu, Fe, Mn, Mo, Ni, and V have also been determined by SS-HR-CS GF AAS being a reference method for samples that are difficult to be brought into solution. The prediction capability of this technique is much higher and requires a smaller number of input data.

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