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Investigation of the spinnability of cellulose/alkaline ferric tartrate solutions

Hai Vu-Manh[a,b,1], Frank Wendler[c,1], Hale Bahar Öztürk[a,1], Thomas Bechtold[a,*,1]

[a] Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstr. 73, A-6850 Dornbirn, Austria
[b] Faculty of Textile-Garment Technology and Fashion Design, Hanoi University of Technology, Hanoi, Viet Nam
[c] Centre of Excellence for Polysaccharide Research, Thuringian Institute for Textile and Plastics Research, Breitscheidstr. 97, D-07407 Rudolstadt, Germany

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ABSTRACT

Dynamic rheology, UV/VIS spectrometry with temperature programming cuvette and reaction calorimetry were conducted on cellulose pulp/FeTNa (NaOH solution containing ferric tartaric acid complex) solutions to investigate their thermostability and spinnability. Color of cellulose/FeTNa solutions changed above 90 °C due to the decomposition of the complex. Thermal activity of cellulose/FeTNa solution started above 130 °C induced by water vapor evolution and complex decomposition. Regeneration of cellulose/FeTNa solutions in a non-solvent (acetic acid and Na-gluconate mixture) resulted in transition from cellulose I into cellulose II structure as revealed by WAXS measurements. Wet-spinning attempts of cellulose/FeTNa solutions yielded fiber-like shaped bodies with a brittle structure.

1. Introduction

Cellulose as biopolymer receives more and more attention regarding to the manufacture of innovative materials beyond the textile sector. Efficient dissolution of cellulose exhibits the starting point for both chemical and physical functionalization (Persin et al., 2011). There are two different routes for cellulose dissolution: *derivatizing* solvents, e.g. formic acid/zinc chloride, carbon disulfide/NaOH, nitrogen tetraoxide/dimethyl formamide, etc. dissolve cellulose with *chemical* interactions, while *non-derivatizing* solvents, e.g. transition metal complex solutions, ionic liquids, *N*-methylmorpholine-*N*-oxide (NMMO, Lyocell process) concern to systems dissolving the polymer physically only by intermolecular interactions. Both processes transform the original supramolecular structure from cellulose I to cellulose II (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). Physical dissolution processes under technical conditions, especially the Lyocell process, involve chemical alterations due to pressure and heat treatments, which cause the degradation of both cellulose and solvent (Rosenau, Potthast, Sixta, & Kosma, 2001; Taeger et al., 1985; Wendler, Graness, Buettner, Meister, & Heinze, 2006; Wendler, Graness, & Heinze, 2005). Therefore, setback of temperature in processing is a necessity avoiding degradation reactions and even exothermicities, so-called thermal runaway reactions, which may end up in deflagrations. In this matter, the search for new and/or application of already well-known solvent systems is an important topic of research.

Swelling-dissolution mechanisms and structural changes of sulfite and sulphate pulp (Unger, Fink, & Philipp, 1995), cotton linters and hydrolysed cotton linters (Pionteck, Berger, Morgenstern, & Fengel, 1996), lyocell, viscose and modal fibers (Vu-Manh, Öztürk, & Bechtold, 2010a; Vu-Manh, Öztürk, & Bechtold, 2010b; Vu-Manh, Öztürk, & Bechtold, 2010c) were intensively studied in FeTNa (ferric tartaric acid complex in NaOH) solution. The fiber diameter, length shrinkage of lyocell fibers and crimping of lyocell yarns in FeTNa solution were also investigated (Kasahara, Sasaki, Donkai, Takagishi, & Hamada, 2010). Viscosity distribution of cellulose was studied by changing the temperature and NaOH concentration of FeTNa solution (Malm, Glegg, & Luce, 1961). A cellulose concentration of above 2% in FeTNa solution was mentioned to form gel-like structures (Klemm et al., 1998).

FeTNa treatment on lyocell yarn with regard to the treatment time, temperature, and excess NaOH concentration was conducted to analyze the weight loss, crystallinity index and tenacity of the yarn (Kasahara et al., 2010). Dissolution and regeneration of microcrystalline cellulose in FeTNa was studied in terms of morphology, crystallinity, thermal stability and degree of polymerization (El-Wakil & Hassan, 2008).

Literature data on chemical interactions of FeTNa/cellulose solutions comprising heat and pressure effects (industrial conditions) are missing. Despite the production of regenerated cellulose

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* Corresponding author. Tel.: +43 557 228 533; fax: +43 557 228 629.
E-mail addresses: Thomas.Bechtold@uibk.ac.at, textilchemie@uibk.ac.at (T. Bechtold).

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(El-Wakil & Hassan, 2008) and Fetnaphane membrane (Naim & El-Tawil, 1982) from cellulose/FeTNa solutions, fiber production studies do not exist in the literature. Furthermore, the maximum cellulose concentration that can be dissolved in FeTNa solution has also not been mentioned yet.

The current communication describes a study on the thermostability by means of rheological, calorimetric and spectroscopic methods and wet-spinning of cellulose/FeTNa solutions. Maximum cellulose concentration dissolvable in FeTNa was studied depending on temperature and mixing shear force. The structure of regenerated cellulose from cellulose/FeTNa solution was evaluated by WAXS and optical microscopy.

2. Experimental procedure

2.1. Materials

MoDo pulp (Domsjö AB, Sweden) with following data was used: α-cellulose content = 93.47%, degree of polymerization (DP) = 610, carboxyl group = 11.12 μmol/g (determined according to Götze, 1967), carbonyl group = 35.9 μmol/g (determined according to Szabolcz, 1961), moisture content = 6.45 ± 0.03%.

Analytical grade sodium hydroxide NaOH (>98%) from Fluka; iron (III) chloride-6 hydrate ($FeCl_3.6H_2O$) (>99%) from Riedel-de Haen AG; tartaric acid ($C_4H_6O_6$) (>99.5%) from Merck and research grade sorbitol ($C_6H_{14}O_6$) from Serva-Feinbiochemica GmbH & Co were used. Analytical grade H_2SO_4 (>98%) from Merck and technical grade sodium gluconate from CHT R. Beitlich GmbH were used for the coagulation-bath after spinning study.

2.2. Methods

2.2.1. Preparation of FeTNa solution

FeTNa solution with a molar ratio of $FeCl_3.6H_2O$:tartaric acid:NaOH as 1:3.28:9.56 were prepared. The concentration of Fe ion was 0.30 M. In addition, 2.5 M free NaOH was added. The procedure was explained in literature (Vu-Manh et al., 2010a, 2010b).

2.2.2. Preparation of cellulose/FeTNa solutions

Two different ways for the preparation of cellulose/FeTNa solutions were used:

a) 3 and 4% cellulose/FeTNa solutions were prepared at room temperature by swelling pulp in FeTNa solution for 16 h. 3% cellulose/FeTNa solution was used for UV/VIS spectroscopy analyses, while 4% cellulose/FeTNa solution was used for optical microscope, reaction calorimetry, WAXS analyses, rheology analyses and spinning experiments.
b) 8 and 12% cellulose/FeTNa solutions were prepared at −9 °C by mixing them in Messkneter H60 (IKA Analysentechnik) (25 rpm) for 5 h. After keeping these cellulose/FeTNa solutions at room temperature for 16 h, they were used for optical microscope (8 and 12% cellulose/FeTNa solution) and rheology analyses (8% cellulose/FeTNa solution).

2.2.3. Optical microscopy analyses

Optical characterisation of cellulose solutions was carried out by means of polarisation microscopy (ZEISS Axiolab) (Kosan, Schwikal, & Meister, 2010).

2.2.4. UV/VIS spectrometry with temperature programming cuvette

A Shimadzu UV-2401 spectrometry was used for monitoring the temperature- and time-dependent changes in 3% cellulose/FeTNa solution. Absorbance/time graphs were plotted by covering a wavelength range of 200–600 μm. The cuvette temperature was adjusted from room temperature to 120 °C. The path length of sample solution was 0.35 mm, which was adjusted by a round-shaped container (Wendler et al., 2005)

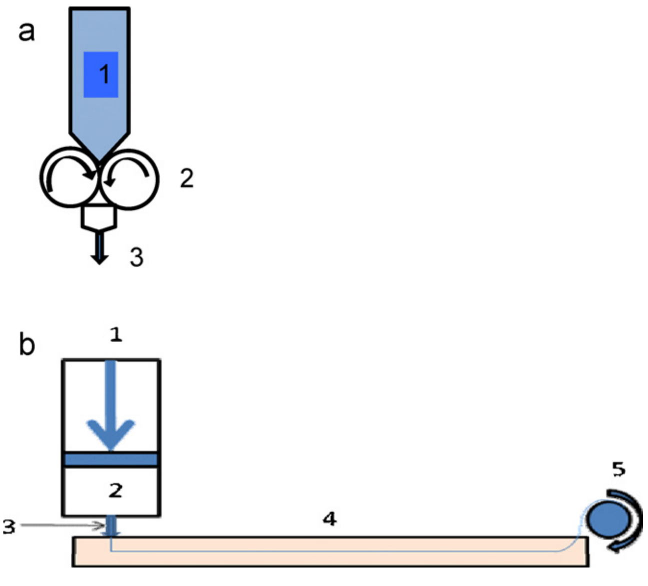

Fig. 1. (a) Wet-spinning equipment with gear pump (1, cellulose/FeTNa solution; 2, pressing gears; 3, spinerette). (b) Spinning equipment with piston (1, self-made piston; 2, cellulose/FeTNa solution; 3, nozzle with a diameter of 500 μm; 4, coagulation bath; 5, rotating drum).

2.2.5. Reaction calorimetry

Thermal investigations of 4% cellulose/FeTNa solution were conducted with the Systag calorimeter RADEX (miniautoclave). The sample solution was placed in the stainless steel vessel (design pressure: 100 bar) equipped with bursting disk and internal temperature sensor. The vessel was kept by a temperature controlled steel/aluminium jacket. The temperatures of vessel and jacket were measured continuously. The vessel was heated with a heating rate of 0.75 K/min from room temperature to 300 °C (Scanning experiment). The temperature rate (dT/dt) and pressure rate (dp/dt) of the sample were investigated in relation to temperature (Wendler et al., 2005).

2.2.6. Dynamic rheology analysis

Dynamic rheology measurements of cellulose/FeTNa solutions were carried out on a rheometer Haake MARS II with electrically heated cone/plate measuring tool (4° angle geometry). Oscillation measurements were provided at 30, 40 and 50 °C and the master curves were calculated for a reference temperature of 40 °C. Master curves were displayed by the illustration of storage and loss modulus regarding to the angular velocity of the cellulose/FeTNa solution samples.

2.2.7. Wide-angle X-ray scattering (WAXS)

4% cellulose/FeTNa solution was prepared at room temperature after swelling for 16 h. The cellulose/FeTNa solution was regenerated by a coagulation-bath containing 600 g sodium gluconate and 300 ml H_2SO_4 in 1000 ml water. The regenerated cellulose was washed with water and further crushed in a triturator in order to prepare a powder-like material, which was placed between two polypropylene films for WAXS measurement. The X-ray graph was obtained by D8 Advance equipment (Bruker AXS GmbH).

2.2.8. Spinning trials

Fig. 1 shows the two methods for the wet-spinning experiments, which are functioning with either gear pump or piston. For

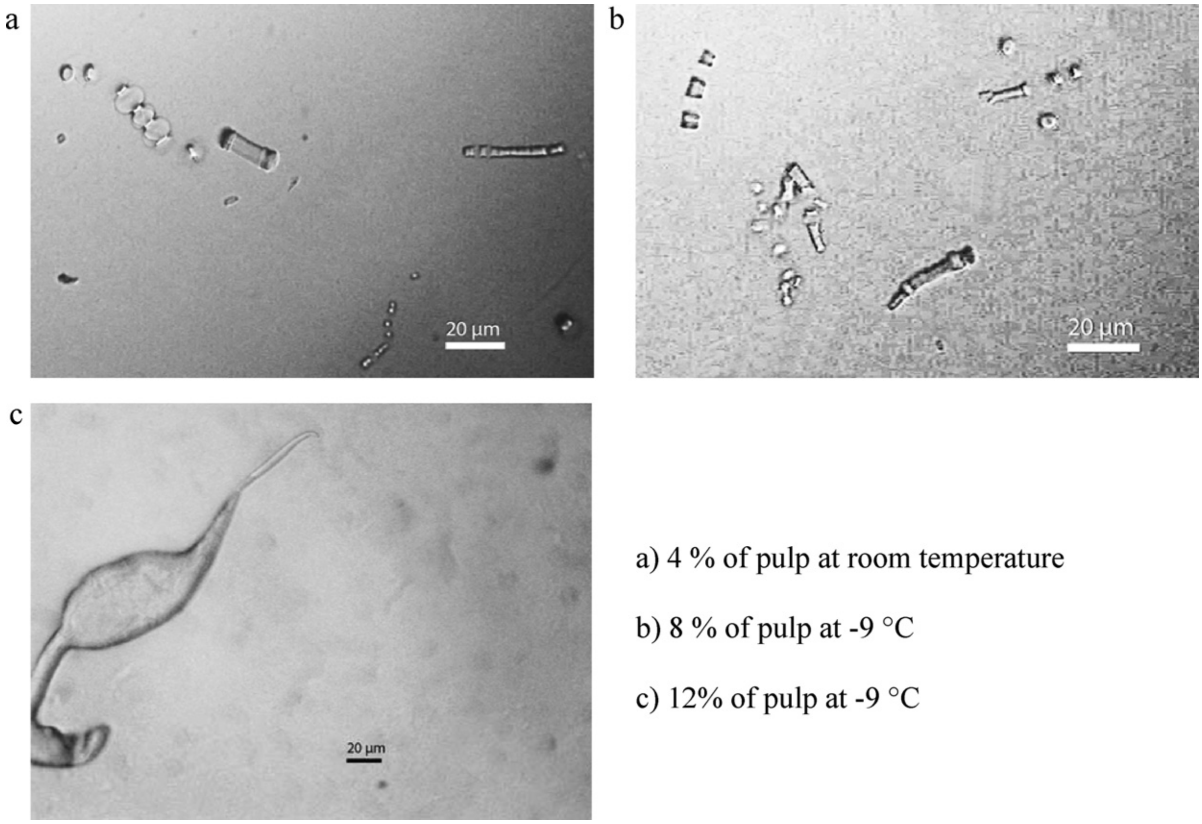

Fig. 2. Optical microscope images of (a) 4% cellulose/FeTNa solution dissolved at room temperature, (b) 8% cellulose/FeTNa solution dissolved at −9 °C by usage of 25 rpm shear force and (c) 12% cellulose/FeTNa solution dissolved at −9 °C by usage of 25 rpm shear force.

the piston-method, the temperature of 4% cellulose/FeTNa solution was 60 °C before passing through the nozzle. The coagulation bath for the shaped regenerated cellulose contained 600 g sodium gluconate and 300 ml H_2SO_4 in 1000 ml water, while the coagulation time was ca. 2 min at room temperature. The fiber-shaped bodies were washed with tap water and then dried at room temperature.

Coagulation bath contained sodium gluconate to remove bound Fe from cellulose and H_2SO_4 to neutralize the alkalinity of FeTNa.

3. Results and discussion

3.1. Cellulose/FeTNa solutions

Various cellulose concentrations (3–12%, w/w) were dissolved in FeTNa solution. At room temperature maximum cellulose concentration dissolved was found to be ca. 4%. By further decrease of temperature and increase of shear force mixing of solution enhanced the cellulose concentration dissolvable in FeTNa solution. Consequently, at −9 °C, the maximum cellulose concentration in FeTNa was found to be ca. 8%. With the usage of shear force (Messkneter H60-IKA Analysentechnik, 25 rpm) at −9 °C, the maximum cellulose concentration to be dissolved in FeTNa solution increased to ca. 12%.

To evaluate the dissolution states of cellulose/FeTNa solutions, optical microscopy analyses were conducted. The solutions were clear in general, while undissolved cellulose particles and fiber residues were also found rarely. Fig. 2 shows optical microscope images of selected cellulose/FeTNa samples, which contain undissolved cellulose as well as the ballooning of undissolved fibers in selected regions.

FeTNa solutions have a transparent green color, which does not change by incorporation of cellulose. Fig. 3 shows the influence of temperature on the absorbance of a 3% cellulose/FeTNa solution. At wavelength from 450 to 750 nm (visible region), the color of cellulose/FeTNa solution was transparent at room temperature, 60 and 80 °C (absorbance ca. 0.1). From 90 °C, the absorbance of cellulose/FeTNa solution became higher, which can be attributed to the decomposition of the cellulose-FeTNa complex structure. Formation of turbid solution from green transparent cellulose/FeTNa solutions can be attributed to (a) precipitation of $Fe(OH)_3$ due to limited thermostability of FeTNa complex, (b) precipitation of $Fe(OH)_2$ due to reduction of Fe^{3+} to Fe^{2+}.

Fig. 4 gives more detailed results to the Fig. 3 showing the influence of cuvette temperature and time on the extinction at $\lambda = 400$ nm of a 3% cellulose/FeTNa solution. The extinction of a 3%

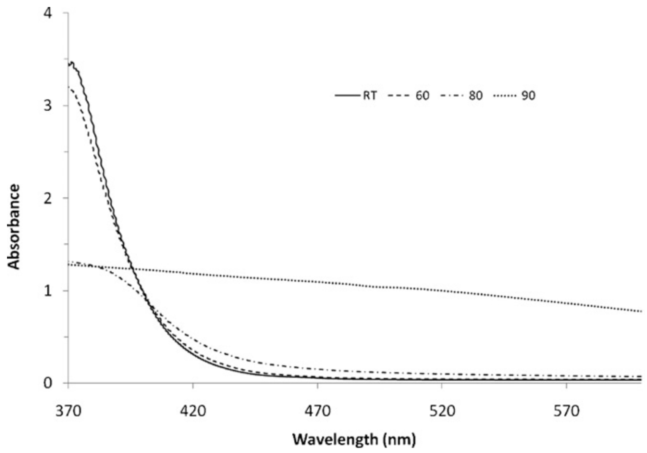

Fig. 3. Changes in UV/VIS spectrum of a 3% cellulose/FeTNa solution at room temperature (RT), 60, 80 and 90 °C.

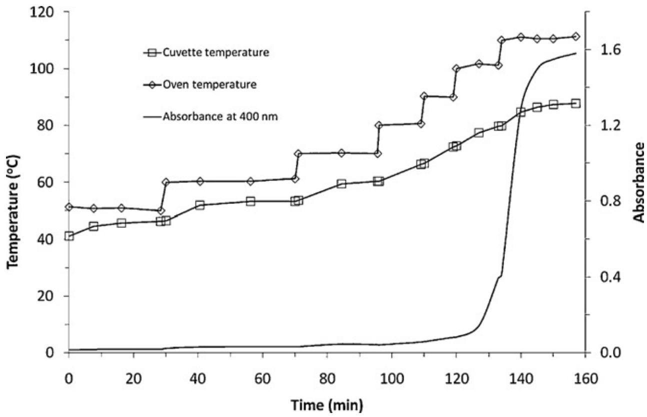

Fig. 4. Influence of cuvette temperature and time on the extinction of a 3% cellulose/FeTNa solution, determined at $\lambda = 400$ nm.

cellulose/FeTNa solution was found to be low (ca. 0.1) at 70 °C, while it became 1.2 at ca. 88 °C.

The temperature at which a change in the color occurred due to the instability of cellulose/solvent mixture can be described in the following order: cellulose/FeTNa (90 °C) < cellulose/NMMO (120 °C) < cellulose/BMIMCl (> 140 °C).

Reaction calorimetry (RC) measurements were conducted to receive a more detailed view of the thermal behavior. Further, RC is usually used as safety measurement tool being more similar to real-time conditions. Especially, in the case of cellulose/NMMO solutions which are crucial with regard to the higher process temperatures between 90 and 110 °C, exothermic reactions can occur due to increase in both temperature and pressure. Using RC, the formation of gaseous degradation products is registered by means of pressure measurement in connection with the increase of temperature (Wendler et al., 2005). Even though cellulose/FeTNa solutions are prepared at RT or lower temperatures, thermostability monitoring over an expanded temperature range exhibits a must for a comprehensive process development.

Fig. 5 shows the scanning of pressure and temperature of a 4% cellulose/FeTNa solution from RT to 300 °C. The onset and offset temperatures at the beginning and end of thermal activity were found to be between 130 °C and 160 °C, respectively. The sample temperature curve shows in this region a slight drop indicating an endothermic event with a generated heat of 209 J/g as shown in Fig. 6 in comparison to tartaric acid, which was included to confirm the calorimetric measurements. The value measured for tartaric acid was 243 J/g. This result corresponds to the literature value of 229 J/g (Li, Zhou, & Huang, 1991). As can be seen the transition peak of the cellulose/FeTNa solution appears earlier, which means that the complex is prone to degrade at lower temperature. This is reflected by the temperature slope with respect to time displayed in Fig. 7. The drop of temperature can be marked at around 160 °C for tartaric acid, which complies with 162 °C found in literature for the melting point (Li et al., 1991). At this temperature tartaric acid starts to degrade. Quite far from this behavior, a degradation temperature of approx. 140 °C followed by a slight temperature enhancement at around 165 °C was ascertained for the cellulose/FeTNa solution. Noteworthy, in view of the pressure measurement a moderate rise is detected from 80 °C in opposite to the pure tartaric acid that possesses a remarkable slope even at 165 °C (Fig. 8). This pressure evolvement at lower temperatures mainly due to water evolution is accompanied by complex decomposition as evaluated above by UV/VIS measurements. Therefore, it can be concluded that the FeTNa complex is thermal stable up to ca. 80 °C.

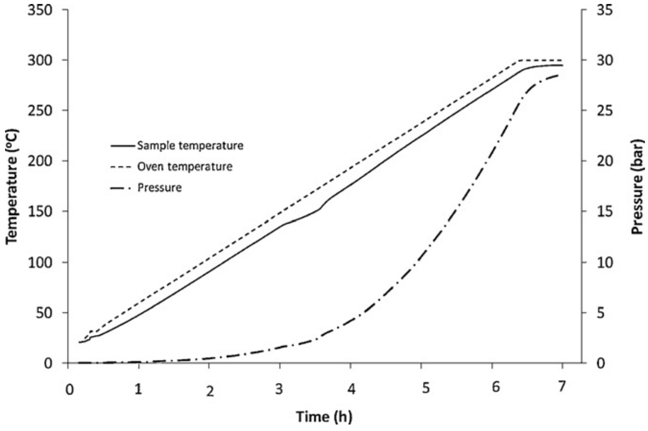

Fig. 5. Reaction calorimetry. Scanning of temperature and pressure of a 4% cellulose/FeTNa solution.

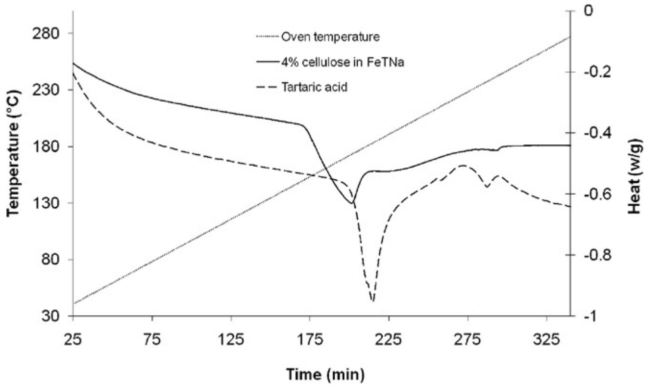

Fig. 6. Reaction calorimetry. Transition enthalpy of a 4% cellulose/FeTNa solution and pure tartaric acid depending on temperature and time.

The maximum pressure rate (ca. 0.0038 bar/s) of 4% cellulose/FeTNa solution was found to be lower than that of cellulose/BMIMCl (ca. 0.0095 bar/s) and cellulose/NMMO solutions (ca. 0.87 bar/s) in the literature. This can attributed to the evolvement of water vapor causing less pressure rate in the case of cellulose/FeTNa compared to deoxygenation products of NMMO and BMIMCl (Dorn, Wendler, Meister, & Heinze, 2008).

3.2. Dynamic viscoelastic properties

Dynamic rheology is a sensitive method to study the gel formation of polymer systems while providing precise indication of gelation time. In this technique, the samples are subjected to small

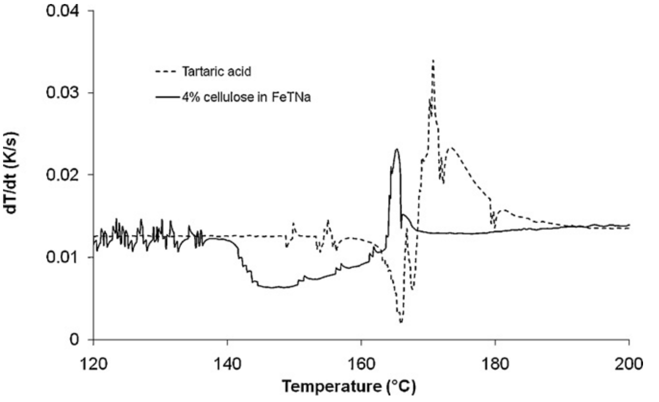

Fig. 7. Reaction calorimetry: Slope of temperature (dT/dt) of a 4% cellulose/FeTNa solution and pure tartaric acid.

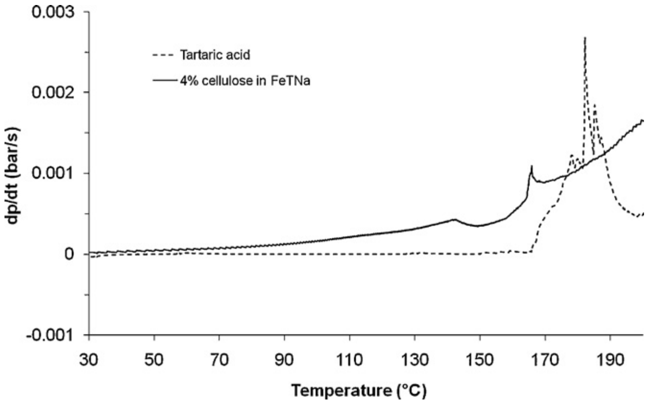

Fig. 8. Reaction calorimetry: Slope of pressure (dp/dt) of a 4% cellulose/FeTNa solution and pure tartaric acid.

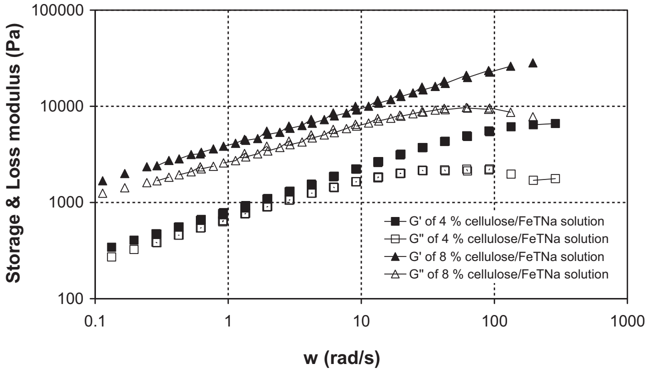

Fig. 9. Storage and loss modulus in relation to angular velocity of (a) 4% cellulose/FeTNa solution and (b) 8% cellulose/FeTNa solution.

amplitude oscillatory deformations, and the stress (τ_{yx}) amplitude is related to strain (γ_o) amplitude by frequency of oscillation (ω), time (t), storage (elastic) modulus (G'), loss (viscous) modulus (G'') as following (Bird, Armstrong, & Hassager, 1987):

$$\tau_{yx} = G'\gamma_o \cos\ (wt) + G''\gamma_o \sin(wt) \tag{1}$$

Fig. 9 shows the storage and loss modulus with regard to the angular velocity of 4 and 8% cellulose/FeTNa solutions. Over the entire range of angular velocity (from 0.1 to 1000 rad/s), the *storage* (*elastic*) *modulus* (G') value was higher than that of loss (viscous) modulus (G''). Hence, *elastic properties* dominate the viscous properties causing the *gel behaviour* of cellulose/FeTNa solutions. Therefore, viscosity determination of FeTNa/cellulose *gel* is not meaningful.

The storage modulus of a 8% cellulose/FeTNa solution was found to be higher than that of a 4% cellulose/FeTNa solution, which shows higher the cellulose concentration, higher the storage modulus (Fig. 9). It suggests that more aggregates and entanglements of the cellulose chains occur at higher cellulose concentration making the cellulose chains stiffer and have more interaction (Cai & Zhang, 2006).

When the storage modulus is scaled approximately with the angular frequency (w), the cellulose solution shows liquid-like properties. If the storage modulus is scaled with the square of angular velocity (w^2) at low frequencies, the cellulose solution shows Newtonian fluid (non-entangled) polymer solution behaviour (Cai & Zhang, 2006), e.g. a 7.6% cellulose/NaOH solution shows Newtonian behaviour at temperatures from 10 to 25 °C (Gavillon & Budtova, 2007).

Viscosity is an important and basic parameter for spinning: too low or too high viscosity of cellulose solution does not form a fiber. Consequently, too low viscosity of a spinning fluid causes the formation of individual drops, while too high viscosity reduces the extrusion rate to impractically slow values (Hudson, 1996). The gel property of cellulose/FeTNa solutions (Fig. 9) is a sign for the problems in spinning tests. Furthermore, spinning process requires cellulose concentrations above 8% for industrial applications towards acceptable productivity.

3.3. Shaping of cellulose/FeTNa solutions

Various spinning techniques are available for different types of polymers. *Melt spinning* method involves the extruding of an undiluted melt of the *thermoplastic* polymer into gaseous or liquid cooling chamber. However, cellulose has thermal degradation temperatures below its melting temperature and thus requires the presence of a solvent to produce a spinnable fluid. Depending on the nature of the solvent, a polymer/solvent mixture can be modified into a filament by dry spinning or wet-spinning method. In *dry spinning*, the polymer is dissolved in a volatile solvent and then is introduced into a drying chamber, where the solvent is evaporated (and recovered) and solid filament is obtained. In *wet-spinning*, the polymer solution is spun into a liquid bath containing a non-solvent to precipitate the filament. Then the filament is washed (Hudson, 1996).

For the current work, spinning trials using gear pump were not successful to produce fiber from cellulose/FeTNa solution, mainly

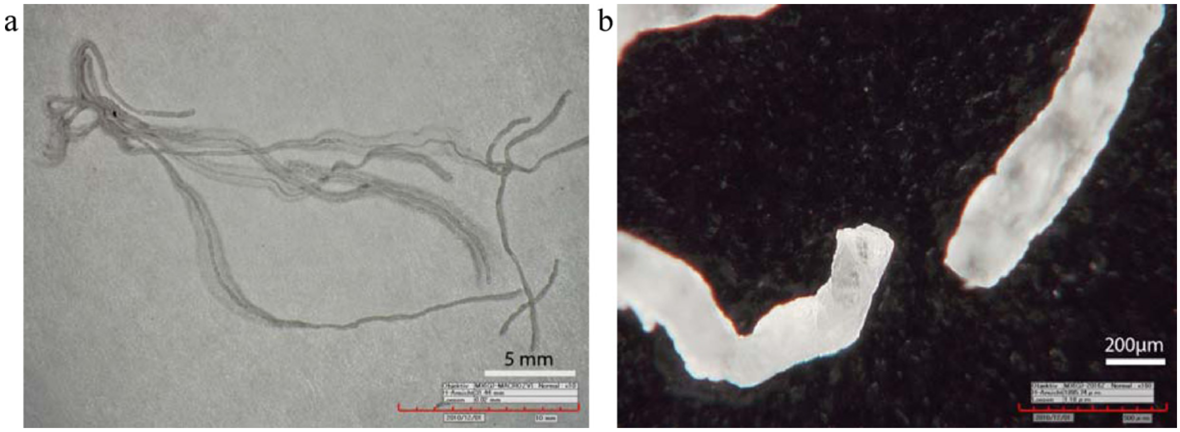

Fig. 10. Optical microscope images of fiber-shaped bodies obtained from the piston method spinning of 4% cellulose/FeTNa solution [The arrows show (a) 10 mm and (b) 500 μm].

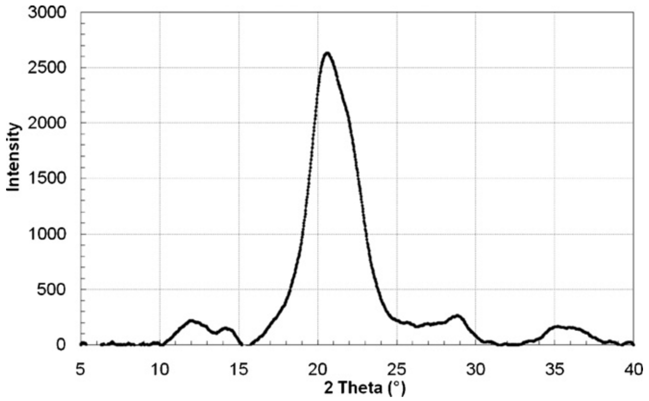

Fig. 11. WAXS graph of regenerated cellulose from 4% cellulose/FeTNa solution.

due to the gel state of the 4% cellulose/FeTNa solution not being able to flow through the *fine* holes of spinneret.

Further trials with piston-method spinning experiments succeeded to produce fiber-shaped bodies through a nozzle with a *hole diameter* of 500 μm. Fig. 10 shows the inhomogeneous surface structure of the bodies. However, fiber-shaped bodies were brittle (elongation at break was less than 8%) so that tensile tests of them could not be achieved. The brittleness of fiber-shaped bodies can be influenced by acid concentration (30% H_2SO_4) and temperature of coagulation bath. Further research should be concentrated on the improvement of tensile properties and surface properties of surface fiber-shaped bodies.

In the literature (Kamide, 2005), the proper H_2SO_4 concentration for the coagulation bath of 5% cellulose/NaOH solution was mentioned to be between 10 and 30% at 5 °C. The higher the temperature of coagulation bath, the lower the concentration of H_2SO_4 in it. Therefore, at 15 °C the H_2SO_4 concentration of the coagulation bath was found to be 3–15% in order to get proper coagulation and good spinnability of cellulosic fibers.

Fig. 11 shows a WAXS image of fibrous cellulosic material obtained from regenerated cellulose/FeTNa solutions. Although some typical spectroscopic features such as the peak at $2\theta = 12^\circ$ (1–10 plane) and $2\theta = 34^\circ$ (0 0 4 plane) are less resolved, the scan clearly proofs the cellulose II structure of the regenerate. No indication is found for structures diverging from the expected one despite the applied uncommon dissolution system.

4. Conclusions

Cellulose shaping for fiber and film production via dissolution of cellulose in FeTNa (NaOH solution containing ferric tartaric acid complex) and regeneration of cellulose in an acidic bath offers important technical advantages.

Cellulose dissolves in FeTNa under moderate conditions, thus cellulose with DP of 610 could be dissolved in FeTNa at *room temperature* up to 4%, which increased to ca. 8% at −9 °C, and to ca. 12% with the usage of shear force at −9 °C. Dynamic rheology analyses expressed that cellulose/FeTNa solutions show gel properties due to their higher storage modulus compared to loss modulus. Thus in experiments for fiber spinning two fields for optimization were identified:

- gel structure of the solution prevents flow through fine holes of spinneret and
- concentration of the cellulose in the solution has to be increased at least to 8% while maintaining viscous behavior instead of elastic gel formation.

The comparison of cellulose/FeTNa solution to both cellulose/NMMO and cellulose/BMIMCl solution showed that cellulose/FeTNa solution does not exhibit the risk of spontaneous exothermic decomposition, but iron-complex decomposed at rather low temperature near 80 °C. In UV/VIS spectrometry the color of cellulose/FeTNa solution changed by iron-complex decomposition at a temperature above 90 °C.

The fiber produced from cellulose/FeTNa solution needs improvement in tensile properties. Further research will be concentrated on dissolution experiments and spinnability trials of cellulose/FeTNa solutions.

Besides the use of NaOH, which is corrosive, all components in the complex solution are non-toxic and will not require extensive treatment of production wastes and effluents, and also traces of the processing solution left in the shaped cellulose will not be harmful. Due to the chemicals used in FeTNa, namely NaOH, tartaric acid and iron (III) salt, the shaped cellulose can easily be produced in food grade quality. Thus such products offer value for both textile and food applications.

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