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Rheological Requirements for Continuous Filament Spinning of Cellulose-Ionic Liquid Solutions

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ABSTRACT

In a dry-jet wet spinning process a polymer solution has to fulfil certain visco-elastic requirements to withstand shear and elongational stresses that are exerted during the spinning procedure. Herein, different rheological aspects and tools are discussed that characterize the spinnability of cellulose-ionic liquid solutions.

INTRODUCTION

The rising prosperity level of emerging economies in the southern hemisphere has triggered a steadily increasing demand for consumer goods. This trend is amplified by an estimated population growth of 20 % (1.4 billion) over the next two decades which urges scientists and politicians likewise to develop new sustainable resource management strategies. Amongst others, this will also affect the textile market. The demand in textile fibres is predicted to rise at a growth rate of 3.1 % p.a. reaching 133.5 million tons by 2030.[1,2] Although synthetic fibres still dominate the textile market, cellulosic fibres play a significant role due to certain inherent properties (moisture management, breathability), which cannot be met adequately by synthetic fibres. Thus, the share of natural and man-made cellulosic fibres is expected to be between 33 and 37 % of the total global fibre consumption and the consumption of cellulosic fibres is expected to increase from the current 3.7 to 5.4 kg per capita by 2030. The cotton production capacities, however, are no longer expandable. Only 3.1 kg of cotton per capita will be available in 2030.[1] This so called cellulose gap will offer new opportunities for man-made cellulosic fibres.

Currently, manmade cellulosic fibres are predominantly produced via the viscose process with a small amount of fibres spun via the Lyocell technique. Both techniques, however, suffer from serious drawbacks such as toxicity and safety concerns. The utilization of large amounts of CS_2 and caustic in the viscose process results in hazardous by-products such as H_2S gases and other volatile thio-compounds which may cause severe stress for the environment. The Lyocell process offers an environmentally benign alternative as the cellulose can be dissolved without chemical modification in the solvent system *N*-methylmorpholine *N*-oxide (NMMO) monohydrate. The cellulosic fibres are coagulated in water and the solvent recovered virtually loss-free.[3] However, the process suffers from the thermal instability of NMMO, the need of high process temperatures, and a limited chemical compatibility of the solvent with other biopolymers and inorganic substances.[4,5] In this context, ionic liquids (ILs) bear great potential as alternative solvents for the Lyocell process. Numerous ILs have been identified as efficient cellulose solvents and proposed for both wet and dry-jet wet fibre spinning.[6,7] In particular, imidazolium based halides and carboxylate ILs have been reported to be suitable for processing of (ligno-) cellulosic material.

However, in a fibre spinning process the polymer melts or solutions have to fulfil defined visco-elastic properties. Extrusion through a spinning nozzle exerts high shear stresses on the respective solution. In the case of dry-jet wet spinning, the fluid filaments would pass an air gap before they enter the coagulation bath where rapid solvent exchange causes the precipitation of cellulose to form solid fibres. Typically, the filaments are stretched in the air gap to increase the longitudinal orientation of the polymer chains and thereby also increase the tensile properties of the resulting fibres. This so called draw causes uniaxial extensional stress on the solution which will cause filament breach if the visco-elastic properties are not suitable to withstand the stress.

Herein, we will discuss some rheological aspects that have to be considered carefully before cellulose dissolving ILs can be promoted for fibre spinning.

SOLUTION STATE

The visco-elastic properties of a cellulose-IL solution do not only depend on the degree of polymerization (DP) and molar mass distribution (MMD) of the cellulosic solute but are also strongly influenced by the IL itself. The interactions between the cellulose molecules and the particular IL will define the solution state of the polymer chains. Attempts to literally shed light on this subject via dynamic light scattering experiments have been reported[8] but are limited due to impurities typically present in ILs. Small traces of water or residual molecular compounds deriving from the synthesis of ILs can form aggregates that disturb the measurement signal. To bypass this problem, the intrinsic viscosity of pulp cellulose in different ILs was determined at different temperatures (25-60 ºC). Eucalyptus pre-hydrolysis kraft (E-PHK) pulp was dissolved in 1-ethyl-3-methylimidazolium dimethylphosphate ([emim]dmp), 1-ethyl-3-methylimidazolium acetate ([emim]OAc), 1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphosphate ([mDBN]dmp), 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc), and 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH]propionate) (Fig. 1). Because of the elevated melting point of [DBNH]OAc, respective solutions were measured at 70 – 90 ºC.

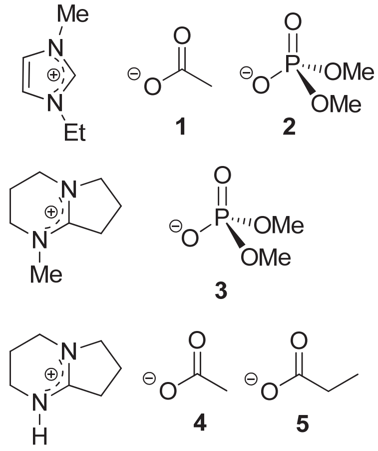

Figure 1. Structure of 1-ethyl-3-methylimidazolium acetate ([emim]OAc, **1**), 1-ethyl-3-methylimidazolium dimethylphosphate ([emim]dmp, **2**), 1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphosphate ([mDBN]dmp, **3**), 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc, **4**), and 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH]propionate, **5**).

Due to the relatively high viscosity of even very diluted cellulose-IL solutions, the kinematic viscosity was determined via measuring the dynamic viscosity with a plate-plate rheometer following a procedure suggested earlier (Fig. 2).[9,10] The density of the neat ILs was measured to calculate the density of the respective cellulose-IL solutions. The apparent molar volume of cellulose and the temperature dependence of the density were neglected as both are smaller than the error introduced via the shear-rheological experiment.[9,10]

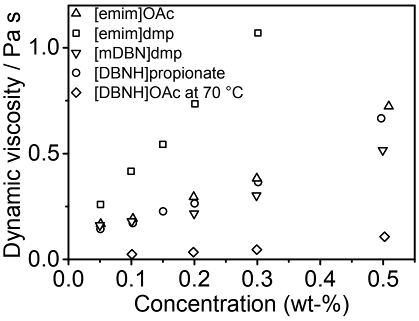

Figure 2. Dynamic (zero shear) viscosities of E-PHK pulp-IL solutions as a function of solute concentration (measurement temperature: 25 ºC).

The intrinsic viscosity was then calculated via a linear fit of the data in a Huggins plot (Fig. 3).[11]

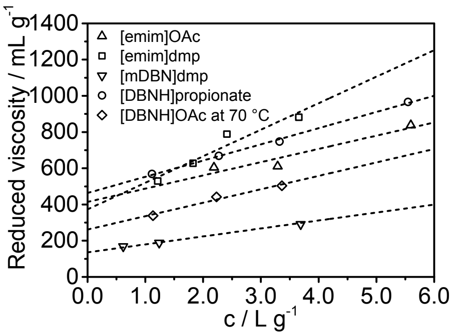

Figure 3. Huggins plot of E-PHK pulp-IL solutions at 25 ºC.

The intrinsic viscosities are summarized in Table 1. E-PHK pulp dissolved in [emim] based ILs and [DBNH]OAc showed intrinsic viscosity values close to 424 ml/g which was found in cupriethylenediamine, a standard cellulose solvent to determine the viscosity-average DP. [mDBN]dmp showed an extraordinary low intrinsic viscosity indicating that its thermodynamic quality as a cellulose solvent are rather poor.

Table 1. Intrinsic viscosities calculated via the Huggins equation.[11]

	25 ºC	35 ºC	45 ºC	60 ºC	70 ºC
[emim]OAc	414	393	370	359	
[DBNH]prop.	464	469	463	453	
[DBNH]OAc					262
[emim]dmp	373	354	339	302	
[mDBN]dmp	136	116	108	102	

SHEAR RHEOLOGY

Shear rheological measurements with a plate-plate rheometer are used frequently to assess the visco-elastic properties of polymer melts and solution with a high accuracy. All spin dopes are also subjected to shear stress in the spinneret though typically with a substantially higher shear rate than accessible with a plate-plate rheometer. Nonetheless, the visco-elastic properties determined via oscillatory measurements are valuable indicators to determine spinnability. The frequency sweep provides the complex viscosity and storage (G′) and loss (G″) moduli of the cellulose solutions. Master curves covering an extended frequency range can be generated by using time-temperature shift factors according to the WLF (Williams-Landel-Ferry) theory. Dynamic moduli and a complex viscosity master curve for a typical E-PHK-[DBNH]OAc solution are depicted in Fig. 4.

The complex viscosity curves can be fitted with different model functions to determine the zero shear viscosity. The Carreau and Cross viscosity models have been proposed, with the latter being more suitable for cellulose-IL solutions and, consequently, used predominantly.[12]

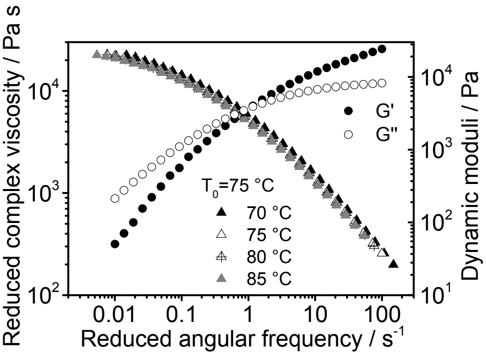

Figure 4. Storage (G′) and loss (G″) moduli and master curve of complex viscosity of a E-PHK-[DBNH]OAc solution (13 wt%) at various temperatures.

The validity of the Cox-Merz rule has to be assumed in order to derive the zero shear viscosity from the complex viscosity curve. However, some authors claimed that the Cox-Merz rule failed in some cases, *i.e.* complex and dynamic viscosity did not superimpose perfectly. Thus, the calculated limiting value of the complex viscosity represents the complex viscosity within the frequency-independent Newtonian plateau but not necessarily the true zero shear viscosity. Also in accordance with earlier reports on highly concentrated cellulose solutions, the regions in which the storage modulus G′ scales with ω^2 and G″~ω were outside the measurement range.

It was found that E-PHK-[DBNH]OAc solutions showed good spinnability when the cross-over point of the dynamic moduli was approximately at 1 s^{-1} and 5 000 Pa, and the "zero shear" viscosity ca. 30 000 Pa s. Since pulp cellulose consists of cellulose chains of different length, respective solutions do not only show a single relaxation time. The dynamic moduli also allow for the calculation of the relaxation time spectrum. It is tightly connected to the MMD of the cellulose. Fig. 5 shows the relaxation time spectrum of a E-PHK-[DBNH]OAc solution at 75 ºC.

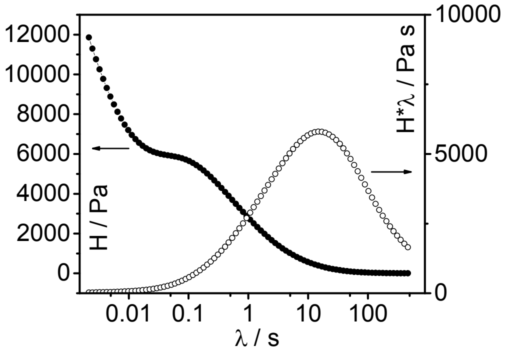

Figure 5. Relaxation time spectrum of a E-PHK-[DBNH]OAc solution (13 wt%) at 75 ºC.

EXTENSIONAL RHEOLOGY

When cellulose solutions are processed to form fibres and films, the polymers in solution are not only subjected to shear stress but also undergo elongational deformation. In particular during dry-jet wet spinning the liquid filaments pass an air gap in which they are drawn to increase the total cellulose orientation via a uniaxial extensional stress. The capillary break-up extensional rheometer (CaBER) allows for the measurement of the apparent transient elongational viscosity and – under certain prerequisites – extensional relaxation time. The latter can be extracted from the measurement data if the elasto-capillary region during the break-up experiment can be identified unambiguously. In order to test if the CaBER is suitable to assess elongational-rheological properties of cellulose-IL solutions, a 10 wt% E-PHK pulp-[emim]OAc solution was prepared and stored at 110 ºC for 8h. This reduced the DP of the dissolved cellulose and, consequently, also the viscosity of the solution (Fig. 6) which facilitated the CaBER measurements notably. The decay of the mid-filament diameter observed in a typical CaBER experiment is illustrated in Fig. 7.

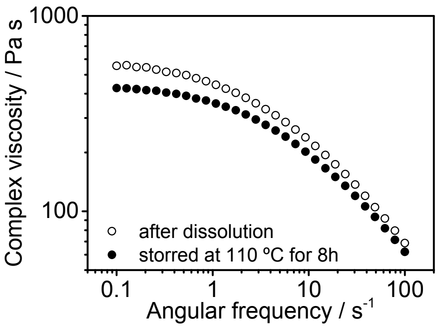

Figure 6. Decrease of the complex viscosity of the E-PHK pulp-[emim]OAc solution (10 wt%) after being kept at 110 ºC for 8h.

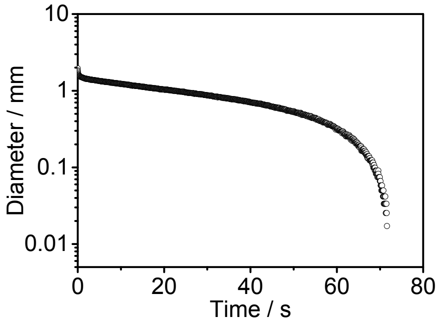

Figure 7. Evolution of the mid-filament diameter vs. time for a E-PHK pulp-[emim]OAc solution (10 wt%) stored at 110 ºC for 8h (measurement temperature: 60 ºC).

A set of forces balancing each other divide the self-thinning of the thread into four regimes.[13] In regime I, the filament thinning profile is ill-defined due to gravitational effects overlapping the capillary forces. Using a local bond number of 0.2, a threshold filament diameter of 1.60 mm upon which gravitation contributes only insignificantly to the filament thinning profile could be calculated.[14] In regime II, the capillary driven flow is resisted by the dominating viscous stress, resulting in a linear decay of the filament diameter.[13,15,16] The subsequent regime III represents a transition phase where visco-capillary balance as observed in regime II is superimposed by an incipient extensional thinning, originating from a pronounced disentanglement and orientation of the cellulose chains. Ultimately, the filament thinning is governed by a balance of the surface pressure and the elastic stress of the unraveling polymer chains. This regime IV is observed only at very high strains and thus at a late stage of the measurement close to filament break-up. Clasen has demonstrated that regime IV can be identified when plotting the extension rate and apparent extensional viscosity versus time (Fig. 8).[13] Regime IV is characterized by a small but distinct rise of the apparent extensional viscosity close to the final break-up (strain-hardening). Concomitantly, the extensional rate should reach a plateau value after rising with time. As illustrated in Fig. 8, neither the rise of the apparent extensional viscosity nor the plateau of the extension rate as described by Clasen could be observed for the aged solution of E-PHK pulp in [emim]OAc.

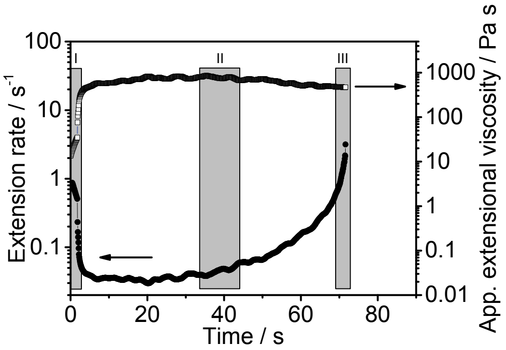

Figure 8. Extension rate and apparent extensional viscosity versus time for the E-PHK pulp-[emim]OAc (10 wt%) solution stored for 8h at 110 ºC (measurement temperature: 60 ºC).

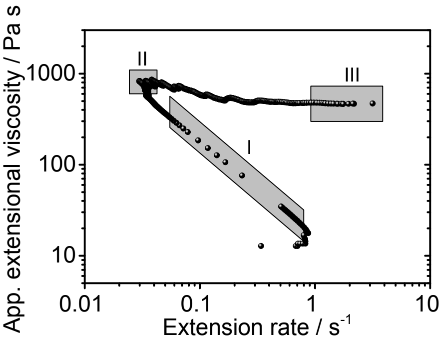

Figure 9. Apparent extensional viscosity as a function of the extension rate for the E-PHK pulp-[emim]OAc solution (10 wt%) stored for 8h at 110 ºC.

Fig. 9 shows the apparent extensional viscosity as a function of the extension rate. Elasto-capillary response would cause a steep rise of $\eta_{E,App}$ towards the end of the measurement which is clearly not observed in our case. Thus, despite degradation of the cellulose a concentration of 10 wt-% is too high and the CaBER measurement is not sensitive enough to detect the elasto-capillary region. This means that extensional relaxation times for high-concentration cellulose-IL solutions cannot be extracted directly from the CaBER experiments.

CONCLUSIONS

Processability of cellulose-IL solutions is highly dependent on their visco-elastic properties. ILs that can dissolve high amounts of cellulose are not necessarily good solvents for e.g. fibre spinning. The respective solutions have to withstand substantial shear and elongational stresses present in several deformation phases (shear in spin capillaries, draw in air gap, after-draw in coagulation bath). Oscillatory shear-rheological measurements provide visco-elastic key parameter that can be used to define the spinning temperature and predict the spinnability. The zero-shear viscosity and cross-over point of the dynamic moduli have to be in a defined frame to allow for stable fibre spinning. Attempts to assess elongational viscosity and relaxation time of cellulose-IL spin solutions with a CaBER failed as the device was not suitable to measure highly viscous and elastic samples.

EXPERIMENTAL

Materials

Eucalyptus urograndis prehydrolysis kraft (E-PHK) pulp (Cuen intrinsic viscosity (ISO 5351-1): 468 ml/g; M_n=79.8kg/mol; M_w=268.7 kg/mol; Bahia pulp, Brazil) was received in the form of sheets and ground by means of a Wiley mill. [Emim]OAc (purity ≥95%) and [emim]dmp (purity ≥98%) were purchased from BASF, Germany and IoLiTec, Germany, respectively, and used as received. DBN-based ILs were gratefully received from the University of Helsinki.

Shear rheology

Shear rheology of all solutions was measured on an Anton Paar MCR 300 rheometer with a parallel plate geometry (25 mm plate diameter, 1 mm gap size). Prior to each frequency sweep, the viscoelastic domain was determined by performing a dynamic strain sweep test to find a suitable strain for subsequent measurements. A time experiment at constant frequency showed no significant water uptake from the laboratory atmosphere at the plate edges within the required testing time. Thus, it was not necessary to seal the edges with paraffin oil as previously suggested.[9,12] Each sample was subjected to a dynamic frequency sweep at various temperatures over an angular velocity range of 0.1–100 s^{-1}. Master curves were generated via WLF (Williams-Landel-Ferry) time-temperature superposition. The shift factor and reduced variables were calculated as described by Sammons et al.[12] Assuming that the Cox-Merz rule is valid, the zero shear viscosity was calculated using the three-parameter Cross viscosity model given by Eq. 1

$$\eta = \frac{\eta_0}{(1 + (\tau\dot{\gamma})^{1-n})} \qquad (1)$$

where τ is a time constant and n is the power-law exponent. The relaxation time, λ, and relaxation time spectrum, $H(\lambda)$, of [DBNH]OAc solutions were calculated from the frequency sweep measurements. The relaxation time, λ, corresponds to the inverse of the angular frequency, ω. λ is associated to the length of the cellulose molecules present in solutions; short molecules show short λ and vice versa. The relaxation time spectrum $H(\lambda)$ is calculated via the regularization method from the loss and storage modulus obtained from the frequency sweep. Eq. 2 and 3 illustrates the relationship between the dynamic moduli and the relaxation time spectrum.[17]

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2.\lambda^2}{1 + \omega^2.\lambda^2}.H(\lambda).\frac{d\lambda}{\lambda} \qquad (2)$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{\omega.\lambda}{1 + \omega^2.\lambda^2}.H(\lambda).\frac{d\lambda}{\lambda} \qquad (3)$$

Extensional rheology

Extensional rheological analyses were conducted on a Thermo Fisher Capillary Break-up Extensional Rheometer (CaBER) at 60 ºC. In this breakup device, the solution is first loaded between two plates. Prior to the actual measurement, the upper plate is rapidly moved up and then held at a fixed vertical displacement. A liquid thread is thus formed and the evolution of the mid-filament diameter is monitored as a function of time by a laser micrometer until its final breakup.[15] Plates of 6 mm were used and the step-stretch defined by an initial and final aspect ratio of 0.66 and 3, respectively (initial and final separation of 2 and 9 mm, respectively). After sample loading, a defined equilibration time of 2 min was waited before the start of the measurement in order to assure full cellulose chain relaxation. Possible moisture up-take during the measurement was prevented by purging a dry air flow of 1.5 ml/min through the measurement cell. The effective sample temperature was determined by a Testo 845 contactless IR thermometer.

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