

Extensional rheology of cellulose-ionic liquid solutions

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ABSTRACT

Various cellulose-ionic liquid solutions were measured with a rotational plate-and-plate rheometer and a Capillary Break-up Extensional Rheometer (CaBER). Comparison of the shear and extensional rheological properties showed good agreement in some cases. The CaBER, however, seems to be more sensitive to small variations in solute composition.

INTRODUCTION

Since almost a decade now, non-derivatizing dissolution of ligno-cellulosic material in so called ionic liquids (ILs) is explored extensively.^{1,2} The term ionic liquids refers to compounds that solely consist of ions and exhibit a melting point below 100 °C. These special salts usually comprise inorganic anions and bulky, organic cations like 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, 1-alkyl-1-methylpyrrolidinium, tetraalkylammonium, guanidinium or phosphonium ions. Reduced interaction between the ions due to their size and charge delocalization and an entropically favoured liquid state lead to the exceptionally low melting points.

In 2002, Rogers *et al.* re-discovered the remarkable capability of ILs to dissolve cellulose directly, *i.e.* without derivatization of the hydroxyl groups, in high concentrations.³ In the meantime, several IL-systems have been reported to be suitable

cellulose solvents. Especially 1-ethyl-3-methylimidazolium acetate ([emim] OAc, Fig. 1) seems to be a promising solvent due to its low viscosity, low toxicity, and good cellulose dissolution properties and was thus studied by many research groups. Non-derivatizing cellulose-dissolution and subsequent regeneration via dry-jet wet spinning provide access to environmentally benign and economically viable biomass processing. Similar to polymer-melt spinning, the cellulose-ionic liquid solution (dope) is spun via an air-gap into a coagulation bath filled with an anti-solvent, where the cellulose is regenerated in the form of value added products like fibers or films. To produce stable filaments in the air gap, however, detailed knowledge of the dope's rheological properties is required.⁴ Unfortunately, only few reports on the rheological properties of cellulose-IL solution have been published. Most of them mainly deal with shear rheological investigations of dilute solutions of microcrystalline cellulose (MCC).

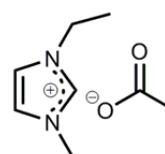


Figure 1. 1-Ethyl-3-methylimidazolium acetate [emim] OAc.

Herein we present two rheological studies on cellulose with high degree of polymerization (DP) in [emim] OAc. The first one deals with influence of the concentration on the rheological properties, whereas in the second the molecular weight distribution (MWD) of the solute was varied. In both cases shear rheological data is compared to elongational-rheological properties assessed by means of a Capillary Break-up Extensional Rheometer (CaBER).

EXPERIMENTAL

Materials

1-Ethyl-3-methylimidazolium acetate ($\geq 98\%$) was purchased from IoLiTec (Germany) and used without further purification. Cotton linters ($[\eta]$: CL1 702 ml/g, CL2 524 ml/g, CL3 909 ml/g) from Milouban, Israel were delivered in the form of sheets and degraded via Kier boiling. Respective blends were prepared by mixing the dry, milled powder.

Instruments and experimental technique

The cotton linters were subjected to Wiley milling and subsequently dissolved in [emim] OAc either by means of a vertical kneader system⁵ or a handheld high shear mixer (IKA Ultra Turrax). The resulting solutions were finally degassed in a vacuum oven at 80 °C and stored under an atmosphere of nitrogen.

Surface tension and density of the dope were determined via KSV CAM contact angle and surface tension meter modified with a dry cell and an Anton Paar DMA515 density meter, respectively.

Oscillatory shear rheology of all solutions was measured on an Anton Paar MCR 300 with a plate and plate geometry. The viscoelastic domain was tested by performing a dynamic strain sweep test and a strain between 0.5 and 5 % was chosen for the frequency sweep measurements. During the measurements, the edges were sealed with a low viscosity paraffin oil to prevent

moisture uptake of the dope from the atmosphere.

Extensional-rheological measurements were conducted on a Thermo Fischer Capillary Break-up Extensional Rheometer (CaBER). Plates of 6 mm diameter were used and an initial and final aspect ratio of 1 and 3, respectively, chosen. The time between completion of sample loading and measurement start was fixed to 60 seconds. The measurement cell was constantly purged with dry air and the temperature determined via a Testo 845 contactless IR thermometer.

RESULTS AND DISCUSSION

Concentration study

To determine the influence of the concentration on both, shear and elongational rheology of cellulose-ionic liquid solutions, cotton linters (CL2, see Table 2) was dissolved in 1-ethyl-3-methylimidazolium acetate [emim] OAc in 1, 3, 5, and 10 %. First, oscillatory measurements were performed to determine the complex viscosity and dynamic moduli as function of the angular frequency.

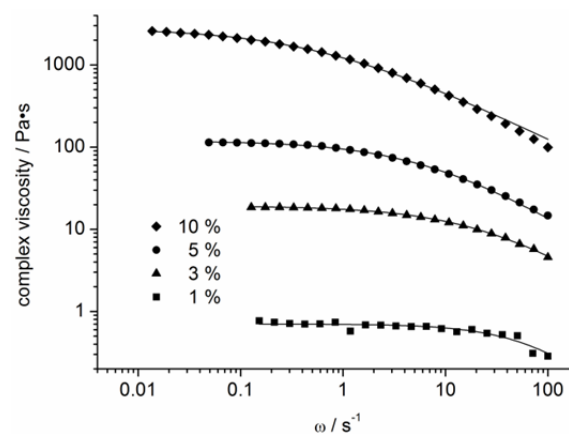


Figure 2. Complex viscosity of CL2-[emim] OAc solutions at 50 °C.

Fig. 2 shows the complex viscosity for the respective solutions at 50 °C. In

accordance to earlier findings for cellulose-IL solutions, pronounced shear thinning can be observed.⁶ Especially at high cellulose concentrations the Newtonian plateau ends already at low frequencies. A three-parameter Cross model (Eq. 1) was then used to determine the zero shear viscosity η_0 .

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^b} \quad (1)$$

To study the relationship of the zero shear viscosity and the concentration the respective values were plotted on a double-logarithmic scale, clearly reflecting the power-law dependency (Fig. 3).

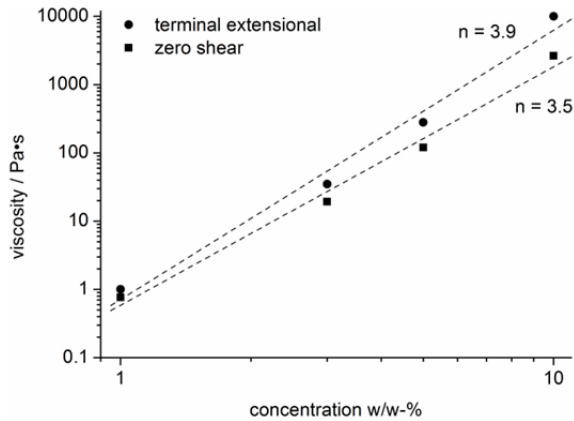


Figure 3. Zero shear and terminal extensional viscosity versus concentration (at 80 °C). In both cases a power-law dependency can be observed ($\eta \sim c^n$).

Loss and storage moduli of the 3, 5, and 10 % solutions at 50 °C are depicted in Fig. 4. Upon increase of concentration the cross over point is shifted to the left, *i.e.* the elastic properties become dominant at lower frequencies.

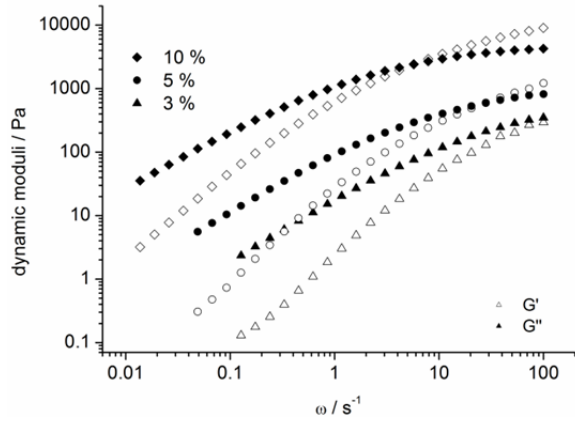


Figure 4. Storage (G') and loss (G'') modulus of CL2-[emim] OAc solutions.

The influence of the temperature on the solutions' rheological properties can be seen from Fig. 5 and 6. Higher temperature lowers the viscosity, extends the Newtonian region, and shifts the cross over point to the right. Thus, effects of increasing concentration can be diminished by rising the temperature. This is especially important for processing high-concentration cellulose solutions, where the viscosity and viscoelastic properties usually have to be within a narrowly defined window.

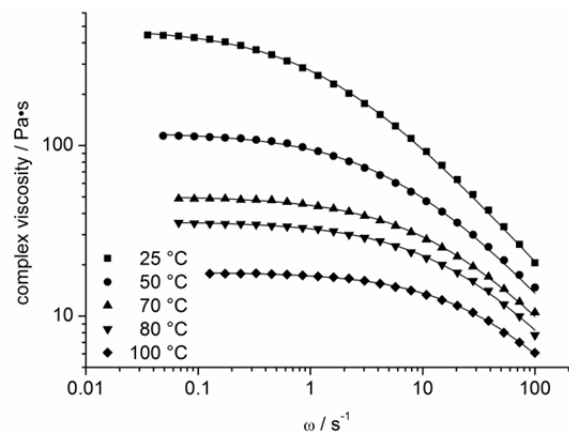


Figure 5. Complex viscosity of 5 % CL2-[emim] OAc solutions at various temperatures.

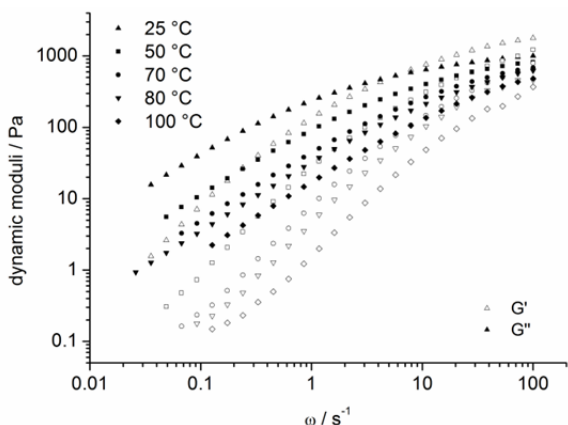


Figure 6. Storage (G') and loss (G'') modulus of 5 % CL2-[emim] OAc solutions at various temperatures.

Extensional rheological behaviour of the solutions was assessed via a Capillary Break-up Extensional Rheometer (CaBER) at 80 °C. In a CaBER experiment, a small amount of sample is placed between two plates (diameter 6 mm, initial distance 3 mm) which are then rapidly separated (final distance 9 mm). After this step-stretch, the experiment drives itself as capillary thinning of the liquid bridge, imposing a uniaxial flow on the fluid diameter. The decay of the mid-filament diameter, from which all properties are calculated, is measured until capillary pinch-off brings the experiment to an end.⁷ The evolution of the mid-filament diameter in the visco-elastic region can be described by Eq. 2.

$$D(t) = \left(\frac{G_0 D_0}{4\sigma} \right)^{1/3} D_0 \exp\left(\frac{-t}{3\tau_0} \right) \quad (2)$$

where D_0 is the initial diameter after cessation of active stretching, σ is the surface tension, and τ_0 the longest relaxation time. G_0 represents the elastic modulus of the longest relaxation time, which is the only one that is excited in this kind of experiments.^{8,9} At late stages of the experiment, the polymer solutes reach their maximum extensibility and the fluid becomes Newtonian. This results in a rapid,

linear drop of the filament diameter which finally leads to the filament rupture.

The results for the concentration series are plotted in Fig. 7. Filament necking for the 10 % solution is extremely slow leading to very long measurement times. The 1 % solution, in contrast, shows an almost Newtonian behaviour with a fast and linear decay of the filament diameter.

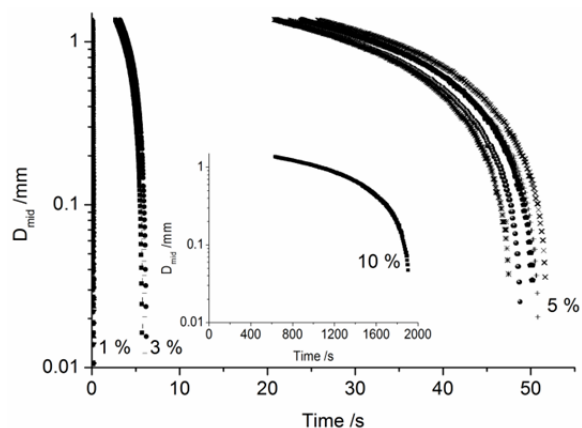


Figure 7. Mid-filament diameter evolution of CL2-[emim] OAc solutions at 50 °C. The 10 % solution is shown as an inset because of the long measurement time.

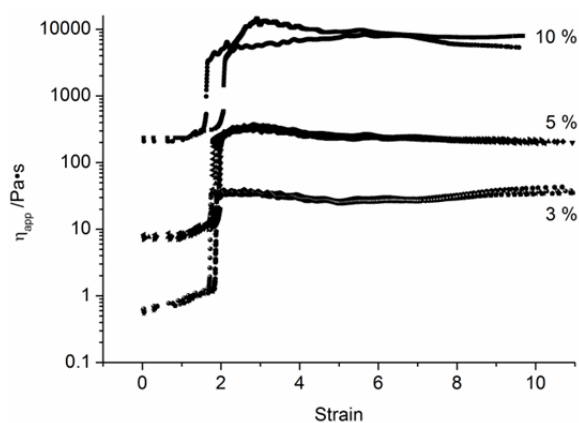


Figure 8. Apparent extensional viscosity of CL2-[emim] OAc solutions at 50 °C. All solutions show typical strain hardening.

The apparent extensional viscosity can be calculated if density and surface tension of the sample at the measurement temperature are known. As can be seen from Fig. 8, all cellulose-IL solutions show strain hardening, resulting in a steady-state plateau

value, the so called terminal extensional viscosity. Similar to the zero shear viscosity, the terminal extensional viscosity shows a power-law dependency on the concentration (Fig. 3). Finally, the two viscosities were plotted against each other, revealing a linear relationship (Fig. 9).

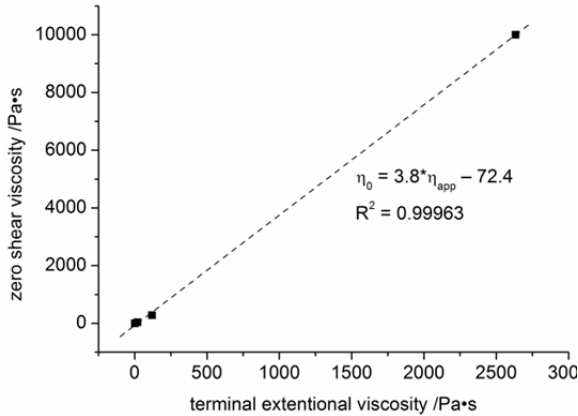


Figure 9. The zero shear viscosity and the terminal extensional viscosity exhibit a linear relationship.

All properties of the cotton linters-IL solutions are summarized in Table 1.

Table 1. Surface tension, density, and rheological properties of the CL2-IL solutions (at 50 °C).

c w/w-%	γ [mN/m]	ρ [kg/m ³]	MCR 300	CaBER	
			η_0 [Pas]	τ_0 [s]	η_{app} [Pas]
1	33.51	1093.9	0.7638	0.68	1
3	31.50	1101.5	19.298	0.88	35
5	31.19	1108.3	120.64	6.6	280
10	25.73	1119.4	2633.9	350	10 ⁵

Influence of the molecular weight distribution.

To investigate the influence of the molecular weight distribution of the cellulosic solute on the rheological properties of the ionic liquid solution, original and degraded cotton linters were blended as summarized in Table 2. The intrinsic viscosity and, thus, the weight average molar mass M_w were kept constant while the poly dispersity index (PDI) was varied. Please note that Blend 1 and 4 have the same intrinsic viscosity whereas Blend 2 and 3 exhibit similar PDI values. All blends were dissolved in [emim] OAc at 9 w/w-% concentration.

The complex viscosities and dynamic moduli are illustrated in Fig. 10 and 11. Blend 1 and 4, and 2 and 3, respectively are indistinguishable in terms of shear rheology.

Table 2. Composition, MWD parameters, and rheological properties of all blends and CL2.

	Composition ^a	$[\eta]$ (ml/g)	M_n^b (kg/mol)	M_w^c (kg/mol)	M_z^d (kg/mol)	PDI	η_0 (Pas)	η_{app} (Pas)	τ_{CaBER} (s)
Blend 1	CL2 524	448	93.6	175.6	299.55	1.88	409.49	450	16
	CL2d 365								
Blend 2	CL3 909	450	69.3	196.4	519.9	2.83	254.62	370	12
	CL3d 309								
Blend 3	CL2 524	433	66.95	192.45	417.15	2.87	258.58	380	14
	CL1 729								
Blend 4	CL1d 189	448	78.5	186.5	375	2.38	424.15	470	15
	CL1 729								
	CL1d 338								
CL2		524	122	214	349	1.8	609.37	630	25

^a Indicates the constituents (d...degraded via Kier boiling) and shows the respective intrinsic viscosities (ml/g). ^b number average ^c weight average and ^d z-average molar mass.

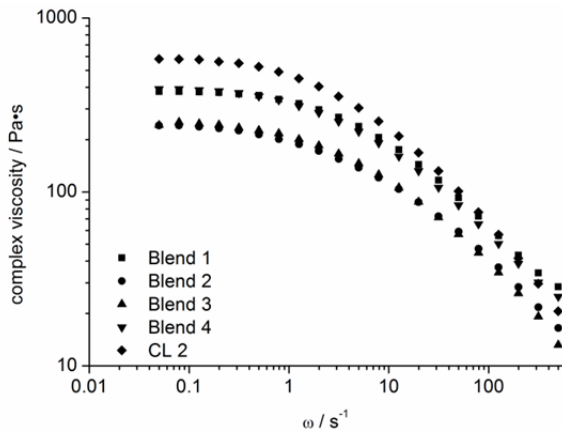


Figure 10. Complex viscosity of the blends dissolved in [emim] OAc (9 %) at 80 °C.

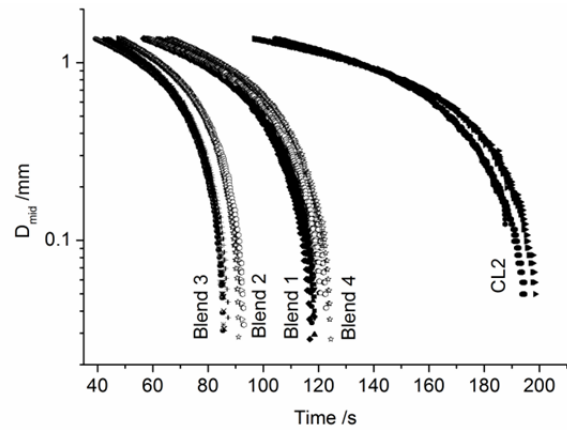


Figure 12. Mid-filament diameter evolution of the blends dissolved in [emim] OAc (9 %) at 80 °C.

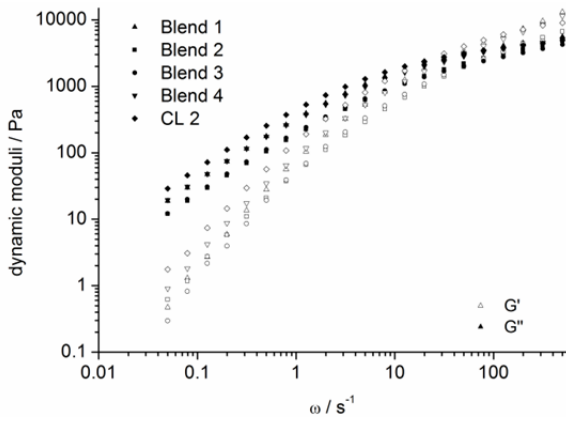


Figure 11. Storage (G') and loss (G'') of the blends dissolved in [emim] OAc (9 %) at 80 °C.

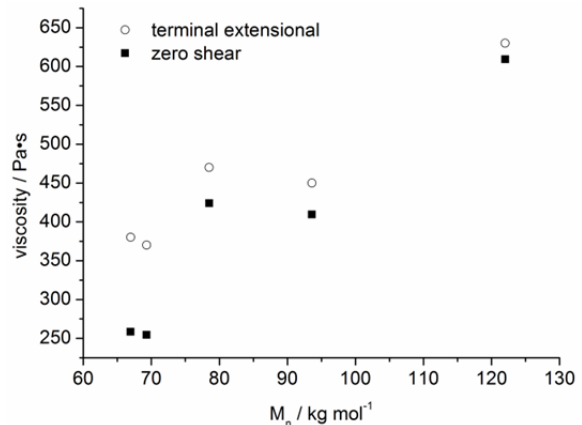


Figure 13. Zero shear and terminal extensional viscosity as a function of the number average molar mass M_n (at 80 °C).

The data obtained via the MCR 300 superpose. In this case the CaBER seems to be more sensitive. Fig. 12 shows the evolution of the mid-filament diameter. All sample curves are well resolved resulting in a different relaxation time for each solution (see Table 2). Both, extensional relaxation time and terminal extensional viscosity rise with increasing number average molar mass M_n . this trend is depicted in Fig. 13. Again, a linear correlation between the zero shear and the terminal extensional viscosity was observed.

CONCLUSIONS

Capillary breakup extensional rheology has shown to be applicable for cellulose-ionic liquid solutions. Zero shear viscosity and terminal extensional viscosity show a power-law dependency on the concentration and were found to be in a linear relationship to each other. The simple experimental procedure and the similarity between the testing principle and the spinning process turn CaBER into a valuable tool for pulp characterization. Especially, since the CaBER seems to be more sensitive to small variations in solute composition.

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