Contribution to dissolution state of cellulose in aqueous amine oxide characterized by optical and rheological methods

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Abstract

The dissolution of cellulose in aqueous amine oxides to isotropic, completely solvated cross-linked solutions is a multiple stage process in microscopic, submicroscopic and molecular ranges. In a suspension of cellulose, water and NMMO at 85°C and with decreasing water content the cellulose undergoes a growing swelling accompanied by an increased flexibility of the chain leading to a heterogeneous phase for the 1,5 hydrate (81,3 % NMMO) to an irreversible transfer of cellulose I into cellulose II and for the 1,2 hydrate (84,4 % NMMO) to a homogeneous, partly solvated gel phase. Discrete inhomogeneities with equivalent spherical diameters greater than 0,5 µm and a concentration greater than 1 µl/l can be analyzed by microscopy and laser diffraction. Rheological parameters and in particular recording of deformation graphs and calculating relaxation time spectra were proven to be efficient for characterization of the solvation occurring during dissolution.

Keywords
Cellulose / cellulose solution / solution state / particle analysis / shear rheology

Introduction

Swelling and dissolution of cellulose in non-derivating solvents and the description of the achieved dissolution state is an important task and is a matter both of scientific and technical interest.

Diluted solutions of cellulose in metal complexes of copper, iron, zinc, nickel etc. with ammonia, tartaric acid, ethylene diamine and Bis- respectively Tris(2-amino-ethyl)amine have superficial analytic importance and are repeatedly described in literature [1-3]. Taking in account technical as well as commercial aspects, concentrated solutions of cellulose became important, as for example solutions of cellulose in copper-ammonia, since the dissolution and coagulation of shaped cellulose should be performed by changing, as far as possible, only one parameter.

With the aqueous amine oxides and in particular with the N-methyl morpholine-N-oxide-hydrate ( NMMO ) there was discovered already in 1936 a solvent system, which can take up cellulose up to 20 wt % whereas its dissolution state undergoes significant changes when slightly changing the water content [4–7].

Highly diluted solutions of one and the same cellulose in NMMO, “ Cuoxam “ or “ Cuen “ exhibit similar behavior and contain comparable intrinsic viscosity numbers with about 340 [ml/g] at 75 °C respectively 290 or 400 [ml/g] at 23 °C. That means assuming free swelling behavior 1 mol of cellulose takes up 480 mol of NMMO. With increasing molecular weight and/or cellulose concentration a transition of the particle solution to a network solution takes place, approaching the so-called critical molecular weight range, where lyotropic mesophases are formed with exceeding cellulose concentration ≥ 20 %.

Technical dissolving and shaping processes favor solutions with 10 – 15 wt % of cellulose, that means one has to deal with isotropic network solutions. These isotropic network solu-
tions are the objective of the following reflections.

Contrary to the described direction the experimental dissolution process, starting from native cellulose, undergoes a dilution from the highly concentrated network solution to the diluted particle solution. Polymer chains of native cellulose are stiffened alongside the chain via intramolecular hydrogen bridge bonds and they are cross-linked each other via existing intermolecular hydrogen bridge bonds between the chains.

Feeding of cellulose into the aqueous NMMO under applied shear forces will cause a simultaneous swelling of the amorphous ranges of cellulose fibers and thereby generate a suspension. With increased evaporation of water in vacuum and rise in temperature and shear force, the swelling increases spontaneously with a mol ratio NMMO: water ~ 1 : 1,5 – 1,2, the differences of the refractive indices of the individual components disappear to a large extent and the remaining gel appears to be largely homogeneously based on corresponding microscopic investigations.

Based on the appearance one could be apt to consider this suspension as a solution. However when paying much closer attention, several facts are contrary to this assumption. The following figures 1 – 4 should make evident the transition of a multiple phase suspension to a microscopically homogeneous gel phase of a solution with 12,5 wt % cellulose, having a Cuoxam DP of about 563 of the dissolved cellulose.

At this state the measurable viscosity will reach a maximum value, one part of the hydrogen bridge bonds is solvated and the chain mobility is increased to such an extent that a non-reversible transition from cellulose I into cellulose II takes place. Wide angle X-Ray spectros-
copy measurements (WAXS) made from samples being swollen in solutions of different NMMO-concentrations, washed and dried, or coagulated and dried after dissolving, have confirmed this transition.

One can see clearly, that the peaks of the cellulose pulp and of the sample, being swollen in dihydrate (76.5 % NMMO) at the one hand and those of the samples being either swollen in 1,5 hydrate (81.3 % NMMO) or dissolved in 1,2 hydrate (84.4 % NMMO) on the other side show a good analogy. That means, the chain mobility in heterogeneous phase (1,5 hydrate) has already reached such an extent, causing a non-reversible transition of cellulose I into cellulose II. Furthermore it can be derived that the transition to the one phase gel does not cause further apparent changes in structure.

Based on the ZERO-shear viscosities at 85 °C and their corresponding standard deviations, measured at various points of a larger sample, one can conclude the existence of an inhomogeneous solution state. With increased shearing, and where necessary, further removal of water, the ZERO-shear viscosity changes in relatively short time in the order of one magnitude and the reproducibility of all measurements is within the limit of errors for this method. Since the molecular weight and the concentration are almost unchanged, the decrease in viscosity should be caused by an increased cleavage of hydrogen bridge bonds, that implies increasing solvation.

At this point, at the latest, there should be posed the question regarding the realized dissolution state and the method for its characterization as well.

We have postulated the ideal dissolution state as follows: Both in microscopic (>5 µm) as well as in sub-microscopic (>0,5 µm) ranges no gel particles can be detected and all hydrogen bridge bonds alongside and between the cellulose chains are completely solvated.

**Measuring methods and results**

For the investigation of the dissolution state in microscopic range a binocular microscope type “Axiolab®” was used, with polarization, λ -
compensation, phase contrast, various filters and a magnification up to 500 : 1 made from Carl Zeiss Jena. With a high degree of certainty, the microscopic viewing enables the unambiguous detection or exclusion of all particles >5 µm if their refractive index is sufficiently different from that of the ambient solvent phase.

The figures 1 – 4 should demonstrate the application limits of the microscopy method. A typical feature of the dissolutions process accompanied with the water / NMMO exchange is the attack in transverse direction to the fiber length axis with a simultaneous forming of spherical gel ranges. When dissolving dry cellulose pulp in monohydrate, however, one can find always an ablation of layers from only the surface.

Laser diffraction method with the HELOS® measuring instrument type BF ( Sympatec GmbH Clausthal is well proven for the investigation of the dissolution state in sub-micron range [8]. The He-Ne-laser with the wavelength of 633 nm lights through a specific measuring cell containing the sample of defined thickness (4 mm and 2 mm) and maintained at a temperature of 85 °C. A Detector measures the optical concentration, classifies the laser light diffraction into 31 particle classes within the range from 0.5 – 175 µm and calculates by use of corresponding software the particle size distribution spectrum. By calibration the optical concentration allows conclusions regarding the particle content as well.

In case of deep colored solutions a certain correction for the optical concentration becomes necessary. The Laser diffraction method even enables the detection of such inhomogeneities, that, exhibit very small differences in refractive indices comparison with the ambient solvent and for that reason cannot be detected by light microscopy.

In figure 6 is given the summary and density distribution of particles in a solution containing 12,3 wt % eucalyptus pulp with a Cuoxam DP of 563 for the dissolved cellulose.

The measured particle volume amounts to 1,3 µl/l of solution with a maximum particle diameter of 18 µm. However, the question remains unanswered whether the "residual particles" have to be considered as cellulosic material itself or as other impurities of cellulose. By suitable choice of dissolution conditions – particularly shear forces and temperature – a relative huge number of diverse cellulose pulps with different sources of consistency can be processed to more or less particle free solutions. Considering the aspect of solution shaping for getting anisotropic shaped bodies we have subdivided the term of solution state and we speak about the solution quality when evaluating the microscopic and submicroscopic ranges, that
means in case of the existence of discrete inhomogeneities.

In molecular range the solution state should differ only by the degree of solvation achieved. That means the network consists of more or less large units crosslinked by hydrogen bonds, which completely dissolve in ideal case. The solution state describes this limited range. In searching for suitable methods, rheological measuring methods were found to promise the best chances of success, since smallest variations in molecular weight, molecular weight distribution and chain branching cause a significant change in rheological parameters like ZERO-shear viscosity, loss and storage modulus, relaxation time etc. For measuring these parameters a Rheometer was used, with temperature controllable cone/plate and plate/plate-sensor of different size ( THERMOHAKE® Karlsruhe ) which enabled sample shearing both in rotational as well as oscillating operating modes and permitting by use of the corresponding software ( Rheowin®, Rheosoft® ) readouts of discrete measuring parameters, master curves and calculated spectra.

For evaluation of the solution state in molecular range we applied the ZERO-shear viscosity $(\eta_0^0)$, the molecular unevenness $U_\eta$ as obtained by rheology, the critical average polymerization degree $(\text{DP}_{\text{crit}})$ and the relaxation time spectra $(H = f(\lambda))$.

More Details of these methods are described in literature [9, 10].

The ZERO shear viscosity changes exponentially in dependence on the molecular weight.

$$\eta_{0,\theta} = K_\eta \cdot M^a$$

$$\text{DP}_{\text{crit}} = 123.5 \cdot \frac{R \cdot T \cdot \rho_L \cdot c_{\text{Cell}}}{G_0}$$

unevenness

$$U_\eta = \frac{\eta_0^0}{\eta_0^\theta} - 1 = \frac{\omega^\theta \cdot \eta_0^0}{\sqrt{2} \cdot G''_0} - 1$$

and relaxation time spectra. The response of relaxation times corresponding to the respective molecular weights should be much more sensitive, as the summary parameter ZERO shear viscosity ever can do.
In Figure 7 is shown the normalized master curve at 85°C for the deformation of a solution containing 12.8 wt % cotton linters (BWL) pulp after 1.5 h dissolving time. The Cuoxam DP of the dissolved cellulose pulp was 608. Storage – and loss modulus were measured with 7100 Pa at a shear rate of 2.7 rad/s and the plateau modulus was 42050 Pa. From these parameters a DP$_{\text{crit.}}$ of 133 and an unevenness of about 2.5 is obtained.

Figure 8 presents a relaxation time spectrum of this solution after 0.5 and 1.5 hours of dissolving time and a subsequent hold-up time of 20 hours at 80°C. Whilst still observing a remarkable decrease in the relaxation times during dissolution, after further 20 hours hold-up time relaxation time keeps virtually constant.

In Figure 9 is given the relaxation time spectrum of a solution of 12.3 wt % eucalyptus pulp (Cuoxam DP$_{L}$: 530) and in Figure 10 the relaxation time spectrum of a 12 wt % softwood pulp solution each after 1.5 hours of dissolving time and further 20 respectively 45 hours hold-up time at 80°C.
From these spectra it can be observed that this method enables a highly differentiated detection of differences in solution state and on the other side, the solution state within the molecular range is less effected by the shear field, but more by the parameters like temperature and time. In dependence on the molecular weight distribution a completely solvated solution, that means a stable state, can be achieved after more or less hold-up times, only.

However, the completely solvated solution is a prerequisite for reproducible measurements. In particular this is imperative for weighted relaxation time spectra where predictions concerning the molecular weight distribution should be derived from. In figure 11 are given the relaxation time spectra of solutions of cotton linters (BWL) cellulose pulp with a Cuoxam DP 1528 and 606 for the dissolved cellulose.
Both spectra indicate bimodal distributions of different width according to the measured unevenness of 2.3 and 2.5 respectively with maximum values for the relaxation time of 12.3/1.1 and 5.3/0.8 s respectively, and according to the measured average polymerization degree of 1528 respectively 606. Using a corresponding calibration of the abscissa ($\lambda = K \lambda \cdot M^n$) predictions regarding the molecular weight distribution should be possible.

**Figure 11.** relaxation time spectra (weighted) for cotton linters cellulose pulps with different molecular weight and molecular weight distribution

**Literature**

2 Klüfers, P.: Lösungsgleichgewichte und Strukturprinzipien in Cellulose-Metall-Netzwerken. Vortrag DFG-Kolloquium 03.06.1997 in Bad Herrenalb
3 Klüfers, P.: Welche Metalle bilden Komplexe mit Cellulosedianionen. Vortrag; DFG-Kolloquium 16.03 1999 in Bad Herrenalb
4 Gränacher, Ch.; Sallmann, R.: Verfahren zur Herstellung von Celluloselösungen. DRP 713486 07.10.1936
5 Johnson, D.L.: Method of preparing Polymers from a mixture of cyclic amine oxides and Polymers USP 5 508 941 02.09.1966
6 Mc Corsley, C.C.: Gelformter Zellulosegegenstand DE 29 13 589 02.03.1979
8 Kosan, B.; Michels, Ch.: Particle analysis by laser diffraction – application and restrictions in the lyocell process Chemical Fibers Int. 49 (1999) 3 50 - 54
9 Michels, Ch.: Beitrag zur Bestimmung von Molmassenverteilungen in Cellulosen aus rheologischen Daten Das Papier 52 (1998) 1 3 - 8