

## Solubility and Solution Rheology of Enzymatically Treated Pulp

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### ABSTRACT

The aim of this work was to study the solubility of chemical pulps and the effects of ZnO and NaOH concentrations on the solution properties. The pulps were mechanically shredded, pretreated using cellulase, and dissolved directly into aqueous sodium zincate. The solubility of pulp was observed visually by a microscope, and the viscosities of solutions were measured by a rotational rheometer and a ball-drop method.

### INTRODUCTION

Cellulose is a biodegradable polymer that is received from renewable agricultural or forest sources. It is the most abundant natural polymer. The enzyme-assisted dissolution method is one possibility for the ecological manufacturing of cellulose products. Vehviläinen et al.<sup>1</sup> and the research group<sup>2-5</sup> have studied the dissolution of cellulose by the cellulase pretreatment. The cellulase treated chemical pulp dissolves directly into aqueous sodium zincate (NaOH/ZnO). Since the pulp dissolves without any use of carbon disulfide, unlike in the viscose method, it is possible to regenerate the cellulose solution into the fibres and films without any harmful emissions during the process. This study focuses on the solubility of enzyme-treated pulps, and the rheological properties of solutions.

### EXPERIMENTAL

#### Materials

Four commercial pulps, Table 1, were shredded mechanically for 5 h with a Baker Perkins Mixer at a cellulose concentration of 20 wt%, room temperature, and thereafter treated with a commercial cellulase preparation (AB Enzymes Oy, Rajamäki, Finland) at pH 5.0, 50°C for 3 h. The intrinsic viscosities of pulps measured by SCAN-CM 15:99, the enzyme dosages used, and the amount of soluble sugars measured by the DNS method<sup>6</sup> are also given in Table 1.

Table 1. Pulps, the enzyme dosages used, intrinsic viscosities of pulps before and after the enzyme treatment, and dissolved sugars after the enzyme treatment.

Pulp	Enzyme dosage (nkat/g)	SCAN viscosity (ml/g)		Dissolved sugars (mg/g) before after
		before	after	
Softwood dissolving pulp	290	400	280	35.1
Softwood dissolving pulp	250	520	340	28.4
Hardwood kraft	250	710	390	19.4
Hemi poor hardwood kraft	250	870	375	27.9

### Preparation of Cellulose Solutions

The enzyme treated pulp was dissolved into NaOH/ZnO as published previously.<sup>7</sup> The pulp concentrations of solutions varied between 1-6 wt%, ZnO concentrations between 0.1-1.3 wt%, and NaOH concentrations between 4.5-6.5 wt%. Wet cellulose (15 % dry content) and NaOH/ZnO solution were mixed together using an overhead stirrer (RW20, IKAWerke GmbH & Co. KG, Staufen, Germany) at 5°C for 5 min. The alkaline cellulose solutions were stored at a deep freezer (-18°C) and were melted in a refrigerator (+5°C) prior to the characterization.

### Characterization of Solutions

The solubility of cellulose pulp was determined visually by optical microscope (Leitz Laborlux D, Ernest Leitz Wetzlar GmbH, Germany) under polarized light. Samples were classified into four groups: (1) a clear solution, (2) a clear solution with 1-2 insoluble fibres, (3) a few insoluble fibres, and (4) a lot of insoluble fibres.

Flow properties were determined using the modified Ball-Drop Method (ASTM D 1343-86) which is based on the falling ball principle. The falling time of the stainless steel ball (1/8", 130 mg) was measured between a measuring distance of 20 cm at a temperature range from 9°C to 20°C.

A steady shear viscosity as a function of shear rate was determined with an Anton-Paar Physica MCR301 (Anton Paar GmbH, Graz, Austria) rotational rheometer using a 50 mm diameter plate-plate geometry with a gap size of 1 mm. All these measurements were made at room temperature (~ 23°C).

## RESULTS

The solubilities of different pulps in NaOH/ZnO are shown in Fig. 1. Softwood dissolving grade pulps dissolved more easily in NaOH/ZnO than the kraft pulps. The hemi poor hardwood kraft dissolved better than the hardwood kraft.

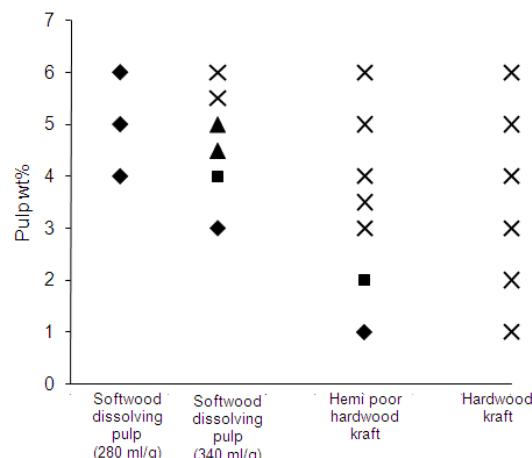


Figure 1. Solubility of pulps in NaOH/ZnO. The samples contain 6.5 wt% NaOH and 1.3 wt% ZnO. Scale: (◆) clear solution, (■) clear solution with 1-2 insoluble fibres, (▲) a few insoluble fibres, and (×) a lot of insoluble fibres.

The effect of ZnO concentration on the solubility was tested with 5 wt% softwood dissolving grade pulp (280 ml/g) and 6.5 wt% NaOH concentration. The clear solutions were obtained with 1.3 and 1.2 wt% ZnO concentration, a few insoluble fibres were obtained with 1.1 and 1.0 wt% ZnO concentration, and a lot of insoluble fibres when the amount of ZnO was less than 1.0 wt%.

The effect of NaOH concentration on the solubility was tested with 4 wt% softwood dissolving grade pulp (280 ml/g) and 1.3 wt% ZnO concentration. The clear solutions were obtained when the amount of NaOH was  $\geq$  6 wt%. The amount of insoluble fibres increased when the NaOH concentration was less than 6 wt%.

The effect of pulp concentration on the viscosities versus shear rate is shown in Fig. 2. All the solutions show shear-thinning behaviour. With increasing cellulose concentration the level of viscosity increased markedly and the critical shear rate for the onset of shear-thinning shifted to lower shear rates. The low-shear-rate

Newtonian plateau was observed with 4 and 5 wt% pulp concentrations, whereas it was not observed with 6 wt% pulp concentration. However, the Newtonian plateau is difficult to observe in high concentration solutions with stiff polymer, as cellulose, although it also exists for high concentrations.

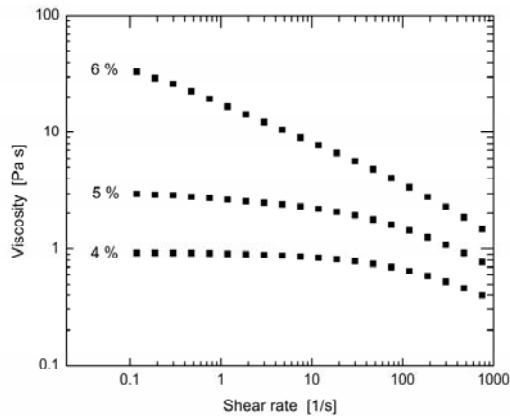


Figure 2. Measured viscosity as a function of shear rate for solutions with cellulose concentrations of 4, 5 and 6 wt% (NaOH 6.5 wt% and ZnO 1.3 wt%). Pulp sample: softwood dissolving pulp (280 ml/g).

The effect of ZnO concentration on the viscosities versus shear rate is shown in Fig. 3. The results reveal that the ZnO concentration, and thus the solubility of cellulose, had a significant effect on the shape of the viscosity curve. With low ZnO concentrations ( $< 1.0$  wt%) there was no viscosity plateau at low shear rates. At higher ZnO concentrations ( $\geq 1.0$  wt%) the solutions had a viscosity curve typically observed for polymer solutions. Moreover, it was observed a lot of insoluble fibres in the solutions with low ZnO concentrations ( $< 1.0$  wt%).

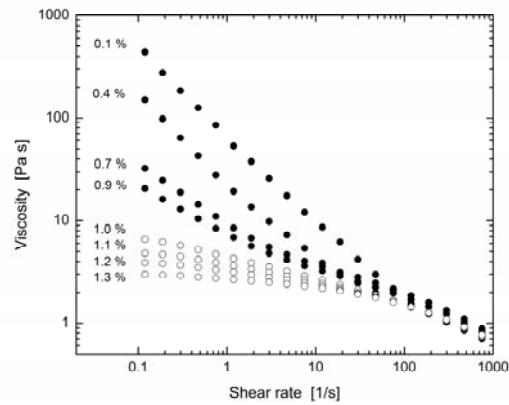


Figure 3. Measured viscosity as a function of shear rate for solutions with ZnO concentrations of 0.1-1.3 wt% (cellulose 5 wt% and NaOH 6.5 wt%): (●) curves without Newtonian plateau and (○) curves with Newtonian plateau. Pulp sample: softwood dissolving pulp (280 ml/g).

The effect of NaOH concentration on solution properties was measured by the ball-drop method as shown in Fig. 4. It was observed the gelation of solutions at low NaOH concentrations ( $< 6.0$  wt%). It was also observed insoluble fibres in the solutions having the gelation behaviour.

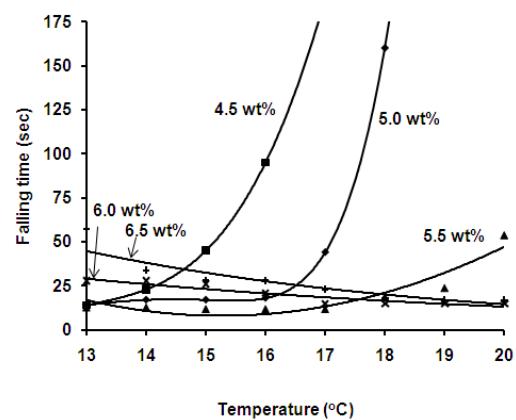


Figure 4. Effect of NaOH concentration on falling ball time with NaOH concentrations of 4.5-6.5 wt% (cellulose 4 wt% and ZnO 1.3 wt%). Pulp sample: softwood dissolving pulp (280 ml/g).

## CONCLUSIONS

Mechanically shredded and cellulase pretreated dissolving pulp dissolves directly into sodium zincate solution. The ZnO concentration has significant effect on the solubility of cellulose, and thus the rheological properties of cellulose solutions. Furthermore, NaOH concentration has to be sufficient to prevent the gelation of solution.

## ACKNOWLEDGEMENTS

This work is carried out in the future biorefinery programme of Forestcluster Ltd. ([http://www.forestclusterportal.fi/index.php/Future\\_Biorefinery](http://www.forestclusterportal.fi/index.php/Future_Biorefinery))

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