

# SOME ASPECTS ON THE ACTIVATION OF DISSOLVING PULPS AND THE INFLUENCE ON THE REACTIVITY IN A FOLLOWING VISCOSE STAGE

LINDA ÖSTBERG and ULF GERMGÅRD

*Department of Engineering and Chemical Sciences, Karlstad University,  
SE-65188 Karlstad, Sweden*

*Received May 24, 2012*

It was found that, for a dissolving pulp, an enzymatic pre-treatment with an endoglucanase prior to viscose preparation did not change the correlation between the gamma number of the viscose dope and the carbon disulphide charge. Thus, the pulp stoichiometry, or reactivity, was not changed by an endoglucanase pre-treatment. It has nevertheless previously been found that the pulp reactivity, measured either by Fock's test or as the filter clogging value ( $K_w$ ), increased for the same type of enzyme pre-treatment. Thus, the pulp reactivity seems to be influenced by the analysis method employed.

**Keywords:** dissolving pulp, *DP*, enzyme, gamma number, reactivity, viscose

## INTRODUCTION

The cellulose molecule is the most abundant organic polymer on earth<sup>1</sup> and it is present in massive quantities in trees and other plants. This molecule acts as an indispensable building block for a large number of substances. In a tree, it acts as a reinforcement material, giving it a surprisingly high strength and bending stiffness. In the paper industry, it is a vital component in the pulp fibres that are used for manufacturing paper and board. However, it can also be used as a raw material for cellulose derivatives and regenerated cellulose.<sup>2</sup> Viscose fibres for textile manufacturing belong to the latter group and these products are gaining in importance due to their capacity to replace cotton and other fossil-based textile fibres, such as nylon and polyester. High tensile strength is required for some viscose products, calling for long cellulose molecules (*i.e.* a high *DP*) in the pulp. The focus of this investigation has been on fibres for sponge cloth for use especially in the kitchen. Such viscose products have to be strong and consequently need to be based on cellulose with a relatively high *DP*.

Since viscose products are based on cellulose, they may be considered as being "green" and environmentally friendly. In the traditional viscose processes, however, large quantities of

sodium hydroxide and carbon disulphide are used; the latter chemical is problematic and hazardous from both ecological and occupational health and safety aspects. Accordingly, the authorities have exerted considerable pressure on the viscose industry to reduce its use. It would therefore be beneficial if a modified viscose process with a lower consumption of carbon disulphide could be developed. One possible way of reducing the consumption of chemicals could be to include an enzyme pre-treatment stage prior to the viscose preparation.<sup>1-3</sup> The objective of this study was therefore to investigate if it is possible to increase the reactivity of a dissolving pulp by an enzyme pre-treatment, if the reactivity was measured either by Fock's test,<sup>4</sup> by the dope filtration resistance test in accordance to Treiber<sup>5</sup> or as the gamma number.<sup>6-8</sup>

## EXPERIMENTAL

### Pulps

The commercial spruce/pine dissolving pulp used, manufactured by two stage (pH 5/pH 1.5) sodium sulphite cooking (TCF), was supplied by Domsjö Fabriker, Sweden. The name of this pulp grade was Domsjö Cellulose 2200 and it had the following properties: viscosity – 18 cP, *DP* – 780, ISO brightness – 92%,  $\alpha$ -cellulose content – 91% and  $R_{18}$  – 94.5%.

One pulp sample of Domsjö Cellulose 2200 was pre-treated in the laboratory using the steam explosion method STEX<sup>11</sup> (3 min, 226 °C) and this resulted in a

pulp (Domsjö, STEX) with properties different from those of the untreated reference pulp (Domsjö, reference), see Table 1.

Table 1  
Properties of the dissolving pulps

Pulp	Viscosity (ml/g)	DP <sub>n</sub>	Mean length of fibres (mm)	Mean width of fibres (µm)
Domsjö, reference	530	745	1.72	25.5
Domsjö, STEX	280	368	1.53	25.4

### Chemicals and enzyme

The enzyme used for the pre-treatment was a monocomponent endoglucanase preparation (Carezyme<sup>®</sup>), provided by Novozymes AS (Denmark). The enzyme activity was determined by the manufacturer and expressed in Endo Cellulase Units (ECU) per unit mass of material as 4500 ECU/g. The chemicals used were sodium hydroxide, NaOH, (purity 99% from VWR International) and carbon disulphide, CS<sub>2</sub>, (purity ≥99% from SIGMA-ALDRICH).

### Enzyme pre-treatment

The enzyme treatment was performed in a glass beaker; the conditions used were 40 °C, pH 7.5 and 5% pulp consistency. The procedure was as follows: a dry pulp sheet was cut into 1x1 cm pieces and 25 g, calculated as oven dry pulp, was added to a beaker with 475 g of de-ionized water. The beaker was placed in a water bath, where it remained until the temperature reached 45 °C, whilst the slurry was continuously stirred. The enzyme was then added to the pulp slurry; the treatment continued for a specified time before the pulp was dewatered to a dryness of approximately 30%. In the following mercerization step, the extra amount of water in the enzyme-treated pulp was noted and compensated for with an extra addition of sodium hydroxide to the mercerization vessel.

### High viscosity viscose preparation

Mercerization was performed by tempering 800 g of sodium hydroxide (18% w/w) in a stainless steel vessel to 45 °C in a water bath. Then, 25 g pulp (calculated as oven dry pulp) was added to the vessel. The slurry was stirred for 20 minutes at 45 °C.

A mesh filter was placed on the bottom of a pressure chamber and the slurry was transferred to it from the stainless steel vessel. Vacuum was applied to the vessel and another mesh filter was put on top of the pulp slurry. The pressure chamber was then placed in the hydraulic press. The load was adjusted to 69-74 kg/cm<sup>2</sup>. The alkali cellulose filter cake that was formed after pressing weighed between 63.0-64.5 g and the pressure time was approx. 2 min.

The alkali cellulose filter cake was torn into smaller pieces by hand and placed in a shredder, where the

alkali cellulose was processed mechanically in order to achieve a larger surface area that could react more easily with the carbon disulphide during the following sulphidation step. The mechanical treatment was continued for 20-30 min at room temperature.

50 g of alkali cellulose was then transferred from the shredder into a glass reactor before it was sealed with a cap. Vacuum was applied to the reactor, which was placed in a water bath at 28 °C. The charge of carbon disulphide was based on the amount of α-cellulose in the alkali cellulose sample. 8.7 g of carbon disulphide was added, i.e. 53%, to a sample of 50 g alkali cellulose, which contained 16.5 g of cellulose (33% of the sample). The carbon disulphide was added with a syringe through a membrane at the top of the reactor. The water bath temperature was raised simultaneously to 32 °C and stirring was started. The slurry was stirred for 2.5 h at 75 rpm.

When the sulphidation was complete, the cellulose xanthate and additional sodium hydroxide (2 wt%) were transferred to the dissolving vessel, giving the viscose dope a chemical composition of 9.5% cellulose and 8.8% sodium hydroxide. The dissolving vessel was connected to a cooling bath and stirring was started. The temperature was held at 5 °C and the stirring was continued for 3 hours. The viscose produced was left to ripen for 16-20 h at room temperature in the dissolving vessel, which was covered with plastic film and placed under a fume hood.

### Analytical methods

The gamma number was determined by a spectrophotometric measurement of the viscose dissolved in sodium hydroxide in accordance to Rahman.<sup>6</sup>

The gamma number was calculated using the formula:

$$\gamma = \frac{A_{303} \times 546.48}{\text{sample weight} \times \% \text{ cellulose}} \quad (1)$$

where 546.48 was derived from the dilution factors, the molecular weight of glucose and the molar extinction coefficient. A molar extinction coefficient of 14822 was used for the calculations in this investigation.<sup>8</sup> The intrinsic viscosity was measured according to ISO 5351-1:2004 and recalculated to

TAPPI T 230 viscosity by means of a conversion curve.

## RESULTS AND DISCUSSION

When the dissolving pulp was treated with different concentrations of the enzyme, prior to the preparation of viscose, its intrinsic viscosity decreased as expected (see Figure 1). The results reflect experiments carried out at constant temperature and pH, i.e. only the enzyme charge was varied. Thus, to avoid a reduction in the strength of the final viscose products, it seemed important to use only low charges of enzyme.

Earlier results had shown that when an enzyme pre-treatment of a dissolving pulp was used the pulp reactivity measured by Fock's test<sup>3,9</sup> or as the filter clogging value<sup>3</sup> increased. It was therefore suggested that an enzyme pre-treatment with an endoglucanase would probably also improve the reactivity of the pulp when the gamma number was the quality parameter. The gamma number was the quality parameter for the viscose grade used for fibre sponge cloths. Should this assumption be correct, then the subsequent viscose preparation for fibre sponge cloths could most probably be carried out with less carbon disulphide, still obtaining the same gamma number. Thus, an environmentally and economically favourable situation would be the final outcome.

Some gamma number results obtained for viscose dopes based on pulps that were pre-treated with low charges of enzymes (4.5 ECU/g) are shown in Table 2. The table shows that for the low enzyme charge no significant influence on the gamma number was obtained. The corresponding results for the experiments using higher charges of enzymes, i.e. 450 and 900 ECU/g, are shown in Figure 2. As can be seen, the required amount of carbon disulphide for a certain gamma number was not affected in this case either. Thus, it seemed that the substitution of the cellulose backbone was not facilitated (or the reactivity of the pulp was not increased) by the endoglucanase pre-treatment, independent of the amount of enzyme charged.

Based on the results obtained, it could be speculated that gamma number, i.e. the degree of substitution, was a stoichiometric property that was only influenced by cellulose properties on a molecular level, like crystallinity, by the presence of hemicelluloses and if the removal of amorphous material had created a more open structure. Similarly, it was proposed that the reactivity according to Fock's test or the filter clogging value were, in both cases, particularly dependent on the presence of fibres and gel in the analysis liquors or in the viscose solutions.

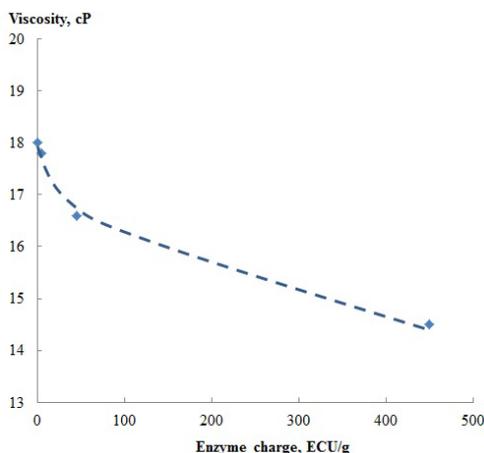


Figure 1: The intrinsic viscosity of viscose samples after enzyme pre-treatment versus enzyme charge. Conditions used: 45 min, 40 °C and pH 7.5. Each point in the figure represents the average of two measurements

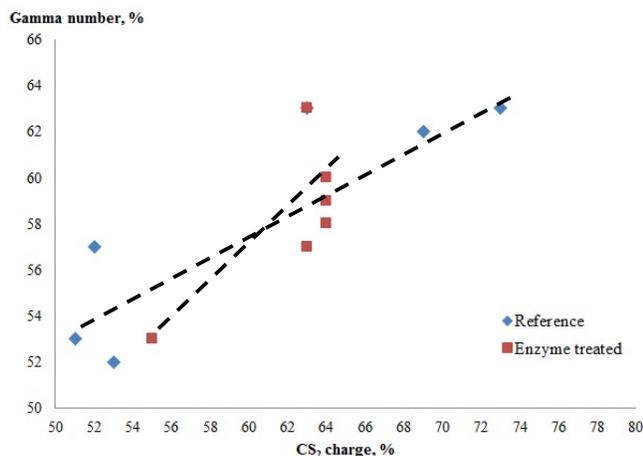


Figure 2: Gamma number of the viscose solution versus the charge of carbon disulphide for laboratory samples with or without enzyme pre-treatment. Enzymatic conditions used: 450 or 900 ECU/g, 2 h, 40 °C, pH 7.5

Table 2  
Gamma number of dissolving pulps, with and without enzyme pre-treatment

Domsjö pulp sample	Gamma number with enzyme (4.5 ECU/g pulp), %	Gamma number without enzyme, %
1	63	60
2	61	63
3	-	61

The carbon disulphide charge was 53%, calculated as g/g pulp

Table 3  
Gamma number of STEX treated dissolving pulp, with or without enzyme pre-treatment

Domsjö pulp sample, STEX-treated	Gamma number with enzyme (4.5 ECU/g pulp), %	Gamma number without enzyme, %
1	62	63
2	60	60
3	-	62

The carbon disulphide charge was 53%, calculated as g/g pulp

It may be also assumed that the improvement in reactivity obtained by the Fock<sup>4</sup> or the Treiber tests<sup>5</sup> was partly due to the reduction in the length of the cellulose chains, i.e. lower DP, which occurred in the enzyme stage. An improvement in reactivity could then be obtained when using other methods that cut chains, e.g. strong acidic treatments. In fact, Henriksson *et al.*<sup>1</sup> reported such results earlier. The fact that the Fock reactivity is improved by lower DP measured as lower intrinsic viscosity has been shown by Javed *et al.*<sup>9</sup> The results presented in Figure 2 indicate, however, that it is not easier to obtain a specific gamma number even if the DP of the cellulose is lower due to the relatively high charge of enzyme.

If an enzyme pre-treatment only resulted in the reduction of the molecular chain length of the cellulose, a higher gamma number could not be expected. Therefore, improved reaction efficiency required instead that, for example, the reactions occur more evenly in the cellulose matrix. Another possibility to improve the reactivity is to make the reactions more efficient as a result of lower losses of chemicals or fewer side-reactions.

Enzymes are large molecules, so it could be expected that they should have a problem to penetrate the fibre cell wall before reaching the cellulose molecules. Pre-treating a dissolving pulp sample using steam explosion (STEX) was therefore performed prior to the enzyme treatment, as this disintegrates the fibers into small fragments (see Table 1) and thus should improve the possibility for the enzymes to reach the cellulose molecules.<sup>10-11</sup>

The gamma number obtained with and without a STEX treatment is shown in Table 3. Thus, it can be seen that the STEX treatment did not improve the influence of the enzyme stage. Thus, the viscose dope showed no significant increase in gamma number for a given charge of carbon disulfide. The bottle neck for the enzyme reaction was apparently not on the fiber level and it could instead be assumed to be on the molecular level. Consequently, there is a difference between the chemical reactions on a molecular level that lead to a certain gamma number and those on a fiber level that lead to certain Fock reactivity or a certain  $K_w$  number. Thus, the expression "pulp reactivity" is not a universal property, but depends, to a large extent, on the method of analysis that is used in a given case.

## CONCLUSION

Endoglucanase pre-treatment of a dissolving pulp results in a lower DP of the cellulose. This reduction in chain length could be a reason for the improved reactivity of a pulp in a following viscose preparation stage, when the reactivity is measured according to either Fock's test or the filter clogging value ( $K_w$ ). These two tests are influenced highly by reactions on the fiber level. The gamma number analysis, on the other hand, which is performed on the viscose dope, is probably not influenced by the DP of the cellulose backbone and it seemed that the gamma number was mainly influenced on a molecular level rather than on a fiber level. Thus, the mechanisms controlling the Fock or the  $K_w$

reactivity on one hand, and the gamma number reactivity on the other, are probably not the same. For a given viscose experiment, these three analyses therefore do not result in the same pulp reactivity.

**ACKNOWLEDGEMENTS:** Thanks are due to Karlstad University and Vinnova/BFP for their financial support, to Domsjö Fabriker AB, Sweden, for supplying the dissolving pulp, to Novozyme AS, Denmark, for supplying the enzymes, to MSc Erik Erhardsson for skillful laboratory work, to PhD Niklas Kvarnlöf for constructive criticism of the manuscript and to Maureen Sondell for linguistic correction of the manuscript.

## REFERENCES

- <sup>1</sup> G. Henriksson, *Biomacromolecules*, **7(6)**, 2027 (2006).
- <sup>2</sup> V. Köpke, D. Ibarra and M. Ek, *Nordic Pulp Pap. Res. J.*, **23(4)**, 363 (2008).
- <sup>3</sup> N. Kvarnlöf, U. Germgård, L. J. Jönsson and C.-A. Söderlund, *Appita J.*, **59(3)**, 242 (2006).
- <sup>4</sup> W. Fock, *Das Papier*, **13(3)**, 92 (1959).
- <sup>5</sup> E. Treiber, C. Rehnström, F. Améen and F. Kolos, *Das Papier*, **16(3)**, 85 (1962).
- <sup>6</sup> M. Rahman, *Anal. Chem.*, **43(12)**, 1614 (1971).
- <sup>7</sup> H. L. Barthelemy and W. Loveleen, *Ind. Eng. Chem. Anal. Ed.*, **17(10)**, 624 (1945).
- <sup>8</sup> J. P. Dux and L. H. Phifer, *Anal. Chem.*, **29(12)**, 1842 (1957).
- <sup>9</sup> M. A. Javed and U. Germgård, *BioResources*, **6(6)**, 2581 (2011).
- <sup>10</sup> P. Bösch, O. Wallberg, E. Joelsson, M. Galbe and G. Zacchi, *Biotechnol. Biofuels*, **3**, 15 (2010).
- <sup>11</sup> M. Kihlman, O. Wallberg, L. Stigsson and U. Germgård, *Holzforschung*, **65(4)**, 613 (2011).