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ANALYSIS OF WOOD CELLULOSE MECHANICAL

DEGRADATION DURING BEATING PROCESS

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ABSTRACT

Dependence of wood cellulose degradation rate on the size reduction method (PFI mill, Valley beater) is monitored. Size Exclusion Chromatography and viscometry method were applied to measure the cellulose polymerisation degree. The highest cellulose degradation degree (mean molecular mass ca. 200 KDa) and the highest value of reaction rate constant (69*10⁻⁸s⁻¹) were reached after using PFI mill. It was revealed that polymerisation degree of cellulose subjected to a beating process depends on the content of primary and secondary minute fraction (so called krill). Size Exclusion Chromatography and viscometric method were used to determine the polymerisation degree of cellulose.

KEYWORDS: PFI mill, Valley beater, cellulose polymerisation degree, viscometry, Size Exclusion Chromatography.

INTRODUCTION

Changes in molecular level cellulose properties (chains shortening) causes fibres weakening and in consequence decrease of – material mechanical resistance. This process, known as degradation, may proceed with a different rate depending on material and different factors presence. Average polymerisation degree (P) of chemical paper-pulp amounts to 700-2000. It influences the fibres strength – if P<100 then there is practically no mechanical resistance, exceeding value of 100 causes fast increase of mechanical resistance. If P>600 then the increase of resistance is relatively low (Przybysz 1997).

Already in the first half of 20th century the influence of cellulose beating time (Staudinger and Dreher 1936) on the polymerisation degree (P) was studied, as well as its influence on the cellulose crystallinity (Hermans and Weidinger 1946) and carboxylic groups content (Staudinger

et al. 1936). Violent increase of beated cellulose solubility in 1 % NaOH was found, which was caused by the synergetic effect of molecular mass (polymerisation degree - P) decrease (Staudinger and Dreher 1936, Forziati et al. 1950, Nelson and O'Connor 1964 a, b, Liang et al. 1993) and crystallinity decrease (Stubicar et al. 1998). Analogical changes were found for FT-IR streching and bending vibrations of wood and cellulose samples beated in the same conditions (Schwanninger et al. 2004). Spectra are very similar. The ratio of absorption bands for 1429.cm⁻¹ and 894.cm⁻¹ (O'Connor et al. 1958) or 1372.cm⁻¹ and 2900.cm⁻¹ (Nelson and O'Connor 1964a) is the crystallinity measure. The processes of oxidation and hydrolysis accompany the mechanical degradation of cellulose.

Described problem was not finally solved in spite of applying many analytical techniques (NMR, FT-IR, chromatography – SEC and HPLC, rontgenographic techniques, strength testing) which were supposed to determine the influence of beating on the usability of obtained fibrous materials. The aim of this paper is to analyse wood cellulose degradation process during mechanical factor action which may cause even low cellulose degradation degree.

MATERIAL AND METHODS

Samples beating using PFI mill

Bleached kraft (obtained from pine wood - SaB1) beating was performed in laboratory conditions according to PN EN ISO 5264-2: 2003 (U) standard in the PFI mill. Beating duration (0-control sample 1, 2, 3, 4, 5, 7 minutes) was measured using timer. Beated pulp after assumed time expiring was tranferred to the defibrator. Then water was added to the volume of 2,5 dm³, pulp was equalized (3000 rpm) within 2 minutes. Water was added to keep the concentration in defibrator on the level of 0.3 %. Obtained fibrous pulp was further mixed with lower rate (1000 rpm). Then it was sampled to determine lubricity and drainage time factor. It was performed using Shopper-Riegler apparatus according to PN EN ISO 5267-1: 2002/AC: 2006 standard. The results of these measurements are collected in the Tab. 1.

Beating duration.min ⁻¹	Lubricity/°SR	Drainage time factor.s ⁻¹
0	14	3
1	16	6
2	21	9
3	30	20
4	39	34
5	55	71
7	72	146

Tab. 1: Characteristic of bleached kraft obtained from pine wood (SaB1) beated in the PFI mill.

Samples were then prepared to chromatographic analysis. Samples of defibered pulp with mass of about 5 g for different beating durations were dried in vacuum drier under pressure of 7 kPa (94 mmHg) in the temperature of 60°C to dry mass. Such a dried cellulose was sampled again, then dissolved and analysed using chromatography (SEC).

The analyses were performed additionally, in which the primary minute fraction (krill)

was separated before beating in PFI mill. This analysis was made in order to obtain data about cellulose fibres behaviour. The residual fibrous fraction was beated in two variants. The first one consists of beating the cellulose fibrous fraction within 2 minutes and then separating the secondary krill. The second one consists of beating the cellulose fibrous fraction within 7 minutes and separating the secondary krill.

All of the fibrous cellulose and krill (primary and secondary) samples were submitted the procedure of preparation to the mean viscosity polymerisation degree analysis developed basing on the PN 92/P-50101/01 standard. Analysis was made using Ubbelohde viscometers, number I and Ic (SCHOTT Instruments). Samples with mass of about 80 mg were collected for dissolution.

Samples beating using Valley beater

Beating of bleached kraft obtained from pine wood (SaB1) was performed in laboratory conditions according to PN EN ISO 5264-2: 2003 (U) standard in Valley beater which is the miniature of industrial open beater.

The procedure of beating in the Valley beater was as follows. Fibres concentration in the beater was 2 %; the charge was 460 g of bleached kraft with 5 % moisture. 0.5 dm³ of beated pulp was sampled after assumed durations: 0 (control sample), 25, 35, 45, 55, 65, 80 minutes. It was then poured to defibrator, diluted with 2 dm³ of water and equalized (3000 rpm) within 2 minutes. Obtained fibrous pulp was diluted to the concentration of 0,3 % and mixed with lower rate (1000 rpm). The pulp was sampled to determine lubricity and drainage time factor. It was performed using Shopper-Riegler apparatus according to PN EN ISO 5267-1: 2002/AC: 2006 standard. The results of these measurements are collected in the Tab. 2.

Beating duration.min ⁻¹	Lubricity/°SR	Drainage time factor.s ⁻¹
0	12	3
25	17	7
35	27	14
45	40	32
55	50	64
65	60	91
80	74	240

Tab. 2: Characteristics of bleached kraft obtained from pine wood (SaB1) beated in the Valley beater.

Chromatographic analysis conditions

Samples were then prepared for chromatographic analysis. Samples of defibered pulp with mass of about 5 g for different beating durations were dried in vacuum drier under pressure of 7 kPa (94 mmHg) in the temperature of 60°C to dry mass. Such dried cellulose was sampled again, then dissolved and analysed using chromatography (SEC). Samples were activated in the sequence: water, methanol, dimethylacetamide (DMAc) and then, after DMAc removal 8 % of (w/v) LiCl/DMAc was added in order to dissolve cellulose. Finally it was diluted to the concentration of 1 % (w/v) LiCl/DMAc.

Molecular-weight distribution analysis was performed using liquid chromatograph.

Nucleogel M-10 (Macherey-Nagel) column (300x7.7mm) was used. Same conditions were applied to all measurements: eluent – 0.5 % (w/v) LiCl solution in DMAc, 1.5-2.0 cm³.min⁻¹ flow, temperature of 80° C.

Polystyrene standards with molecular mass in the range of 580 Da – 6850 Da were used to calibrate. The Mark-Houwink universal calibration was applied to determine the celluose molecular -weight distribution. Following parameters of calibration were used:

 $K_{PS} = 17.35 \times 10^{-3} \text{ cm}^3$. g⁻¹ $\alpha_{PS} = 0.642$ (for polystyrene, Timpa 1991).

 $K_{cel} = 2.78 \times 10^{-3} \text{ cm}^3$. g⁻¹ $\alpha_{cel} = 0.957$ (for cellulose, Bikova&Treimanis 2002).

RESULTS AND DISCUSSION

SEC chromatography allows to degradation mechanism analysis. Mean molecular weight, molecular weight distribution and degradation process rate constant is possible to calculate basing on these measurements. Model system, in which wood cellulose forming suspension in water is beated, is in PFI mill and Valley beater. The results were applied to estimate kinetic parameters of degradation process. The dependence of cellulose mean molecular weight on time is generally linear for small degradation progress. The dependence for higher degradation degrees (lower mean molecular mass) is nonlinear. To make the uniform description of observed dependences possible, degradation process kinetic model was assumed. The reciprocal of weight-average polymerisation degree, obtained with SEC analysis for degradated cellulose samples, are presented as the time function in the Fig. 1 and Fig. 3.

Applied co-ordinate system allows for simple description of cellulose degradation process kinetic. All of presented dependences are of linear character. It proves that kinetic model of pseudo-zero order describes analysed phenomenon correctly. Rate constants of cellulose degradation were determined basing on kinetic equation for this model:

$$\frac{1}{P_{w}} = \frac{1}{P_{w,0}} + kt$$

where: P_{w} is the weight-average polymerisation degree, $P_{w,0}$ is the weight averagepolymerisation degree before the degradation process, k is rate constant and t is time. Degradation process both in Valley beater and PFI mill is similar (Fig. 1 and 3). The dependence of the reciprocal polymerisation degree on time shows random character of degradation process (linear dependence – Fig. 2 and 4). Significant difference is observed between values of process rate constant. For the Valley beater it is equal to $(3.84 \pm 0.16) \times 10^{-8} \text{s}^{-1}$, for the PFI mill it is equal to $(69\pm4) \times 10^{-8} \text{s}^{-1}$, which is one order of magnitude more. These result is compatible to other observed relationships – changes of lubricity and drainage time factor (Tab. 1 and 2) are also much faster for the PFI mill.

Beating of cellulose pulp in the PFI mill causes significant decrease of cellulose molar-average molecular mass. Cellulose polymerisation degree was analysed with viscometry method in order to find the cause of high degradation degree. The primary "krill" fraction was separated before beating, and the residue was beated within 2 and 7 minutes. In both versions secondary "krill" was separated after beating. All samples were analysed according to "Material and Methods".

Fibrous pulp is obtained as a result of sulfate pulp processing. It consists of two parts: fibrous fraction and primary "krill" fraction. Viscometric-average molecular mass differs significantly for both fractions – for fibrous fraction it is equal to 1114 and for primary "krill" it is equal to 950. Primary "krill" content in industrial cellulose pulp amounts to 5 % (according to Przybysz 2007).



Fig. 1: Changes of weight-average molecular mass of paper cellulose during PFI beating.

Fig. 2: Dependence of the reciprocal polymerisation degree on time for paper cellulose degradation during PFI beating.



Fig. 3: Changes of weight-average molecular mass of paper cellulose during Valley beater refining.

Fig. 4: Dependence of the reciprocal polymerisation degree on time for paper cellulose degradation during Valley beater refining (PFI mill data added for comparison).

Changes of viscometric-average polymerisation degree of fibrous fraction after 2 and 7 minutes of beating were also analysed. The polymerisation degree for fibrous fraction was equal to 1098 and 1080 (suitably). It means that degradation degree of fibrous fraction during beating is very small. Changes of polymerisation degree are observable for secondary "krill", after separating it from fibrous fraction. Polymerisation degree is equal to 900 after 2 minutes of beating and 799 after 7 minutes. Polymerisation degree of cellulose from fibrous fraction (after separation of secondary "krill") was in parallel equal to 1112 and 1128. The "increase" of cellulose polymerisation degree in fibrous fraction is caused by separation of "krill" and its different content in fibrous fraction. Summarizing, removal of "krill" with lower polymerisation degree causes the increase of polymerisation degree in relation to total original sample. Results of viscometric-average polymerisation degree (P_v) measurements of pine bleached kraft cellulose fractions beated in PFI mill are presented in the Fig. 5.

Primary and secondary "krill" were not separated during analysis of degradation degree of cellulose from paper pulp obtained from pine wood and beated in PFI mill and Valley beater.



Fig. 5: Changes of viscometric-average polymerisation degree (P_v) of pine bleached kraft during beating in the PFI mill.

It is probably one of the reasons of significant differences in analysed molecular mass during beating (especially for PFI mill). Possible errors of polymerisation degree determination are caused by incomplete dissolution of the cellulose sample, errors in weighing or changes of concentration of diethylenecopperdiamine hydroxide (CuEN) during storage. A process of the cellulose oxidation also influences the polymerisation degree analysis.

CONCLUSIONS

Using of the PFI mill causes higher cellulose degradation (average molecular weight of about 200 kDa) than Valley beater appication. Also the highest value of reaction rate constant ((69±4)×10⁻⁸s⁻¹) was stated for PFI mill. Process of fibres shortening, which decreases polymerisation degree of cellulose, takes place in the PFI mill most effectively. The content of primary and secondary minute fraction ("krill") influences the polymerisation degree of bleached cellulose from pine wood.

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