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Characteristics of Kraft Pine Pulps with Different Degrees of Delignification

Abstract
A comparison was made of the fractional composition and properties of two kraft pine pulps (conventional and 'hard') which differed considerably in their levels of delignification. Several methods of analysis, namely with the MorFi apparatus, optical microscopy in vision mode, scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (WAXS) were used. It was shown that the fibres of 'hard' pulp (kappa number 68) show less damage, greater length and width, a higher mass per unit length (coarseness) and are more resistant to transversal deformation in comparison to the conventional pulp (kappa number 28). From the results obtained, it follows that 'hard' pulps are the fibrous semi-product which is better designed for oxygen delignification than are pulps produced in the conventional way.

Key words: *kraft pulps, degree of delignification, morphology of fibres, structure of fibres, SEM, AFM, WAXS.*

Introduction

The quality of the final product (the paper) depends on the raw material used, the pulping and bleaching methods and also on the conditions of the paper sheet formation finishing. The pulping process is the very important first step in this chain. During this process, about 50% mass of the raw material dissolves and the strength potential of fibres decreases by two times because pulping usually takes place at high temperatures and pressures. Recently, a tendency to interrupt pulping at a higher kappa number (>40) followed by oxygen delignification has been noted [1]. This solution aims at better utilisation of the oxygen effect on lignin in order to shorten the kraft pulping and maintain the strength potential of the wood fibres and the high pulp yield to as great an extent as possible. At the Institute of Papermaking and Printing, the modified sulphate-pulping technology for both softwood and hardwood was devised. This paper presents the comparative characteristics of conventional kraft pine pulp fibres (with a kappa number of about 30) and high-yield kraft pine pulp fibres (with a kappa number of about 70) destined for two-stage oxygen delignification. Conventional microscopic photographs show the changes in pulp fibres resulting from the pulping process. When necessary to show details which are difficult or even impossible to perceive in visible light, the SEM and AFM techniques are used. Thanks to much higher magnification, these methods allow all changes taking place to be detected. Fractional composition and fibre morphology were analysed with the use of the MorFi apparatus from Techpap (France) [2].

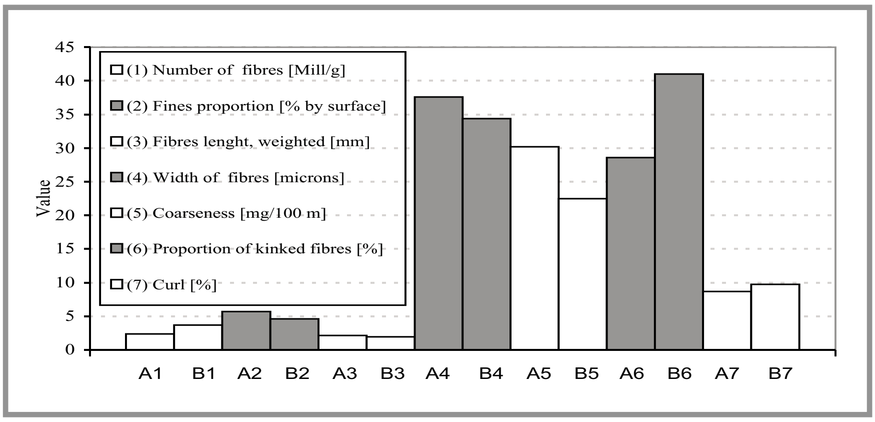

Figure 1. *A comparison of fractional composition and fibre morphological characteristics of laboratory-made pulps with different degrees of delignification, A - kappa number 68; B - kappa number 28.*

Table 1. *Characteristics of kraft pine pulps recorded with the MorFi apparatus.*

Kappa number	Fractional composition		Dimensions of fibres				Characteristics of fibres	
	Number of fibres	Proportion of fine elements	Average fibre length: arithmetical	Average fibre length: weighted	Width of fibres	Coarseness	Proportion of kinked fibres	Curl
	million/g	% by surface	mm	mm	µm	mg/m	%	%
68	2.378	5.68	1.569	2.133	37.6	0.302	28.6	8.70
28	3.695	4.61	1.418	1.947	34.4	0.225	41.0	9.75

Aim of the Study

The aim of this study was to compare the fractional composition and properties of two kraft pine pulps which differed considerably in their levels of delignification (conventional and 'hard' pulps).

Experimental

Subject of the study

We used two laboratory-obtained kraft pine pulps with kappa numbers of 28 and 68 respectively [3].

Optical microscopy in vision mode

We used a Biolar PI Microscope coupled with a CCD camera connected to a computer in our observations; a MultiScan Base v.8.08 system working in a Windows environment enabled us to save the photographs of the fibres [4].

A fractional composition of pulps and fibre characteristics with the use of the MorFi LB01 apparatus (Techpap, France) [5]

The MorFi apparatus measures many different indices specifying the fibre composition of pulps, the fibres' dimensions and statistical distribution, as well as other indices, including:

- ***kinks of fibres*** arising in the areas of fibre cell wall dislocation, in so-called weak points of fibres, where breaks can occur under mechanical strains. These are identified as sudden kinks (slope) changes during the fibre length calculation.
- ***curl of fibres***, a deformation with a character of soft twists (in opposition to sharp kinks). The curl index is calculated from the following equation:

$$Curl = (1 - l/L) \cdot 100$$

where:
l - length of fibre after curling (bow),
L - total fibre length; and

- ***fine elements***, any objects present in the pulp whose dimensions are too small for it to be considered as a fibre (by default a length less than 200 microns and/or a width less than 5 microns).

Scanning Electron Microscopy (SEM)

The fibre surface and its cross-section were analysed with the use of a JSM 5500LV (JEOL) scanning electron microscope in the secondary electrons (SE) mode. The observations were carried out with an accelerating voltage of 10 kV,

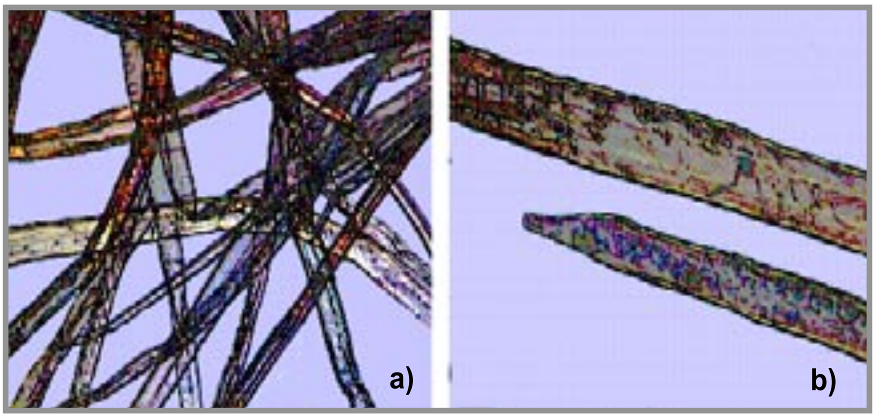

Figure 2. *Kraft pine pulp, kappa number 68; a - magn. 130×, b - magn. 170×.*

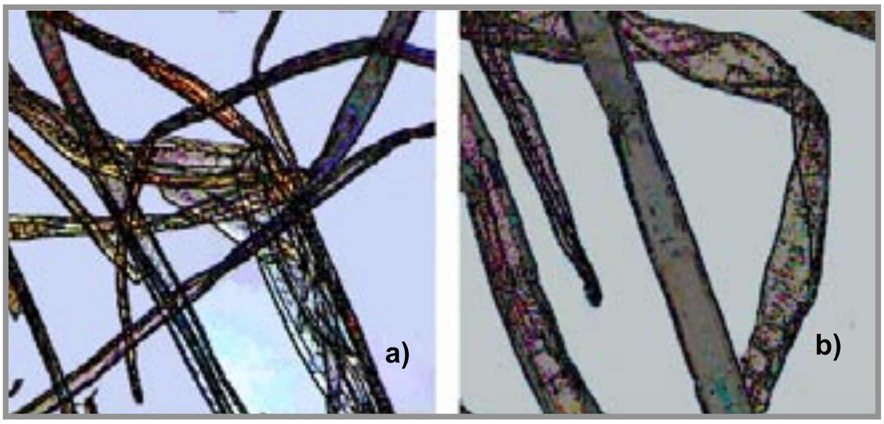

Figure 3. *Kraft pine pulp, kappa number 28; a - magn. 130×, b - magn. 170×.*

Figure 4. *Cross-sections of fibres, kraft pine pulp (kappa number 68).*

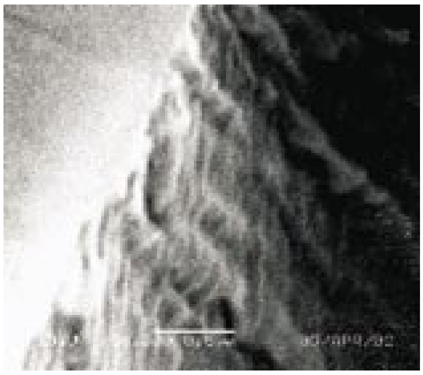

Figure 5. *Topography of lumen surface, kraft pine pulp (kappa number 68).*

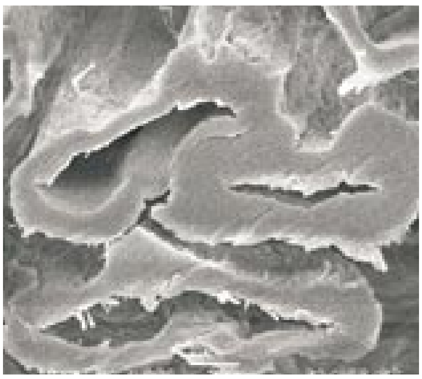

Figure 6. *Cross-sections of fibres, kraft pine pulp (kappa number 28).*

Figure 7. *Topography of lumen surface, kraft pine pulp (kappa number 28).*

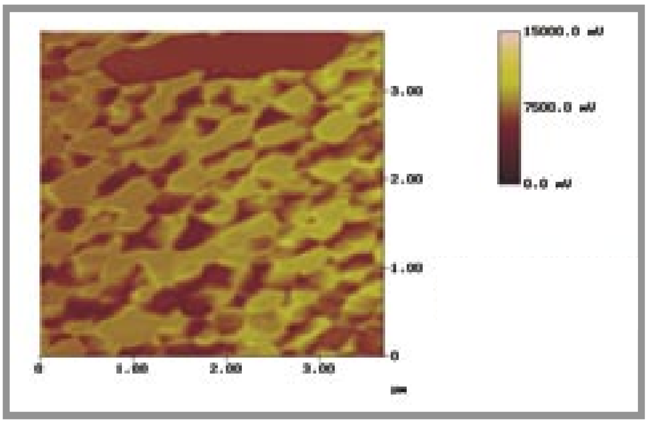

Figure 8. Surface of fibre, kraft pine pulp (kappa number 68).

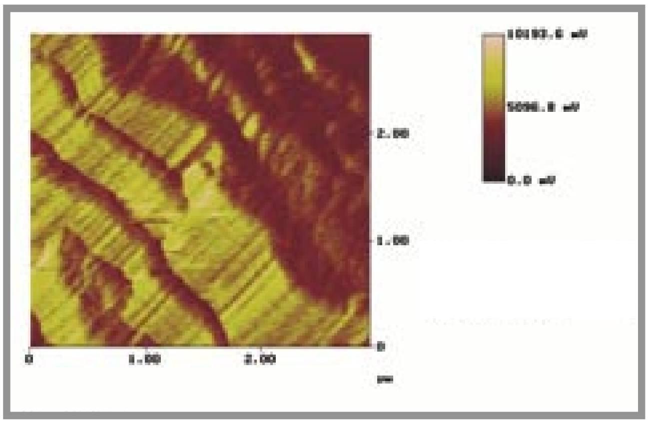

Figure 9. Surface of fibre, kraft pine pulp (kappa number 28).

and the microphotographs were taken at a magnification of 50 to 10000×. The microscope can also operate in a low-vacuum mode (gas pressure in the sample chamber of 1-100 Pa).

Atomic Force Microscopy (AFM)

The Metrology Series 2000 apparatus (Molecular Imaging, USA) in contact mode and with a scanning frequency of 1-4 Hz was also used for the observations [3].

Diffraction of X-rays (WAXS)

X-ray investigations were performed with the use of the URD-6 apparatus (Seifert) under the following conditions: CuKα radiation, accelerating voltage 40 kV, anode current intensity 30 mA. A monochromatic beam was obtained by applying the impulse height analyser. The scintillation meter was used as a detector. X-ray diffractographs were obtained by the step method within a range of deflection angles from 3° to 60°, using a step of 0.1° and impulse counting time of 20 s [3].

Results

A comparison of fractional composition and morphological characteristics of the fibres of both kraft pine pulps (kappa number 28 and 68) was made on the basis of the computer image analysis with the MorFi apparatus (Table 1, Figure 1).

This data shows that the pulp with a kappa number of 28 contains considerably more fibres per gram (3.7 million, compared to 2.4 million in the pulp with a kappa number of 68). The former's fibres are also shorter, have lower width and coarseness and a higher content of kinked fibres (41% compared to 29% in the pulp of kappa number 68) and also a curl index higher by about 12% (Table 1).

On Figures 2-3, prepared with the optical microscope in vision mode (CCD camera and computer) the fibres of both pulps are shown. From a comparison of Figures 2 and 3, it follows that pulp fibres with a kappa number of 68 are stiffer and their cell walls are less damaged than those of the pulp with a higher degree of delignification (kappa number 28).

From the SEM observations, it follows that fibres with a lower cooking degree are less susceptible to deformations, as seen in Figures 4 and 6. The fibrillar structure of the fibre wall is also tighter, as is visible on the internal surface of the lamella (S3) surrounding the lumen (Figure 5 and 7).

The observations with use of the AFM method indicate that on the surface of the kraft pine pulp fibres (kappa number 68) there is lignin and cellulose - the latter in a partly uncovered form (Figure 8). On the surface of the pulp with the kappa number of 28 (Figure 9), the exposed crystallites of cellulose can be seen.

The investigations with the use of X-ray radiation (WAXS) show that the progress in delignification results in an increase in the degree of crystallinity (the percentage share of the cellulose crystalline phase) in kraft pine pulp from 61.7% (kappa number 68) to 63.2% (kappa number 28) and in the dimensions of the polymorphic form of cellulose (cellulose I) from 36.1 Å (kappa number 68) to 38.5 Å (kappa number 28).

Conclusions

Observations with the following microscopic methods - optical in vision mode, electron scanning microscopy (SEM) and computer image analysis in MorFi apparatus - has shown that in comparison to the conventional pulp with a kappa number of 28, fibres of 'hard' pulp (kappa number 68) are less damaged, longer, maintain a higher mass per unit of length (coarseness) and a higher width, and are also less susceptible to transversal deformation but have a lower degree of crystallinity. The method of atomic force microscopy (AFM) demonstrated that lignin and cellulose appear on their surface, the latter in a partly uncovered form. On the surface of the fibres of kappa number 28, the cellulose fibrils can be seen with great clarity, together with the exposed cellulose crystallites. The pulp fibres with a kappa number of 68 have retained greater strength potential, and are therefore a better half-product for oxygen treatment.

Acknowledgement

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