

Influences of Surface Chemical Composition on the Mechanical Properties of Pulp as Investigated by SEM, XPS and Multivariate Data Analysis

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Os efeitos da composição química total e da superfície nas propriedades mecânicas (MP) da polpa kraft de eucalipto foram investigados usando cromatografia líquida (HPLC), microscopia eletrônica de varredura (SEM), espectroscopia de fotoelétrons de raio X (XPS) e análise de componentes principais (PCA). Imagens em SEM das regiões fraturadas durante testes de rasgo (TrID), tração (TsID) e estouro (BuID) em amostras refinadas mostraram deformação das fibras e uma baixa proporção de fibras quebradas, indicando rupturas inter-fibras no arranjo fibroso. TrID de amostras não refinadas foi afetado pela cobertura superficial de lignina (SLig), enquanto que TsID e BuID foram afetados pela cobertura superficial de extrativos (SExt) e carboidratos (SCar). Após o refino, TrID foi afetado por ácidos urônicos presentes na xilana e a influência da composição química total foi muito mais pronunciada. Nossos resultados indicaram que as ligações fibra-fibra foram o fator limite para as MP mais do que a resistência das fibras individuais. Uma estratégia combinando modificação da superfície das fibras com a preservação de polisacarídeos durante a polpação foi sugerida para aprimorar as MP desse material.

The effects of bulk and surface chemical composition on the mechanical properties (MP) of eucalyptus kraft pulp were investigated using Liquid Chromatography (HPLC), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Principal Component Analysis (PCA). SEM images of fractured regions during tear (TrID), tensile (TsID) and burst (BuID) tests of refined pulps showed fibre deformation and low proportion of broken fibres, indicating an inter-fibre failure in the sheet network. TrID of unrefined samples was affected by lignin surface coverage (SLig) while TsID and BuID were affected by surface coverage of extractives (SExt) and carbohydrates (SCar). After refining, TrID was affected by uronic acids (UA) in xylan and the influence of bulk composition was more pronounced. Our results also indicated that the fibre-to-fibre bonding rather than the individual fibre strength was the limit factor for MP. A strategy combining surface modification and preservation of polysaccharides in pulping was suggested to improve the MP of this material.

Keywords: eucalyptus, cellulosic fibre, surface composition, mechanical properties, XPS, PCA

Introduction

Surface chemistry of pulp fibres has attracted remarkable research interest, especially in the latest years. The idea that surface characteristics play an important role in pulping, bleaching and papermaking processes was subject for many reported studies.¹⁻³ Surface investigations are relatively complex due to intrinsic characteristics of wood materials such as component location in fibre wall and modifications introduced by the different processes. Generally

spectroscopic techniques using high vacuum interfaces are applied to achieve surface sensitivity of a few nanometres and X-ray Photoelectron Spectroscopy (XPS/ESCA) has been proposed to determine the surface composition of carbon and oxygen and then estimate coverage of lignin and extractives.⁴ This approach considered that after solvent extraction, usually with acetone or dichloromethane, only carbon from lignin and carbohydrates remain on the surface. Recently, resistance to solvent extraction and other contamination sources have been proposed as possible interference to this estimation, but under strict experimental set up there is no certain evidence if the interference is significant.⁵⁻⁷ XPS can also be used in the high-resolution

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mode and a curve fitting of C1s peak gives information about chemical bonds and different oxidation states.⁴ This approach was not used here.

Scanning Electron Microscopy (SEM) has been extensively applied for studying morphology and ultrastructure of fibres.⁸ Fibre swelling,⁹ fibrillation and collapse,¹⁰ fracture and shape¹¹ and interactions with rosin size¹² were reported. However, in spite of the good lateral resolution achieved, the surface composition of carbohydrates, lignin and extractives are not assessed using this technique.

Theoretical models for pulp and paper mechanical properties were proposed considering two distinct levels, one for the individual fibre and other to sheet network. Models for individual fibre are based on the concept that cellulose, hemicellulose and lignin associate to form a composite in the fibre cell wall.¹³ Models for the sheet network are based on a broad class of structural and hydrogen bond theories.¹⁴ Theories for tensile and tear strength usually combine influences from individual fibre strength and fibre-to-fibre bonding depending on the refining level.¹⁵⁻¹⁷ In these theories it is suggested that the energy consumed by the fibre failure dominates over bond breaking and pull-out of the sheet network when fibres are refined to the maximum strength level. In a general overview, models do not consider any bulk or surface chemical composition parameter.

The establishment of relations between chemical composition data and other fibre properties is complex, but the use of multivariate data analysis showed to be useful to identify physical and chemical differences between kraft pulps using Principal Component Analysis (PCA) and Partial Least Squares (PLS).^{18,19} PCA can also be applied for exploratory data analysis using loading plot disposition. In this plot variables located on line through the origin are correlated with extent determined by their PC value.²⁰

In the present study, SEM was used to investigate the hand sheet fractured regions and PCA was applied in an exploratory data analysis using load plots containing surface composition from XPS, bulk chemical composition and mechanical properties.

Experimental

Pulping conditions and characterization of pulps

Wood of *Eucalyptus grandis* trees, eight years old, was used to make chips employing an industrial chipper. Chip fractions in the width range of 2-5 mm and length range of 16-45 mm were selected for kraft pulping using a bar and

hole chip classifier. Four pulp samples were obtained by digesting in a 20 L laboratory reactor using active alkali 15.5, 18.1, 23.3 and 28.5 % as NaOH, respectively. The reactor conditions, the same in all experiments, were: pulping temperature 165 ± 2 °C, heating rate 2.8 ± 0.1 °C min⁻¹, sulfidity 27.2 ± 0.1 % as NaOH, wood/liquor ratio of 4:1, H factor of 400 ± 20 and 1000.0 g of chips (o.d.). After pulping the unbleached pulp samples were washed with tap water until the pH of the filtrate was around 6.8 to simulate industrial conditions. Samples were identified according to the active alkali used in pulping as A15, A18, A23, A29.

D-glucose, D-xylose, D-mannose, L-arabinose, D-galactose and L-rhamnose were determined in acidic pulp hydrolyzates using HPLC-PAD.²¹ Uronic acids were determined according to the Scott method.²² The polysaccharide composition of pulp samples was calculated according to Janson.²³ Acid insoluble and soluble lignins were determined according to Effland²⁴ and TAPPI UM 250, respectively. The content of acetone-extractives was determined according to SCAN CM 49:93. Kappa and intrinsic viscosity (IV) were determined according to TAPPI T 236:85 and SCAN C15-16:62, respectively. Degree of polymerization (DP) of cellulose was estimated using IV and the amount of hemicelluloses in the pulp.^{25,26} Pulps were refined in an Papirindustriens Forsknings Institut (PFI) mill using 1500, 3000, 4500 and 6000 revolutions according to ISO 5264/2. All mechanical properties were measured on pulp hand sheets prepared with a Rapid Köthen apparatus using deionised water and properly conditioned at a temperature of 23 ± 1 °C and relative humidity of 50 ± 2 %. Tear (TrID), burst (BuID) and tensile (TsID) indices were determined according to ISO 5270. Elastic modulus (EM) was determined according to ISO 1924/2 and bending index (BeID) according to ISO 2493. Scott bond (SB) was measured according to TAPPI UM 403. At least 10 handsheets were analysed for each mechanical property. All unrefined and refined pulp samples were characterized, however, only results of maximum strength levels were presented for refined samples. The analytical variations were determined by calculation of coefficient of variation (CV) for each property. Measured CVs ranged up to 7%.

Surface analyses

Scanning Electron Microscopy (SEM) images were obtained using a JEOL JSM T300 microscope operated in secondary electron mode and accelerating voltage of 20 kV. Fractured regions of pulp hand sheets obtained in different strength tests were previously coated with Au for

150 s using a BALTEC MED 020 coating system equipped with a rotating base. At least ten spots were observed on each fractured region of three similar hand sheets. One micrograph of each fractured region was carefully selected to represent the dominant pattern observed during the analysis. X-ray Photoelectron Spectroscopy (XPS) data of pulp hand sheet surfaces were obtained with a Physical Electronics PHI 5500 ESCA instrument equipped with a monochromatic Al K α X-ray source operated at 200 W. The charge compensation was done by an electron flood gun. The pass energy was 187 eV, the take-off angle was 70°, the measurement time was 10 min and the analysed area was 1 mm². At least three different spots were measured on each sample in order to determine the analytical variations. Quantification of surface atomic composition was performed by using sensitivity factors from the instrument supplier and a Shirley background correction. Surface coverage of lignin (SLig) and extractives (SExt) were estimated using the method proposed by Ström and Carlsson.⁴ In this method, low-resolution XPS spectra were measured on unextracted and acetone extracted samples. The O/C peak ratio was calculated and used to estimate the SExt and SLig according to the equations (1) and (2), respectively.

$$\text{SExt} = \frac{O/C_{(\text{after extraction})} - O/C_{(\text{before extraction})}}{O/C_{(\text{after extraction})} - O/C_{(\text{extractives})}} \times 100 \quad (1)$$

$$\text{SLig} = \frac{O/C_{(\text{after extraction})} - O/C_{(\text{carbohydrates})}}{O/C_{(\text{lignin})} - O/C_{(\text{carbohydrates})}} \times 100 \quad (2)$$

The $O/C_{(\text{extractives})}$ in the equation (1) was the theoretical value for oleic acid, *i.e.*, 0.11. In the equation (2), the $O/C_{(\text{lignin})}$ used was of 0.33, while the theoretical O/C ratio of 0.83 of cellulose was used for $O/C_{(\text{carbohydrates})}$.^{2,4-7} Surface coverage of carbohydrates (SCar) was estimated according to Carlsson⁵ using the equation (3). The measured CVs for SLig, SExt, SCar ranged up to 4%.

$$\text{SCar} = 100 - \text{SLig} \quad (3)$$

Multivariate data analysis

Principal component analysis (PCA) is a multivariate data analysis method suitable for describing major trends in a data set and also the relations between samples and between variables. In PCA, a multivariate matrix **X** with *m* rows and *n* columns, with each sample being a row and each variable being a column, is decomposed as the sum

of the outer product of vectors **t_i** and **p_i** plus a residual matrix **E**. The **t_i** vectors are known as scores and give information on how samples are related to each other. The **p_i** vectors are known as loadings and give information on how the variables are related to each other. A detailed description of PCA method can be found in literature.²⁰ Two matrices were done to study effects of bulk and surface chemical composition on mechanical properties of unrefined and refined samples, respectively. In the first matrix, TrID, TsID, BuID, BeID, EM, DP, SLig, SExt, SCar, cellulose/hemicellulose ratio (CHr) and the contents of cellulose (CEL), xylan (XYL), uronic acids (UA), extractives (Ext) and total lignin (Lig) were introduced as columns while the four pulp samples were added as rows, forming a 4 x 15 data matrix. In the second matrix aiming at studying refined samples, SB was added to the bulk and surface chemical composition and mechanical properties forming a 4 x 16 data matrix. Both matrices were autoscaled, *i.e.*, adjusted to zero mean by subtracting the original mean of each column and then adjusted to unit variance by dividing each column by its standard deviation. The latter operations and PCA were performed using a computer program (MATLAB 6.0).

Results and Discussion

Characterisation of the different pulps

The variation in active alkali (AA) in pulping produced pulps with different physicochemical properties and chemical composition (Table 1). Lignin, hemicelluloses and extractives were removed and macromolecular degradation of cellulose was observed according to IV and estimation of DP. Xylan was the hemicellulose that remained in all pulps. The content of UA was assumed as the sum of 4-*O*-methylglucuronic and hexenuronic acids. The kappa numbers were similar as the commercially used for production of printing and tissue papers. The CHr varied extensively due to removal of xylan.

Figure 1 present the XPS low-resolution spectrum obtained for sample A15 after extraction with acetone. Carbon and oxygen were the main elements present on the surface but low contents of aluminium, calcium and silicon were also observed. These elements can be originally present in wood or introduced by pulping liquor. Unrefined and refined samples were extracted with acetone and the surface elemental composition obtained. Results from XPS for extracted and non-extracted samples including the O/C ratios are presented in Table 2.

The surface chemistry of the pulps was also significantly affected by changing in AA (Table 3). Surface

Table 1. Chemical composition and physicochemical properties of *E. grandis* kraft pulps obtained with different active alkali levels. Active alkali (AA) as %NaOH, kappa number (KP), intrinsic viscosity (IV) as cm^3g^{-1} . Cellulose (CEL), xylan (XYL), total lignin (Lig) and extractives in acetone (Ext) as % of pulp dry weight. Uronic acids (UA) as mol/100 mol xylose. Degree of polymerization (DP) estimated considering contents of CEL and XYL in each pulp.²⁵ Cellulose/hemicellulose ratio (CHR) was also calculated

Sample	AA	KP	IV	DP	CHR	CEL	XYL	UA	Lig	Ext
A15	15.5	23.7	1152	5559	5.0	80.1	16.2	18.3	3.2	0.3
A18	18.1	21.9	1121	5304	5.3	81.4	15.3	16.7	2.8	0.3
A23	23.3	15.5	915	4075	6.4	84.1	13.2	12.2	2.3	0.2
A29	28.6	11.9	684	2856	7.4	86.5	11.7	11.3	1.6	0.1

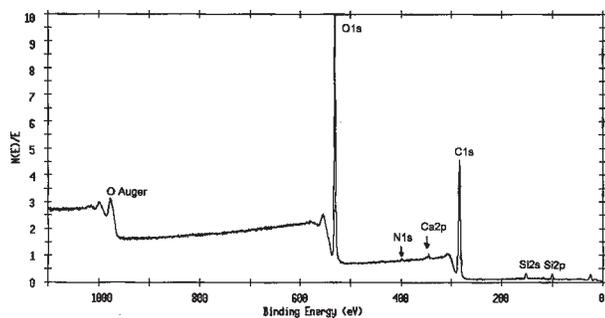


Figure 1. XPS spectrum for sample A15 after acetone extraction.

coverage of lignin was reduced while surface coverage of carbohydrates and extractives increased. The deposition of extractives and exposure of carbohydrates in eucalyptus pulping was previously discussed.²⁷ Mechanical properties of unrefined pulp samples were extensively affected by pulping conditions. The SR was similar for all unrefined samples and was apparently not affected by changes in chemical composition caused by pulping.

Refining changed the surface chemical composition of fibres (Table 4) in comparison with the unrefined pulps (Table 3). Surface lignin was removed while carbohydrates increased. Surface extractives increased for sample A15

and decreased for samples A18, A23 and A29. Modifications of fibre surfaces during refining of eucalyptus were discussed previously.²⁸ The maximum strength level obtained in refining is presented in Table 4. The number of PFI revolutions necessary to achieve this level increased according to the AA used in pulping, probably due to removal of hemicelluloses and disordered cellulose.²⁹ Samples produced with low AA required less refining and achieved higher levels of TrID than to the samples obtained with high AA.

Investigation of handsheet fractures by SEM

The extent of refining affects significantly the fibre morphology and the sheet network. Unrefined or slightly refined fibres have a tubular shape with limited contact areas and the sheet network is plenty of empty spaces, even for samples extensively degraded in pulping such as A29 (Figure 2). Fibrillation apparently contributes to fibre-to-fibre bonding already at 1500 PFI revolutions as layers and fibrils extending from one fibre to another could be observed. As the refining continued to 6000 PFI revolutions, fibres collapsed, contact areas and fibrillation increased and the

Table 2. Surface elemental composition of unrefined and refined pulps (before and after acetone extraction) as analysed by low-resolution XPS. The identification of refined samples shows the number of PFI revolutions used to achieve the maximum level of mechanical properties. Results expressed as % atomic

Samples	Al	Si	Ca	C	O	O/C
A15	traces	0.9	0.3	61.8	37.0	0.60
A15 ext	0.7	2.5	0.3	59.9	36.6	0.61
A15 - 3000	1.2	1.4	0.5	58.1	38.8	0.67
A15 - 3000 ext	1.1	2.9	0.4	56.0	39.6	0.71
A18	0.7	0.8	0.4	59.6	38.5	0.65
A18 ext	0.7	2.5	0.3	57.5	39.0	0.68
A18 - 4500	1.0	1.3	0.5	57.4	39.8	0.69
A18 - 4500 ext	1.2	3.1	0.5	55.3	39.9	0.72
A23	0.7	0.9	0.4	59.0	39.0	0.66
A23 ext	0.6	2.5	0.3	57.2	39.4	0.69
A23 - 6000	0.9	1.2	0.4	56.9	40.6	0.71
A23 - 6000 ext	0.9	2.8	0.4	55.5	40.4	0.73
A29	0.7	0.8	0.3	58.9	39.3	0.67
A29 ext	0.8	1.2	0.3	55.7	42.0	0.75
A29 - 6000	0.9	1.1	0.4	57.1	40.5	0.71
A29 - 6000 ext	0.9	1.4	0.4	55.3	42.0	0.76

Table 3. Surface chemical composition as estimated by XPS and mechanical properties of unrefined pulp hand sheets. Surface coverage of carbohydrates (SCar), lignin (SLig) and extractives (SExt) as % area. Bending index (BeID) as $\text{mNm}^2\text{g}^{-1}$, tear index (TrID) as $\text{mNm}^2\text{g}^{-1}$, tensile index (TsID) as Nmkg^{-1} , burst index (BuID) as $\text{kPam}^2\text{g}^{-1}$, elastic modulus (EM) as MNmkg^{-1} . Schopper-Riegler drainability (SR) was also measured for each sample

Sample	SR	SCar	SLig	SExt	BeID	TrID	TsID	BuID	EM
A15	15	56	44	2.0	2.2	6.0	32.6	1.1	7.0
A18	17	70	30	5.3	2.2	4.5	37.5	1.3	7.3
A23	17	72	28	5.2	2.8	4.0	24.6	0.9	5.8
A29	16	84	16	12.5	2.6	3.2	20.4	0.7	4.7

Table 4. Surface chemical composition as estimated by XPS and mechanical properties of refined pulp hand sheets at the maximum strength level. Surface coverage of carbohydrates (SCar), lignin (SLig) and extractives (SExt) as % area. Bending index (BeID) as $\text{mNm}^2\text{g}^{-1}$, tear index (TrID) as $\text{mNm}^2\text{g}^{-1}$, tensile index (TsID) as Nmkg^{-1} , burst index (BuID) as $\text{kPam}^2\text{g}^{-1}$, elastic modulus (EM) as MNmkg^{-1} , Scott bond (SB) as Jm^{-2} . Schopper-Riegler drainability (SR) was also measured for each sample

Sample	SR	SCar	SLig	SExt	BeID	TrID	TsID	BuID	EM	SB
A15 - 3000	26	76	24	6.0	1.9	16.1	71.9	4.0	8.7	199
A18 - 4500	30	78	22	4.9	1.6	12.4	82.7	4.9	9.6	275
A23 - 6000	38	80	20	3.2	2.0	9.2	66.5	4.1	8.3	309
A29 - 6000	34	86	14	7.7	2.4	8.7	56.6	3.3	7.6	283

sheet network became more compact. Consequently, strength properties were drastically improved in comparison with unrefined samples (Table 4).

SEM images were obtained in the fractured regions of sheets tested on burst, tear and tensile methods at the maximum strength level achieved by refining (Figure 3). Only a few broken fibres were observed, mainly for burst tested samples. Most of the fractures observed in fibres were located in their extremes, probably due to a thin wall in this region³⁰ or indentation produced during refining.³¹ Fibre curling produced during refining³² was observed for all samples and a clear example was the burst fracture of sample A18. Fibre deformations were also present indicating viscoelastic behaviour of individual fibres that resisted to breaking, for example in the tear test of sample A23. It was clear in all cases here that fibre-to-fibre bonds were preferably broken instead of individual fibres, independently of the carbohydrate degradation in pulping. This does not agree with theories of tear and tensile,¹⁵⁻¹⁷ probably because eucalyptus fibres are much shorter than other hardwoods.²⁹ On the other side, these results evidence that the nature and extent of the fibre bonds significantly affect the mechanical properties of eucalyptus sheets. This makes the contribution of surface chemical composition an important factor.

The relation between mechanical properties, bulk and surface composition of unrefined samples

The effects of fibre and surface chemistry on mechanical properties of unrefined pulps were investigated to assess

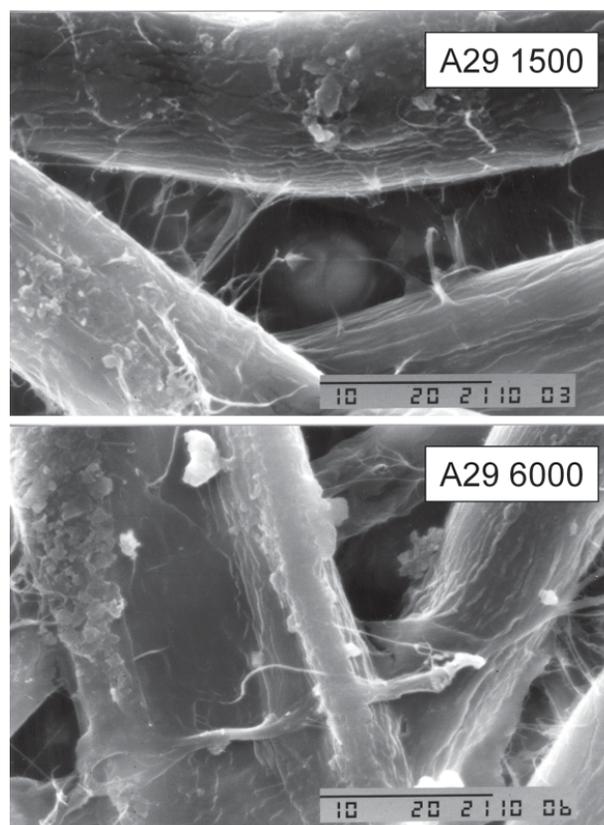


Figure 2. Effects of refining in the hand sheet network and fibre morphology. Fibre collapses after refining and fibre-to-fibre bonds increases by external fibrillation. Magnification of 3500x, scale of 10 μm .

the impacts of modifications caused by pulping. The PCA score plot showed a clear separation of the pulp samples according to the differences in AA used in pulping (Figure

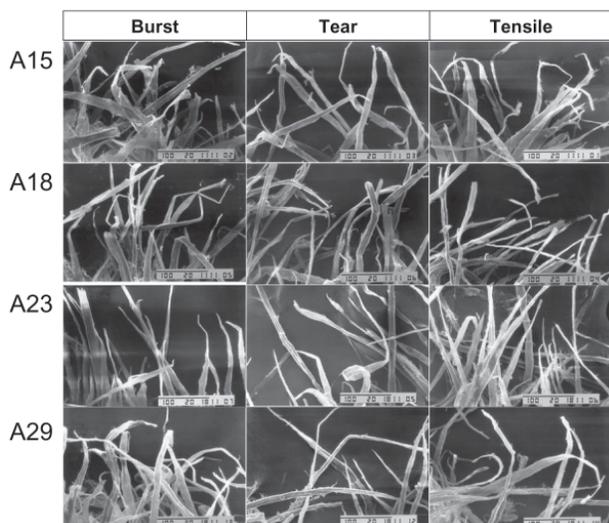


Figure 3. SEM images of fractured regions in tensile (TsID), burst (BuID) and tear (TrID) tests of hand sheets of pulp samples A15, A18, A23 and A29. Refining levels were selected according to the highest strength obtained for each pulp sample. Magnification of 450x, scale of 100 μm .

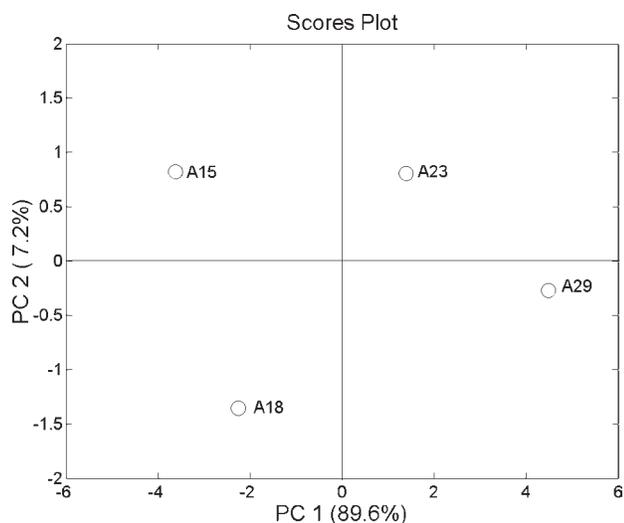


Figure 4. Score plot of PCA using bulk and surface chemical composition, DP and mechanical properties of unrefined A15, A18, A23 and A29 pulps. Samples were clearly separated by PC1 and PC2.

4). The PC1, describing 89.6% of the variation, separated samples obtained with lowest and highest levels of AA, while PC2, describing only 7.2% of the variation, separated samples obtained with closer AA levels.

The loads plot showed that samples obtained with lower AA had higher mechanical properties and less degradation of polysaccharides (Figure 5). However, bending index (BeID) was the unique mechanical property favoured by using higher AA levels in pulping. When both PCs were considered, it seemed that the influence of surface chemical composition on mechanical properties was more pronounced than the contribution from the bulk. This

observation is reasonable considering that unrefined fibres are not collapsed and not extensively entangled in the network, with limited contact areas.³³ SLig was related to tear (TrID) and bending (BeID) indices while SExt and SCar were related to burst (BuID) and tensile (TsID) indices. The elastic modulus (EM) was not related to TrID and BeID. Thus, these properties apparently have no influence of bonded area that is considered for EM in different theories.¹⁴ It was previously reported that lignin is present as patches in fibre surfaces³⁴ and can be originated either by deposition during pulping or from remnant middle lamella.² Based on this information, the effect of SLig on TrID can be explained due to a contribution of lignin layers to the frictional forces to pull out individual fibres from the sheet network.¹⁶ In case of BeID, the presence of lignin layers or islands probably favoured a laminar shearing towards the z direction, decreasing the resistance of the sheet network to the bending force.³⁵ The effects of SExt and SCar on TsID and BuID can be asserted mainly to the reduction of fibre-to-fibre bonding caused by extractives³⁶ deposited on fibre surfaces during pulping.^{2,27}

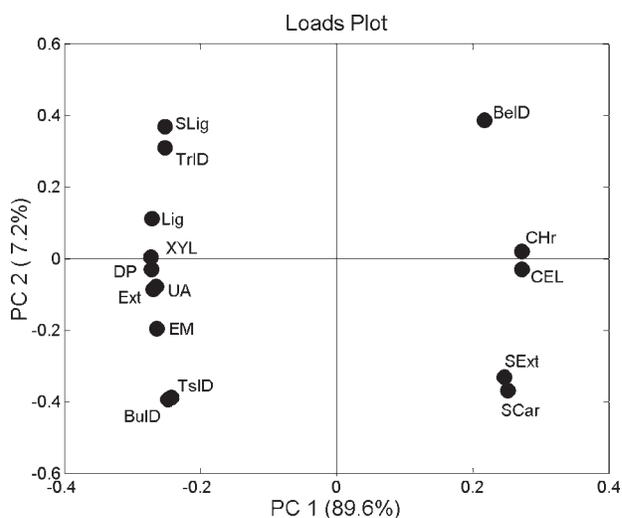


Figure 5. Loads plot of PCA using bulk and surface chemical composition, DP and mechanical properties of unrefined pulp samples. SLig affected TrID and BeID while TsID and BuID were affected by SCar and SExt.

The relation between mechanical properties, bulk and surface composition of refined samples

Refining modifies the morphology and chemistry of fibre surfaces and improves contact fibre-to-fibre due to collapse of lumen, liberation of fibrils and increase in fibre flexibility.³¹ The PCA score plot for the matrix containing mechanical properties and bulk and surface composition of refined samples showed a separation in different quadrants in a similar way as observed for unrefined pulps (Figure 6).

According to PC1, describing 80.7% of the variation, the refining response of the pulps had a clear influence of the AA used in pulping, *i. e.*, pulps less degraded developed higher levels of strength using lower number of PFI mill revolutions. The loads plot was significantly changed in comparison with the unrefined samples (Figure 7). TrID was affected by uronic acid (UA) side groups in xylan. These groups were preserved in pulping by using low AA and fast pulping cycles. Considering both PCs, bulk and surface composition apparently contributed in the same extent to the mechanical properties. The increase in SCar and reduction of SExt induced by refining favoured the fibre-to-fibre bonding as indicated by Scott bond (SB) and the PC1. However, samples less degraded in pulping and with higher contents of xylan had also the higher levels of mechanical properties. During mechanical load the forces applied to the network are transmitted to the individual fibres via inter-fibre bondings and the contribution of bulk composition is ascribed to a nanocomposite involving cellulose fibrils embedded in a matrix containing hemicelluloses and lignin.¹³ Removal of xylan was suggested previously to replace the flexible cellulose-hemicellulose-cellulose bond by a more rigid cellulose-cellulose bond.³⁷ According to this information, samples obtained here with high AA and refined at the maximum strength would be expected to present a high proportion of broken fibres in the SEM analysis of fractured regions. However, the fibre-to-fibre bonding developed by refining was preferentially broken, indicating that strength properties of eucalyptus pulp can be further improved if inter-fibre bonding is increased. Potential strategies for improving mechanical properties are discussed in the next section.

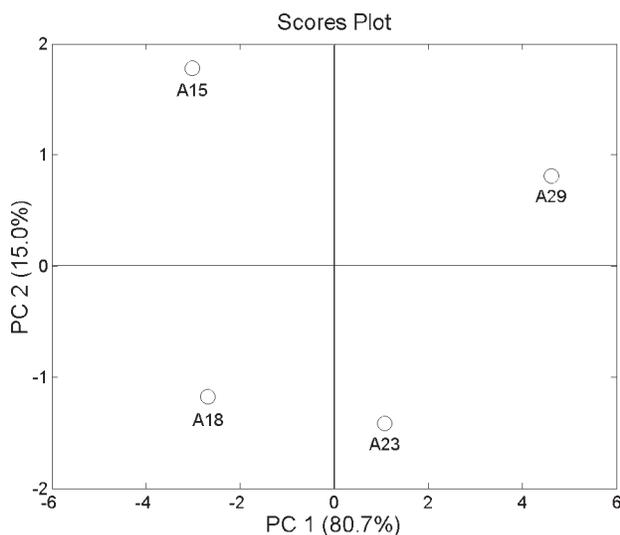


Figure 6. Score plot of PCA using bulk and surface chemical composition, DP and mechanical properties of refined A15, A18, A23 and A29 pulps. Samples were clearly separated by PC1 and PC2.

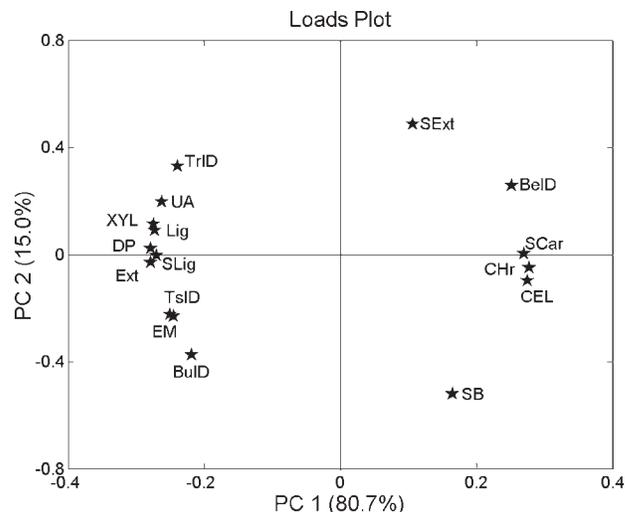


Figure 7. Loads plot of PCA using bulk and surface chemical composition, DP and mechanical properties of refined pulp samples. Bulk and surface chemical appeared to have similar influence on mechanical properties.

Strategies for improving the mechanical properties of eucalyptus pulps

The mechanical properties of eucalyptus pulps, particularly TsID and TrID, are 40% and 20% lower than for softwood pulps, respectively. This characteristic limits the increase in paper machine speed for printing papers and use of eucalyptus pulp in packaging products. A strategy combining retention of polysaccharides in pulping and chemical modification of fibre surfaces seems to be a good alternative for improving strength properties. Retention of carbohydrates by using fast pulping cycles and preservation of non-relocated xylan was recently suggested³⁸ and is expected to improve the strength at the nanocomposite level and the fibre flexibility. Different methods for surface modification³⁹ or addition of mannans⁴⁰ were recently reported to increase the fibre-to-fibre bonding, even for commercial pulps. The strategy of combining pulping and surface modification can provide special eucalyptus pulps with high strength properties at low cost. This strategy should be further investigated.

Conclusions

We investigated the effects of bulk and surface chemical composition of eucalyptus pulp on the mechanical properties of unrefined and refined fibres. For unrefined pulps the surface composition affects the mechanical properties rather than the bulk composition. Refining changes the surface composition and improves fibre-to-fibre contact. As a consequence, the mechanical properties are affected by bulk and surface composition. Observation

of fractured regions shows inter-fibre bonding failure instead of broken fibres. Based on this finding a strategy of combining preservation of non-relocated xylan by using fast pulping cycles and surface modification of fibres to improve bonding was suggested.

Acknowledgements

Support from Suzano Papel e Celulose and Åbo Akademi Process Chemistry Centre are acknowledged. Prof. Maria do Carmo Gonçalves and Lúcia Carvalho are acknowledged for the use of JEOL JSM T300 microscope. Part of this work was presented at the International Symposium on Wood and Pulping Chemistry, Nice, France, June 2001.

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Received: May 16, 2004

Published on the web: February 21, 2005

FAPESP helped in meeting the publication costs of this article.