

EFFECT OF BEATING AND SIZING ON
THE SURFACE PROPERTIES OF
Eucalyptus globulus FIBRES

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ABSTRACT

In this work attention has been focused on the effect of papermaking operations like beating, sheet forming and sizing on the physical/chemical surface properties of bleached *Eucalyptus globulus* kraft fibres. Inverse Gas Chromatography (IGC) was used to determine the dispersive component of surface free energy ((sd) and the acidic/basic character (according to the electron acceptor/donor Lewis concept) of the solid surface (pulp fibres and pulp handsheets). The results have shown that beating increases essentially the fibres acidic character. Sheet forming caused a great decrease in (sd and significant increments in the adhesion works of both acidic and basic probes, diminishing the ratio between the two. Nonetheless, the surface of handsheets still exhibited an acidic character. The influence of sizing on the handsheet did not change significantly the dispersive component of the surface energy but decreased the difference between the adhesion works of the acidic and basic probes, rendering the sized handsheet surface more amphoteric.

INTRODUCTION

The present work focuses on the quality of the Portuguese *E. globulus* pulp and is part of a more extensive work whose main objective is to study the relationship between chemical and physical properties of fibres and sheets and the functional properties of the paper made with this pulp, in order to assess their contribution to the printing/office papergrades performance. Since fibre surface properties decisively influence the final product quality it is not surprising the large number of works concerning the study of the surface energetics of cellulose fibres and paper and their interaction with ink (Banerjee 1991; Santos 2001). Adhesion between these phases is directly related to the dispersive and acid-base properties of both components and therefore the knowledge of these parameters is of major importance.

Some studies have been undertaken to investigate the effects of the cooking (Shen 1999; Aquino et al. 2002) and bleaching processes (Aquino et al. 2002) on surface and strength properties of *E. globulus* kraft pulps. These studies have revealed that these properties are highly dependent on the cooking and bleaching conditions. For

instance, high cooking temperatures strongly decrease fibre surface free energy and the introduction of a previous oxygen stage during bleaching largely enhances the acidic character of fibres (Aquino et al. 2002). However, the effect of subsequent papermaking operations, like refining and sizing, is still not well known.

To improve bonding properties, pulps are normally submitted to beating (a mechanical process in which fibres undergo high shear and compression forces in the presence of water), which decreases pulp drainability, paper porosity and optical properties and increase mechanical resistances. In addition, to enhance paper resistance to liquid penetration and also to improve surface characteristics, materials like AKD (alkyl ketene dimer) are added to the stock furnish in a paper mill operation called sizing. The purpose of the present study is exactly to examine changes on the surface characteristics of fibres due to beating and of handsheets due to sizing. Comparisons are also made between fibre surface energetics in pulp (milled) and in handsheets in order to investigate the effect of fibre bonding during sheet formation.

Inverse gas chromatography (IGC) has been currently used to characterize the surface of many inorganic and organic materials (polymers, coatings, wood, pulp, paper, etc.) (Belgacem 2000). This technique enables the evaluation of several surface parameters, namely the dispersive component of surface free energy, arising from London and Van-der-Waals forces, and the acid/base character according to the Lewis concept (i.e., ability to accept and donate electrons). IGC is very similar to conventional gas chromatography (GC), the main difference being the fact that the material under study is the stationary phase introduced into the chromatographic column whereas the compounds injected (probes) have well known properties. As mentioned above, in this work, the packed materials under investigation are milled pulp and pulp handsheets.

IGC DATA ANALYSIS

In IGC, an inert carrier gas elutes a minute quantity of a probe molecule through a column packed with the material under study. Due to the interactions between the two phases, the probe molecules are retained for a certain time, t_r , known as the retention time, which is used to calculate the net retention volume, V_n , according to equation (1)

$$V_n = (t_r - t_0)F.J \tag{1}$$

where t_0 is the dead retention time of the marker probe (in this case, natural gas), F is the carrier gas flow rate (measured by a digital flow meter) and J is the correction factor for gas compressibility (Belgacem et al.1995). Determination of the dispersive component of surface free energy. Assuming that experiments take place at in-

finite dilution, the free energy of adsorption of the probe on the stationary phase surface per mole, (G, can be determined from the retention volume, Vn, according to

$$\Delta G = -RT \ln(Vn) + C_1 \tag{2}$$

where R is the ideal gas constant, T is the absolute column temperature and C1 is a constant which depends upon the chromatographic column and the reference state (Dorris and Gray 1980). Considering that the dispersive and specific components, respectively (Gd and Gs, are additive, as suggested by Fowkes (Fowkes 1987), Equation (2) can be rewritten as

$$\Delta G^d + \Delta G^s = -RT \ln(Vn) + C_1 \tag{3}$$

On the other hand, the free energy of adsorption can be related to adhesion work, Wa (Dorris 1980), according to

$$-\Delta G = N.A.Wa \tag{4}$$

where N is Avogadro's number and A the cross-sectional area of the probe to be tested (Table 2). If non polar components (like alkanes) are used, only dispersive interactions occur and the adhesion work is given by

$$Wa = 2(\gamma_s^d \gamma_l^d)^{1/2} \tag{5}$$

where (sd and ld are, respectively, the dispersive components of surface tension of the solid (stationary phase) and the liquid.

Substituting Equations (4) and (5) in Equation (2) leads to:

$$2N(\gamma_s^d)^{1/2} A(\gamma_l^d)^{1/2} + C = RT \ln(Vn) \tag{6}$$

The slope of the straight line, referred to as the reference line, obtained by plotting RTln(Vn) versus 2N((ld)1/2A, for a homologous alkane series (Figure 1(a)), leads to the determination of (sd for a given temperature.

Determination of the surface acid-base properties. Acid-base characteristics of fibres surface are determined by analysing the interaction of the polar probes with the solid surface and quantifying the deviation from the reference line, leading to the estimation of the specific free energy, (Gs, as

$$-\Delta G^s = RT \ln(Vn) - RT \ln(Vn_{ref}) \tag{7}$$

where Vnref is the retention volume established by the n-

alkanes reference line (Equation (1)), Vn being now the retention volume of the polar probes. This calculation is also illustrated in Figure 1a).

The adhesion work between the polar probes tested and the fibres, Was, can be evaluated from the specific free energy, given by Equation (7), as

$$Wa^s = \frac{RT}{N.A} \ln\left(\frac{Vn}{Vn_{ref}}\right) \tag{8}$$

By carrying out experiments at different temperatures, it is possible to determine the enthalpy and entropy of adsorption, respectively (Hs and Ss, from the plots of (Gs/T versus 1/T according to the following equation:

$$\frac{\Delta G^s}{T} = \frac{\Delta H^s}{T} - \Delta S^s \tag{9}$$

The acidic and basic constants, respectively Ka and Kb, are calculated using Equation (10) from the linear relationship (Hs/AN* vs DN/AN* for the series of polar probes tested (Figure 1(b)), characterized by different AN* (acceptor) and DN (donor) numbers (Table 2).

$$\frac{(-\Delta H^s)}{AN^*} = Ka \frac{DN}{AN^*} + Kb \tag{10}$$

MATERIAL AND METHODS

Sample preparation. Eucalyptus globulus pulp was produced in a laboratory MK digester by the kraft process (160°C cooking temperature, 16% active alkali charge, as Na2O, and 30% sulphidity) and bleached by applying a DEDED sequence to achieve a brightness of 90% ISO (sample A). In order to analyse the changes on the surface energetics due to the beating process, a portion of the bleached pulp was beaten in a laboratory PFI mill to achieve 30° Schopper Riegler (sample B). Both samples A and B were milled before being packed into the column. To study the influence of sheet formation and sizing on the surface characteristics of fibres, handsheets were made (according to ISO 5269/1-1979) with the beaten pulp without (sample C) and with AKD (sample D). The sizing agent emulsion was added to the pulp suspension after addition of sodium hydrogen carbonate (0.1%) which is the reaction catalyst. After strong mixing, laboratory round sheets were formed and subjected to drying (for AKD curing) during 10 min at 80°C. The AKD amount was adjusted to obtain 180 s HST (Hercules Sizing Test) level. Table 1 summarizes the characteristics of the several samples tested.

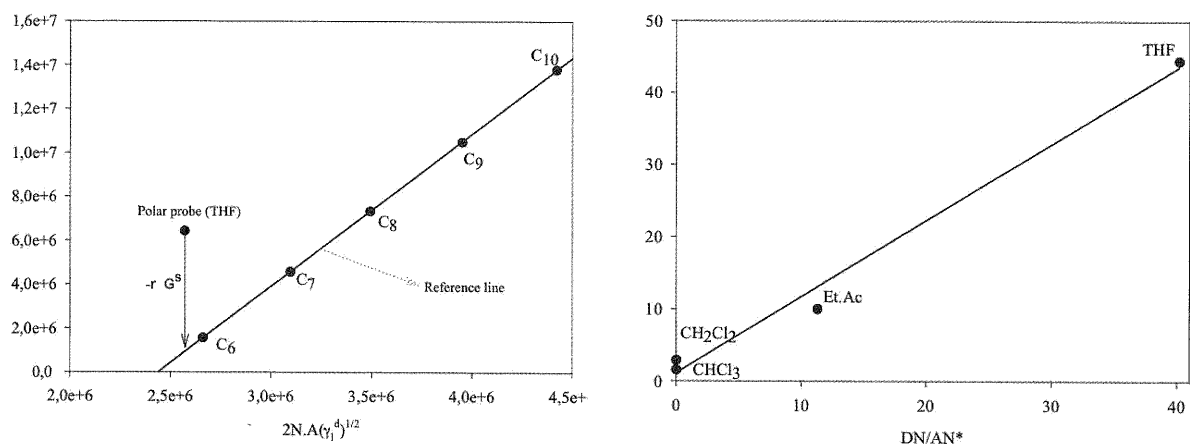


Figure 1. Determination of (a) sd (Eq. 6) and G_s (Eq. 7) for the basic probe THF; (b) acidic and basic constants (Eq. 10) for a sample tested in this work (sample C).

	Sample A	Sample B	Sample C	Sample D
Sample type	milled pulp	milled pulp	handsheet	handsheet
rpm to 30°SR		1200	1200	1200
Grammage (g/m2)			80	80
Sizing (mg AKD/10 g of pulp)				75

Table 1. Summary of sample characteristics

IGC Technique. In the present work a Perkin Elmer 8410 gas chromatograph equipped with a hydrogen flame ionization detector was used for IGC data collection. The instrument was connected to a Kompensograph Siemens integrator. Stainless steel columns, 0.5m long and 0.4mm i.d., were degreased, washed and dried before packing. Samples A and B were milled and samples C and D were cut into small pieces about 2 mm (2 mm. 1.3 g of pulp, on average, and approximately 2 g of handsheets were packed into the columns using a vacuum pump. The packed columns were conditioned overnight at 105° under a helium flow before any measurements were taken.

Experiments were carried out at column temperatures between 40 and 60°C, at 5°C intervals, in order to evaluate the variation of (sd with temperature as well as the enthalpies of adsorption for the polar probes. The injector and detector were kept at 180 and 200°C, respectively. Helium was used as carrier gas and its flow was selected to ensure that neither absorption nor diffusion of the probes would occur inside the column. Minute quantities of probe vapour (<1_L) were injected into the carrier gas flow to ensure that the experiments took place at infinite dilution. The probes, whose properties are listed in Table 2, were of chromatographic grade and used as received. Although several polar probes were used, the results reported for the acid-base characteristics were estimated from the work of adhesion with tetrahydrofuran (basic probe) and chloroform (acidic probe). Replicated measurements were performed with two columns prepared

in the same way. Retention times were the average of at least five injections. The retention times were determined graphically according to the Conder and Young method (Kamdern 1992). From the retention time measured for a given probe (t_r), the corresponding net retention volume (V_n) was calculated (Equation 1). Natural gas with 83.7% methane was used to determine the dead retention volume.

(1) Tetrahydrofuran; (2) Diethyl ether

RESULTS AND DISCUSSION

Determination of the dispersive component of surface free energy. The dispersive component of the surface tension, (sd , using Equation 6, and its variation with temperature ($d(sd)/dT$) are presented in Table 3 and Figure 2.

	Sample A	Sample B	Sample C	Sample D
sd (mJ/m2), 40°C	45.02±0.38	48.16±0.48	31.25±0.02	33.39±0.04
r^2	0.995	0.998	1.000	0.999
$d\ sd/dT$ (mJ/m2K)	-1.06	-1.28	-0.61	-0.57

Table 3. Dispersive component of surface tension, (sd , and its variation with temperature for all the samples tested.

Although the modifications to which pulp A was submitted (beating, handsheet formation and sizing) greatly affect the sample surface properties, all the values obtained for (sd are consistent with those published in literature for this type of materials (Belgacem 2000). Comparing samples A and B (refining effect), a slight increase in both (sd and $d(sd)/dT$ can be detected. This was somehow expected since beating increments the amount of hydroxyl groups accessible at the surface and consequently the total area available for bonding. Therefore, the surface ability to establish dispersive interactions slightly increases. The dependence of (sd on temperature (Figure 2) also increases for pulp B, denoting a

Polar probes	A (Å2)	Id (mJ/m2)	AN* (kJ/mol)	DN (kJ/mol)	Alkanes	A (Å2)	Id (mJ/m2)	AN* (kJ/mol)	DN (kJ/mol)
Chloroform	44.0	25.0	22.6	-	C6H14	51.4	18.4	-	-
Dichlormethan	31.5	27.6	16.3	-	C7H16	57.0	20.3	-	-
THF(1)	45.0	22.5	2.1	84.2	C8H18	62.8	21.3	-	-
DEE(2)	47.0	15.0	5.9	80.5	C9H20	68.9	22.7	-	-
Acetone	42.5	16.5	10.5	71.2	C10H22	75.0	23.9	-	-
Ethyl acetate	48.0	19.6	6.3	71.7					

Table 2. Characteristics of IGC probes (Santos et al. 2001).

higher entropic contribution to the surface free energy.

The effect of sheet-forming can be examined by comparing sample B (milled pulp) and sample C (handsheet). Packing the column with the latter resulted in a much lower value of the dispersive component of surface free energy and of its temperature dependence (about half). This is most probably due to the fact that fibres attach to each other during sheet formation creating a more dense structure and consequently a lower number of sites remains available for the establishment of interactions of dispersive nature.

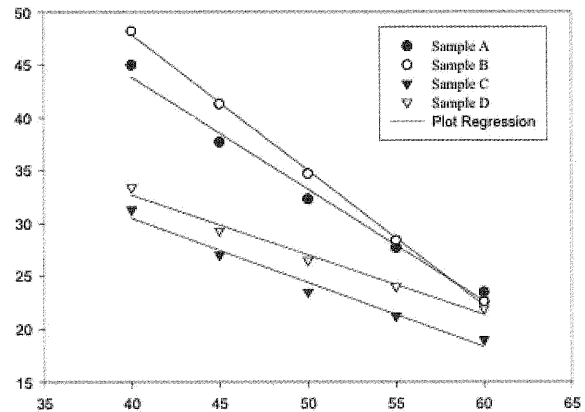


Figure 2. Variation of the dispersive component of surface tension with temperature for the various samples.

Regarding the influence of sizing, expressed by the differences between the results obtained for samples C and D, no significant change was detected for the surface energy, despite other authors having reported a decrease in this parameter with sizing (Shen 1998; Belgacem 2000). Possible explanations for this are probably the differences in the sizing procedure and the fact that, in this work, its effect was evaluated in handsheets instead of pulp fibres.

Acid-base characteristics. Although the discussion is mainly based on the results obtained for THF (basic probe) and chloroform (acidic probe) at 40°C, the acidic/basic character of the samples was evaluated using all the polar probes referred in Table 2. The results found for

the adhesion works (derived from Equation (8)) as well as the acidic and basic constants (calculated from Equation (10)) are presented in Table 4.

	Sample A	Sample B	Sample C	Sample D
Wa(THF)/Wa(CHCl3), 40°C	8.7	11.4	5.4	2.0
Ka/Kb	2.0	3.1	1.8	1.0

Table 4. Ratio between the adhesion works with tetrahydrofuran (Wa(THF)) and chloroform (Wa(CHCl3)) and between the acidic and basic constants (Ka and Kb, respectively).

From the results obtained for the ratios between the adhesion works, it can be concluded that, excluding sample D that is nearly amphoteric, all the samples have a predominant acidic character which decreases in the following order:

sample B> sample A> sample C> sample D.

This tendency is corroborated by the values of the Ka/Kb ratios, determined from the adsorption enthalpies, revealing a good qualitative correlation between the two methods.

The increase of the acidic character of sample B (beaten pulp) in relation to sample A can be explained by the greater amount of hydroxyl groups together with carboxyl groups at the surface of the first, as a consequence of the beating action. As Figure 3 shows, the higher ratio Wa(THF)/Wa(CHCl3) exhibited by sample B is essentially due to the increment in the adhesion work with THF since the adhesion work for the acidic probe is similar to that of sample A.

Comparing the milled pulps (samples A and B) and the handsheets (samples C and D), it is evident the considerable increase of the adhesion works with both basic and acidic probes for the handsheet samples. On the other hand, it is clear from Figure 3 that the differences between the adhesion works of the acidic and the basic probes decreased from sample C to sample D, due to sizing. In addition, the ratio Ka/Kb not only decreased but is for sample D equal to unity, denoting that sizing renders the sample more evenly bipolar. The loss of acidity with sizing is consistent with other studies reported elsewhere

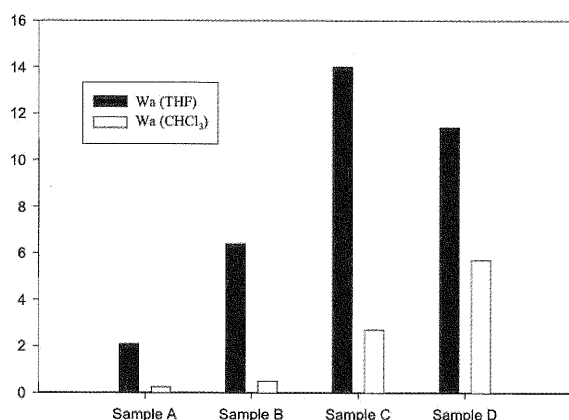


Figure 3. Adhesion works with basic (THF) and acidic (CHCl₃) probes of all samples at 40°C.

(Shen 1998), and is likely to be related to the basic nature of AKD, which must have formed strong covalent bonds with the fibres surface, decreasing the percentage of acidic sites.

CONCLUSIONS

In this work, Inverse Gas Chromatography was used to study the influence of beating, sheet forming and sizing on surface energetics of bleached Eucalyptus globulus kraft fibres. Milled pulps or pieces of handsheets were used as solid substrates.

The results have shown that beating although increasing only slightly the dispersive component of surface free energy greatly enhances the acidic character of the fibres surface, probably due to the greater amount of hydroxyl and carboxyl groups accessible at the surface.

The process of sheet formation widely decreases the ability of establishing dispersive bonds, resulting in much lower values for (sd. Nevertheless, the specific (acidic/basic) interactions with the polar probes greatly increase, especially with the basic probe (THF), and therefore the acidity of the surface (according to Lewis' concept) is preserved.

Because of the basicity of AKD and also due to the strong bonds formed between this sizing agent and the fibre surface, the available electron accepting sites decrease and the sized handsheet surface becomes more amphoteric.

Although sizing plays an important role to control spreading and ink penetration at the paper surface, sheet forming is probably the stage during papermaking that most contribute to the changes of the surface properties of fibres.

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