Atomic force microscopy to determine the surface roughness and surface polarity of cell types of hardwoods commonly used for pulping

M. Meincken*

ATOMIC FORCE MICROSCOPY CAN BE USED to determine the surface roughness and surface polarity of different cell types originating from hardwood species. This analytical method allows images representing the topography and polarity of a surface to be captured simultaneously at a molecular (nanometre) resolution. The distribution of hydrophilic (polar) groups on these cell surfaces influences the subsequent processing of woodpulp in paper manufacture. These surface properties of fibres, vessel elements and parenchyma cells were investigated for *Acacia mearnsii, Eucalyptus grandis, E. dunnii* and *E. macarthurii.* A clear distinction was observed between the cell types and the species in terms of polarity and surface roughness. All four species are currently being used for paper manufacture in South Africa, but not with equal success. This study may help to explain the differences in pulp quality obtained for the various species.

Introduction

The surface properties of wood fibres used for papermaking have a strong influence on paper quality. Fibre, however, is often used in the pulp and paper industry as a collective term to refer to various cell types. In softwoods the 'fibres' consist mainly of tracheids and parenchyma cells, whereas in hardwoods they include fibres and a larger proportion of vessel elements and of parenchyma cells.[2] It is well established that morphological characteristics, such as fibre length, the ratio of fibre length to width, and fibril angle influence the mechanical properties of paper.[1] The relationship between paper properties and fibre morphology is not as pronounced for hardwood species, however, as it is for softwoods. This can be explained by the heterogeneity of cell types in hardwoods in contrast to the more homogeneous distribution of cells in softwoods.

The surface roughness of fibres is also believed to affect paper strength, as it determines the ability of fibres to interlink with each other or filler particles.[3] The chemical composition of pulp fibres determines the ability of colloidal filler particles to bond to the fibre surface and affects the inter-fibre bonding. Lignin, for example, has a detrimental effect on the strength of paper,[4] whereas the presence of anionic components on the fibre surface was found to increase paper strength.[5]

The presence of polar, or hydrophilic, groups on the fibre surface can improve the interaction with filler or binder particles and other additives that attach to the fibre via hydrostatic forces.[6] The main contributor of free hydroxyl groups on the fibre surface is hemicellulose, which acts as a coupling agent between the cellulosic micro-fibrils and lignin. Both lignin and extractives are relatively hydrophobic in nature and are reported to impair paper strength.[7] Paper quality is affected not only by the quantity of polar groups in the fibre, however, but also by their distribution on the fibre surface.

The wood species also greatly influences pulp quality. The main focus of the work reported here was to determine the differences in surface properties according to species and cell type. I compared two species that are commonly used for papermaking in South Africa, namely *Acacia mearnsii* and *Eucalyptus grandis,* with two others that are less important as pulpwood material, *E. dunnii* and *E. macarthurii*. The latter two produce pulp of a different quality from the others, which could be because they have a higher lignin content. Nevertheless, all four species are used as pulpwood in mixtures, to augment the source material available for paper manufacture.

I determined the surface roughness and the surface polarity of fibres, parenchyma cells and vessel elements of these four tree species, with atomic force microscopy (AFM), but not the effect of these surface properties on subsequent processing (such as pulping and bleaching). AFM has been employed to study the topography and morphology of fibre surfaces by several groups.[8–13] The high resolution (in the nanometre range) of the microscope allows the observation of structures with molecular dimensions. On the other hand, this sensitivity limits the scan range for rough samples, such as solid wood. The surface polarity of a suitable sample can be determined simultaneously from the topographic image by means of a digital pulsed force mode (DPFM) controller. This additional device allows the determination of the adhesion between the sample and the probe at each scan point,[14,15] resulting in a surface 'map' where different adhesive forces are revealed by the image contrast pattern. From this image it is possible to distinguish the polar and the non-polar parts of the surface, and hence to determine an average adhesion value for the surface examined, which can be regarded as the average surface polarity.[16] Surface roughness was determined from the topographic images by measuring the deviation from the average height recorded.

Experimental

Pieces of each of the four debarked tree species, measuring 6–8 mm in thickness, were obtained using a Wigger pilot size wood chipper. Untreated wood fibres were prepared in the form of bundles by cutting small pieces (about 200 μm in diameter and 3 mm long) from these chips with a microtome. Individual cells were then obtained by maceration with Jeffrey's solution (a mixture of equal parts of 10% nitric and chromic acids). This botanically accepted technique is regarded as a mild way of dissolving the lignin-rich middle lamellae between the cells and thereby liberating individual cells.[17] All fibres were kept in distilled water prior to imaging.

Untreated fibre bundles were attached to an AFM sample holder with double-sided adhesive tape, whereas macerated fibres were spread on a 1 cm^2 glass slide mounted on a sample holder and left to dry for 12 hours. The adhesion due to capillary forces between the cells and the glass substrate was sufficient to keep the samples in place during imaging. Images were acquired with the fast scan axis parallel to the longitudinal cell axis, in order to minimize shear forces.

Surface roughness was derived from a topographic image and the average adhesive force from an adhesion image, both of which were acquired simultaneously. Measurements were obtained with a Veeco Multimode AFM with a Witec DPFM controller. Images were acquired with a silicon force modulation cantilever (Nanosensors) with a nominal spring constant of 2.8 N/m. Untreated silicon has a natural oxide surface layer with hydroxyl bonds. These OH groups are adsorp-

*Department of Forest and Wood Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa. E-mail: mmein@sun.ac.za

tion sites for water molecules and the surface is therefore hydrophilic. A conventional silicon tip with SiO_2 groups at the surface will consequently show a higher adhesive force on a hydrophilic than on a hydrophobic surface.[15,18] The image of the adhesion force therefore represents the hydrophilicity (polarity) of the sample, where lighter and darker parts represent more and less hydrophobic compounds, respectively. The value of the adhesive force is given by $V_{adh}kS$, where V_{adh} is the average voltage value determined from the adhesion image, k is the spring constant of the cantilever and S the sensitivity of the photodiode.[15] In this case, S was 500 nm/V. A higher value of the adhesive force represents a more hydrophilic (more polar) surface.

It was not possible to identify the different cell types on the surface of untreated wood because the heterogeneous surface makes imaging with AFM difficult. In this study, therefore, only the individual cells of macerated fibres were examined. Each image was recorded with a scan size of $2\,\mu m \times 2\,\mu m$ and a resolution of 256×256 pixels. The surface roughness and adhesive force of each image were therefore determined from an average value of all 65 536 (256×256) individual measurement points. For each tree species, five images were acquired of fibres, parenchyma cells and vessels, respectively.

Results and discussion

Surface polarity

Figure 1 illustrates a topographic and an adhesion image of a macerated *E. grandis* parenchyma cell. Different cell types observed through a transmission microscope are illustrated in Fig. 2. Figure 3 shows adhesion images acquired subsequently for different *E. grandis* cell types. The average adhesive force is determined from a histogram of the kind shown in Fig. 4.

The average adhesive forces determined for the three cell types of the four species are summarized in Table 1. The forces measured on the fibre surfaces of *A. mearnsii* and *E. grandis* were similar. For the former, the surface polarity of parenchyma cells was in the same range as for the fibres, whereas for *E. grandis* it was about 50% higher than for fibres. The surface polarity of vessel elements was around 35% less for both species. The similar surface polarity of all three cell types for these two species might explain why these trees yield pulp of a comparable quality and are therefore often used together as pulpwood. The fibres of *E. dunnii*, on the other hand, had a significantly higher (about double) surface polarity than *E. grandis* and *A. mearnsii*, the parenchyma cells were as hydrophilic as the fibres, and the surface polarity of vessel elements were comparable to that of *E. grandis* and therefore only about 20% of the value determined on the fibre surface.

The surface polarity of *E. macarthurii* fibres was slightly higher than for *E. grandis* and *A. mearnsii*. The parenchyma cells displayed a much lower surface polarity (half that of the fibre surface) than for all other species. The vessel elements were comparable in their polarity to those of *A. mearnsii*.

The significantly higher polarity of *E. dunnii* fibres and the lower polarity of the *E. macarthurii* parenchyma cells may explain why these trees yield pulp of a

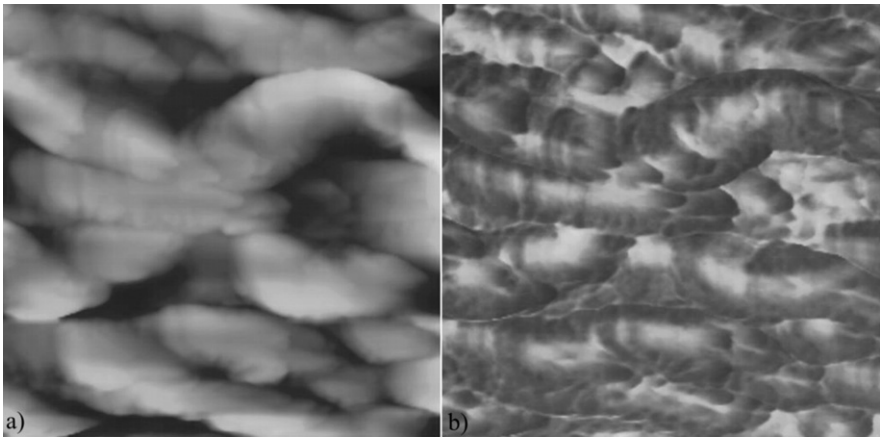

Fig. 1. Topographic (**a**) and adhesive force (**b**) images of the same macerated parenchyma cell from *Acacia mearnsii*. Scan range: 2 µm × 2 µm. A clear distinction is evident between polar (light) and non-polar (dark) areas.

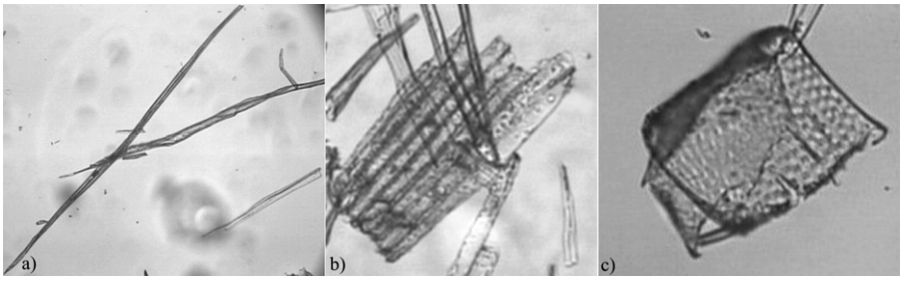

Fig. 2. Different cell types of *A. mearnsii* as seen through a transmission microscope: **a**, fibres; **b**, parenchyma cells; **c**, vessel element; ×50 magnification. AFM analysis was subsequently performed on surfaces of each cell type.

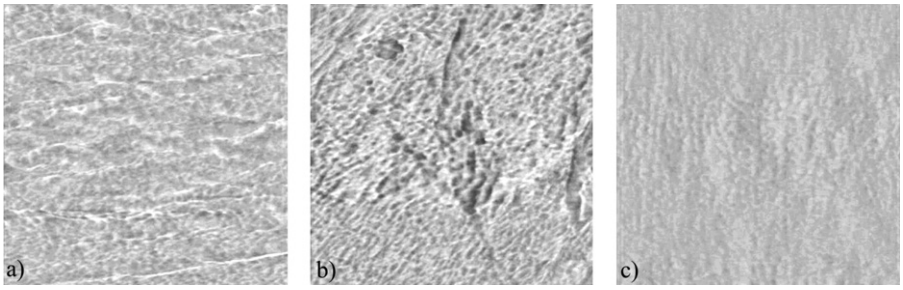

Fig. 3. Adhesive force images of a fibre (**a**), parenchyma cell (**b**), and a vessel element (**c**) from *Eucalyptus grandis*. Scan range: 2 µm × 2 µm.

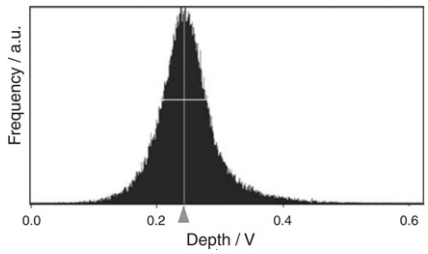

Fig. 4. Typical histogram of the distribution of grey values in AFM images such as those of Fig. 3, indicating average surface polarity and its standard deviation.

Table 1. Average adhesive force (nN)* measured on the surface of different cell types after maceration for different species.

Wood species: Cell type	*A. mearnsii*	*E. grandis*	*E. dunnii*	*E. macarthurii*
Fibre	510 ± 65 (448 ± 83)†	460 ± 83 (404 ± 74)†	1248 ± 57	615 ± 86
Parenchyma cells	577 ± 71	698 ± 94	1228 ± 52	363 ± 57
Vessel elements	393 ± 100	288 ± 65	248 ± 53	397 ± 82

*± Standard deviation. †Corresponding value of native fibre.

Table 2. Average surface roughness (nm)* measured on the surface of different cell types after maceration for different species.

Wood species: Cell type	*A. mearnsii*	*E. grandis*	*E. dunnii*	*E. macarthurii*
Fibre	19 ± 5 (18 ± 5)†	21 ± 6 (14 ± 6)†	26 ± 17	32 ± 14
Parenchyma cells	26 ± 10	41 ± 25	15 ± 10	15 ± 9
Vessel elements	14 ± 13	19 ± 9	16 ± 8	13 ± 8

*± Standard deviation. †Corresponding value for native fibre.

different quality from the other two species. Vessel elements have a generally detrimental effect on pulp quality and their lower surface polarity might partly be the reason.

Table 1 also lists values of the surface polarity of native wood fibres and macerated fibres of *A. mearnsii* and *E. grandis*, which indicate the influence of maceration. In both cases the polarity of the macerated fibres lies within the standard deviation of the value for native wood fibres (510 ± 65 nN and 448 ± 83 nN for *A. mearnsii*, respectively; and 460 ± 83 nN and 404 ± 74 nN for *E. grandis*, respectively). The differences in surface polarity due to maceration were therefore not significant.

Surface roughness

The average surface roughness values determined on the three cell types for the four species are given in Table 2. The values for *A. mearnsii* and *E. grandis* had a fairly narrow distribution, but a significantly wider range for *E. dunnii* and *E. macarthurii*. The broader distribution in values for the latter two species could be a further indication of why *E. dunnii* and *E. macarthurii* produce pulp of a different quality from that derived from the others, because enhanced fibre surface roughness may hinder the fibre-to-fibre contact and therefore result in a lower paper quality.

Table 2 also compares the surface roughness of native and macerated *E. grandis* and *A. mearnsii* fibres. For *A. mearnsii* the surface roughness after maceration lay within the standard deviation of the value determined on native fibres, so the difference was not significant. In the case of *E. grandis*, surface roughness increased slightly after maceration, which can be explained by the removal of the lignin-rich outer cell wall and the liberation of cellulosic fibrils. The surface roughness values of *E. grandis* and *A. mearnsii* parenchyma cells were higher than those for *E. dunnii* and *E. macarthurii*. The values determined on vessel elements show a relatively wide distribution around 65% of the average, and their average was lower than those determined on the other cells for those two tree types.

Conclusions

It was possible to determine the surface polarity of wood fibres, parenchyma cells and vessel elements with a combined AFM–DPFM. A clear difference in surface polarity between the cell types was detected. Furthermore, this variation between cell types depended on the tree species, and could partly explain the differences in their pulp quality.

Cells from *A. mearnsii* and *E. grandis* had similar surface polarities. The corresponding values for *E. dunnii* and *E. macarthurii*, on the other hand, differed significantly from these. The surface polarity of *E. dunnii* fibres and parenchyma cells was noticeably higher, and this could result in flocculation of cells and fibres and therefore impact adversely on paper quality. The surface polarity of parenchyma cells from *E. macarthurii* was significantly less than that of the other species and comparable to the surface polarity of vessel elements. Too low a surface polarity will decrease the ability of fillers and additives to bind to the fibres and fines and therefore result in reduced paper strength.

The surface roughness of *E. grandis* and *A. mearnsii* fibres had similar average values with a narrow distribution, whereas for both *E. dunnii* and *E. macarthurii* the deviation from the average value was greater. Increased surface roughness might have a negative effect on paper quality, as it hinders the fibre-to-fibre contact and results in voids in the paper.

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