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EVALUATION OF PAPER TWO SIDEDNESS WITH SEM/AFM MICROSCOPE TECHNIQUE

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ABSTRACT

The atomic force microscopy AFM and scanning electron microscopy SEM micrographs show non-uniformly distributed grainy particles with various shapes on the paper surface. However, AFM studies revealed the features of the paper surfaces are probably caused by different physical and chemical processes. The height feature and roughness parameters may be used to make automated measurements between images. AFM methods are likely to be useful for detecting topographical changes on surface structures as well as for the clarification of the surface dislocation phenomena such as; two sidedness.

KEYWORDS: Atomic force microscopy, scanning electron microscopy, cellulose, paper surface, two sidedness, scan area, microtopography.

INTRODUCTION

Paper surface is typically composed of cellulose fibres which have polymeric structure at various sizes from nanometers up to many microns (Paavilainen 1990). However, the property denoting difference in microstructure between its top (felt) and bottom (wire) sides usually called two-sidedness of paper (Roberts 1991, Scott et al. 1995).

The structural difference between the different sides of the paper, is generally associated with production on standard Fourdrinier paper machines, where asymmetric water drainage through only wire side of the sheet. As the paper is formed on the wire section, water drains from the bottom of the sheet by gravity and suction, and carries with fines. Thus, concentrate on the top side of the sheet, resulting in differences in some surface properties on the felt side in comparison to those on the wire side. Two-sidedness is a problem in many paper grades. Poorly bonded coarse filler detach particles more easily from the upper surface and cause problems, particularly during printing.

AFM is a recently developed scanning probe microscope that allows direct examination of materials in their ambient conditions. It has been proven to be a powerful technique for the characterization of materials surface at the nano scale. One of the greatest advantages of AFM over traditional techniques such as; optical and electron microscopes, is its ability to obtain information from the surface in aqueous or dry conditions directly (Anon 2000, Hansma et al. 1992). The three dimensional (3D) images may be obtained without specific sample preparation and yield more complete information than the two dimensional (2D) profiles. It can also provide clear measurement of step heights, independent of differences between solid materials.

The non-contact mode AFM usually operated in air or liquid; the cantilever is oscillated at its resonant frequency and positioned above the surface so it only taps the surface for a small fraction of its oscillation period. It is useful when imaging very soft samples. However, its imaging generally provides low resolution and can also be hampered by the contaminants or poorly immobilized layer which can interfere with oscillation.

The contact mode AFM where the tip scans in close contact with the sample is the common mode used in the force microscope. The measurement of the forces interacting between the tip and the surface are obtained using a cantilever with a characteristic spring constant (k).

The most familiar use of the AFM is in creating 2D or 3D images of a solid material. Recently, it has been applied successfully to studies of inorganic and organic materials from polymer research to nanotechnology studies. Examples include plasmid DNA (Hansma et al. 1992), biological applications (Ratneshwar and Scott 1994), a variety of membranes (Le Grimellec et al. 1994), and plasma-modified surfaces (Mahlberg et al. 1999, Sahin 2001, 2007). Other types of treatments (Lelarge et al. 1999), and surface coatings (Dahla et al. 1999), have also been studied using various AFM techniques.

However, the contact mode is probably the only AFM method which can obtain high resolution images from intended materials. But one of the drawbacks of contact with the sample is that there may exist lateral forces on the sample as the drip is over the specimen. These shear forces could disturb features in the image. But this is only in the case of very soft and fragile materials such as; biological tisssues and very thin polymers. Denes et al. (1997) and Denes and Young (1998) reported that the contact mode AFM micrographs had the capability to provide new information on the materials, especially, at the atomic level.

Although a number of researchers have attempted to predict AFM and its capability on lignocellulosic materials, further study is necessary to fully explain to papermaking industry. It may represent a powerful tool for paper surface imaging, and its application in this area warrants further investigation.

In the current work, the feasibility of imaging the paper surfaces by means of contact mode AFM was studied and results were compared to those from conventional SEM technique. The ultimate objective of this study was to increase our knowledge of the fundamental phenomena taking place in the papermaking process and to find correlations between the felt and wire side of sheets (two sidedness), in terms of quantity surface roughness.

MATERIAL AND METHODS

Bleached kraft paper was used to study the sheet network structures. Surface chemical compositions of samples were evaluated by the use a Perkin-Elmer (PHI) 5400 X-ray photoelectron spectroscopy (XPS) unit (Perkin-Elmer Corporation, Norwalk, CT).

An ATI-Mattson research Series IR (ATR-FTIR) was used to evaluate the chemical groups on the paper surfaces. All ATR-FTIR measurements were performed in the 500-4000 cm^{-1} wavenumber region.

The paper samples were vacuum coated by evaporation with platinum and examined by a Hitachi 450 scanning electron microscope. The accelerating voltages used, varied from 1 to 15 kV depending on the level of intended resolution.

A contact mode AFM (Digital Instruments Nanoscope II, Santa Barbara, CA), was utilized in order to investigate surface topography close to the atomic level. A standard silicon nitride type NP-20 probes supplied by Digital Instrument Company was used in all experiments. The standard NP-20 probes that have four cantilevers with different geometries attached to each probe, resulting in different spring constants, are shown in Fig. 1 (Anon 2000).In this installation; nominal tip radius of curvature: 20-60 nm; cantilever lengths: 100 & 200 μm; cantilever configuration: V-shaped; reflective coating: gold; sidewall angles: 35° on all 4 sides.

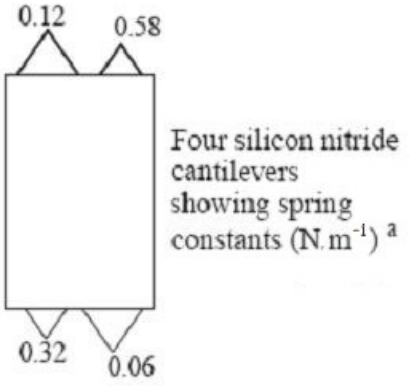

Fig. 1: Typical standard silicon nitride probe, NP-20

Images from the samples were obtained various cantilevers that having spring constant (k) from 0.06 to 0.58. It was observed that cantilever that having k of 0.06 (smallest among four cantilever) gave the best results with AFM analyses of paper. For that reason, comparison among AFM micrographs was made with using only this cantilever. The size of the scan area varied from 0.5 μm to 15 μm. The samples were attached to the sample holder with double-sided tape. Repeatable images of the paper was taken using same size cantilever in order to be able to compare the results.

The following AFM parameters were chosen as key descriptors of paper surface topography: mean (m), average roughness (R_a), root-mean-square roughness (RMS or R_q), respectively.

The mean value (m) is defined as the arithmetic mean of all height data obtained from an AFM surface scan. It represents the absolute Z-value of the cross section of peaks and valleys for a rough surface.

The mean roughness (R_a) is the average deviation of the measured Z-values from the mean plane. For the paper surfaces, it may be considered as half the average peak-to-valley depth. It is calculated using the following equation (Anon 2000):

$$R_a = \frac{\sum_{i=1}^{N} |Z_i - Z_{cp}|}{N} \quad (1)$$

where: Z_i is the current Z value, Z_{cp} is the Z value of the center plane and N the number of points within the given area.

The root-mean-square (R_q) describes the standard deviation of an entire distribution of the Z-values within a given area and is calculated using the following equation (Anon 2000):

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{ave})^2}{N}} \quad (2)$$

where: Z_{ave} is the average of the Z within the given area, Z_i is the current value, and N is the number of points within the given area.

The formulas used by the AFM software to compute these numbers were found the automatically. The measurement of surface roughness by means of R_q and R_a are presented in current study for ease in understanding.

RESULTS AND DISCUSSION

According to X-ray photoelectron spectroscopy XPS analysis, full bleached kraft paper consisted only of carbon (C_{1s}) and oxygen (O_{1s}) that are characteristic for cellulose. But, the felt side has only marginally higher oxygen to carbon ratio (O/C: 0.76) in comparison to wire side (O/C: 0.73). This variance indicates that the present types of paper surface are chemically similar to allow a surface determination. However, it is impossible to identify significant differences in the absorption patterns of the felt and wire side from ATR-FTIR diagrams, which indicates that the two surfaces are made of similar chemical functionalities; the broad peak at 1000-1100 cm^{-1} which is attributed to the stretching of the C–O and C-C-O groups; CH_2 bending at 1370 cm^{-1} and in-plane OH bending C–OH at 1400 cm^{-1}. The surface chemical variations in terms of two sidedness of same paper substrate were studied and a detailed description has been provided by Sahin (2007).

The SEM micrographs for felt and wire side of sheets are shown in Figs. 2, 3, respectively. Those typically indicate fibrous, quite rough and unhomogeneous structures. The roughness features were retained: some deep and large empty spaces among randomly laid fibers forming a netlike pattern on the surface were realized. However, it was expected that some fines and short fibers will retain in the wire side, which leads to a non-uniform distribution of particles through the thickness of the sheet. But, comparison of the both side with SEM, even scan area up to 10 μm (Fig. 2c and 3c) did not reveal any distinctive differences on paper. Moreover, none of the micro roughness could be in-situ, because the standard sample preparation (surface coating) methods were used to fix paper for SEM characterization, have proven inadequate roughness evaluation. Mahlberg and et al. (1999) claimed SEM did not give enough information on the polymer surface at the atomic level and had limited depth resolution, which did not enable the detection of morphological features of much less than microns. Similar results have been observed with bleached paper and the 2D SEM images lack the resolution that cannot capture the exact shape of sheet network features.

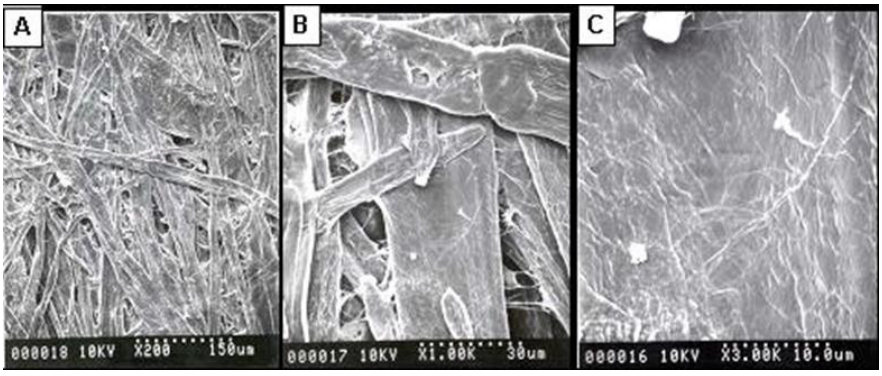

Fig. 2: SEM micrographs of paper at various magnifications (felt side)

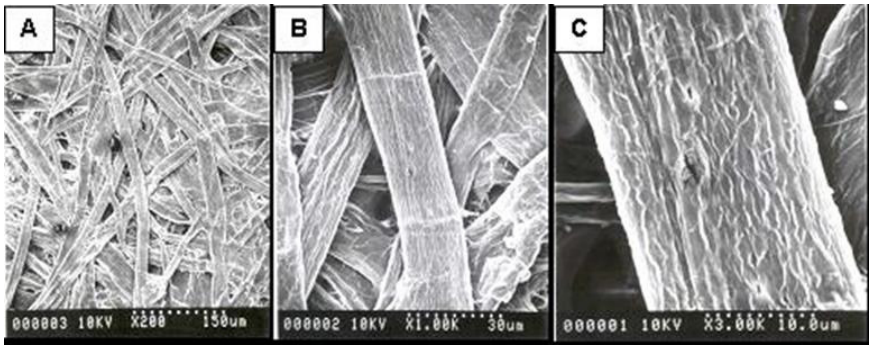

Fig. 3: SEM micrographs of paper at various magnifications (wire side)

Hanley and Gray reported (1995), that AFM could be used during evaluating the paper surface properties. This is based on determination of surface roughness values and direct micrograph of surface. It was also suggested AFM may be considered as a method that is non-destructive to surfaces (Mahlberg et al. 1999). Hence, AFM technique at the various magnification levels was used for evaluating surface topography of the paper. It was concentrated on observations of microstructure differences and roughness measurements on the felt and wire side of sheet.

Typical 2D AFM micrographs with scan area ranging from 0.5 μm to 15 μm are presented in Fig. 4a-f, respectively. It can be noticed that no special features are visible with the 2D micrographs. However, various surface morphologies: (a) large, valley type asperities (b) small, closely spaced asperities, (c) closely spaced, relatively smooth asperities, and (d,e,f) large, widely spaced, ridge-and-valley type asperities can be visible. But obtained surface height histograms correspond to the cantilever deflection during cyclic up and down movements (Fig. 4). These may be practically useful for determining surface topographpical feature (Z-range). It can provide quantification of the distribution spread of measured heights. Moreover, the small steps in the nano range which are not apparent in the SEM micrographs, can be easily seen with AFM. It is also evident that paper is not soft enough for effective imaging, at least in cantilever with spring constant of 0.06. This is in good agreement with the results of some other studies (Denes et al. 1997, Denes and Young 1998). Kopycinska-Müller et al. (2006) found that the nanoscale tip-surface contact was very complicated and could not be easily described in terms of simple, ideal geometries.

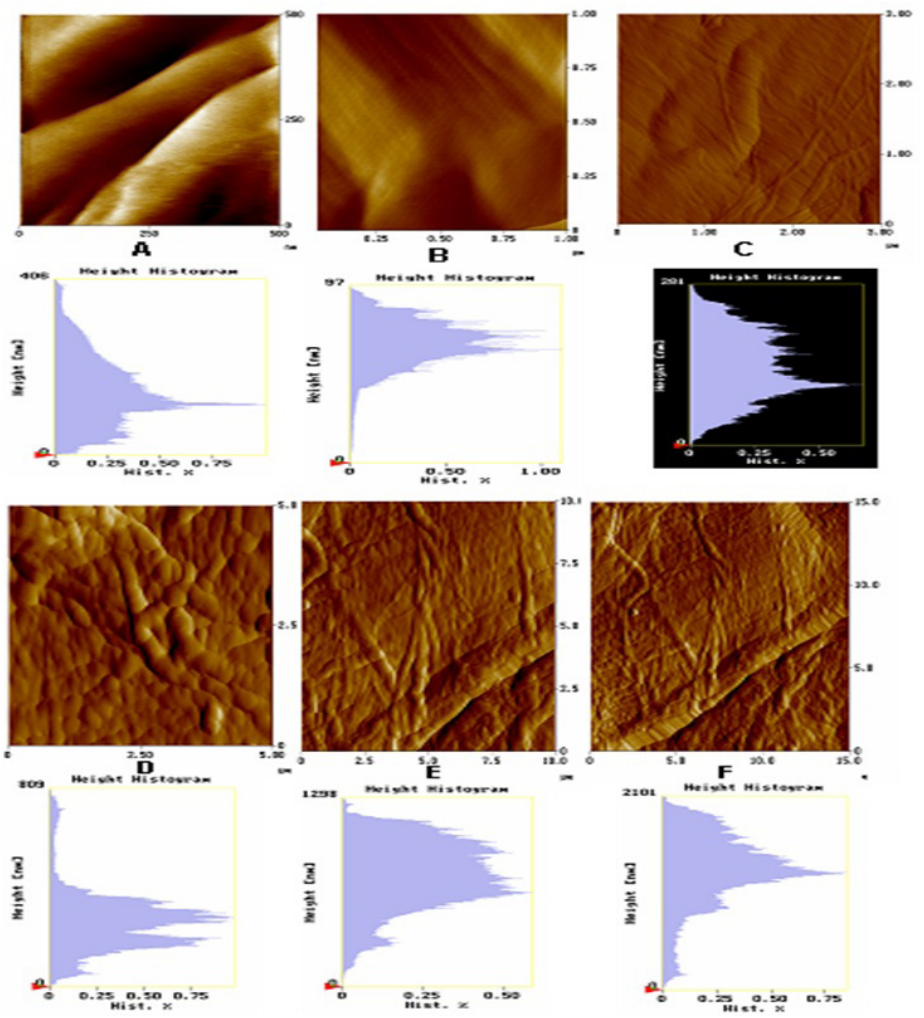

Fig. 4: The 2D AFM images of paper surface at various magnifications with surface height histograms; a) 0.5 μm, b) 1.0 μm, c) 3.0 μm, d) 5.0 μm, e) 10 μm and f) 15.0 μm.

Typical 3D AFM micrographs of the same samples for felt side is given in Fig. 5. Those clearly reveals a distinct differences and no such structure can be visible in 2D micrographs in both AFM and SEM. The 3D appearance permitted a better understanding of the topographic characteristics of the paper surface. The gradual increase in the particle grain size with the image scan area can be realized. It typically indicates randomly laid various irregular fine structures which was an indication of a deposition some substance on the surface. According to Tappi Standard T 261, the word "fines" is used for cellulosic objects small enough to pass through a conical hole having a minimum diameter of 76 μm.

However, the fuzzy character of micrographs at submicrometer magnification were

associated with difficulty of obtaining satisfying images from 3.0 x 3.0 µm scan areas and lower (Figs. 4 a-c, 5 a,b). While larger features such as inhomogeneous laid network structure with various heights occurred on the surface, these particles were not clearly visible. Similar problems were encountered while trying to achieve high magnification such as 15 x 15 µm. Cellulose particles, which have essentially no permanent charge, were not fixed stably enough to image properly beyond these levels. It was hypothesize that the fuzzy appearance of the surface at low magnification is encountered due to the cellulose chains moving under the AFM tip. For that reasons, determination and quantification of paper two sides was made with 5µm and 10µm scan area level.

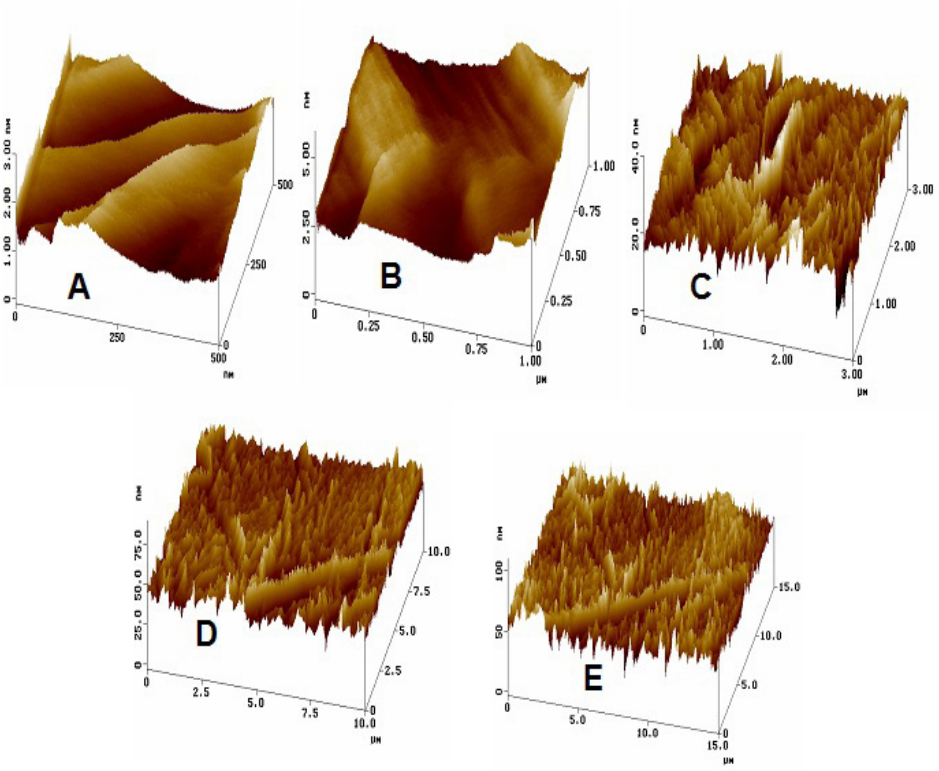

Fig. 5: The 3-D AFM images of paper surface at various image area a) 0.5 µm, b) 1.0 µm, c) 3.0 µm, d) 10 µm and e) 15.0 µm.

The close relationships between cantilever deflection range (Z-range) and image scan area were observed. Analysis of AFM images of the paper yielded R_a values between 10.073 and 310.82 nm and R_q values between 13.048 to 400.52 nm, scan area ranging from of 0.5 to15 µm. Those increase in the same order as image size but in each case, the trend is marginally the same for both parameters (R_q and R_a).

As seen in Fig. 6, the R_a and R_q directly proportional depend on AFM image scan size. The surface raughness (R_a) is the increase in surface area, due to roughness, over a flat plane with the same X and Y dimensions.

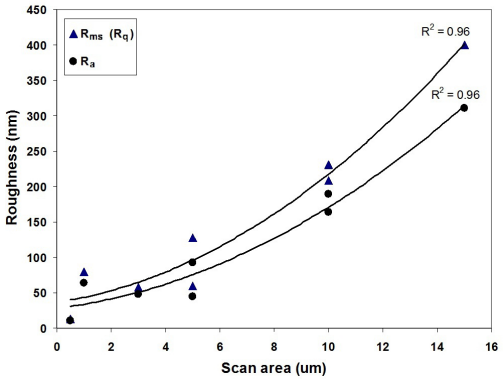

Fig. 6: The correlation of surface roughness and scan area for paper determined by AFM

The micro topographic properties of two surfaces presented in Tab. 1 are comparable and statistically found.. It was observed that felt side has higher grain size (Z-range) compared to wire side under same magnification level (809 nm vs 462 nm). However, the calculated m is typically nonzero because all data points are measured with respect to the starting elevation of the AFM probe tip. But the mean value was quite small and negligible. Moreover, based on the quantification of paper surface roughness properties, it can be clearly distinguish at least two types of surface: moderately rough (wire side), and rough (felt side) at atomic level as realized in Tab. 1.

Tab.1: Typical AFM values for paper surface microtopography

	5.0 µm	**10µm**
Felt side		
Z range (nm)	809	1299
Mean (nm)	0.05	0.02
Rms (R_q) (nm)	127.47	231.20
Grain size (nm)	0-809	0-1298
Wire side		
Z range (nm)	462	1210
Mean (nm)	0.03	0.023
Rms (R_q) (nm)	59.73	208.22
Grain size (nm)	0-462	0-1210

Compared felt and wire side surface roughness root mean square (R_q) at 5 µm and 10 µm scan area is shown in Fig. 7. From automated surface measurements, the R_q for felt side was calculated to be approximately two times higher than wire side at 5.0 µm scan area (127.4 nm vs 59.7 nm). The distinct two sidedness, that corresponds to two different surface types, seems to exist. This suggested surface topography of paper at atomic level is strictly related to the particle sizes; hence the increased fines in bottom (wire side), results in a decreased roughness at atomic level are realized in Fig. 7.

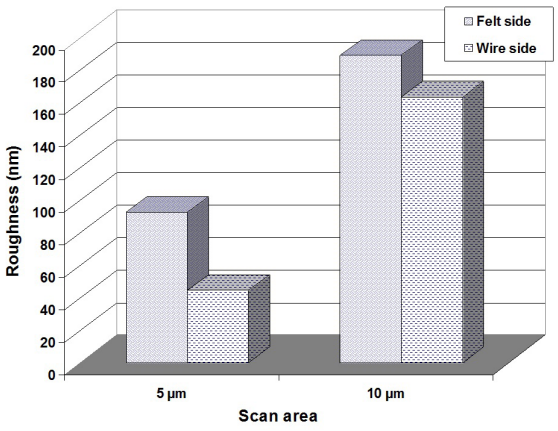

Fig. 7: Comparative surface roughness properties of paper determined by AFM

This is probably due to small particles that can be arranged better in wire side compared to the felt during sheet forming processes.

CONCLUSIONS

The 3D micrographs provided by AFM offered interesting information concerning the paper surfaces. Experiments strongly suggest that AFM represents a powerful tool for the imaging and determination of the paper surface microstructure. Minimal sample preparation, high (submicrometer) magnifications, and the capability of easy quantification of structures represent some of AFM's unique characteristics.

It defined the AFM imaging parameters appropriate for paper and obtained high quality images. The sample preparation methods presented here will enable the examination of paper products and the chemical processes associated with its surfaces and interlayer using contact mode AFM.

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