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HYDRATION OF REFINED CHEMICAL PULPS STUDIED BY MICROWAVE SPECTROMETRY

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ABSTRACT

A bleached sulfate pulp has been refined in a disk refiner to different degrees : from 15 to 75° SR (720 to 70 CSF). Different water contents ranging from 40 to 90 % by volume (70-90 % by weight), have been obtained by centrifugation of small samples of ca.30 mg o.d. weight. The samples have been analyzed by microwave spectrometry performed in a cavity at 5GHz. The theory of small perturbations of a resonant cavity allows the determination of the dielectric losses ϵ''_s of the hydrated material. The slope of the lines : ϵ''_s vs. moisture content is an index of the hydration of pulps. At the same water content (in the range 70 to 90 % by weight), we have shown that refining increases the hydration, which can be defined as the transformation from free water to bound water.

INTRODUCTION

Cellulose-water interactions

Water plays a major role in the formation of paper : it is the dispersing and carrying agent of cellulose fibers throughout process and it pulls and holds the fibers together on the paper machine. The strong interaction between cellulose and water was emphasized by Goring when he stated that "liquid water may be regarded as the amniotic fluid of paper" (1).

The hydrophilic properties of cellulose are due to the chemical constituents, namely the hydroxyl (OH) groups, located along cellulose chains. The OH- groups are capable of hydrogen bonding with water molecules, and thus impart specific properties to the water directly in contact with, or in the vicinity of them. These properties are different from those of water not directly in contact with cellulose. The properties of "free" and "bound" water have been reviewed by Boesen (2) and more recently by Corte (3). The water associated with cellulose does not dissolve salts, does not freeze, and is more firmly bound to cellulose, as shown by the heat of wetting and by desorption isotherms. As stated by Corte : "Water tends to structure itself because of the polarity of its molecules. Cellulose tends to impose some structure on the water in the vicinity of its surface because of its hydroxyl groups"(4).

Beating and refining

It is commonplace to say that refining is an important part of the papermaking process. The main effects of refining on chemical pulp fibers are well known and have been categorized as follows :

- Internal fibrillation or fiber swelling, measured by the Water Retention Value (5) or by the increase in fiber width (6).
- External fibrillation and fine elements production, which bring an increase in the specific surface of pulp and lower the freeness (7).
- Fiber shortening, measured optically (8), or by the decrease in weight of the long fiber fraction in any of the various pulp classifiers (9).
- Fiber activation (10) and defects removal (11).

All of these processes occur to varying degrees during refining, and determine the end product properties. They occur under interesting conditions, from the viewpoint of the papermaker, because of the affinity of water and cellulose. Water penetrates and swells the cell wall, it plasticizes the amorphous hemicelluloses (12), and prevents fibers from crushing or destruction during refining.

The present report deals with the evolution of the interactions between cellulose and water during refining as seen by microwave spectrometry.

Refining and cellulose-water interactions

Recent works have been published on this subject with apparently contradictory results. Yamauchi and Murakami (13) have interpreted the increase in electrical specific conductivity with beating as a consequence of the opening of the fiber wall structure, and the increased contribution of dissociative (carboxyl) groups, to conductivity. Hatakeyama et al. (14) have shown that beating does not change the crystalline structure of cellulose microfibrils, with the density column method and with X-Ray diffraction. Moreover, DSC measurements have shown that the number of non-freezing water molecules attached to the hydroxyl groups in the amorphous region kept a constant value throughout beating. The authors conclude that the structure on the molecular level was not affected by beating.

Conversely, Atalla et al. (15) have shown by NMR studies that extensively refined pulps exhibit enhanced molecular mobility, suggesting that physical disruption through beating has extended to a molecular level. It seems that each method, with its own sensitivity, "sees" a different amount of more or less bound water.

The effects of beating on pulps hydration have been studied by microwave spectrometry coupled with BET measurements, and the results presented in previous works (16, 17). The conclusion of Henry et al. was that the water mobility in the vicinity of the hydroxyl groups was restricted with beating, leading to an increase in thickness of the perturbed layer. However, the experiments had some deficiencies : the pulp sample was subjected to dehydration during the measurements causing sample contraction ant thus volume reduction. Since the volume is an important parameter when dealing with microwaves, the experiments have to be done under static conditions with a known volume of pulp samples. This has been done in the work presented here.

PRINCIPLE OF MEASUREMENT

Microwave spectrometry

Molecules which have a dipole moment such as water are oriented in the direction of the electric field to which they are subjected. Their free rotation is however hindered, due to interactions with the surrounding molecules. The frequency at which the molecules are no longer able to rotate is the frequency of relaxation. The quantity that describes the behaviour of a dielectric under the influence of a microwave field is the complex permittivity ϵ^* .

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad (1)$$

ϵ' is the dielectric constant or permittivity. It describes the dispersion of the wave by the medium.
ϵ'' is the loss factor that governs the amount of energy which is absorbed by the medium and converted into heat.

In the case of ionic materials, losses also occur by conduction

$$\epsilon^* = \epsilon' - j[\epsilon'' + \frac{\sigma}{2\pi f \epsilon_0}] \tag{2}$$

where σ is the conductivity, f the frequency and ϵ_0 the dielectric constant of vacuum.

The dielectric losses are maximum at the frequency of relaxation. Water has different relaxation domains, depending on its physical state : solid (KHz), adsorbed or bound water (MHz), free water (GHz). The microwave range (1 - 100 GHz) has specific action on free water ; it is therefore used for heating as well as detection and measurements.

Cavity perturbation technique

The method is based on the measurement of the electromagnetic field perturbation of a resonant cavity, by a small sample which has been inserted into it. The technique is briefly presented by Metaxas and Meredith (18). It has been developped by Henry and Berteaud (19), and applied to many materials.
The dielectric properties can be computed through the measurement of the shift of the cavity resonant complex frequency from its original unperturbed value of ω_0^* to a new perturbed value of ω^*, and by the measurements of the change in the cavity Q-factor values, again with and without the insertion of the sample.

$$\frac{\omega^* - \omega_0^*}{\omega^*} = \frac{F - F_0}{F} + \frac{1}{2} j \left[\frac{1}{Q} - \frac{1}{Q_0}\right] = \epsilon_0 (\epsilon^* - 1) \frac{\iiint_V E^* E_0 \, dV}{4W} \tag{3}$$

where F_0 , F , Q_0 , Q are the frequencies and Q-factor of unperturbed and perturbed cavity respectively, E^*, E_0 are the electric fields inside the sample and in the cavity, V is the cavity volume and W is the total stored energy in the cavity.

The sample dielectric constant ϵ_S' and the loss factor ϵ_S'' are found after integration and separation of the real and imaginary parts respectively, giving

$$\frac{\Delta F}{F} = K_S V_S \frac{1}{V} [\epsilon_S' - 1] \tag{4}$$

$$\Delta(\frac{1}{Q}) = \frac{K_S}{2} V_S \frac{1}{V} \epsilon_S'' \tag{5}$$

where V_S is the sample volume and K_S the depolarizing factor. K_S describes the fact that the field inside the sample is not the same than in the surrounding medium. K_S depends mainly on the sample shape which does not change throughout the experiments (see below). $\Delta(\frac{1}{Q})$ is measured for the sample and then for pure water in place of the sample.

The ratio of the two quantities allows the calculation of ϵ''_s

Thus :
$$A = \frac{\Delta(\frac{1}{Q})\,\text{sample}}{\Delta(\frac{1}{Q})\,\text{water}} = \frac{K_s V_s \epsilon''_s}{K_W V_W \epsilon''_W} \tag{6}$$

and
$$\epsilon''_s = A \frac{K_W}{K_s} \frac{V_W}{V_s} \epsilon''_W \tag{7}$$

where A and V_s are measured and K_W / K_s , V_W and ϵ''_W are constant.

The device used for the measurement is described in Fig 1.

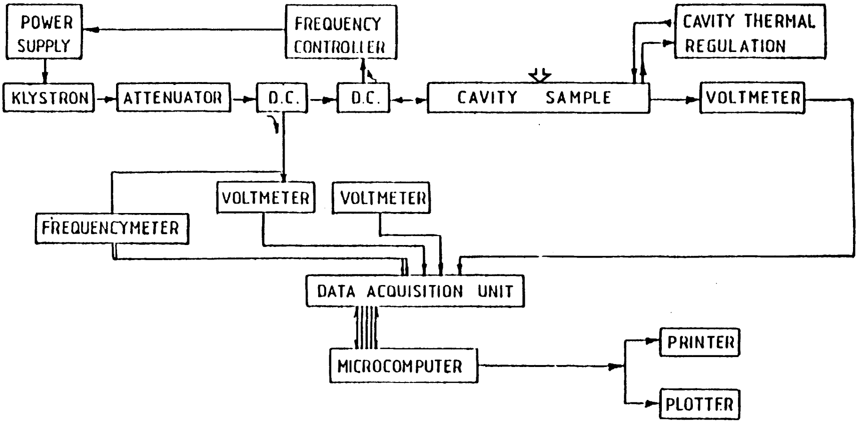

Fig. 1 : Experimental device. The sample is inserted into the cavity at the place indicated by the white arrow.

The microwaves are produced by a klystron in a resonant cavity. At 5GHz, the vibration is of the mode TEO,1,63. The quality factor is 4000 ; the volume is 3 dm^3.
In the following, we will consider the relationship between ϵ_s'' and the amount of water in the sample.

Variation of ϵ'' with moisture content

The general shape of the curves of ϵ'' vs. moisture content is shown in fig. 2. It is obtained by dielectric properties measurement of a sample subjected to continuous dehydration (16, 17). Refining shifts the curves towards the low values of ϵ'' . The point Mc is the dielectric critical moisture content (termed Dc in ref 16). Below this point, water is bound to cellulose surface in the first unimolecular layer. It occurs at around 10 % for cellulose materials. Above this point, water is more free to rotate in the electric field. The slope of the curves at low water content (20 % on a wet basis) is indicative of the level of interactions between cellulose and water (20). The higher the slope, the "freer" the water. As said above, these curves are obtained under dynamic conditions, with strong sample shrinkage.
The work presented here deals with the results of dielectric measurements performed at a higher water content (above 70 %) under

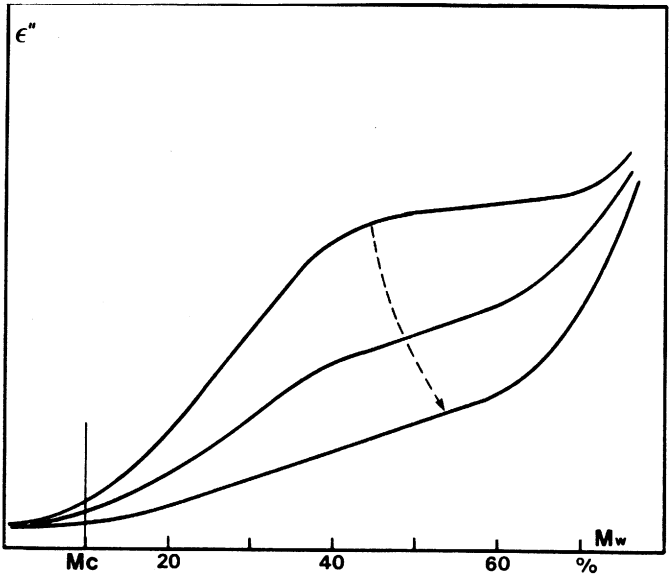

Fig. 2 : Variation of ϵ'' vs. Moisture content (Mw in percent) indicated in weight of water divided by weight of wet sample. The arrow indicates beating.

EXPERIMENTAL

Pulp refining

A bleached sulfate softwood (95 % Scots pine) from Cellulose du Rhone et d'Aquitaine (C.D.R.A.) was refined in the pilot plant shown in fig. 3. A specific edge load of 1.2 Ws/m was kept constant throughout the refining by gap adjustment. The pulp underwent several passes through the refiner until the desired amount of refining was obtained. Seven samples were taken from the suspension during the course of refining. The pulp properties measured were : Schopper-Riegler, Water Retention Value (under 3000 g) and weighted average fiber length (WAFL) with the Kajaani FS-100 Fiber Analyzer. For each sample, eight handsheets have been formed using a Rapid Kothen sheet-former. The apparent density and tensile index of the sheets were measured according to standard ISO methods, and appear with pulp properties in Table 1.

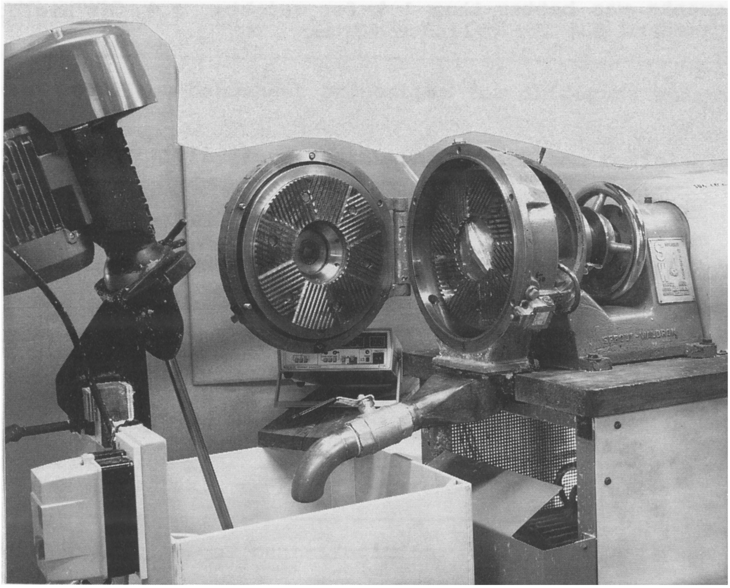

Fig. 3 : The C.T.P. pilot plant refiner is a modified Sprout-Waldron 12" single disk refiner.

Dielectric measurements

The dielectric properties of the seven samples were measured using small aliquots of pulp. The measurements are made on cylindrically shaped pads having different water contents, in the range of 70 to 90 % (wet basis). The various consistencies were obtained by serial centrifugation of the aliquots to remove water. The sample holder used, consisted of a tube with a teflon ring. A small sample of pulp was placed into the ring.
After centrifugation, the sample was introduced into the cavity for dielectric measurement. The volume of the sample (0.25 $10^{-6}m^3$) was small compared to the volume of the cavity ($3.10^{-3}m^3$). The fibermat was then weighed and its diameter and thickness were measured with a calliper-rule for volume calculation. The same sample was reintroduced into the ring and centrifuged to increase its consistency for further measurements. The speed of the centrifuge and time of centrifugation were both increased after each cycle (see Table 2) . After four complete cycles, the sample began to shrink and lose its cylindrical shape. It was then ovendried (3 hours, 105° C) and weighed. We were thus able to compute the volume fractions of water, cellulose and air at each step. This tedious method of carrying out the experiment ensured a constant shape (cylindrical) to the sample, and thus a constant value of K_S throughout refining. The calculation of ϵ''_S was possible with the knowledge of V_S . The precision of measurements was better than 1 % for weights, 2 % for dielectric properties and 5 % for cylinder volume.

RESULTS

Pulp properties

Pulp and handsheet properties are presented in Table 1.

Sample number	1	2	3	4	5	6	7
Refining Energy (kwh/t)	0	20	60	105	190	270	360
°SR	15	16	19	24	46	61	74
Water Retention Value :							
dry basis (g/g)	1,07	1,17	1,32	1,48	1,63	1,87	2,08
wet basis (%)	52	54	57	60	62	65	68
WAFL (mm)	1,93	1,90	1,86	1,81	1,68	1,62	1,48
Sheet apparent density (kg/m^3)	564	580	603	631	656	699	736
Tensile Index (Nm/g)	24	33	42	49	57	68	77

Table 1. Pulp and handsheet properties for different energy inputs.

The pulp conductivity is constant throughout the refining and is equal to 200 μS/cm.

Sample volumes after centrifugation

Four conditions of centrifugation were used in this experiment, and are presented in Table 2.

Condition	1	2	3	4
Speed (t/min)	780	1180	1580	1980
Time (min)	4	6	8	10
Speed x time (10^3 t)	3,1	7,1	12,6	19,8
Number of g (approx)	70	160	300	450

Table 2. Conditions of centrifugation.

The value of speed x time is used to represent the conditions of centrifugation in fig. 4. One can notice that the number of g is about one order of magnitude below the one for WRV measurements.

The ovendried weight of samples is indicated in Table 3.

Sample number	1	2	3	4	5	6	7
o.d. weight (mg)	46,9	29,5	21,6	27,1	25,6	26,3	32,7
Range of water content studied :							
Volume water/volume sample (%)	45-77	55-70	30-63	38-72	50-90	47-88	68-92
Weight water/weight sample (%)	71-80	78-84	74-88	72-87	80-88	73-86	87-92

Table 3. o.d. weight of pulp samples and range of water content. studied. Numbers 1 to 7 are the references of each pulp as defined in Table 1.

The variation of each sample volume with the conditions of centrifugation is shown in fig. 4.
All refined pulps show a decrease in volume with centrifugation. The unrefined sample remains at a constant value ; this is due to the felting effect of unrefined fibers.

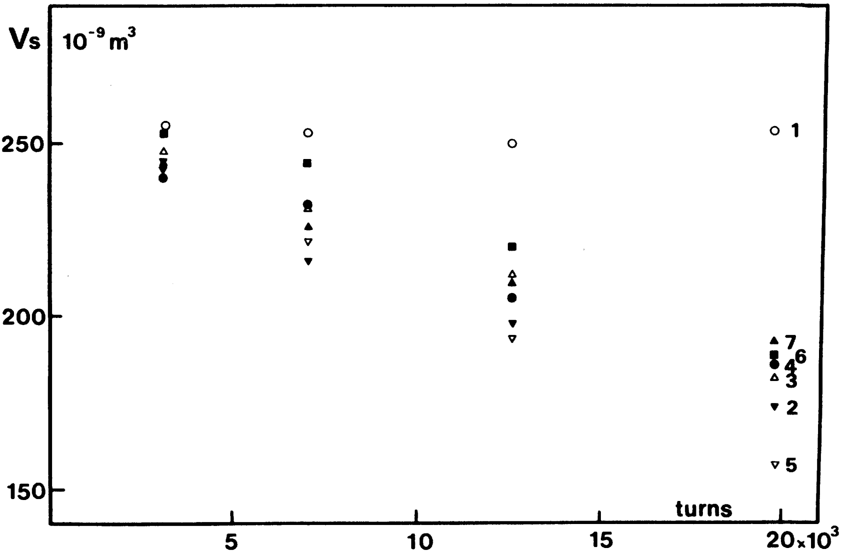

Fig. 4 : Variation of the volume of the sample (Vs) vs. centrifugation conditions represented as the product of time of centrifugation x speed of centrifugation. The numbers indicated beside the symbols refer to Table 1.

Dielectric measurements

The values of ϵ_s'' as a function of water content by volume are presented in fig. 5. This graphical representation shows little distinction amongst the different pulps. As a first approximation, we have assumed that the values of ϵ_s'' for each sample have a linear dependence upon water content and we have used a linear reression analysis to construct straight lines.

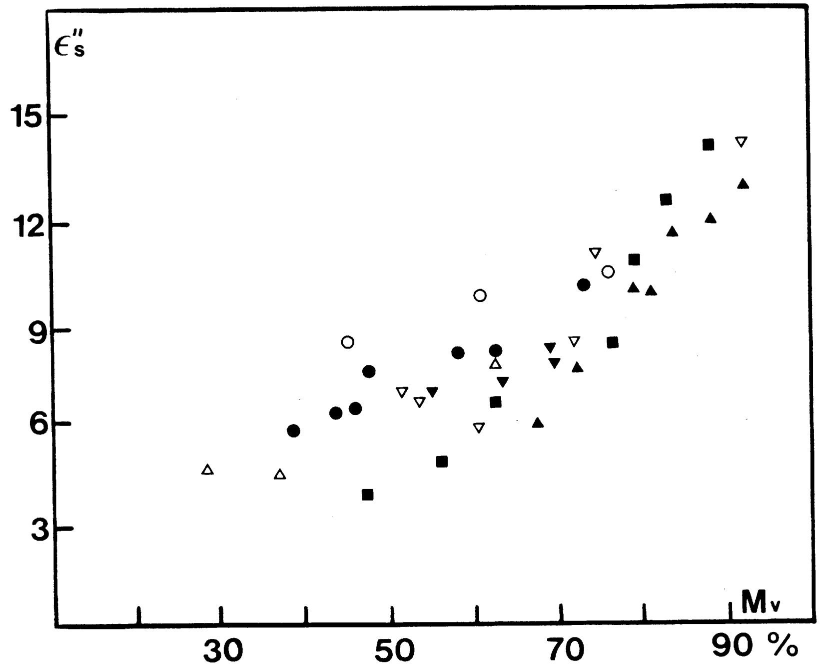

Fig. 5 : Variation of ϵ_s'' vs. moisture content (Mv in percent) indicated by volume of water divided by volume of wet sample.

As shown in fig. 6, where the lines have been spread along the y-axis for clarity, an increase in the degree of refining causes an increase in the slope of the line for the same range of water contents. The values of the slopes have been calculated (see Table 4).

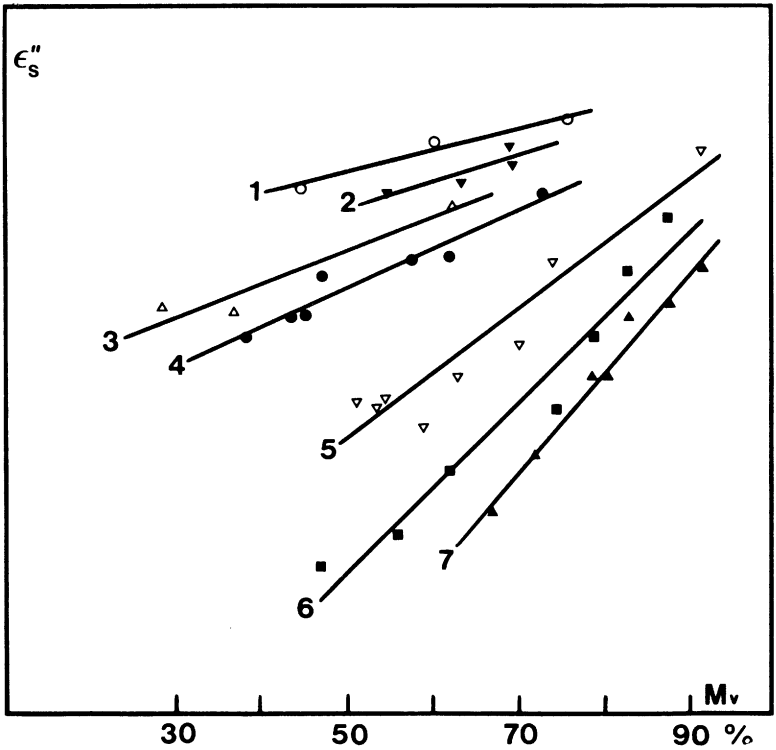

Fig. 6 : Variation of ϵ_s'' vs. moisture content : as in fig. 5, except that straight lines have been drawn using linear regression analysis. The lines have then been spread along the y-axis for clarity.

As first conclusion, we can say that the measurement of the dielectric losses of a pulp sample makes it possible to distinguish the refining degree of the pulp independently of its water content (in the range 40-90 % by volume).

Sample n.	1	2	3	4	5	6	7
Slopes	6,3	7,6	9,7	11,2	18,4	25,0	28,8

Table 4. Values of the slopes of ϵ_s'' vs. moisture content.

DISCUSSION

The analysis of the dielectric properties of a ternary mixture is not simple. We shall not enter here into the theory of the dielectric behaviour of mixtures of water, cellulose and air. We shall however propose a simple explanation for the decrease in the slopes of the lines, ϵ_s'' vs. water content. The three constituents of the sample contribute additively to its dielectric properties. The contribution of cellulose and air are however very low compared to that of water (ϵ'' cellulose $= 0,1$, ϵ'' air $\simeq 0,0$, ϵ'' free water $= 17$).

The slope of ϵ_s'' vs. water content for the unrefined pulp is lower than that for refined pulps. This means that for an unrefined pulp, a decrease in the water content from 80 % to 50 % for example, produces a smaller change in the dielectric properties of the pulp than the same water content decrease for a refined pulp. This phenomenon becomes more pronounced as the degree of refining increases. A high value of ϵ_s'' is indicative of water which is loosely bound or free to rotate. Therefore, since ϵ_s'' is decreasing, the water molecules must be becoming more tightly bound as refining proceeds.

Though this tendancy is evident from the values of the slopes calculated, we cannot ignore two deficiencies of this work :

i. The range of water content is not the same for each pulp : pulp number 3 for example has been studied from 30 to 60 % water by volume, whereas pulp number 7 has been studied from 70 to 90 %. A complete study would have required additional experimentation.

ii. A non linear analysis would probably have been a better approximation of the actual situation (see for example the experimental points obtained for pulp number 6), and would have allowed detailed calculation.

Two explanations of increased water binding with refining can be proposed :

i. Refining produces an increase in the specific area within the fiber wall. More cellulosic-hydroxyl groups are thus available for H-bonding with water molecules, and more water can be bound to cellulose. We must note, however, that B.E.T. measurements performed at 10 % moisture content (much lower than the range studied here), show no increase in specific area with beating (16).

ii. Refining causes an increased molecular mobility of short chain polysaccharides which are then able to bind more water molecules in their vicinity. This mechanism can be described as the partial solvation of polymers (21). It explains the "wet" or "slimy" feel that develops in a stock as it is beaten.
The movement of molecular segments is also accounted for by the diffusion theory of adhesion to explain interfibre bonding (22).

It is possible that these two mechanisms coexist.

CONCLUSION

This work has shown clearly that dielectric properties measurements allow us to distinguish between refined pulps. It is thus possible to quantify the degree of pulp refining or beating by an index of its dielectric properties. At the same water content (in the range 70-90 % by weight), the water present within the fiber wall has different properties depending on the degree of refining of the pulp. The refining produces an increase in the affinity between cellulose and water. The causes of this enhancement must be explained at the molecular level and this work does not allow us to give a definitive answer to this question.

The meticulousness required for sample preparation and measurement is a major drawback for the transposition of this methodology in mill laboratories.

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Transcription of Discussion

HYDRATION OF REFINED CHEMICAL PULPS STUDIED BY MICROWAVE SPECTROMETRY

P. Noe

Dr. N. Gurnagul, PPRIC

Would you expect the thickness of the perturbed layer to increase due to external fibrillation on the surface of the fibre?

Dr. P. Noe

I think this is not a phenomenon of simple external fibrillation, it goes further to a molecular level. External fibrillation has to do with fibrils being stripped out of a fibre - I think this is another level of explanation.

Dr. L.G. Odberg, STFI, Sweden

I prefer my explanation that it is mostly an area increase. I would like to point out that if you take bleached softwood fibres and beat them, then you get 10-20% increase of the absorbed water in the 20-90 RH area.If there is so little perturbation for the first layers it is hard to see why the water molecules further out should be more perturbed.

Dr. P. Noe

I think B.E.T is maybe too simple to explain how things occur. You can imagine that a short chain polysaccharide for example, is hydrated and in this case what would be the surface in terms of B.E.T?

Dr. L.G. Odberg

When we are in the 20-90% relative humidity area the pulps have less fibrils protruding from the surface, they must have more or less collapsed. But we should remember that you are working in a suspension -I have been working in the 20-90% humidity area.

J.F. Waterhouse, Institute of Paper Science & Technology, USA

One point of clarification - were your pulps once dried or never dried in these experiments?

Dr. P. Noe

Our pulps have been used as dry lap then refined and not re-dried.

J.F. Waterhouse

I wonder if the explanation here is in the drying because in the work that you quote of Hatakeyama's they did not find any change in the bound or non-freezing water with refining but Graminsky did some work a few years ago,(ACS Symposium). I am not sure if it was ever published, but he showed the same result that you did and it seems the result is mainly attributed to having the fibres once dried. Using a never dried fibre will not give you the change in non-freezing water with refining.

Dr. P. Kolseth, STFI

As I understand this you are measuring the dielectric constants on a pad that has been centrifuged and I would say that those pads are not homogeneous. How does this affect the analysis of their dielectric properties?

Dr. P. Noe

I do not know. Microwave measurements can be used to measure the fibre orientation and three works have been published on this subject. When dealing with fibre orientation influences the measurement, but in this case free water is the most important thing with a dielectric constant much higher than cellulose. It is not homogeneous, of course, but I do not think it influences the measurement.

Dr. P. Kolseth

May I then follow up with a question? In Figure 6 you have separated all the lines but if you look at Figure 5 they are all in a mess.

Dr. P. Noe

I agree.

Dr. P. Kolseth

If you have a non-homogeneous sample for the dielectric measurements, would it be the scatter between the samples that produces this scatter and should you not then draw a smooth curve of increasing loss with more water through all your data points?

Dr. P. Noe

This is a good question. There is something else in the experiments that means we cannot have absolute values for dielectric measurements and I don't know what it is.