

Development of a FTIR Spectroscopy for the Determination of Paper Strength

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ABSTRACT

Inter-fiber bonding is improved by refining resulting in higher Young's modulus. This effect is consistent to the changes of FTIR absorption intensities associated with the hydroxyl groups in the pulp samples. A PLS model, which is established to correlate the FTIR spectral data with the Young's modulus of the pulp samples for predicting the elastic Young's modulus of paper, is statistically robust.

INTRODUCTION

Paper is a network of wood fibers which are mainly composed of cellulose, hemicelluloses and lignin. Paper strength is governed by two factors: strength of individual fibers and inter-fiber bonding (Page, 1969). Paper products with high strength such as linerboards are often used for packaging. Because of their functions strength properties, such as tensile stiffness, ring crush and modulus of elasticity, are very important. These properties are associated with hydrogen bonds between fibers. The hydrogen bonds form when a hydroxylic group (OH) bonds to an electro-negative atom such as oxygen. The hydrogen bonding is usually a linear chain such as O-H...O, where "..." denotes the hydrogen bond and "-" a covalent bond. In cellulosic materials, the hydrogen bonds principally go from the primary hydroxyl groups on the sixth carbon atom, and join to the hydroxyls on the third carbon atom on an adjacent cellulose molecule. There are also two hydrogen bonds, between an OH(6) and the OH(2) in the neighboring pyranose ring, and from an OH(3) to the oxygen in the following pyranose ring (see Figure 1).

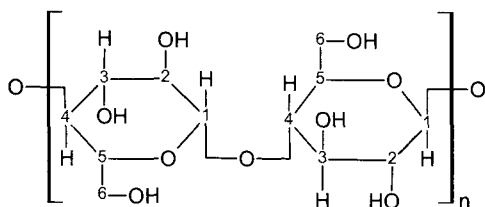


Fig.1. A chemical structure of cellulose

The mechanism of hydrogen bonding results in the attraction of water to the hydroxyls of cellulose molecules. Caulfield (1978) proposed that the water between two cellulosic surfaces forms hydrogen-bonded chains through the interface. As water is removed from the wet web, the surface tension of water draws fibers together. The chains become shorter, and the hydroxyl groups on

the fiber surfaces come into contact to form direct hydrogen bonds.

In the wet state, cellulose fibrils are more flexible and more hydrogen bonds can be easily formed than in a dry state. The ultimate determinant of consolidation of the wet web is the formation of hydrogen bonds between the surfaces of cellulose fibers, fibrils and fragments after they have been brought close enough together by earlier influences (wet pressing and surface tension). This bonding firmly joins together the component parts of the sheet resulting in the sudden transformation on the paper machine of an extremely weak web into a firm, hard strong sheet of paper. The mechanical properties of the fibers in a paper sheet are therefore related to the presence of hydrogen bonds. Robertson (1966) identified the onset and development of hydrogen bonding at approximately 50% solids content at which the elastic modulus of paper starts to increase rapidly during drying.

Carboxylic groups already present in the fiber wall or created during the impregnation, pulping or bleaching operations are also components of hydrogen bonding. Carboxylic groups promote fiber swelling and contribute to improved flexibility and conformability of the fiber wall. High contents of carboxylic acid groups on fiber surfaces may also increase inter-fiber bond strength. The swelling of pulp fibers always takes place inwards into the lumen because external swelling is restricted by the presence of the outer secondary wall and primary wall. It is only when the outer secondary wall or the primary wall has been removed that the pulp can show external swelling.

Refining, or beating, delaminates fiber wall and, if excessively degree of refining is applied fibers could be cut to form fines. The delamination exposes the carboxylic groups in the fiber wall and increases the swelling degree, flexibility and conformability of wet

fiber. Fines to some extent help link the two fiber surfaces more closely together in the wet state improving sheet consolidation and bond formation because they have a large specific surface area. In practice the effect of refining is essential for improving the contact areas and bonding between fibers, and hence the Young's modulus. In the paper mills, the freeness or Schopper-Rieghler of pulps is often measured to control refining.

Previous studies (Ellis and Bath, 1940; Marrinan and Mann, 1956) on hydrogen bonding of cellulosic fibers by FTIR spectroscopy were reported but there was no intention to formulate a reliable predictive model for the paper strength. The objective of this work is to collect FTIR spectra of refined pulps and use these spectra to study the development the tensile stiffness of the pulps at different refining levels.

EXPERIMENTAL METHODS

A high yield softwood kraft pulp processed in a paper mill with the Kappa 95 was collected after the wash press. The pulp was diluted with deionized water to make up a total of 23 litres with consistency of 1.6%. The pulp slurry was beaten using a Valley beater at room temperature. Different beaten pulp samples were withdrawn after checking the pulp freeness. Two round handsheets (diameter = 15 cm) of 40 and 120gsm were made for each beaten pulp sample. Thick handsheets were gently pressed at a pressure of 2 bars to further remove water and consolidate the sheets. All samples were stored in a conditioned room maintained at 23°C and 50% relative humidity for two days before being tested.

Infra-red transmission spectra of the thin handsheets were obtained using a PerkinElmer FTIR spectrometer (GX model). The spectra were recorded in absorbance units. Each sample was scanned 8 times at 4 cm⁻¹ resolution and scan interval of 1 cm⁻¹ and the average spectrum was

accounted. All handsheets were cut into 15 mm wide by 10 cm long strips, and the Young's modulus was measured by an Instron (5566 model). All tests were carried out in the conditioned room. A standard load was applied to the strip at a constant speed of 10 mm per minute until the sample snapped off. From the stress versus strain curve, the Young's modulus was then computed in the load range of 4–20N.

The obtained spectra are correlated with the measured Young's modulus using Spectrum Quant+™ program. The method provided by the program is based on Partial-Least-Squares (PLS1). This technique involved two steps. The first step, which was known as calibration or model construction, identified the Principal Components of the spectra obtained from the standard samples. The Principal Components were abstract spectra that contained features accounting for the most spectral variance in the data set and were independent of the others. The second step involves the validation of the model using samples that were not used in the calibration.

RESULTS AND DISCUSSION

The hydrogen bonds exist in both fiber wall and on surface of refined fibers. However, only hydrogen bonds between surfaces of fibers are directly responsible to the tensile strength of paper.

In this study the obtained FTIR spectra of refined pulp samples are recorded and some are shown in Figure 2. These spectra show significant effects of refining on the absorption intensity at 3346, 2902, 1161, 1109 and 1041 cm⁻¹. The band at 2902 cm⁻¹ is corresponding to C-H stretching, and the rest are associated with the O-H absorption. As the refining level is increased, it is anticipated that more hydroxyl groups in fibers are exposed and so the absorption intensity of the O-H groups.

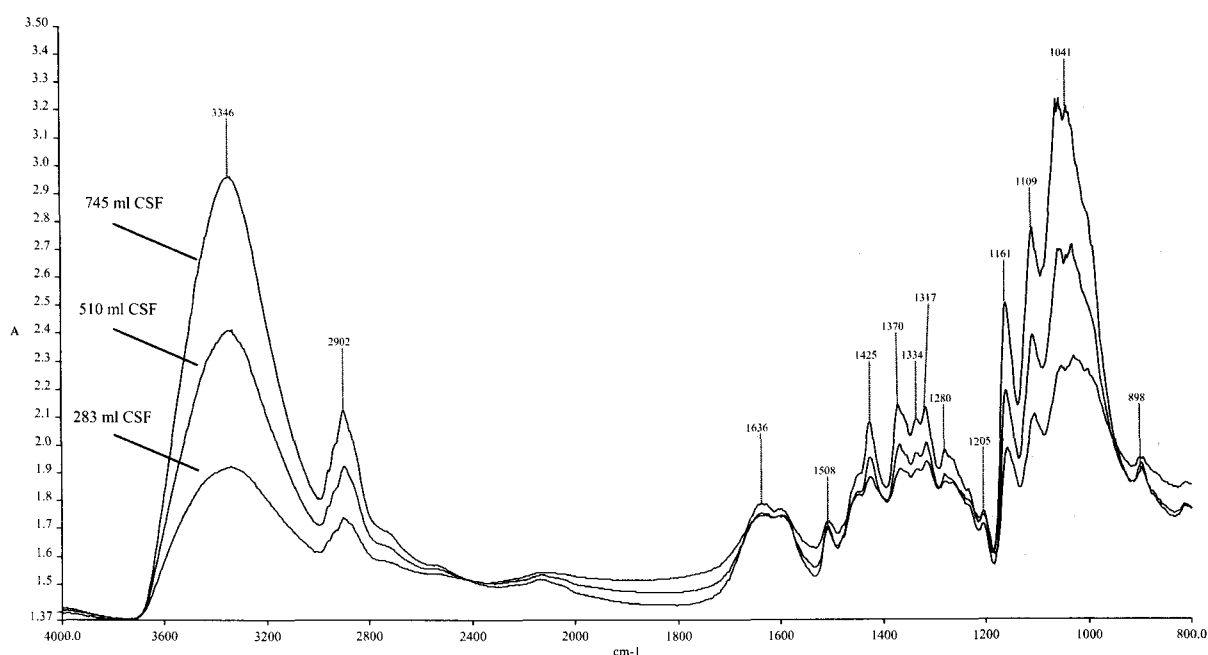


Fig.2: FTIR transmission spectra of kraft pulp beaten at different levels.

We are also interested in the presence of the carboxylic groups, which are highly relevant to fiber-fiber bonding. However, the absorption intensity of the carboxylic group at 1725-1700 cm^{-1} range is not evident in our spectra. The absence of this characteristic band could be due to the low concentration of this group in the pulp samples.

The Young's modulus of the 120 gsm handsheets was measured and summarized in Table 1. It was evident that the Young's modulus increases with the degree of refining, consistent with the development of additional hydrogen bonding sites as shown by the FTIR spectra.

Sample id	Freeness (ml)	E (MPa)
X0	745 \pm 5	533 \pm 40
X1	705 \pm 5	1086 \pm 70
X2	654 \pm 5	1530 \pm 60
X3	577 \pm 5	2009 \pm 110
X4	510 \pm 5	2276 \pm 60
X5	447 \pm 5	2341 \pm 100
X6	347 \pm 5	2527 \pm 100
X7	312 \pm 5	3265 \pm 130
X8	283 \pm 5	3391 \pm 150

Table 1: Elastic Young's modulus of kraft pulps with different freeness

In order to formulate a PLS model to correlate the spectral data with the Young's modulus five random samples from Table 1 were used. The calibration was performed using the absorption regions where the hydroxylic groups were identified, typically regions of 3700-2800 cm^{-1} and 1180-920 cm^{-1} . The PLS1 analysis basically sorted out the spectral data which relate to the elastic Young's modulus of

paper and then put them in a form of linear matrix equation. The coefficients of the matrix equation were determined by optimizing the x and y-variances. The x-variance shows the cumulative amount of spectral variance as a percentage of total and the y-variance shows the cumulative amount of property variance (Young's modulus) as a percentage of total. The PLS1 analysis resulted in two principal components which contain most spectral data relating to the strength property of paper. These components can explain about 99.9% of the variance in X-matrix and 96.8% of the variance in Y-matrix. The calibration as shown in Figure 3 shows a nearly perfect agreement between the spectral data of the calibration samples and the Young's modulus.

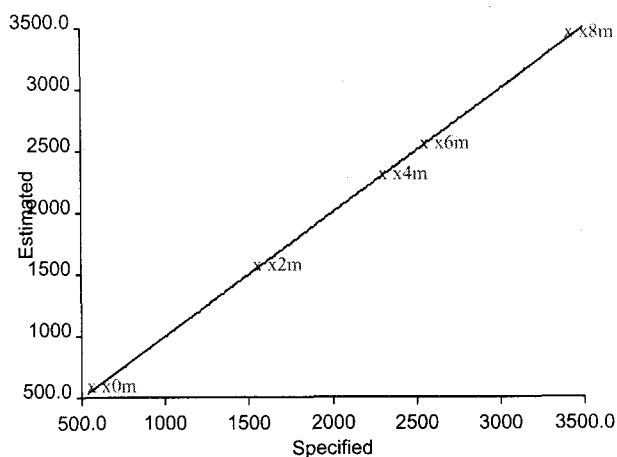


Fig. 3. PLS1 analysis, Estimated vs Specified Young's modulus of paper

The PLS model accuracy was then tested using four additional refined kraft pulp samples. The comparison of the predicted values and the measured Young's modulus, as shown in Figure 4, has a regression coefficient of 99%, confirming the accurate predictability of the model.

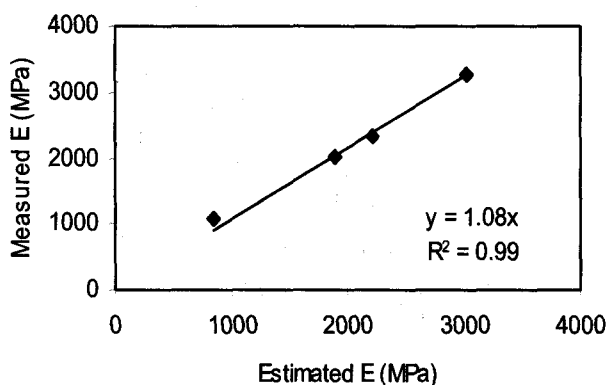


Fig. 4. Comparison between the Young's modulus values obtained from Instron measurement and predictive model.

CONCLUSION

This work reveals the effect of refining on Young's modulus of a high-yield Lo-Solids™ kraft pulp. The results suggest that interfiber bonding is improved by refining, resulting in higher Young's modulus. This effect is consistent to the increasing trend of the absorption intensity of the FTIR spectra associated with the hydroxylic groups in the pulp samples. A robust PLS model can be established to correlate the FTIR spectral data with the Young's modulus of the pulp samples, for predicting the elastic Young's modulus of paper.

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