

Effect of Chitosan Addition on the Surface Properties of Kenaf (*Hibiscus cannabinus*) Paper

Alireza Ashori*, Warwick D. Raverty¹, and Jalaluddin Harun²

Iranian Research Organization for Science and Technology (IROST), P.O.Box 15815-3538, Tehran, Iran

¹Commonwealth Scientific and Industrial Research Organization (CSIRO),

Private Bag 10, Clayton South, VIC 3169, Australia

²Institute of Advanced Technology, University of Putra Malaysia (UPM), 43400 Serdang, Selangor D.E., Malaysia

(Received December 10, 2004; Revised May 16, 2005; Accepted May 26, 2005)

Abstract: The present paper studies the effect of chitosan, cationic starch and polyvinyl alcohol (PVA) as sizing agents to enhance surface properties of kenaf paper. The polymers were incorporated into the sheets by spray application. The results clearly showed that the addition of chitosan to a sheet formed from beaten fibers had excellent improvement in surface properties, compared to the effect of other additives. Sizing quality of cationic starch fairly matched with the sizing quality of chitosan, however, it was able to reduce the water absorption potential of paper more than chitosan at a same concentration. In most other properties, particularly the most important property for printing papers, surface smoothness, chitosan-sized papers are superior to the paper sized with cationic starch or PVA.

Keywords: Chitosan, Surface properties, Handsheet, Kenaf, Paper, Film-forming, Papermaking

Introduction

Papermaking fibers as they come from the pulp mill require additional processing prior to being made into paper. This processing, called "stock preparation", consists of mechanical treatment (beating/refining), and the inclusion of a variety of chemical additives intended to alleviate potential processing problems, or to impart improved strength or surface properties. Modification of the fiber properties is the primary reason for using polymeric paper additives. These materials bond well to the fiber surfaces and are capable of bridging inter-fiber distances, thereby establishing bonds between fibers and fibrils that would not have otherwise formed.

Many synthetic chemical additives are used in paper manufacture to improve or enhance the strength and printability of paper. A number of these synthetic additives are non-biodegradable and may cause environmental problems and some pose occupational health and safety risks to paper industry workers [1]. Many of the problems posed by use of synthetic chemical additives may be overcome through the use of biopolymers. Many biopolymers are biodegradable, non-toxic and environmentally more benign than their synthetic counterparts, so there is a trend to use these materials where possible in papermaking [1,2]. Chitosan is a chemically modified biopolymer (derived from the shells of certain crustaceans) that has shown potential to improve both the strength and the printing properties of papers based on wood fiber [2-5]. No investigations have been published on the use of chitosan, to improve the surface properties of paper made from kenaf (*Hibiscus cannabinus*) fibers.

This paper reviews the laboratory work to investigate the surface properties of handsheets by applying chitosan as a sizing agent at various concentrations during sheet formation. Sizing potential of chitosan was compared with two most widely used sizing agents, polyvinyl alcohol (PVA) and cationic starch, in order to highlight the advantages and drawbacks of chitosan as a sizing agent.

Experimental

Materials

Bleached kenaf kraft pulp (BKKP) was used after PFI mill beating. High-molecular weight chitosan was a Vanson product (USA), a material with 85.4 % deacetylation, and molecular weight of 9×10^5 g/mol. The cationic starch used in this study was made from tapioca and was obtained from National Starch and Chemical Co. It contained about 17 % amylose and 83 % amylopectin and had a degree of substitution of 0.036. PVA is available as a white granular solid that can be dissolved in hot water. Fully hydrolyzed (98.4 %) PVA with molecular weight of 0.43×10^5 g/mol was used in this experiment.

Methodology

In this work, the chitosan solution was prepared by dissolving in 1 % acetic acid at room temperature by stirring for 6 h (the pH was adjusted with 3 % NaOH to pH 5), whereas the PVA was prepared by dissolving in distilled water and heating on a hot plate with a magnetic stirrer at 95-100 °C for 20-25 min. The cationic starch was prepared by suspending of starch powder in distilled water and heating to 95 °C on a water bath with periodic stirring and then holding the suspension at this temperature for 25-30 min after the onset

*Corresponding author: ashori_a@yahoo.com

of gelatinization. The solutions were then diluted with distilled water, and refrigerated prior to use. Different dosage solutions of polymers were sprayed onto a preformed (untreated) handsheet, just after it was removed from the sheetmold. At this point the sheet contains about 30 % fiber and 70 % water, which allows rapid and uniform distribution of sprayed polymer within the wet fiber web. In order to simplify the experiment no other additions, such as alum and AKD, were added to the slurry.

Determination of Surface Properties

Properties of paper surface were determined following TAPPI Test Methods [6] and TAPPI Useful Methods [7]. The brightness of handsheets was measured using a Technibrite Micro TB-1 instrument (using a 457 nm filter to remove any influence arising from fluorescence) according to T 452 om-98. Roughness was measured using Bendtsen UM535 method. Air resistance of paper was determined according to T 460 om-02 (Gurley method). Water absorption capacity of paper was determined using the Cobb Test, T 441 om-98. Oil absorption of surface was determined according to Dutch Standard NEN 1836 using an IGT printability tester, model AIC2-5. Surface strength of sized paper was determined using the Dennison wax pick test according to T459 om-99. The film forming characteristics of papers sized with polymers were investigated at 10-15 sample areas using a Scanning

Electron Microscope (SEM, model JSM-6400, JEOL). The retention of chitosan on paper was analyzed using the Kjeldahl method. The retention was calculated from the difference between the nitrogen content determined in the chitosan-sized paper and the corresponding value obtained using paper without chitosan. Oil absorption of surface was determined according to Dutch Standard NEN 1836 using an IGT printability tester, model AIC2-5. Because of the option of improving the smoothness of the laboratory-made papers by calendering (a process used for this purpose on almost all commercially-made printing papers), only the smoother (glazed) side of each laboratory-made sample was tested for surface properties.

Results and Discussion

Effect of Chitosan Addition on Surface Properties of Paper

One property of chitosan is its ability to form films that improve the surface properties of paper when it is applied to the surface of the sheet [8]. At the outset of this study, it was considered that its film forming capacity should be influenced either by concentration, or by technique of addition. The chitosan was prepared in solutions with different concentrations and applied to the papers with constant volumes. The film forming characteristics of the papers were then investigated using

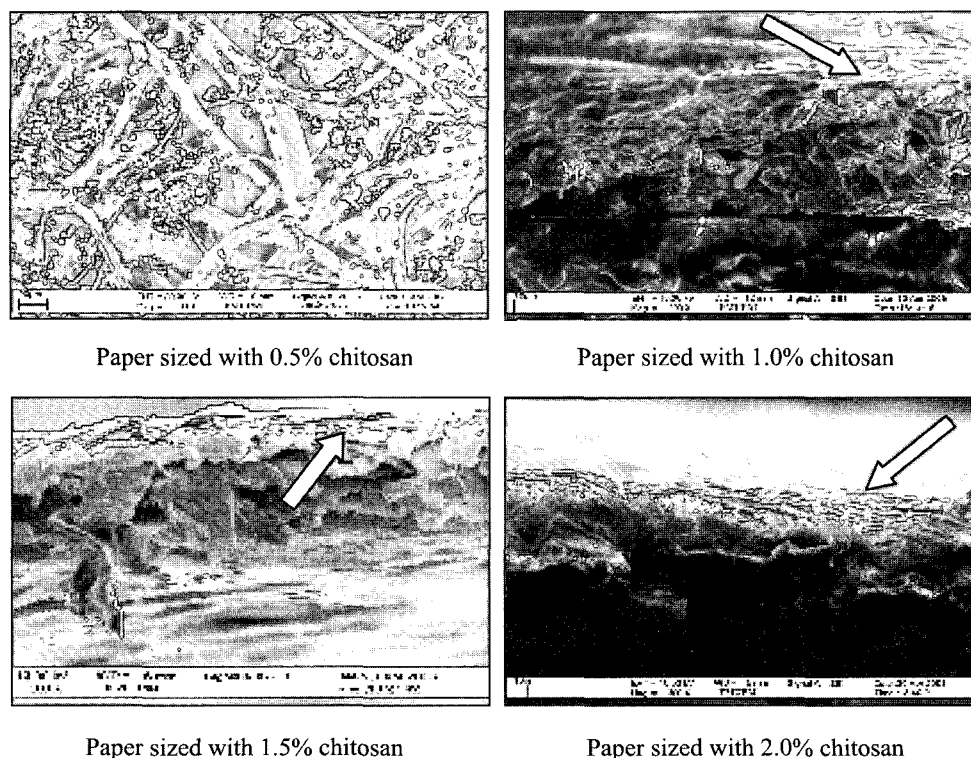


Figure 1. Film forming potential of chitosan at different concentrations. Arrows show the lighter regions on the surface of the fiber which are attributable to chitosan film formation.

SEM. Figure 1 demonstrates the film forming potential of chitosan when the spray technique was used at the concentration of 0.5-2 %.

At the concentration of 0.5 %, chitosan was unable to develop any film on the paper surface. At lower concentrations chitosan migrates into the paper bulk due to its lower viscosity [1]. However, at 1 % or higher concentration, chitosan was able to form a film on the paper surface. Comparison of the control (unsized) paper with chitosan-sized paper indicates that chitosan concentration influences its film forming potential. Wieczorek and Mucha [9] and Lertsutthiwong *et al.* [2] reported similar observations. Higher chitosan concentration results in better film forming through the higher viscosity of its aqueous solutions.

Table 1 shows the properties of paper sized with chitosan. Brightness and opacity are very important parameters for printing paper. Addition of chitosan reduced brightness a little (0.4-1 %) and increased the opacity, but the changes were not significant.

One of the most important properties of paper is an ability to control the penetration of various liquids, particularly those based on water [10]. The water absorption (C_{60}) results for the control and the paper sized with low (0.5-1 %) concentrations of chitosan could not be obtained, i.e. the water penetrated the paper too quickly for a meaningful measurement to be made. However, the observation indicates that higher (beyond 1 %) concentrations of chitosan could reduce (29 %) water absorption of sized paper. A reduction in water absorption may provide more appropriate absorbency characteristics in paper for improving printability.

Porosity is one of the most important factors which influence the absorption of ink vehicles. Ink vehicles are drawn into the pores and inter-fiber spaces of paper by capillary action. Coated papers provide higher and better-controlled ink holdout than uncoated papers because of their lower porosities (as paper becomes less porous, the air resistance readings increase when measured by the Gurley method) of their coatings [11]. Air resistance of the sized paper with 2 % chitosan increased approximately 46 %. If air resistance is indicative of porosity, this result suggests that either the numbers of pores in the paper are reduced, or their sizes are diminished.

Paper roughness (or its inverse, the surface smoothness) is commonly considered as one of the properties of paper that has an influence on its printability [12]. As shown in Table 1, the roughness values (Bendtsen) of chitosan sized papers decreased considerably compared to control sheets and the improvement is greater than that achieved with PVA, or cationic starch. The corresponding increase in smoothness is probably attributed to the continuous film on the surface of paper sized with 2 % chitosan.

Surface strength is also very important for quality printing. Surface sizing can cement the surface fibers, fines and fillers to the body of the sheet and improve the scuffing resistance and "linting" (removal of partially or poorly bonded fibers from uncoated paper surfaces during printing) of the paper surface in the course of printing [1]. Surface strength increased nearly 4 points on the wax pick scale (a very significant increase in printing terms) after applying 2 % chitosan.

In Table 1, it is shown that chitosan made the paper more resistant to oily materials. The control sheet gives a high oil absorption stain length, which is consistent with its greater roughness. The chitosan-sizing reduced the oil absorption of kenaf papers by about 14 %, which is higher than the values of PVA or cationic starch. The reduction in oil absorption indicates that sizing reduces the paper porosity. The data agree well with the air resistance results. Lertsutthiwong *et al.* [2] also reported that film-forming polymers laminate the voids in the fiber network of paper, resulting in a reduction in paper porosity and lower oil absorption or penetration.

The data demonstrate that the concentration of the chitosan solution used does in fact influence film forming characteristics and other surface properties of the kenaf paper as well. According to Lertsutthiwong *et al.* [1], another important parameter that should be influenced by chitosan concentration is the size pickup in the course of sizing. This is expected to be the case due to the correlation of chitosan concentration with the viscosity, which is in turn expected to influence the size pickup volume. A possible explanation for the chitosan pickup might relate to the rheology and character of the chitosan solution. Starch and PVA have low viscosity and can penetrate fibers quickly, whereas chitosan is very viscous and might stay more at the surface of paper during

Table 1. Effect of chitosan on surface properties of kenaf paper

Parameters	Concentrations				
	0 %	0.5 %	1 %	1.5 %	2 %
ISO brightness (%)	88.4 ± 0.6	88.6 ± 0.3	88.0 ± 0.2	87.4 ± 0.3	87.5 ± 0.1
Opacity (%)	82.5 ± 0.4	82.8 ± 0.2	83.3 ± 0.1	84.5 ± 0.2	90.7 ± 0.2
Bendtsen (ml/min)	56 ± 13	64 ± 9	39 ± 8	35.4 ± 10	29 ± 5
Air resistance (s/100 ml of air)	720 ± 3	850 ± 4	880 ± 4	924 ± 7	1049 ± 6
Water absorption (g/m ²) [†]	—	—	—	29.5 ± 0.6	28.4 ± 0.3
Surface strength (wax pick test)	12A	13A	14A	16A	16A
Oil stain length (mm)	80 ± 2	77 ± 1	73 ± 0.5	69 ± 1.5	69 ± 1

[†]Chitosan could not improve water absorption property at lower concentrations.

drying. On this basis chitosan pickup may be expected to be relatively low and film formation will be favored [1].

Effect of Cationic Starch Addition on Surface Properties of Paper

Cationic starch has been widely used for sizing and coating because of its good strength, stability and tendency to bind strongly to cellulosic fibers. SEM photomicrographs showed that cationic starch behaved similarly to PVA in the concentration range of 0.5-1.5 %. At 2 % concentration, however, in contrast to PVA it formed a uniform film over the surface of the paper (Figure 2).

Table 2 shows that cationic starch changed all of the paper properties significantly. For example, at 2 % concentration the surface strength and resistance to water absorption increased to a greater extent compared to the paper sized with 2 % chitosan or 2 % PVA. The surface roughness (Bendtsen) of the paper sized with 2 % cationic starch was, however, 21 % higher than the roughness of paper treated with PVA. On average, air resistance was also higher for cationic starch-sized paper compared to PVA-sized paper. Surface strengths of cationic starch sized papers were higher for all concentrations compared with PVA- and chitosan-sized papers.

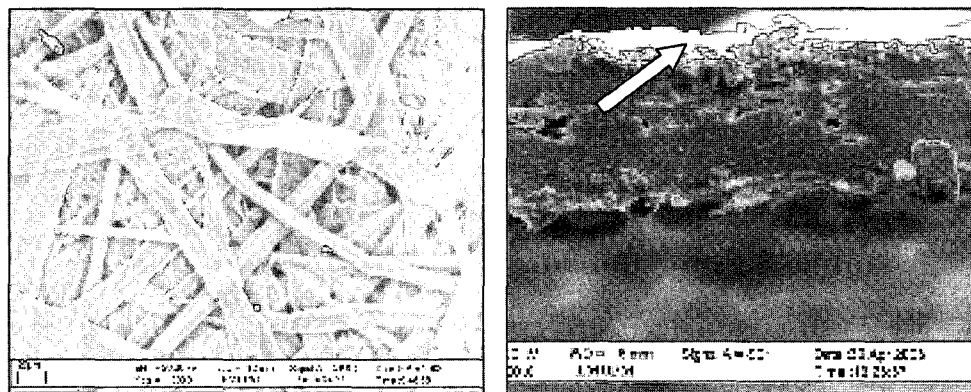
The adsorption of cationic starch, and indeed cationic

polymers in general, is influenced by a wide range of factors. These include fiber factors such as surface area and surface charge [13]; polymer factors such as charge density, molecular weight and conformation; and furnish factors such as pH, ionic strength, temperature, anionic trash etc. All of these factors influence the degree of electrostatic attraction in some way, and hence the adsorption of cationic starch.

The main driving force for adsorption of cationic polymers on to paper fibers is the electrostatic attraction. The mechanism of adsorption is generally accepted to be an ionic bond between the carboxylate groups of the fiber and the cationic groups of the polymer. However, some researchers have disputed this hypothesis, finding no correlation between the carboxylate content of the fibers and the levels of adsorption. In the case of cationic starch, other adsorptive forces such as H-bonding are also thought to be operated [13].

Effect of PVA Addition on Surface Properties of Paper

PVA is a sizing agent of choice due to its excellent bonding strength and ability to enhance brightness. The PVA-sized paper did not develop a film at any concentration up to 2 %. As mentioned earlier, PVA has low viscosity and tends to penetrate into paper fibers rapidly. Lertsutthiwong *et al.* [2] also observed that PVA did not form a film at 2 % concen-



Paper sized with 1.5% chitosan

Paper sized with 2.0% chitosan

Figure 2. Film forming potential of cationic starch at different concentrations. Arrow shows the lighter regions on the surface of the fiber which are attributable to cationic starch film formation.

Table 2. Effect of cationic starch on surface properties of kenaf paper

Parameters	Concentrations				
	0 %	0.5 %	1 %	1.5 %	2 %
ISO brightness (%)	88.4 ± 0.6	88.9 ± 0.1	89.2 ± 0.2	89.7 ± 0.2	89.5 ± 0.3
Opacity (%)	82.5 ± 0.4	81.0 ± 0.1	80.7 ± 0.1	80.9 ± 0.2	79.5 ± 0.1
Bendtsen (ml/min)	56 ± 13	65 ± 10	79 ± 11	99 ± 10	107 ± 10
Air resistance (s/100 ml of air)	720 ± 3	869 ± 3	886 ± 5	890 ± 3	954 ± 4
Water absorption (g/m ²)	—	26.7 ± 0.8	24.8 ± 0.7	23.2 ± 0.9	21.6 ± 0.4
Surface strength (wax pick test)	12A	14A	16A	16A	18A
Oil stain length (mm)	80 ± 2	81 ± 1	78 ± 0.5	77 ± 1	75 ± 1

tration, but at 10 % concentration (a concentration that is probably not economically justifiable in the great majority of commercial papermaking operations), it was able to make a uniform film over the surface of paper.

Air resistances of papers sized with 0.5 % and 1 % PVA were almost 6-12 % lower than the control (Table 3). This is opposite to our earlier observation concerning chitosan- and cationic starch-sized papers, possibly because the majority of PVA penetrated into the fibers and did not reduce the size of the pores in the paper web. The roughness (Bendtsen) increased about 20 % at 2 % concentration. PVA-sizing showed no change in the resistance to water absorption compared to the unsized control. This high water absorption of PVA-sized paper is a considerable drawback in practical terms because higher water uptake can induce linting in offset printing papers [2]. The surface strength of PVA-sized papers (as measured by wax pick) increased marginally, but to a much smaller degree than the case with cationic starch- and chitosan-sized papers.

From a practical perspective, the surface properties of the PVA-sized paper were slightly inferior to the paper sized with either chitosan or cationic starch. The results indicate that PVA is unable to enhance most surface properties significantly, such as water absorption, air resistance, smoothness, and opacity.

Effect of Chitosan as an Additive in Surface Sizing

Retulainen *et al.* [14] stated that the mechanical properties of paper depend on inter-fiber bonding, and so it is most probable that chitosan exerts its beneficial effects on paper by increasing the inter-fiber bond strengths. The structural configuration of chitosan might explain some differences in performance when compared with PVA and cationic starch. The chemical structures of chitosan and PVA are linear polymer chains, while starch is composed of amylopectin, which is branched. Starch has α -linkage, which causes it to take helical form, while chitosan has β -linkage, which translates it into straight molecular chains. These chains are more conformable, which facilitates accessibility of their functional groups for bonding to a cellulose surface. Furthermore, both chitosan and cationic starch possess amino or ammonium

groups, which give a strong cationic character to chitosan and cationic starch, while PVA does not contain this functionality. PVA is nonionic in character. Possibly the reduction in rate of water absorption for chitosan-sized paper can be explained by the fact that its solutions have high viscosity which slows the rate of penetration of further water through the chitosan coating film once the surface becomes wet. Another advantage of the use of chitosan as a sizing agent identified by Lertsutthiwong *et al.* [1] is the fact that it remains attached to the fibers in the papermaking process and so reduces the biochemical oxygen demand (BOD) load in the effluent in contrast to starch, much of which detaches from the fiber and so creates additional BOD load.

Cellulosic fibers and chitosan form a compatible fiber-binder system. Due to their chemical similarity, they readily form hydrogen bond to one another. Lertsutthiwong *et al.* [1] reported that the hydrogen bonding between solid surfaces is restricted to a few hydrogen bonds due to the difficulty of achieving the required geometry (i.e. separation of less than 0.1 nm). The authors concluded that forming a film between fiber crossings by polymers could overcome this problem and lead to strong bonds by 'welding' the surfaces together. The hydroxyl groups of chitosan have the potential to form hydrogen bonds with weakly polar areas of fiber surfaces,

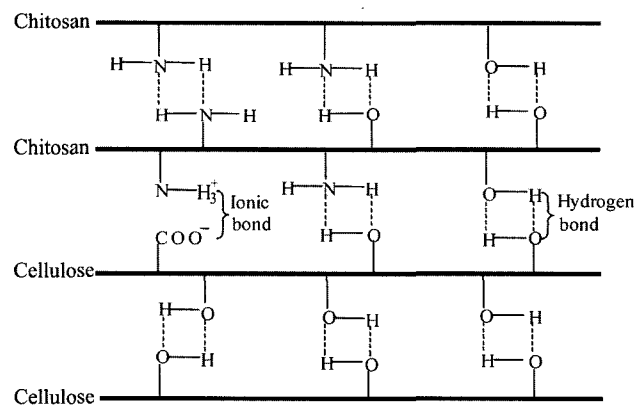


Figure 3. Idealized representation of bond formation in the cellulosic fiber-chitosan bonding system.

Table 3. Effect of PVA on surface properties of kenaf paper

Parameters	Concentrations				
	0 %	0.5 %	1 %	1.5 %	2 %
ISO brightness (%)	88.4 ± 0.6	88.5 ± 0.1	89.3 ± 0.2	90.2 ± 0.3	90.6 ± 0.3
Opacity (%)	82.5 ± 0.4	81.2 ± 0.1	80.4 ± 0.1	79.7 ± 0.1	78.9 ± 0.1
Bendtsen (ml/min)	56 ± 13	53 ± 8	47 ± 7	41 ± 7	45 ± 8
Air resistance (s/100 ml of air)	720 ± 3	640 ± 01	682 ± 2	797 ± 1	875 ± 2
Water absorption (g/m ²) [†]	—	—	—	—	—
Surface strength (wax pick test)	12A	12A	13A	13A	14A
Oil stain length (mm)	80 ± 2	80 ± 0.5	79 ± 1	79 ± 1	78 ± 2

[†]PVA could not improve water absorption property and the results were failed.

therefore contributing to paper strength development if the fibers come sufficiently close in order to meet the required geometry conditions. Therefore, the film-forming potential of chitosan not only facilitates the formation of van der Waals forces between the fibers, but also provides suitable conditions for hydrogen bonds to occur. Figure 3 is an idealized representation of the cellulosic fiber-chitosan system, showing the bonding between two cellulose molecules and two chitosan molecules.

Conclusion

The object of this study was to improve surface properties of BKPP using three polymer additives, particularly the naturally-derived polymer chitosan. Chitosan solubilized with acetic acid, and hence in the form of the acetate salt, was incorporated into the sheets using spray application. The film formation of chitosan, cationic starch and PVA on the surface of fiber networks was found to be different. Comparing chitosan, cationic starch and PVA at the same concentration, papers sized with chitosan produced the best surface properties, with exception of resistance to water absorption (Cobb Test). The most probable reason for the superior performance of chitosan is its ability to make electrostatic (ionic) bonds with the anionic charges of the fibers, networks [15], and also the high viscosity of its solutions in water [2].

The overall conclusion is that chitosan is recommended as an additive in conventional surface sizing to enhance surface properties for printing kenaf paper.

References

1. P. Lertsutthiwong, S. Chandkrachang, M. M. Nazhad, and

- W. F. Stevens, *Appita J.*, **55**(3), 208 (2002).
2. P. Lertsutthiwong, M. M. Nazhad, S. Chandkrachang, and W. F. Stevens, *Appita J.*, **57**(4), 274 (2004).
3. M. Nishiyama, *Annals of the High Performance Paper Society, Japan*, No. 23, 11 (1983).
4. G. G. Allan, J. P. Carroll, Y. Hirabayashi, M. Muvundamina, and J. G. Winterowd, *Material Research Society Symposium Proceedings*, **197**, 239 (1990).
5. M. Laleg, "Proceedings 87th Pulp and Paper Technical Association of Canada, Annual Meeting - Technical Section", pp. C67-C75, 2001.
6. "TAPPI Test Methods", Tappi Press, Atlanta, GA, 2002.
7. "TAPPI Useful Methods", Tappi Press, Atlanta, GA, 1991.
8. P. Jenvanitpanjakul and S. Shinagawa, *J. of Porous Materials*, **6**(3), 239 (1999).
9. A. Wiczorek and M. Mucha in "Proceedings of International Conference on Chitin and Chitosan Euch'i's 97", (A. Domard, G. A. F. Roberts, and K. M. Vårn Eds.), pp.890-896, Lyon, France, 1997.
10. F. J. Micale, S. Iwasa, and J. Lavelle, "Proceedings of 41st TAGA (Orlando)", pp.309-329, 1989.
11. W. H. Bureau, "Graphic Arts Technical Foundation (GATF)", pp.44-139, Sewickley, PA, 1989.
12. J. S. Pellinen and M. Luukkala, *Sensors and Actuators A*, **A49**, 37 (1995).
13. S. Malton, K. Kuys, I. Parker, and N. Vanderhoek, *Proceedings of 51st Appita Annual General Conference*, **1**, 37 (1997).
14. E. Retulainen and I. Nurminen, *Paperi ja Puu-Paper and Timber.*, **75**, 499 (1993).
15. M. Laleg and I. I. Pikulik, *Nordic Pulp and Paper Research Journal*, **6**(3), 99 (1991).