CHITOSAN AN EFFECTIVE SURFACE SIZING AGENT IN PAPERMAKING PROCESSING

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Abstract

The present paper studies the effect of biopolymer chitosan as a sizing agent to improve printability properties of kenaf handsheets. Sizing potential of chitosan was compared with two most widely used sizing agents, polyvinyl alcohol and cationic starch, in order to highlight the advantages and drawbacks of chitosan. The polymers were incorporated into the sheets by spray application. This study clearly demonstrated that the use of chitosan could improve the printability and print quality of kenaf paper in terms of water and oil absorption, ink penetration, print density, gloss and surface roughness for offset printing.

Key words: sizing, pulp, chitin, strength properties, topography, ink penetration

Introduction

Among the many properties of paper, one of the most important, is its ability to control the penetration of various liquids, particularly those based on water (Micale et al. 1989). Paper surface chemistry influences the water absorption properties of paper and interactions between a paper surface and a printing ink (ink setting). In other words, surface energy is a property that determines how the liquid phase and the solid phase react with each other. Processes those impact resistances to liquid penetration in paper are called sizing processes. There are two types of such processes; internal sizing and surface sizing. Internal sizing consists of mixing the sizing agent with the fibrous furnish and forming the entire mass into a sheet containing a relatively uniform distribution of fibers and sizing agent.

Surface sizing differs from internal sizing in that the sizing agent is applied to the surface of the paper where it cements the fibers to the body of the paper and deposits a more or less continuous film on the paper surface. The advantage of surface sizing in the case of writing and printing papers is that a film is produced on the surface of the paper that will not catch the pen when the paper is written on and will not pick if the paper is printed with tacky inks. Surface sizing is oftentimes more important than internal sizing for writing papers, printing papers, and certain grades of wrapping papers. Surface sizing is usually done in a size press, or on the calendars. Another means for applying sizing agent (such as starch and /or other surface-sizing ingredients) to the paper web is by spraying (Casey 1981).

Many of the problems posed by use of synthetic chemical sizing agents 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 in papermaking to use these materials where possible (Lertsutthiwong 2002, 2004). 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 (Lertsutthiwong 2002, Laleg 2001, Allan et al. 1990). No investigations have been published on the use of chitosan, to improve the surface properties of paper made from non-wood fibers.

The purpose of the present study is to investigate the surface properties of handsheets of applying chitosan, as sizing agent 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.

Material and Methods

Materials: Bleached kenaf (*Hibiscus cannabinus*) pulp was used after PFI mill beating to 307 CSF. 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. 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 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.

Properties of papers surface were determined following Tappi Test Methods (2002) and Tappi Useful Methods (1991). Roughness was measured using Bendtsen and PPS as per T 535 um-91 and T 555 om-99, respectively. Specular gloss of paper was determined using a Technidyne glossmeter according to Tappi T 480 om-99. The surface energy of paper is commonly determined by contact angle measurement. The contact angles as functions of time were determined using distilled water as the wetting liquid in a Fibro 1100 DAT (FIBRO Systems AB, Sweden). Oil absorption of surface was determined according to Dutch Standard NEN 1836 using an IGT printability tester, model AIC2-5. The AltiSurf®500 profilometer, was used to study surface details. This instrument was manufactured by Cotec-CCA (France). Because 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

Result

Dynamic absorption test (DAT)

Among the many properties of paper, one of the most important, is its ability to control the penetration of various liquids, particularly those based on water. Paper surface chemistry influences the water absorption properties of paper and interactions between a paper surface and a printing ink (ink setting).

Figure 1 shows a reduction in contact angle during the 12 s after application of a droplet on the surface of the sample. As expected from the nature of sizing agents that are intended by definition to increase contact angles between water and paper, the sized papers have better water resistance than the unsized control sheet. Of the papers made in the laboratory, the cationic starch sized paper has the greatest and most stable water absorption properties followed by the chitosan.

Oil absorption

At the moment of printing, a quantity of oil (or "varnish") is absorbed by the surface of the paper. This amount is determined by the absorption of liquid in the surface recesses (roughness) and the absorption into the paper pores at the surface. The sum of the two phenomena determines the oil absorption (or "varnishability"). In the case of the varnishability test the length of the stain made by the standard varnish determines its oil absorption level. A low oil absorption paper creates a long stain, while from the standpoint of printing penetration, a long stain indicates a low roughness/absorption of paper.

Table 1 shows that all of the sizing agents used in this investigation made the paper resistant to oily materials. The unsized sheet gives a high oil absorption stain length, which is consistent with its greater roughness. Chitosan-sizing reduced the oil absorption of kenaf papers by about 14%, which is more than PVA or cationic starch. The reduction in oil absorption indicates that sizing had reduced the paper porosity. The data agree well with the air resistance results. Lertsutthiwong et al. (2004) 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.

Ink transfer

Ink transfer or ink demand - the amount of ink needed for a given level of optical density on the paper, or the level of density achieved with a given amount of ink - is the most direct and also the most important printability factor.

The ink demand of chitosan-sized paper, in comparison with that of the unsized sheet, was clearly reduced (Table 1). It may be related to the strong film-forming properties of chitosan, which reduces porosity (Lertsutthiwong et al. 2004). Mattila et al. (2003) states that the pore structure in the paper is a key factor in ink transfer. Porosity is one of most important factors which influences the absorption of ink vehicles. Ink vehicles are drawn into the pores and inter-fiber spaces of paper by capillary action.

Print density and ink penetration

The ink density, and hence the print quality, is dictated by the paper quality. Uncoated paper gives a lower print density than coated due to its greater ink absorption, with resulting loss of gloss (Senden et al. 2000). It is evident that the ink penetration of sized papers, in particular chitosan sized paper, is less than that of the unsized sheet. A possible explanation for the ink penetration differences between unsized and sized papers is the differences in porosity between the two types of paper. Senden et al. (2000) found that the ink penetration depth can be affected by the pore morphology of paper. Printing paper requires, at the microscopic level, pores with uniform size and distribution in order to let the ink vehicle penetrate into the paper while leaving the ink pigment particles on the surface. If the pores are large, the ink particles may penetrate into the sheet, depending on their size distribution (Lertsutthiwong, 2004).

The unsized sheet had a higher ink transfer and ink penetration depth compared with chitosan-sized paper. Mattila et al. (2003) stated that the amount of ink applied has a significant influence on the ink penetration depth. A greater amount of ink applied to the paper surface causes more ink to penetrate deeper into the paper structure.

Ink penetration and print density have a close relationship to ink absorption ability of paper. Penetration of ink into the paper and variation in the ink layer thickness reduce the optical efficiency of a given amount of ink on the paper (Oittinen and Saarelma, 1998). In general, all sized papers gave low (oil and water) absorption and porosity values. On this basis the ink penetration of sized papers may be expected to be less than that of the unsized sheet. The fact that sized papers provide higher and better controlled porosity-based ink holdout than unsized paper because it is reflected in their higher air resistance measurements. As mentioned previously, the air resistance of the sized paper with chitosan increased (i.e. it is less porous). As a general conclusion, sized kenaf-based papers have lower ink penetration and greater ink density than unsized papers, with chitosan having the best ability to promoted these properties of the sizing agents examined.

Another probable factor in determining the efficiency with which a particular polymer-based sizing agent promotes low ink penetration and ink density is the interaction between the ink and the polymer. In the case of chitosan-sized paper, the offset ink vehicle may not be able to penetrate rapidly. This will cause more ink pigment to remain on the surface of paper, resulting in high print density.

Gloss contrast

In this study, measurements of the gloss value of unprinted and printed-papers were made using a Technidyne instrument. The difference between print gloss (snap) and paper (unprinted) gloss, measured at an incident light angle of 75°, are shown in Table 1. The highest values of gloss contrast occur where the paper is not glossy but the roughness is small. The gloss contrast of kenaf (sized or unsized) papers is significantly different to that of the commercial printing paper.

In general, the lowest in gloss values come from uncoated papers that have a matt finish and therefore exhibit the lowest specular (glossy) reflectance component and highest diffuse reflectance component. The print gloss value, obtained after the application of ink, depends not only on the surface gloss of the paper, but also on the degree of absorption of ink into the paper. Kenaf sized papers had lower ink penetration than the unsized control sheet and the print density and gloss contrast are consequently higher.

Surface topography

A 3D topographic map of a paper surface is a color-coded reconstruction of the surface, as viewed from a position normal to and above the surface. The surface is defined from the top of the highest fiber to the bottom of the deepest open pore. A topographical map is a matrix of pixels, i.e.

a series of consecutive pixel points, in both the *X* and *Y* directions. Each point represents a specific height on the surface (Conners and Banerjee, 1995). Udupa et al. (2000) pointed out that the 3D representation of the surface topography provides a clear indication of pits, scratches, peaks and troughs existing on the surface.

A comparison of the 3D surface maps (Figure 2) reveals that the topography of the unsized sheet surface has higher peaks and lower depressions. All 3D topographical maps are usually color-coded for height, with the highest points indicated in white and successively lower areas indicated by red, yellow, green, blue and black colors. The increasing area of the paper surface occupied by white, red and yellow colors indicates how the smoothing of the surface improves with the various sizing agents used. The smaller pores appear almost unaffected, remaining relatively constant in all the images.

The increasing area of the paper surface occupied by white colors indicates how the smoothing of the surface improves with the various sizing agents used. The smaller pores appear almost unaffected, remaining relatively constant in all the images. The surface of chitosan sized paper has a flatter topography than the surface of the unsized sheet (Figure 2). The surfaces of the cationic starch- and PVA-sized papers are also flatter, than the surface of the unsized sheet, but not as flat as the chitosan-sized paper.

The enhancing of surface property is related to the structure of chitosan. It has an aminoglucose backbone, with hydroxyl groups and a positively charged (at pH 5) ammonium group, giving it film-forming characteristics. Its film-forming potential creates new areas for fiber-fiber adhesion and its cationic nature (i.e. positively charged amino group) initiates ionic linkages by undergoing ion exchange reactions of the following type (Ashori et al., 2005).

Conclusions

The following conclusions can be drawn:

1. The cationic starch sized paper had the most stable water resistance properties, followed by chitosan-sized paper.
2. The oil absorption of sized papers was lower than unsized paper with chitosan sizing providing the highest oil resistance levels.
3. Of the sizing agents examined, chitosan gave the lowest ink demand and ink penetration and the highest print density, both of which are desirable features in high quality printing papers. Both PVA-sizing and cationic starch sizing gave print densities and ink penetrations than were intermediate between chitosan and the unsized control sheet, which gave the lowest values for these properties.
4. All of the topographic parameters of surface roughness measured in this study indicated that the surface of chitosan-sized paper was smoother than the surfaces of the other papers examined.
5. Overall kenaf paper sized with chitosan gave the best mix of desirable printing paper properties and was superior to kenaf paper sized with either cationic starch or PVA.

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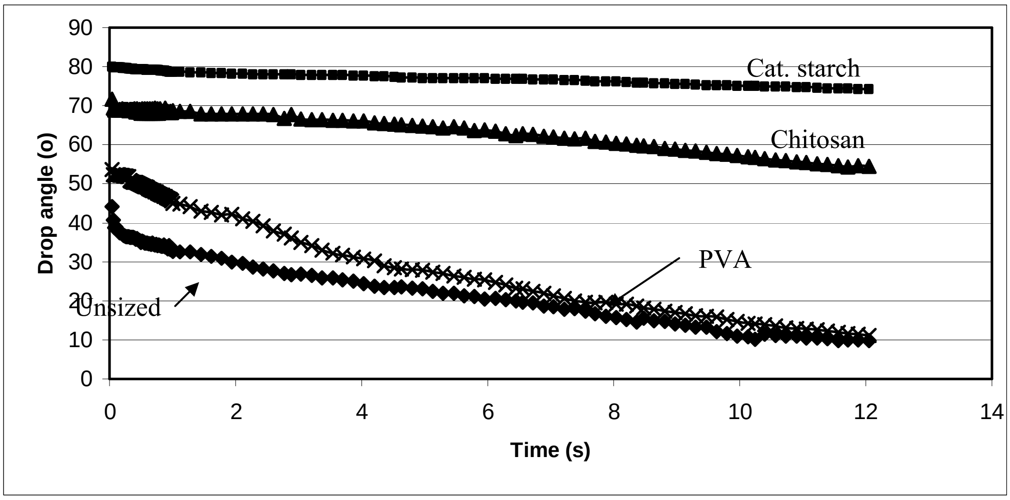

Figure 1 : Absorption properties of different papers as a function of time

Table 1. Printability properties

Paper type†	Bendtsen, mL/min	PPS, µm	Ink transfer, g/m^2	Print density	Oil stain length, mm	Gloss, %			Ink penetration, µm
						Paper	Print	Snap	
Control sheet	56	5	1.99	1.44	80	6	16	10	49.4
K-Chitosan	35	3.9	1.65	1.64	69	6	19	13	40.7
K-PVA	45	5	1.89	1.50	78	7	18	11	42.9
K-Cat.starch	98	5	1.34	1.49	77	7	18	11	43.1

† All tests were performed on the glazed (plate) side of the handsheets

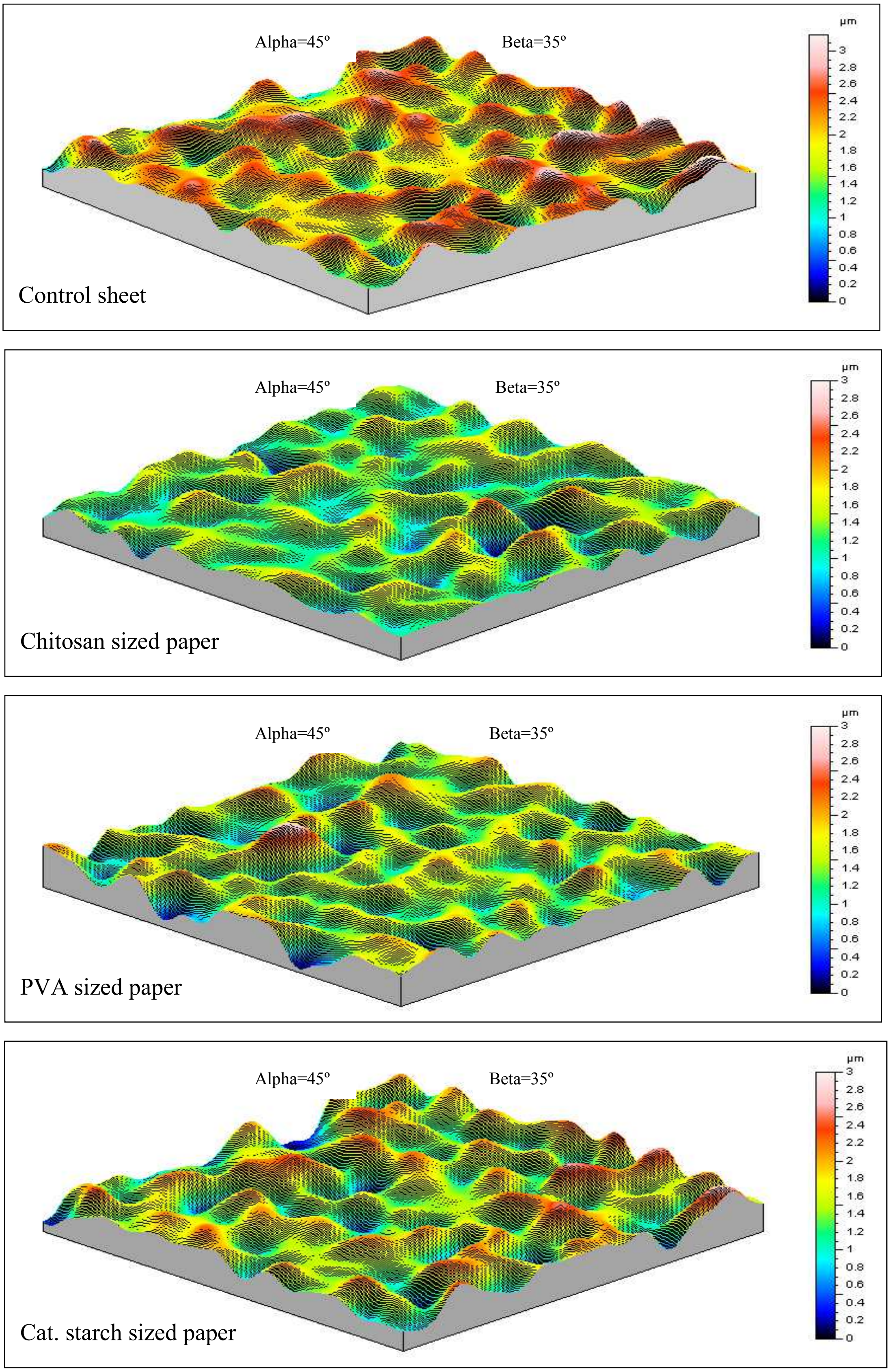

Figure 2 : Three-dimensional topographic maps of unsized and sized papers