

A Study of Wet and Dry Strength Properties of Unaged and Hygrothermally Aged Paper Sheets Reinforced with Biopolymer Composites

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ABSTRACT: Biopolymers and their composites were added during the formation of unbleached Kraft bagasse pulp paper sheets to improve the mechanical strength properties of the produced hand sheets. The biopolymers (cellulose, chitosan, and chitosan-cellulose composite) were either crosslinked or noncrosslinked and they were added in series of concentrations from 0.1% to 1.5%. The characterization of the samples using the Fourier transform infrared (IR) technique identified differences in the intensities of the characteristic IR absorption bands for chitosan, cellulose, and their composites, these differences are due to the various degrees of hydrogen bonding. The surface morphology of the biopolymers composites and the treated paper sheets were studied using SEM technique. Both the equilibrium moisture sorption and the diffusion coefficient of the paper sheets containing 1% additives were evaluated at regular time intervals. The long-term stability of the treated paper with biopolymers was verified by exposing the treated and the untreated sheets to hygrothermal ageing. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40761.

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INTRODUCTION

Cellulose fibers are bounded to each other by hydrogen bonds. The distance between the fibers affects directly the strength of the bonds and consequently reflected in the mechanical strength properties of the resulting paper sheet. Water molecules play an important role in strengthen the interfiber's linkages, in case of large excess of free water, the wet strength of the paper sheets and paper board become weak,¹ because the excess water molecules have increased the distance between the fibers. The wet strength is the mechanical strength of the remaining paper after complete soaking in water.² To improve the wet strength of paper sheets, a number of resins and polymeric materials such as urea, phenol-, and melamine-formaldehyde resins³ are used as wet strength agents (WSA), in addition to polyacrylamide, poly(methyl methacrylate),⁴ and vinyl acetate–vinyl chloride copolymer.⁵ The WSA is working in two steps: first, it adheres to the pulp by adsorption and then it forms a network that limits the swelling of cellulose fibers, i.e., inhibiting the disruption of fiber–fiber contacts when paper is rewetted.² A good strengthening additive should also be nontoxic and preferably

natural and biodegradable to comply with the environmental regulations.^{2,6} Chitosan is known to be a nontoxic, biodegradable, antibacterial, and odorless renewable bioresource. Chitosan is a derivative of N-deacetylation of chitin, a naturally occurring polysaccharide from crustacean and fungal biomass origin, which is the second most naturally abundant biopolymer next to cellulose and is readily available from seafood wastes. The chemical formula of chitosan is 2-amino-2-deoxy-(1-4)- β -D-glucopyranose. Much attention has been paid to the industrial applications of chitosan in the past decade.⁷ It has been identified as the potential dry and wet strengthen additive for paper making.⁸ Chitosan additives increase the strength of wet towels, grocery bags, and disposable diapers.⁹ Chitosan and its derivatives (carboxymethyl–chitosan and chitosan–acetate) are used as reinforcement agents for both recent paper and weak historic documents.^{10–12} Polymer blending is increasingly used as a method for producing polymeric materials with specific designed properties.¹⁰ Chitosan blends with poly(vinyl alcohol) and gelatinized starch are used as paper filler to increase paper

strength due to their strong ionic interactions. A blending polymer of cellulose and chitosan is widely used due to: (a) cellulose is the most abundant natural biopolymer with relatively strong mechanical strength and (b) cellulose has similar polysaccharide backbone chemical structure such as chitosan which provides the possibility of producing a homogeneous blend that have the unique properties of both materials. However, chitosan is not convenient in case of age-acidified documents due to its partial dissolution in acidic environment, so, a modification to the chitosan takes place using crosslinking. Crosslinking agents, e.g., glutaric dialdehyde, ethylene glycol diglycidyl ether, and epichlorohydrin (EP) is used to enhance the chemical resistance of chitosan to acidic and alkaline mediums. Highly reactive polyamido-amine-EP resins are used to produce paper grades with high wet strength. EP resins are very suitable agents for neutral and alkaline paper manufacturing and it comply with the environmental aspects.¹¹

Natural degradation processes lead to the formation of acids on the paper sheet; these acids enhance the acid-hydrolysis of cellulose lead into considerable changes in the mechanical, optical, and chemical properties of the paper sheets. These changes in the paper properties cause damaging to the structure of the paper sheet, increasing brittleness, yellowing, and leading to general loss of the material quality. Understanding and finding methods to reinforce the old weak paper is a relevant issue for the preservation of historic documents in archives, libraries, museums, and has its implications in the papermaking industry.

The research objective is to study the effect of the natural biopolymer additives to cellulose fibers during the formation of a paper sheet with its possible applications in both papermaking and conservation of paper documents. The effects of the different biopolymers and composites concentrations on the improvement of paper strength properties in the dry and wet state will be studied. The additives and their interaction with the paper sheets will be characterized using SEM and Fourier transform infrared (FTIR) techniques. The equilibrium moisture sorption (EMS) and diffusion coefficient of the treated paper sheets will be evaluated at different time intervals. The long-term stabilization effect of the strengthening agents will be evaluated by applying hygrothermal ageing to the treated paper samples.

EXPERIMENTAL

Materials and Chemicals

Unbleached Kraft bagasse pulp (Edfo Mill, Egypt) [15% NaOH, 5% Na₂S, 0.05% anthraquinone (AQ)-based on raw material (oven dry pulp) at 160°C for 2 h and 1 : 6 liquor ratio] has the following characteristics according to the specified TAPPI standard methods: α -cellulose 64.0% (T 203 om-83), pentosane 27.5% (T 223 om-84), and lignin 4.8% (T 222 om-88). Chitosan, commercial grade (Oxford Laboratory, India) with 90–95% degree of deacetylation, was used. Cellulose powder Avicel PH-101, sodium hydroxide, acetic acid, and EP pure grades were from Fluka.

Preparation of the Chitosan-Cellulose Composite

The chitosan-cellulose composite was prepared according to the protocol in Li and Bai.¹³ Chitosan flakes (6 g) were added to

300 mL of 2% (w/w) solution of acetic acid in a beaker and were heated to 40–50°C under constant stirring at 200 rpm for 6 h. Cellulose powder (6 g) was mixed with 50 mL water and heated at 40–50°C under stirring. The suspended cellulose solution was added drop wise to the chitosan solution at 50°C under continuous stirring for 1 h. The blended solution was then injected in droplets into a 1M NaOH solution to form hydrogel beads. The chitosan-cellulose hydrogel beads were allowed to stay in the NaOH solution with slow stirring for another 12 h for hardening. The hardened beads were then washed with deionized (DI) water in a large beaker until the pH of the solution was the same as that of the fresh DI water. The beads were then washed with ethanol and acetone.

The crosslinking of the chitosan-cellulose hydrogel beads with EP was carried out as follows: 100 mL DI water was added to 3 g of chitosan-cellulose composite under stirring and the pH was adjusted to 12 with 1M NaOH. Then, 50 mL NH₄OH and 0.8 mL (EP) were added and the sample was maintained at 80°C under reflux for 2 h.¹⁴ The insoluble crosslinked chitosan-cellulose product was collected by vacuum filtration and washed with ethanol and water until neutrality. The same experiment was performed for crosslinking of cellulose and chitosan separately.

Hand Sheet Formation

The pulp was beaten to 30° SR in a Jokro mill beater according to the Swedish Standard Method. Hand sheets with a basis weight of 68 g m⁻² were formed and different concentrations of cellulose, chitosan (dissolved in 2% acetic acid), chitosan beads, and chitosan-cellulose composite and the crosslinked derivatives (0.1–1.5% w/w) were added in the mixer. The prepared sheets were dried at 103°C using a drum dryer. All paper samples were conditioned at 23°C and 50% relative humidity (RH) for 24 h before measurements.

Hygrothermal Ageing

Moist heat ageing in hermetically closed glass tubes (35 mm internal diameter (ID) × 147 mm, 144 mL) was performed at 100°C for 5 days in a dry oven (Heratherm, Thermo Scientific) according to ASTM standard method D6819-02E02.¹⁵ The paper samples were conditioned for at least 24 h at 23°C and 50% RH, and the humidity in the tube is supplied and buffered by the paper and stabilized between 50 and 60%.¹⁶

FTIR and SEM

FTIR of chitosan and its derivatives was carried out in transmission mode using the KBr disk technique using a JASCO FT/IR 3006. Scanning electron microscopy (gold coating, Edwards Sputter Coater, UK) was performed using a Jeol 6310 (Jeol Instruments, Tokyo, Japan) system running at 5–10 kV.

Equilibrium Moisture Sorption

Paper sheets containing 1% additives (cellulose, chitosan, chitosan-cellulose composite, and crosslinked additives) were placed in Petri dishes and stored in a desiccating chamber at 25°C for 2, 4, 6, 24, 48, 168, and 336 h, to progressively remove residual moisture. The moisture sorption isotherms were determined by the gravimetric method.¹⁷ In each case, 1 g of the dry sample was placed in an aluminum foil in desiccators with a gauze

holding tray containing a saturated solution of sodium chloride salt to provide 75% RH. The sheets were weighted at time intervals until the equilibrium was attained. The EMS was determined using eq. (1):

$$\text{EMS} = (M_t) / M_d \times 100\% \quad (1)$$

where (M_t) is the moisture content at time t and M_d is the dry weight of the material. The diffusion coefficient is the most important parameter for water absorption because it shows the ability of solvent molecules to penetrate the fibers inside the structure of the paper sheets. The following equation was used to determine the diffusion coefficient.¹⁸

$$M_t / M_\infty = 4 / L(D/\pi)^{0.5} t^{0.5} \quad (2)$$

where M_∞ is the moisture content at the equilibrium, L is the thickness of the sample, and D is the diffusion coefficient.

Mechanical Strength Testing

Elongation at break (%) was measured by Adamec Lhomargy instrument (DY-20B) according to the standard method NF: Q03-004 July 1986, where a co-axial stress is applied to the paper sample. Samples were tested at a speed of 10 mm min⁻¹ with the 100 decaNewton (daN) load cell. The data were processed with Test Works 4 (MTS Systems Corp.) software. Break length (BL) was calculated as follows:

$$\text{BL (m)} = \frac{\text{Tensile strength} \times 6.67 \times 10,000}{R} \quad (3)$$

where BL is breaking length (m), T is tensile strength (kg) on 15 mm strip, and R is basis weight (dry) (g m⁻²).

Zero-span tensile strength (zsTS) was measured with a Pulmac instrument (TS 100) according to TAPPI standard T231 cm-96. When measured on samples as conditioned, it is referred to as dry zsTS. The measurement carried out after saturating the paper sample with water upon 1 min immersion in DI water before mounting in the pulling jaws is referred to as wet zsTS. Wetting the paper allows to eliminate interfiber bonding, and intrinsic fiber resistance alone to be measured. The value obtained (P) is transformed applying the formula:

$$\text{zsTS} = (P - P_0) \times 5.64 (\text{daN mm}^{-1}) \quad (4)$$

where $P_0 = 2$ (constant of the instrument).

RESULTS AND DISCUSSION

FTIR Spectroscopy

The specific features of cellulose, chitosan, and its derivatives were investigated using the FTIR spectra as shown in Figure 1. The bands at 3000–3445 cm⁻¹ are attributed to —NH₂ and —OH stretching vibrations in chitosan and cellulose.¹⁹ The absorption band at 3445 cm⁻¹ is higher in cellulose, chitosan, chitosan beads, and chitosan-cellulose composite than in the corresponding crosslinked samples. The difference is due not only to the difference in the primary structure between the non-crosslinked and crosslinked (biopolymers and composites) but also to the occurrence of a more ordered level of packing of the macromolecules in the networks (crosslinked samples). The appearance of shoulders at 3317, 3223, and 3110 cm⁻¹ in chitosan beads is attributed to intermolecular hydrogen bonding involving the —OH(6) and —OH(3).^{20,21} The decrease in the

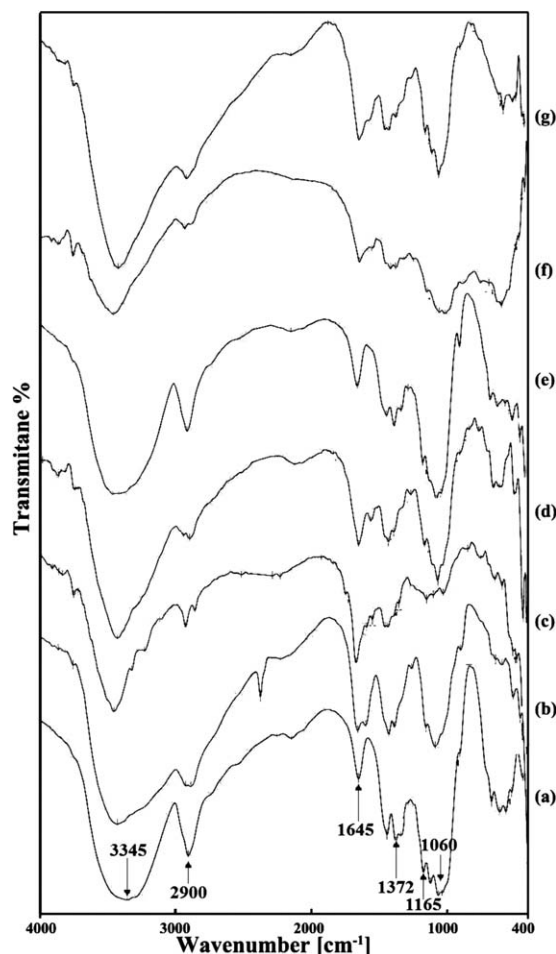


Figure 1. FTIR spectra for (a) cellulose, (b) chitosan, (c) chitosan beads, (d) chitosan-cellulose composite, (e) crosslinked cellulose, (f) crosslinked chitosan beads, and (g) crosslinked chitosan-cellulose composite.

band intensity at 2900 cm⁻¹ (—CH vibration of —CH₂, CH₂OH from C (6) in cellulose and chitosan) for the cross-linked samples is due to the reaction between EP and (cellulose, chitosan, and chitosan-cellulose composite). A new shoulder appeared at 1740 cm⁻¹ in the chitosan beads sample which is attributed to the ester or the carbonyl groups in the side chains of chitosan. The absorption band at 1640 cm⁻¹ is attributed to the adsorbed water molecules vibration, the carbonyl groups in case of cellulose and the acetamide group in case of chitosan.²² At 1640 cm⁻¹, chitosan additives (chitosan, chitosan beads, chitosan-cellulose composite, and crosslinked chitosan-cellulose composite) have the highest intensities due to the hydrogen bonding between the side chains of cellulose and chitosan. The absorption band at 1590 cm⁻¹ in the chitosan sample which is related to the amino group (—NH₂) was shifted to 1550 cm⁻¹ in chitosan beads, chitosan-cellulose composite, crosslinked chitosan beads, and crosslinked chitosan-cellulose composite, whereas chitosan beads show the highest intensity of this band. The lower intensity of this band in the crosslinked chitosan-cellulose composite indicates that some of the amino groups were consumed or sheltered by the crosslinking reaction. The increase in the intensities of the bands related to —CH or

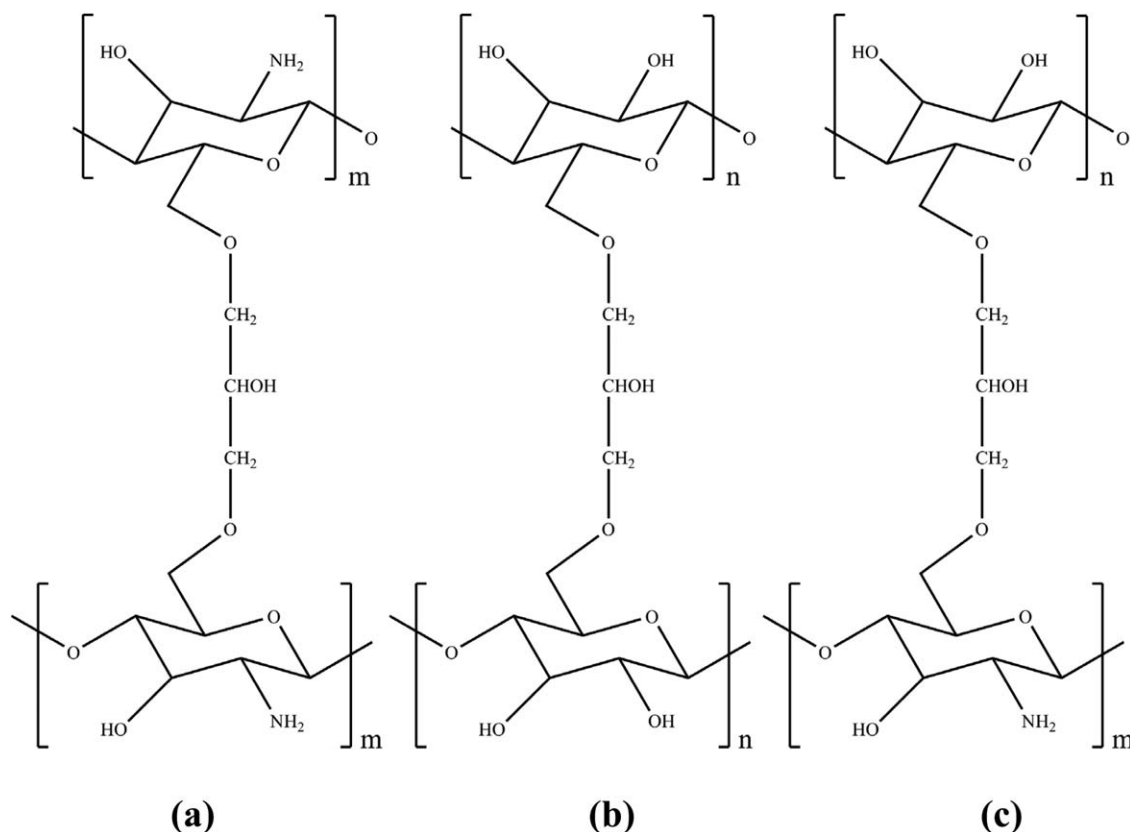


Figure 2. Reaction products for crosslinked (a) chitosan, (b) cellulose, and (c) chitosan–cellulose composite.

$-\text{CH}_2$ vibrations ($1430, 1370, 1315, 1280 \text{ cm}^{-1}$) in cellulose and chitosan reflects the new formed bonds in chitosan beads, chitosan–cellulose composite, and in the crosslinked samples. The increase in the intensity of the bands at 1160 cm^{-1} and 1060 cm^{-1} which belong to C–O–C and C–O ether vibrations, methoxy, and β -O-4 links is due to the crosslinking of cellulose, chitosan, and chitosan–cellulose composites.²³ The crystallinity index (CrI) of the product resulting from the crosslinking reaction using EP was higher than that of the noncrosslinked additives. CrI is defined as the ratio of the intensity of the 1425 cm^{-1} band which represents C–H asymmetric deformations in $-\text{CH}_3$ and $-\text{CH}_2$ over the intensity of the 900 cm^{-1} band which represent the asymmetric out of plane ring stretching in cellulose due to the β -linkage and also to the amorphous (disordered) portion of cellulose. This high crystallinity index is due to the increase in the amino groups and to the long side chains which were formed by the reaction of EP with the amino groups of chitosan. So the net hydrogen bonding between $-\text{OH}$ or $-\text{OH}$ and $-\text{NH}$ has increased and accordingly, crosslinked reaction product of the chitosan and cellulose network using EP has been released as shown in Figure 2.

Surface Morphology of Chitosan-Cellulose Composite

Figure 3 shows the surface morphology of cellulose, chitosan, chitosan beads, chitosan–cellulose composite, and its crosslinked derivatives. The morphology of chitosan beads differs from that of chitosan; the beads are flatter, thicker, and smoother. This is

due to the diffusion of NaOH into the center of the particles. The chitosan–cellulose composite shows a more spherical shape. The crosslinking reaction with EP increased the compactness of the network of cellulose, chitosan, and chitosan–cellulose composite but simultaneously it maintained its porosity.

Effect of the Additives on the Paper Mechanical Strength Properties

The mechanical properties of the different paper samples are substantially influenced by the individual characteristics of the cellulose fibers (dimension, strength, and intrafiber bonding²⁴), the fiber network structure of the paper (distribution of the fibers within the sheet upon formation) and the nature, concentration, and chemical properties of additives. Bonding comes primarily through the formation of hydrogen bonds. The bonding strength depends on the fiber contact area and the intrinsic strength per unit area of contact. Figures 4 and 5 show the BL and dry zero-span tensile strength (dry zTS) of the paper sheets treated with different concentrations (0.1–1.5% w/w) of noncrosslinked, crosslinked, and composites additives. A high improvement in BL and dry zTS of the paper sheets occurred upon adding a minimal concentration of cellulose, chitosan, and its derivatives (0.1% and 0.25%). The highest increase was upon the addition of cellulose. Beyond 0.25% of additives a plateau BL and dry zTS value is reached. The presence of basic functions on each chitosan unit enables its solubility in the dilute aqueous acidic solution which makes

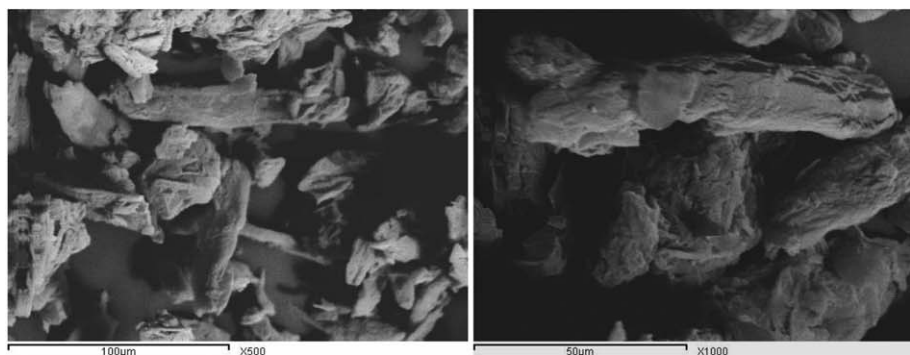
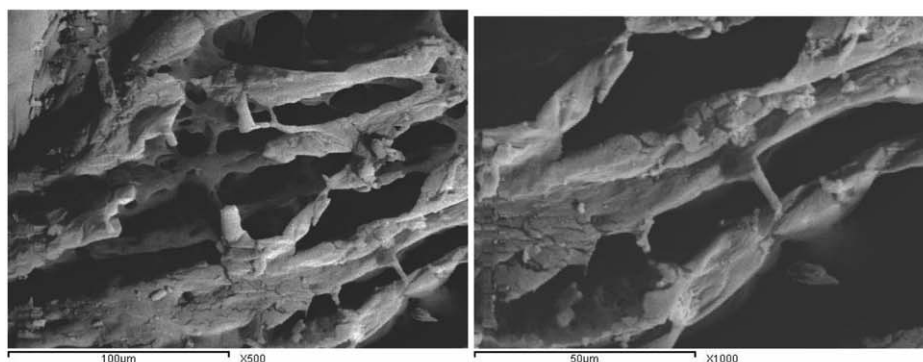
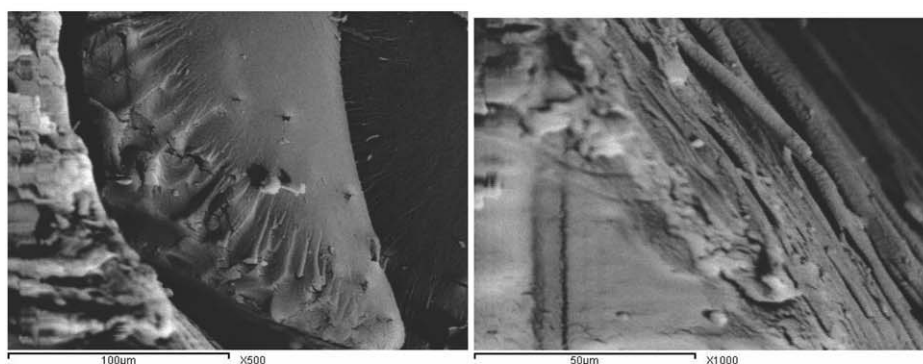
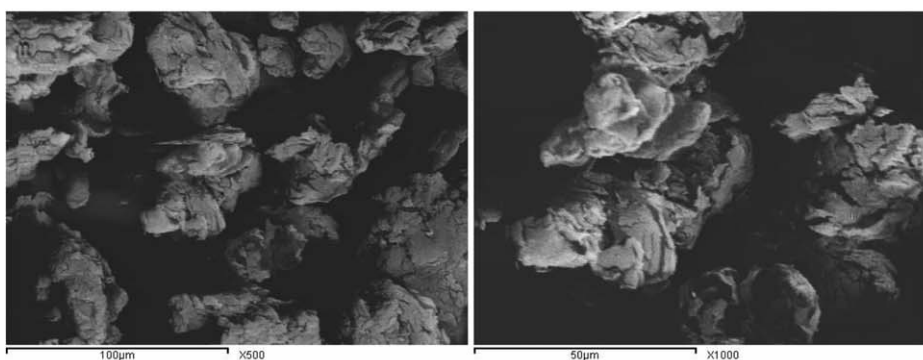
**(a) Cellulose****(b) Chitosan****(c) Chitosan beads****(d) Chitosan-cellulose composite**

Figure 3. Surface morphology of (a) cellulose, (b) chitosan, (c) chitosan beads, (d) chitosan–cellulose composite, (e) crosslinked cellulose, (f) crosslinked chitosan, and (g) crosslinked chitosan–cellulose composite.

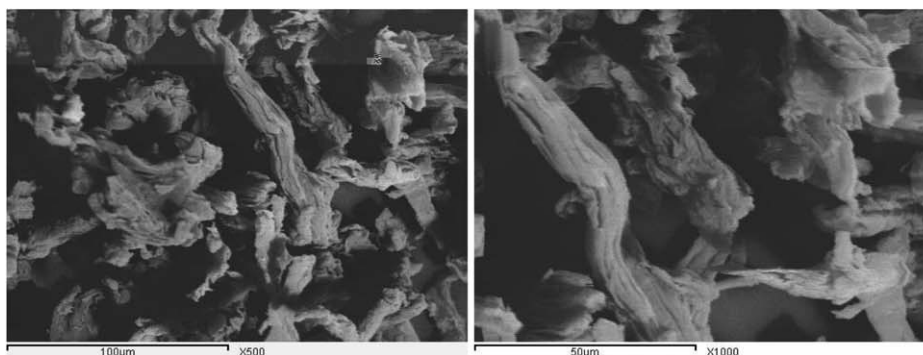
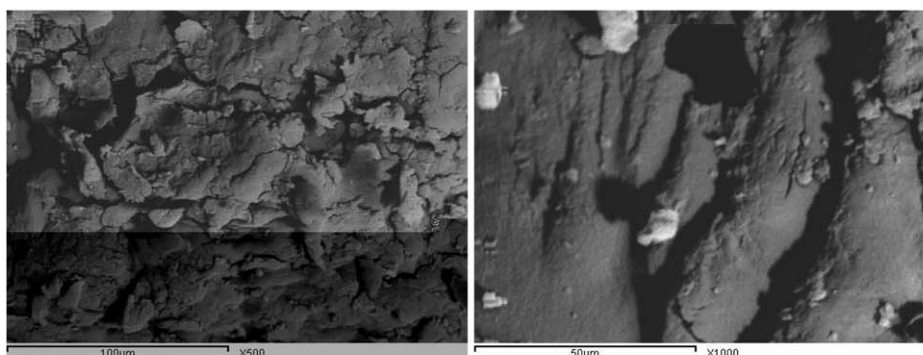
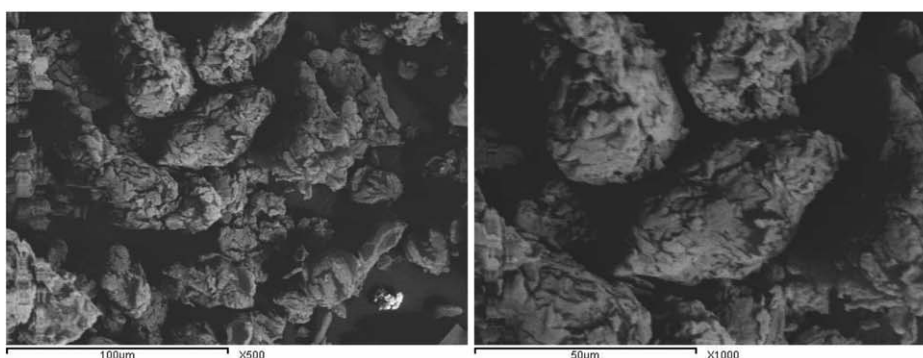
**(e) Crosslinked cellulose****(f) Crosslinked chitosan beads****(g) Crosslinked chitosan-cellulose composite**

Figure 3. Continued.

it substantive to paper pulp (naturally anionic). This increases the cross-linking efficiency between the fibers.^{8,25} Moreover, the —NH_2 functional group in chitosan is capable of ionic or covalent bonding with the paper fiber surface during the paper making process. This enhances bonding produces a film which firmly adheres to the fibers and offers adhesive resistance to rupture. The addition of chitosan and its derivatives during the paper sheet formation led to an improvement of the mechanical resistance properties of the sheet. This is attributed to the increase of interfiber bonding and chemical compatibility between the added material and the cellulose fibers in the paper sheets. Due to their chemical similarity, chitosan and cellulose fibers readily form hydrogen bonds. Lertsutthiwong et al.⁶ reported that the hydrogen bonding between solid

surfaces is restricted to a few hydrogen bonds due to the difficulty of achieving the required geometry. Forming a polymer film covering the fiber crossing areas could overcome this problem and lead to stronger 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, 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 6 represents an idealized cellulosic fiber-chitosan system, showing two cellulose molecules, two chitosan molecules, and their bonding.²⁶

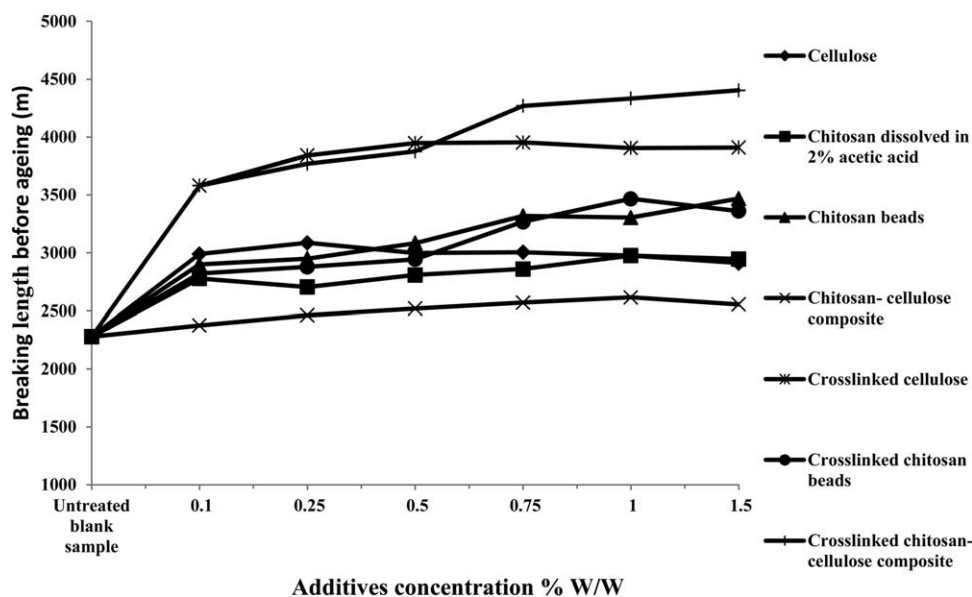


Figure 4. Breaking length of the unaged paper as a function of additives concentration.

Mechanical Strength of Wetted Paper Sheets

Two principal mechanisms explain the development of wet strength in paper. The first mechanism suggesting that once an additive is distributed on the fibers (and perhaps diffuses into the hemicelluloses and lignin), it self-crosslinks forming an insoluble network around and through the fibers and the fibers contact areas. When the treated paper is rewetted, this network inhibits the fiber swelling and separation thus preserving a fraction of the original dry strength; this is called the protection mechanism. The other mechanism is the reinforcement mechanism which describes the reaction of the additive with cellulose (or hemicelluloses) to form covalent bonds between cellulose molecules and presumably, between fibers. These linkages supplement and reinforce the natural hydrogen bonding in the dry sheet. Being covalent, the bonds are not disrupted by water and

they add their aggregate strength to the structure of wet fibers. It is rational to assume that the reinforcement mechanism is also accompanied by some level of polymer crosslinking. These polymers are likely self-cure in paper as they do when dried alone.² BL depends on both inter and intra-fiber bond strength. However, most wet-strength materials produce pulps which results in weak fiber-fiber bonds, and consequently, the strengthened additives are usually most effective if they enhance the fiber-fiber contacts.²⁷ Figure 7 shows that the mechanical strength of the paper sheets was highly affected after wetting with a decrease of about 50% compared with the dry zsTS. However, all the additives led to an increase of the wet zsTS. For chitosan-cellulose composite (1% w/w additive concentration), the dry zsTS was 156 daN mm^{-1} and the wet zsTS was 97 daN mm^{-1} . The crosslinked derivatives showed the most

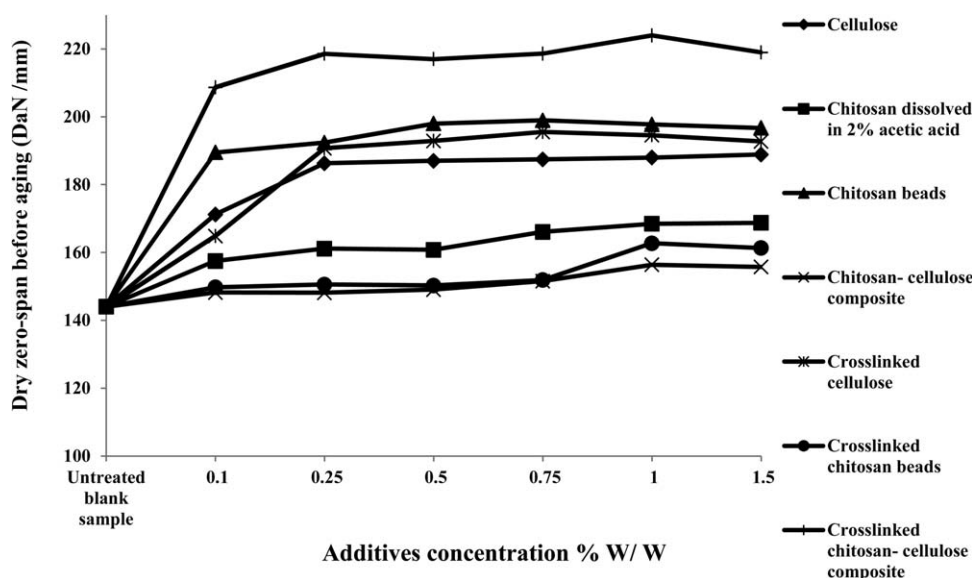


Figure 5. Dry zero-span tensile strength of the unaged paper as a function of additives concentration.

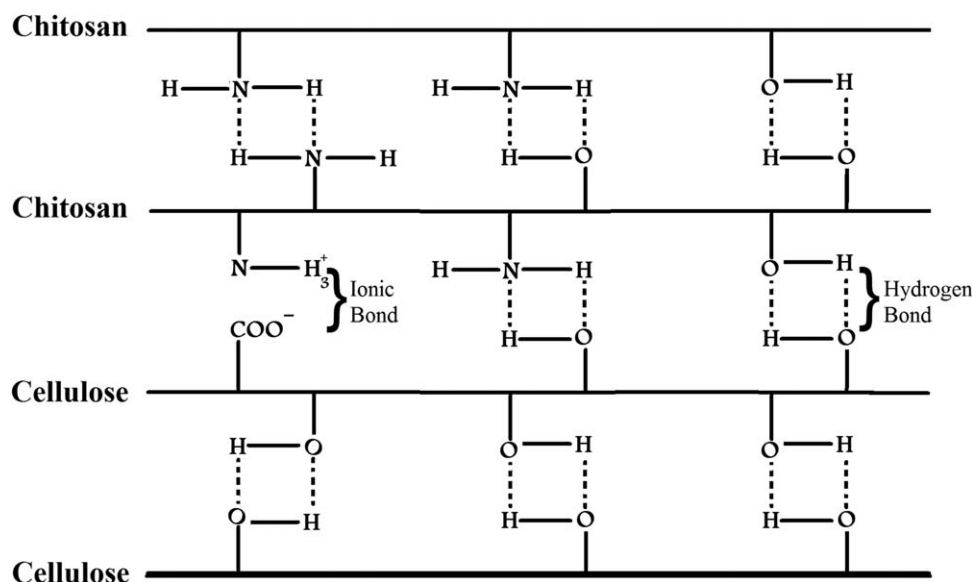


Figure 6. Representation of bond formation in the cellulosic fiber-chitosan system.

improved wet zTS even at low concentration. It increased further with additives concentrations up to 1%, about 86 and 82% in the case of chitosan beads and crosslinked chitosan–cellulose (1%) compared with the untreated paper, respectively. This is attributed to the fact that chitosan beads and crosslinked chitosan–cellulose composite increase the interfiber hydrogen bonding. The lower wet-web strength of paper sheets at higher concentrations of cellulose, chitosan additives, and chitosan–cellulose crosslinked derivatives might be due to a damage that occurred when the sheets were peeled from the blotter.⁷

Surface Morphology of Paper Sheets (SEM)

The film forming characteristics of the paper sheets were investigated using SEM. Figure 8 shows the surface morphology of the unbleached Kraft bagasse pulp hand sheets treated

with the different additives. The surface of the unmodified fibers differed from that of the modified fibers. One property of chitosan is its ability to form films which improve the surface properties of paper.²⁶ The additive particles were more firmly and effectively adhered and bonded to the fiber surfaces and enhanced the chemical compatibility to the cellulosic pulp fibers.²⁸ Figure 8 shows the dispersion state of the fibers in the paper web. In the untreated sheet, the fibers are randomly distributed, whereas in the treated sheets, the fibers are more homogeneously dispersed. Upon addition in the paper pulp, the additives disperse on the surface as well as into the fibers and chemically crosslinked with the cellulose fibers.²⁹ Therefore, the network crossings form confines the motion between fibers and consequently reduces the expansion of the fibers and the deformation of the sheets.

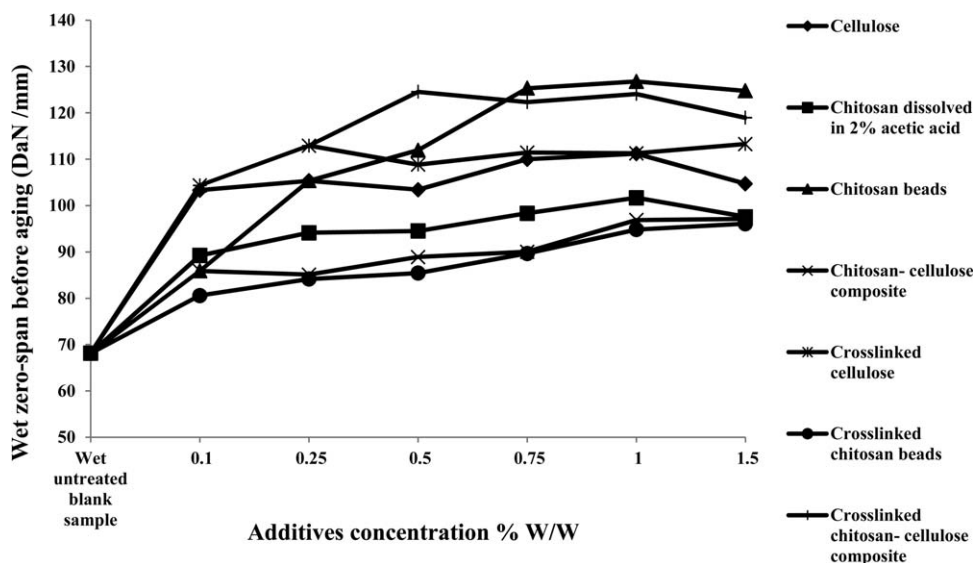


Figure 7. Wet zero-span tensile strength (wet zTS) of unaged paper as a function of additives concentration.

Table I. Effect of Different Types of Additives on the Amount of Moisture Absorbed by Paper Sheets at Different Time Intervals

Additive	Moisture absorbed % (w/w)						
	2 h	4 h	6 h	24 h	48 h	168 h	336 h
No additive (untreated sheet)	0.865	0.973	0.676	2.649	3.055	3.271	3.36
Cellulose	1.007	1.684	2.016	3.343	3.572	5.103	5.231
Chitosan in 2% acetic acid	1.03	1.539	2.025	2.666	3.27	3.05	3.38
Chitosan beads	1.05	1.357	1.931	2.745	3.077	3.409	2.93
Chitosan–cellulose composite	1.091	1.539	2.102	2.666	3.27	3.05	3.329
Crosslinked cellulose	0.584	0.661	0.793	3.072	3.799	4.760	6.046
Crosslinked chitosan beads	0.596	0.731	1.649	2.841	2.543	3.49	6.71
Crosslinked chitosan–cellulose composite	0.678	0.838	1.054	1.973	2.73	3.405	2.703

Equilibrium Moisture Sorption

The moisture sorption is an important feature for the foresee use of the paper (such as for packaging purposes) because the moisture content and the moisture exchange rate with the surrounding environment is a crucial factor in the natural degradation rate of cellulose with time.³⁰ Moisture absorption by paper results from the interaction between water molecules and the many hydroxyl groups on the cellulose chains. Different factors affect the moisture absorption in paper such as the presence of hydrophobic (lignin fragments) or hydrophilic moieties and the presence of additives in the paper manufacturing. Table I shows the evolution of moisture absorption in the paper samples at short time intervals. In case of the untreated paper, the moisture absorption was rather stable in the interval 0–6 h (0.865% after 2 h to 0.676% after 6 h) and reached 2.649% after 24 h. Subsequently, no significant change in the moisture absorbed was recorded in the interval 48–336 h and it reached 3.36% after 336 h. The hydrophobicity of the residual lignin fragments present in the unbleached Kraft pulp paper explains the resistance for moisture absorption in the initial time intervals and the low level of moisture absorption obtained after 336 h. Cellulose, crosslinked cellulose, and crosslinked chitosan beads additives enhanced the total moisture absorption of the paper sheets in comparison with the untreated paper sheet (5.2, 6.04, and 6.7% after 336 h, respectively). The addition of cellulose powder enriched the paper surface with hydroxyl groups which interacted with water molecules and increased the moisture absorption capacity of the sheet. In the case of crosslinked

cellulose, the swelling ability of the cellulose macromolecule network and the presence of the hydroxyl groups of the crosslinked network made the paper sheets more prone to moisture absorption. The high swelling ability of the crosslinked chitosan beads enhanced the moisture absorption of the paper sheet. On the other hand after a long time interval, chitosan dissolved in acetic acid, chitosan beads, chitosan–cellulose composite, and crosslinked chitosan–cellulose composite showing similar moisture absorption as the untreated paper (3.38, 3.41, 3.33, and 3.40%, respectively). This is due to the steric occupation of the chitosan macromolecules on the fiber surface via intermolecular interaction of the hydrogen bonds and the coordination bonds between the cellulose's (hydroxyl groups) and the chitosan's ($-NH_2$) groups. This intermolecular interaction reduced the accessibility of the hydroxyl groups to moisture. The presence of cellulose and chitosan in the crosslinked system or in the blend system increased the degree of crosslinking and the physical bonds between cellulose and chitosan which in turn reduce the swelling behavior of both systems. Such systems thus cannot enhance the moisture absorption capacity of the paper.¹⁸ The penetration of water molecules through the paper negatively affect the mechanical properties of the sheet resulting in debonding of the physical forces (van der Waals) and disrupting of the hydrogen bonding between the cellulosic chains and/or the additives on the paper sheet surface. The diffusion of the water molecules inside the paper sheet occur via capillary transport mechanism.³¹ The capillary mechanism involves the flow of water molecules at the

Table II. Effect of Different Types of Additives on the Diffusion Coefficient of Moisture Inside the Paper Sheets at Different Time Intervals

Additive	Diffusion coefficient						
	2 h	4 h	6 h	24 h	48 h	168 h	336 h
No additive (untreated sheet)	1.57 E -07	2.13 E -08	6.85 E -09	4.63 E -09	4.75 E -09	5.73 E -09	3.02 E -09
Cellulose	1.13 E -07	2.53 E -08	2.02 E -08	8.36 E -09	4.47 E -09	1.82 E -09	9.34 E -10
Chitosan in 2% acetic acid	3.09 E -08	2.31 E -08	8.24 E -09	6.67 E -09	4.09 E -09	1.09 E -09	6.04 E -10
Chitosan beads	4.38 E -08	1.7 E -08	1.61 E -08	5.72 E -09	2.48 E -09	1.01 E -09	4.36 E -10
Chitosan–cellulose composite	4.96 E -08	3.46 E -08	1.24 E -08	1.00 E -08	6.13 E -09	1.63 E -09	8.92 E -10
Crosslinked cellulose	1.78 E -08	3.31 E -09	2.64 E -09	2.56 E -09	1.58 E -09	1.28 E -10	3.60 E -10
Crosslinked chitosan beads	3.98 E -09	1.83 E -09	1.08 E -09	4.18 E -09	5.30 E -10	2.08 E -10	2.00 E -10
Crosslinked chitosan–cellulose composite	1.97 E -07	1.89 E -08	1.58 E -08	7.40 E -09	5.12 E -09	1.82 E -09	7.24 E -10

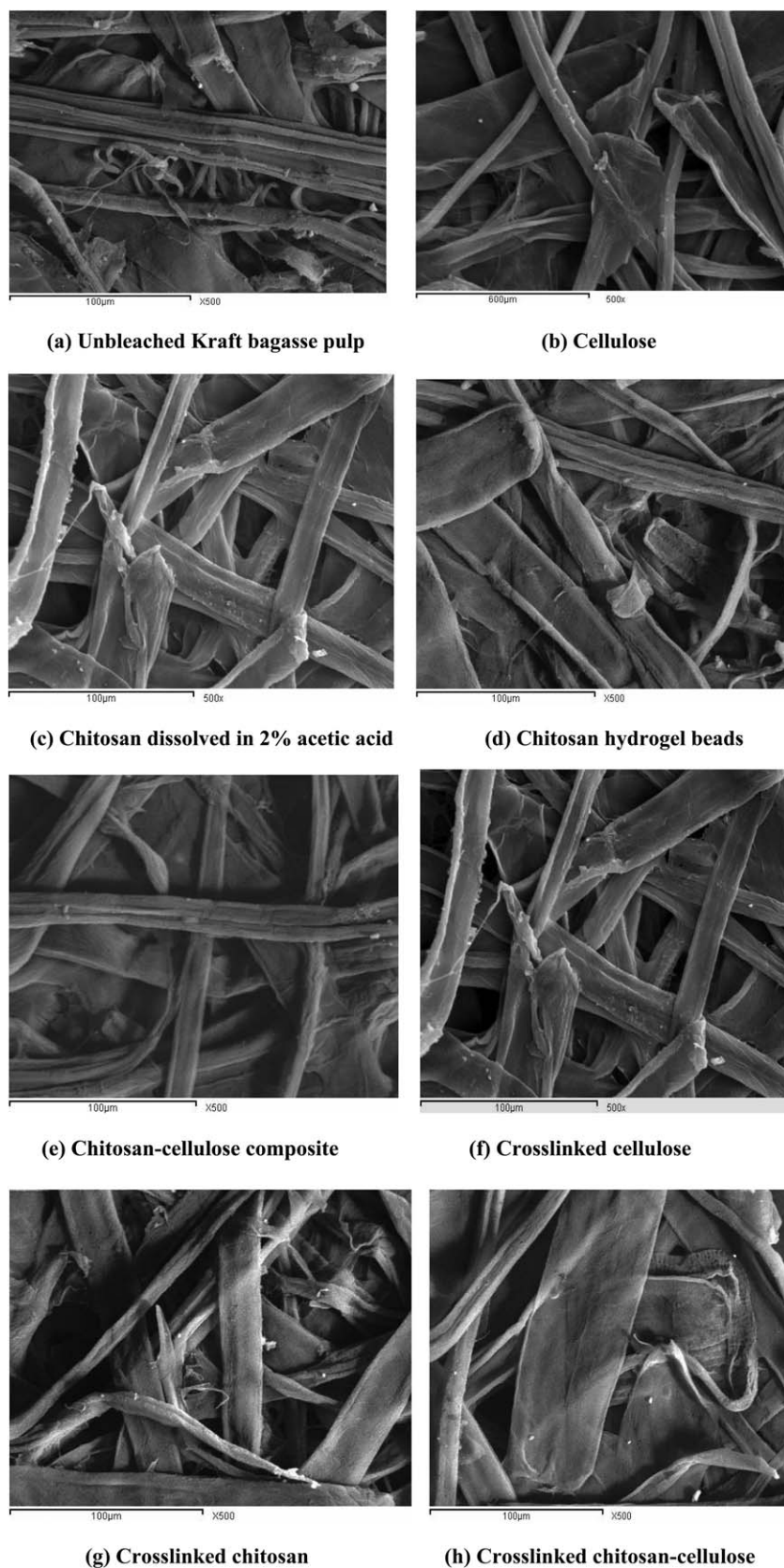


Figure 8. SEM micrographs of (a) Kraft bagasse pulp blank sheet, sheets treated with (b) cellulose, (c) chitosan dissolved in 2% acetic acid, (d) chitosan beads, (e) chitosan–cellulose composite, (f) crosslinked cellulose, (g) crosslinked chitosan, and (h) crosslinked chitosan–cellulose composite.

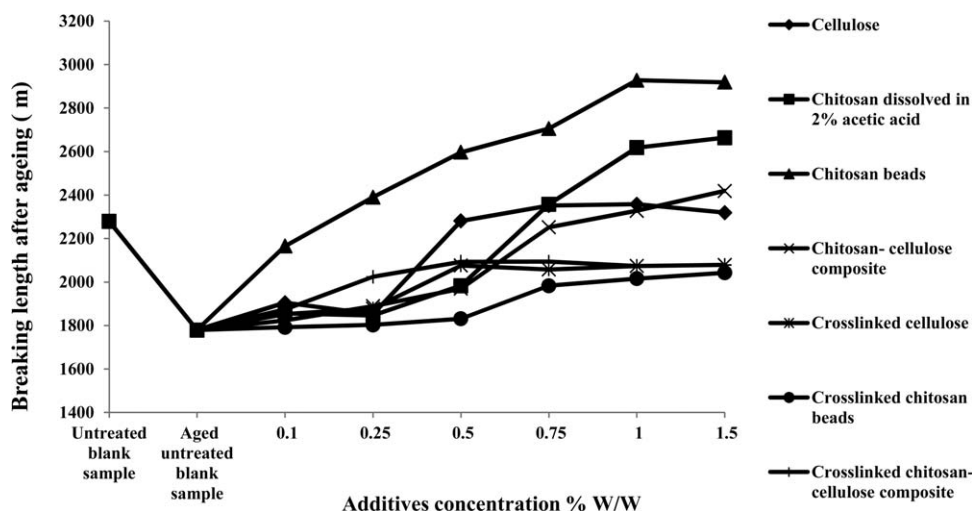


Figure 9. Breaking length of aged paper sheets as a function of additives concentration.

surface interface of fibers because of incomplete wetting of the interior of the fibers. Diffusion occurs through the micro gaps formed between the cellulosic chains and the additives. Table II shows the effect of the different additives on the diffusion coefficient of moisture inside the paper sheets. The values of the diffusion coefficients are high for all samples in the first time intervals (2–4 h) but after longer time intervals they decrease. The diffusion coefficients are divided into two groups, where one group comprises the paper sheets with noncrosslinked additives and the other group those with crosslinked additives. At early time intervals, the diffusion coefficient values of the former are higher than those of the latter. This is due to the crosslinking physical action which acts as a barrier against water molecules diffusion inside the paper sheet. The treated paper with crosslinked chitosan beads had the highest resistance to water molecules flow (lowest diffusion coefficient values) at short- and long-time intervals. Using different additives (noncrosslinked and crosslinked) modu-

lated the resistance of the water molecules flow inside the paper sheet but in all cases increases it.

Effect of Hygrothermal Ageing on the Mechanical Properties of Paper

The changes in zTS initiated by the ageing process are used to evaluate the damage of the cellulose chains caused by oxidation and hydrolytic processes which led to weaker fibers.^{24,32} The zTS represents a more sensitive tool to monitor the effects of ageing on the paper sheets than the tensile strength.³³ Figures 9–11 show that, as expected, BL and zTS of untreated and treated paper sheets decreased upon ageing. However, in general, the aged samples containing the additives showed better mechanical strength than the aged untreated samples. The results also indicate that the dry zTS of the samples containing chitosan is practically as low as that of the untreated aged sheet at all chitosan concentrations. This attributed to the increase of

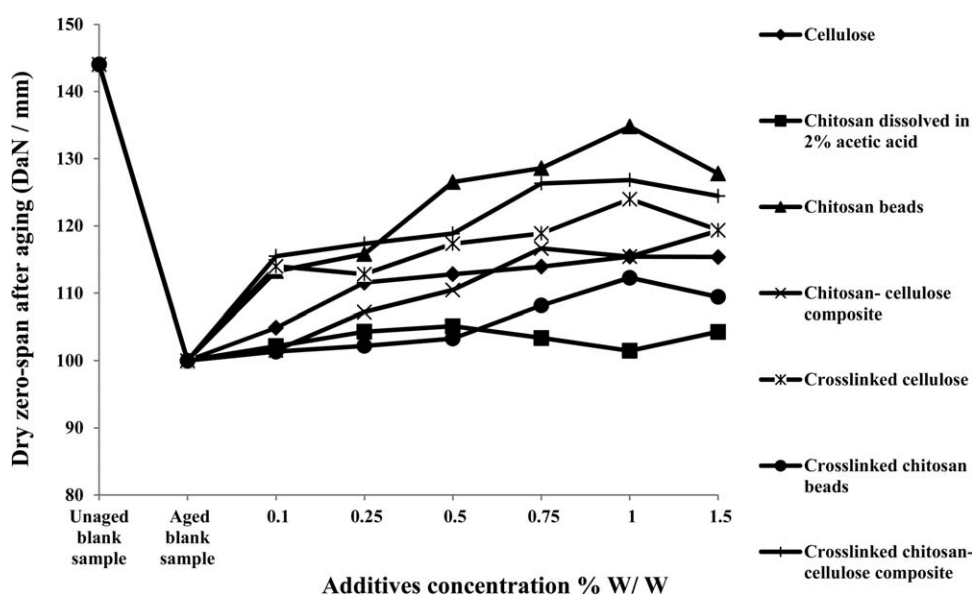


Figure 10. Dry zero-span of aged paper sheets as a function of additives concentration.

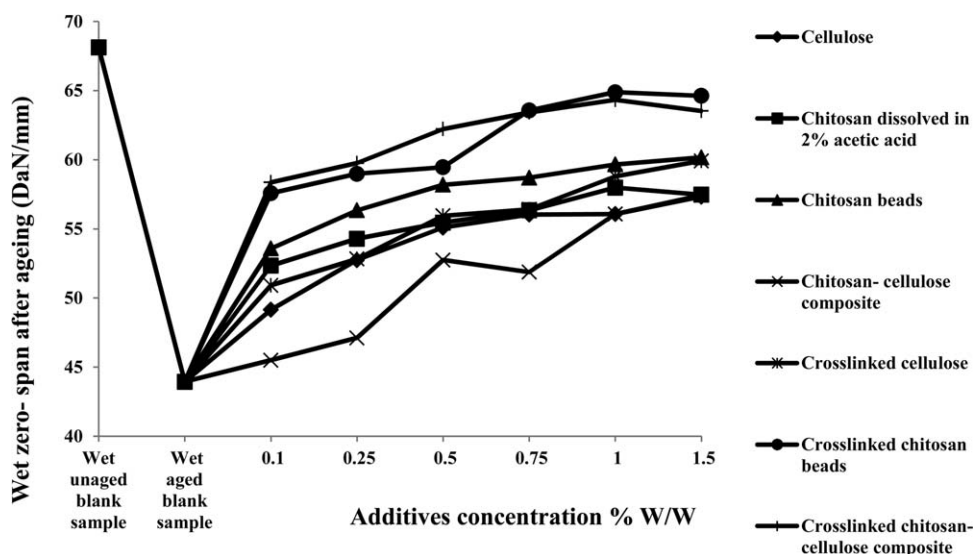


Figure 11. Wet zero-span of aged paper sheets as a function of additives concentration.

stiffness of the film formed on the paper sheet. In case of treated paper with crosslinked cellulose, crosslinked chitosan, and crosslinked chitosan–cellulose composite, the ageing resulted in an increase in the mechanical properties with increasing additives concentration compared with the untreated aged samples. This attributed to the increase of adhesion forces between the additives and the cellulose fibers. The interfiber bonding is a function of both bonded area and bond strength, thus the increase in tensile BL suggests a corresponding increase in bond strength per unit bonded area. It follows therefore that more and/or stronger bonds are formed with ageing. The rate of formation of such bonds with ageing is related to the BL of the unaged sheets which in turn is related to the original bond strength of the blank sample (untreated unaged). The results indicate that the changes in the mechanical properties occurring in paper upon ageing are caused by a gradual reduction in fiber strength accompanied with a decrease in interfiber bonding.³⁴ Ageing resulted in a decrease in the mechanical strength for both untreated and treated sheets but in case of the treated sheets, the additives preserved a very large portion of the mechanical strength of the paper sheets. The quality and the long-term stability of the paper materials produced from cellulose fibers are determined by the extent of degradation reactions taking place upon ageing. In case of cellulose, primarily the glycosidic bonds are hydrolyzed and the hydroxyl groups on the glucopyranose rings are oxidized. The hydrolysis process (which is mostly acid-catalyzed) induces cellulose chain breakage. The keto and the aldehyde groups are formed on the cellulose chain as a result of the oxidation. These groups are prone to further oxidation, which in combination with ongoing hydrolysis leads to the formation of small oxidized molecules among which are organic acids that in turn can promote further hydrolysis.³⁵ The hydrolytic and oxidative processes are thus related to one another and precede simultaneously.^{19,36} In addition to cellulose, unbleached Kraft bagasse pulp contains hemicelluloses and lignin, which degrade faster and more easily than cellulose. Acidic degradation compounds from cellulose and hemicelluloses such as acetic acid, formic acid, and other

short chain acids^{37,38} accelerate the degradation of the unbleached paper sheets in the absence of other acidity controlling factors. The mechanism of the production of the volatile acids could include the breaking of the C₅–C₆ bond on C₆ oxidized cellulose or the opening and the subsequent fragmentation of a glucopyranose ring.³⁹

CONCLUSION

Addition of chitosan, cellulose, and chitosan–cellulose composite as noncrosslinked or as crosslinked additives improves the mechanical properties of paper sheets (BL and zero-span strength for wet and dry paper sheets). This improvement is progressive with the increasing additive concentration up to 1%. The addition of chitosan and its derivatives increases the stability of the paper sheets. The SEM technique indicated a change in the surface morphology of the treated paper sheets in comparison with the untreated sheets. This change is due to the modification of the properties of the fiber network. The presence of noncrosslinked and crosslinked additives enhances the resistance to the penetration of water molecules inside the treated paper sheets which decreases the water molecules role in aging and degradation of paper.

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