

Cellulose fiber networks reinforced with glutaraldehyde–chitosan complexes

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ABSTRACT: In this study, glutaraldehyde–chitosan complexes (GA–chitosan) were prepared and were used as functional additives to enhance the strength properties of cellulose fiber networks. The adsorption and distribution of GA–chitosan on the surface of cellulose fiber were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. The effects of glutaraldehyde dosage and GA–chitosan to fiber ratio on the strength properties, including wet-strength, wet-web strength, and dry strength, were investigated. GA–chitosan did not require high temperature curing and had good cross-linking rates at room temperature. Samples treated with GA–chitosan exhibited significant improvements in their mechanical properties. Wet tensile index and wet-web tensile index (both at 50% solids), and dry tensile index, were increased by about 1300, 190, and 115%, respectively. The GA–chitosan additive developed in this study provides a useful approach to prepare high-performance value-added specialty wood-fiber based products. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42375.

KEYWORDS: cellulose and other wood products; coatings; crosslinking; fibers; mechanical properties

Received 21 January 2015; accepted 13 April 2015

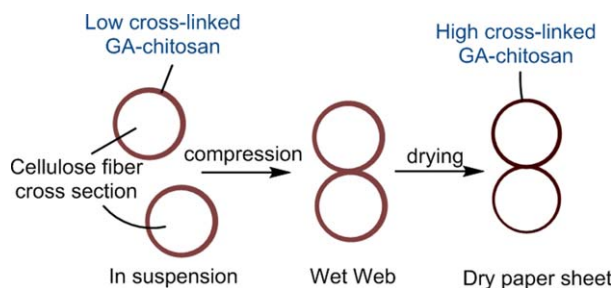
DOI: 10.1002/app.42375

INTRODUCTION

One of the key functionalities for many paper grades, such as tissue, packaging, and printing and writing papers, is their wet strength properties.¹ Wet-strength of cellulose fiber networks (i.e., the tensile index of rewetted fiber network) depends not only on fiber characteristics but also on the abundance and the strength of fiber–fiber joints.^{2,3} Various strength additives are commonly used to “bridge” between adjacent fibers and improve fiber–fiber bonding. Examples of such additives are dialdehydes that could cross-link cellulose fibers by reacting with hydroxyl groups of cellulose chain. In particular, glyoxal and glutaraldehyde have been reported to be good cross-linkers and to improve mechanical properties of cellulose fiber networks.⁴ The cross-linking reaction between aldehydes and cellulose could be catalyzed by acid, metal, or ammonium salts.^{5,6} The most frequently used catalysts are aluminum, magnesium, and zinc salts of inorganic acids. However, aluminum, magnesium, and zinc salts are toxic and would contaminate the paper. Furthermore, these additives require curing at elevated temperatures for the cross-linking reaction to occur at reasonable rates. For instance, earlier studies have shown that without curing, glutaraldehyde addition reduced the dry strength of Kraft paper by 3.2%.⁴ As a mainstream, polymeric wet-strength additives

have been used extensively to enhance the wet-strength of cellulose fiber networks.⁷ In this case, the surface of cellulose fibers is often modified *via* the adsorption of functional polymers. These functionalized fibers can be subsequently cross-linked during the papermaking or drying processes and hence improve fiber–fiber joints. Given that papermaking fibers are usually negatively charged, wet-strength polymers are best to contain cationic groups such that they can absorb on to the fibers through ion exchange mechanism. Examples of such polymers include polyamidoamine–epichlorohydrin (PAE),^{8,9} urea–formaldehyde,¹⁰ melamine–formaldehyde,¹¹ glyoxal polyacrylamide,¹² polyvinylamine,¹³ poly(maleic acid),^{14,15} poly(vinyl alcohol),¹⁶ and cationic poly(vinyl alcohol)¹⁷.

The application of cationic polymers has been proven to be an effective method to enhance the wet-strength properties of cellulose fiber networks by orders of magnitude. For instance, addition of 2.0–6.0% PAE has been reported to improve the wet-strength of paper by 900–1400%.¹⁸ However, because of the growing environmental concerns in recent years, there have been a steady trend to replace synthetic polymers with eco-friendly alternatives that could reduce our dependence on petroleum-derived chemicals.¹⁹ For example, cationic starch²⁰ and carboxymethyl cellulose (CMC)²¹ were shown to improve



Scheme 1. Preparation of GA-chitosan-modified cellulose fiber network. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fiber-fiber joints and paper strength properties²². Similarly, oppositely charged polyelectrolyte pairs, such as PAE/CMC,^{23,24} CMC/polyvinylamine,²⁵ and CMC/chitosan,^{26,27} were reported to be effective wet-strength additives. Others reported the use of cationic aldehyde starch (CAS) to cross-link bleached Kraft pulp fibers through covalent bonding that improved the wet-web strength (i.e., the tensile index of never-dried sample) by about 50% at 2.0% CAS loading and 50% solids.²⁸ In a more recent study, adipic acid dihydrazide was used to cross-link CMC-coated cellulose fibers in suspension and resulted in an increase

of ~500% in wet-web strength at 40% solids.²⁹ Another naturally derived cationic polymer of interest is chitosan. Chitosan is the deacetylated products of chitin which is the second abundant natural polymer on earth.^{30,31} It bears amino and hydroxyl groups and can be readily absorbed on the surface of cellulose fibers *via* ion exchange reaction. Chitosan is proven to be an effective wet-strength additive.³²⁻³⁴ For instance, an improvement of ~50% in wet-web strength of hardwood Kraft pulp at 50% solids was reported at 2.0% chitosan loading.³³ Chitosan complexes, such as chitosan-guanidine⁷ and chitosan-CMC,²⁷ have been also reported in the literature and were used as strength additives.

Chitosan could be cross-linked by dialdehydes, such as glyoxal, succinaldehyde, and glutaraldehyde (GA).³⁵ In this case, the 2-amino group of glucosamine residue of chitosan reacts with the aldehyde group to form a Schiff base.^{30,36} Additional details regarding this cross-linking reaction can be found elsewhere.^{30,35,36} In this work, we used glutaraldehyde cross-linked chitosan (GA-chitosan) as an eco-friendly wet-strength additive. It was found that GA-chitosan was significantly more effective than chitosan alone in enhancing the strength properties of cellulose fiber networks. GA-chitosan was first coated on cellulose fibers in pulp suspension through ion exchange reaction and was further cross-linked during drying to form a strong

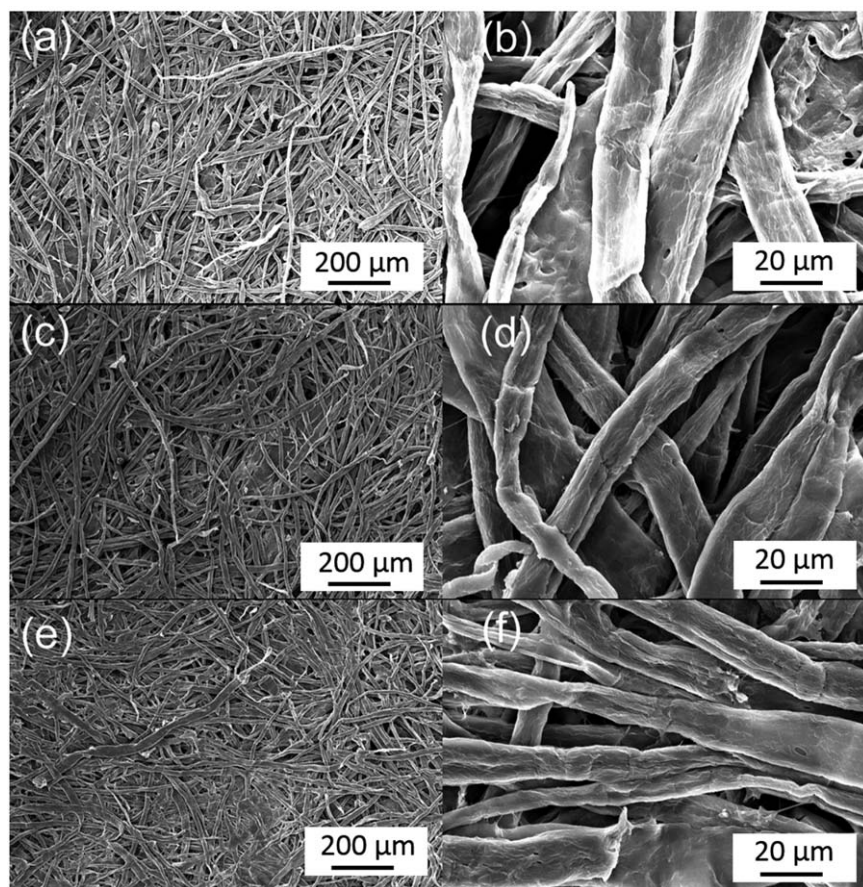


Figure 1. SEM images of cellulose fiber networks: (a,b) pristine, (c,d) treated by chitosan (chitosan/fiber = 0.1 g/2 g), and (e,f) treated GA-chitosan (GA/chitosan/fiber = 0.08 g/0.1 g/2 g).

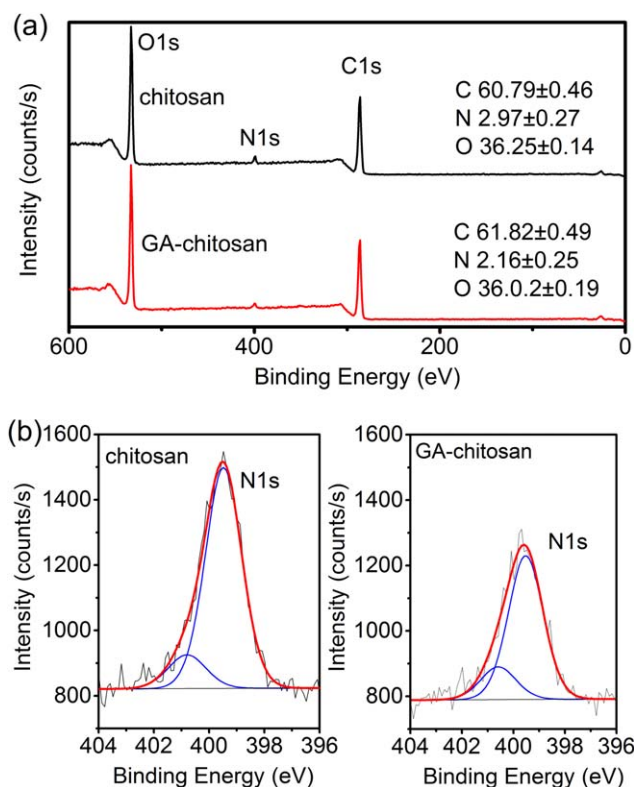


Figure 2. (a) Typical XPS Spectra of cellulose fibers treated by chitosan and GA-chitosan. (b) XPS N1s narrow scans with the curve fit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water-resistant joint between adjacent fibers. The effects of GA dosage and GA-chitosan/fiber ratio on the strength properties of cellulose fiber network were investigated. In contrast to conventional wet-strength agents like PAE, this additive has acceptable cross-linking reaction rate at room temperature,³⁷ which eliminates the need for high temperature curing and results in the energy saving. Hence, GA-chitosan additive developed in this work could be readily adopted in the production of various grades of paper such as tissue, towel, packaging, printing, and writing grades.

EXPERIMENTAL

Materials

Eucalyptus hardwood bleached Kraft pulp was supplied by Fibria Celulose (Brazil). Chitosan with a low molecular weight, glutaraldehyde (GA), and acetic acid were purchased from Sigma-Aldrich (Canada) and used as received. All experiments tested used the tap water.

Sample Preparation

Hardwood fiber suspension with a consistency of 0.5 wt % was prepared using a pulp disintegrator. This suspension was subsequently concentrated to 20 wt % using a 32- μm standard sieve. Chitosan solution (2 wt %) was prepared by mixing 2 g of chitosan, 2 g of acetic acid, and 96 g of water for 2 h under stirring. The fiber suspension was subsequently dispersed in chitosan solution under vigorous stirring to obtain a suspension

containing 2 wt % of fiber. The final chitosan/fiber ratio was varied from 0.0125 g/1 g to 0.2 g/1 g by adjusting the chitosan loading. After 30 min, glutaraldehyde solution (25 wt %) was added into the mixture under strong stirring and was allowed to react for another 30 min. The amount of GA solution was varied from 0.005 to 0.04 g depending on the target GA level. The resulted suspension was diluted to 0.1 wt % and used to prepare samples with a target grammage of 100 g (dry fiber) m^{-2} in a British handsheet making machine according to Tappi Standard T205. Samples were then pressed between blotters at 350 kPa for 5.5 min to partially remove water and were allowed to dry at room temperature for 24 h. For wet-web strength tests, sheets were compressed between plastic films at 350 kPa for 5.5 min and were cut into even strips. These strips were allowed to dry until the target water content (varying from 22 to 65 wt %) was achieved. Control samples containing untreated cellulose fibers were also prepared under similar conditions.

Characterizations and Measurements

Cellulose fiber networks were characterized using scanning electron microscopy (SEM, JSM-6610LV, JEOL, Japan). Before SEM observations, all samples were sputter-coated with gold to improve the conductivity. The surface composition of cellulose fiber networks was analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha XPS Spectrometer (ThermoFisher, East Grinstead, UK) using monochromatized Al K α X-ray source. These samples were run at a take-off angle (relative to the surface) of 90° with a spot area (on a 90° sample) of 400 μm^2 . Charge compensation was provided. The position of the energy scale was adjusted to place the main C1s feature (C–O) at 286.5 eV. A survey spectra was first obtained (pass energy = 200 eV) followed by the C1s, N1s, and O1s regions at high energy resolution (PE = 25 eV). Relative atomic percentage was taken from the latter three spectra. The instrument control and all data processing was performed using the software (Avantage) provided with the instrument. Samples were also analyzed using a time-of-flight secondary ion mass spectrometry (ToF-SIMS) IV instrument (ION-TOF GmbH, Münster, Germany) equipped with a liquid metal ion gun (LMIG) with a Bi³⁺ cluster primary ion source. The target current of the primary ion beam was typically 1 pA and had a pulse width of 10 ns before bunching for spectroscopy and imaging at a spatial resolution of better than 100 nm. Ion masses were determined by a time-of-flight analyzer with a mass resolution of five significant figures allowing accurate mass assignment. The tensile index was measured in a SinTech Universal Testing Machine with a 1-kN load cell according to TAPPI Standard T494. For each sample, five strips 25 mm wide with a span of 100 mm were tested at an elongation rate of 14 mm min^{-1} . For wet-strength test, each strip was soaked for 30 min in water and its saturated water sorption was measured after removing the water on surface. Wet-strength and wet-web strength were measured at various solid contents ranging from 20 wt % to about 70 wt %. For this reason, wet samples were allowed to dry partly in air for varying periods of time until the target solids contents were achieved prior to the tensile testing.

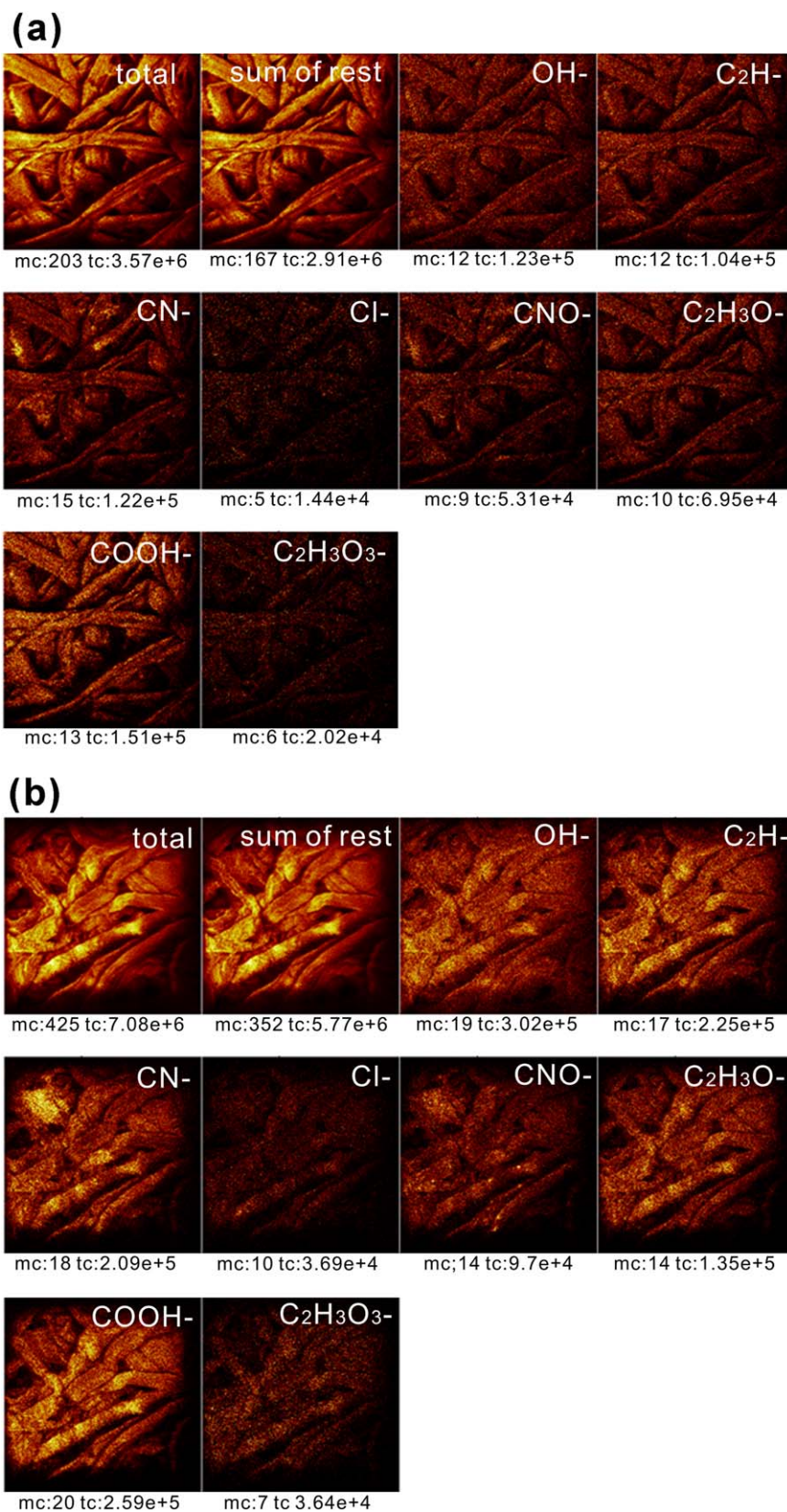


Figure 3. ToF-SIMS images of cellulose fiber networks treated by chitosan (a) and GA-chitosan (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

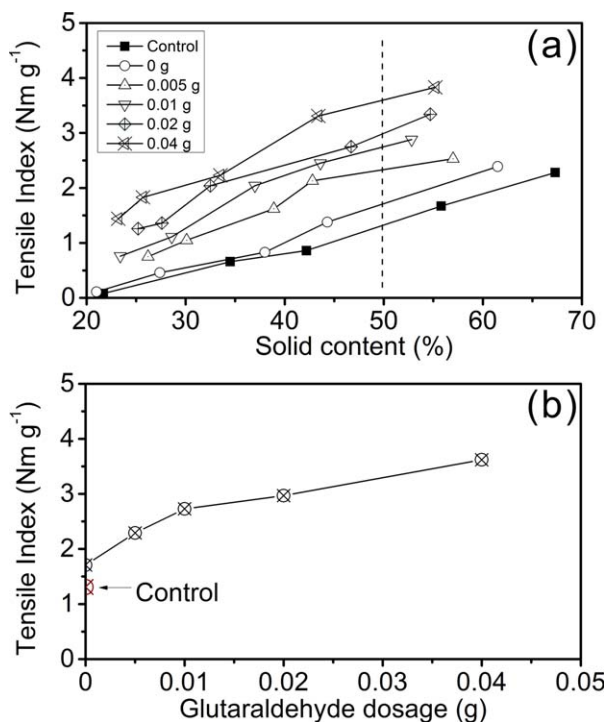


Figure 4. Wet-web tensile index of samples: (a) as a function of solids content at various glutaraldehyde (GA) dosages and (b) at 50% solids as a function of GA dosage. Chitosan/fibers ratio was kept as 0.1 g/1 g. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Characterization of GA–Chitosan Treated Samples

Scheme 1 shows the process for the preparation of GA–chitosan modified sheets. Glutaraldehyde and chitosan could form polymers with larger molecular weights and even micorgels through cross-linking reactions.³⁷ GA–chitosan cross-linking products are expected to adhere to the surface of fibers and develop more contact areas by bridging between adjacent fibers during the sheet forming process. The unreacted functional groups could undergo additional cross-linking reactions during the drying process and further improve the fiber–fiber joints. From literature, the larger the size of these cross-linked polymers, the greater the improvement in the strength properties of samples.³⁸ Figure 1 shows SEM images of cellulose fiber networks. It can be seen that cellulose fiber networks treated by GA–chitosan had less surface pores and appeared smoother compared to pristine cellulose fiber networks and samples treated with chitosan alone. This observation suggests a greater extent of polymer adsorption on the fiber surfaces in GA–chitosan treated samples.

XPS spectra for cellulose fibers treated by chitosan and GA–chitosan are shown in Figure 2(a). Both cellulose fibers show the presence of oxygen, nitrogen, and carbon atoms on their surfaces. The average atomic percentages of elements were calculated from three spectra. C/N ratio were 20.5 and 28.6 for cellulose fibers treated by chitosan and GA–chitosan, respectively, whereas for C/O ratio were 1.67 and 1.72, respectively. The increase in the percentages of carbon and oxygen in GA–chito-

san treated sample confirms the adsorption of GA on the fiber surface. The resolved N1s spectra for two cellulose fibers are shown in Figure 2(b). Two peaks were identified and the peak at 399.5 eV was assigned to amine group, whereas the peak at 400.8 eV was assigned to imino and amide groups.^{39,40} N1s_(399.5)/N1s_(400.8) for cellulose fibers treated by GA–chitosan was 4.52, which was smaller than that for cellulose fibers treated by chitosan alone (6.28). This result indicates that some amine groups reacted with glutaraldehyde and formed imino groups.³⁰ In addition, ToF-SIMS analyses were coupled with XPS to examine the distribution of chitosan on the surface of cellulose fibers. To locate chitosan, CN⁻, and CNO⁻ fragments, which

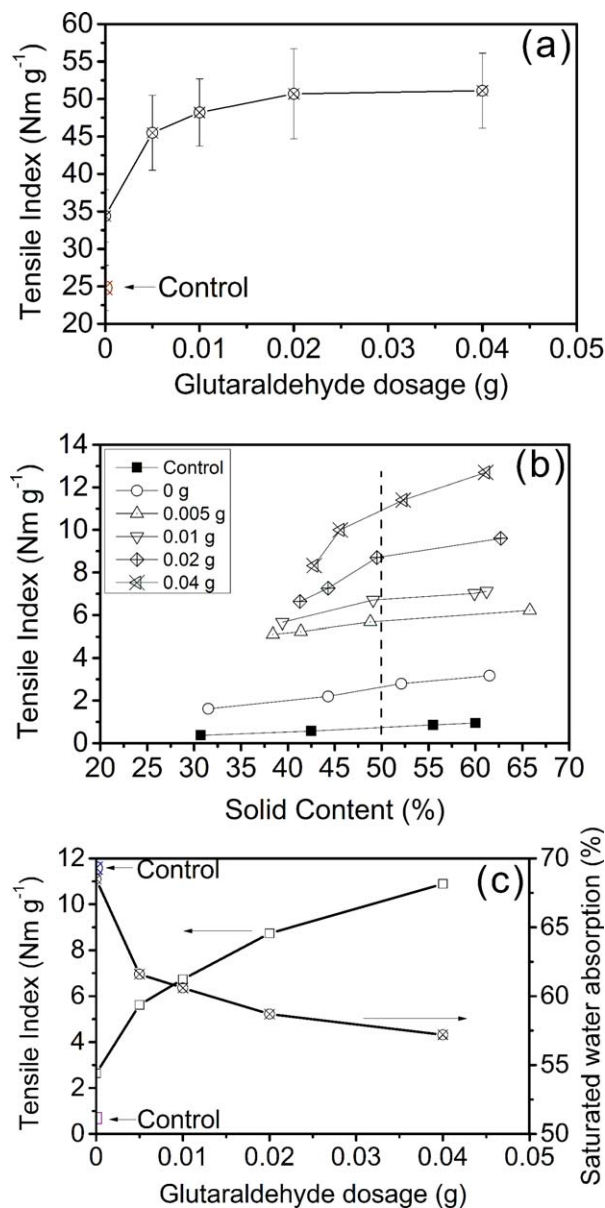


Figure 5. Effect of glutaraldehyde (GA) dosages on the mechanical properties of samples. (a) Dry tensile index, (b) wet tensile index, and (c) wet tensile index at 50% solids and the saturated water absorption. Chitosan/fibers ratio was 0.1 g/1 g. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

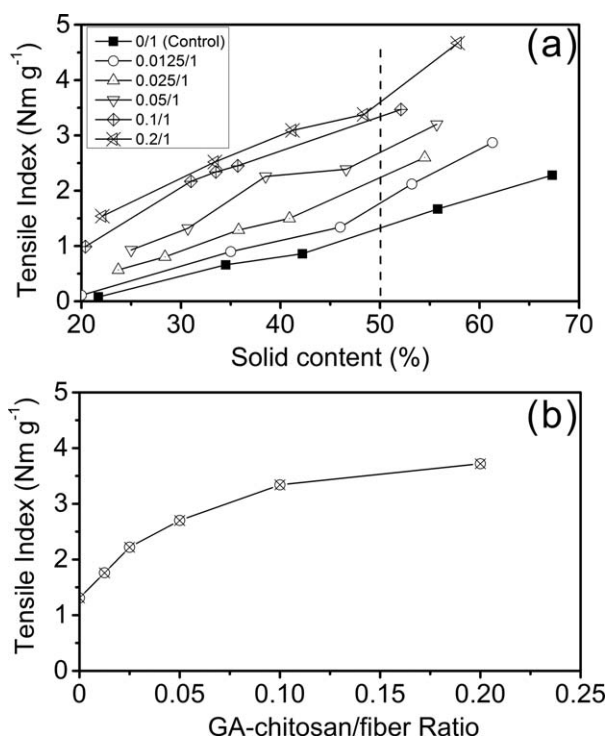


Figure 6. Effect of GA–chitosan/fiber ratio on: (a) wet-web tensile index as a function of solids contents, and (b) wet-web tensile index at 50% solids. GA/chitosan feed ratio was 0.2 g/1 g.

could be attributed to chitosan, were identified. Figure 3 illustrates the spatial distribution of these fragments on fiber surface. In this figure, yellow spots indicate the presence of CN^- and CNO^- fragments, and the intensity of the color is directly related to the ion concentration. Based on these images, the treated fibers were uniformly covered by CN^- and CNO^- , which indicated a uniform distribution of chitosan on the fiber surface. Moreover, the yellow intensity of CN^- and CNO^- for cellulose fibers treated by GA–chitosan was found to be higher than that of cellulose fibers treated with chitosan alone, which indicates a larger amount of chitosan was absorbed on the GA–chitosan treated fibers.

Effect of Glutaraldehyde Dosage

Figure 4 shows the effect of GA dosage on wet-web tensile index at a constant chitosan loading of 0.1 g/1 g fiber. As expected, the wet-web tensile index shifted upward with increasing GA dosage. This trend is better highlighted in Figure 4(b) that shows the wet-web tensile index of samples at a constant solids content of 50%. Based on this figure, the wet-web tensile index with a GA dosage of 0.04 g was 3.7 Nm g^{-1} that was significantly greater than 1.3 Nm g^{-1} measured for the control sample (pristine cellulose fiber network). Figure 4(b) also shows that the wet-web tensile index of chitosan treated samples (i.e., no GA added) was only slightly greater than that of the control (1.7 Nm g^{-1}). The dry tensile index of samples also increased with increasing GA dosage [Figure 5(a)] but reached a plateau at a GA dosage of about 0.02 g/1 g fiber. The dry tensile index was 50.7 Nm g^{-1} at a GA dosage of 0.04 g, 24.5 Nm g^{-1} for the control and 34.9 Nm g^{-1} for the sample treated only by chitosan. These find-

ings indicate that GA–chitosan is a more effective strength additive than chitosan alone in both wet and dry states.

Figure 5(b) shows the effect of GA dosage on the wet tensile index of samples. It was found that wet tensile index shifted upward with increasing GA dosage. Wet tensile index at 50% solids was 10.8 Nm g^{-1} at a GA dosage of 0.04 g that was an improvement of 1250% in comparison with the control (0.8 Nm g^{-1}) [Figure 5(c)]. However, this effect was less than linear and greater GA loadings had a diminishing return on the wet-strength of the sample. Increasing the GA dosage resulted in an increase in the extent of cross-linking reaction and formation of larger GA–chitosan products that covered fiber surfaces. Therefore, the strength properties were enhanced by increasing

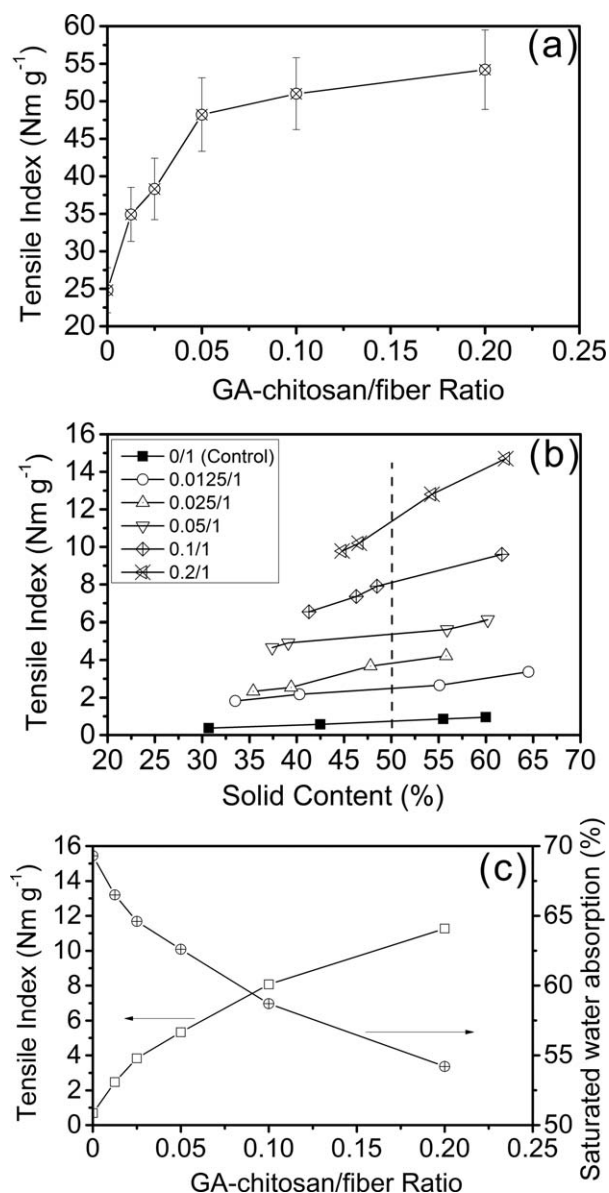


Figure 7. Effect of GA–chitosan/fiber ratios: (a) dry tensile index, (b) wet tensile index at various solids contents, and (c) wet tensile index at 50% solids and saturated water absorption of cellulose fiber network. GA/chitosan ratio was kept as 0.2 g/1 g.

GA dosage. However, with further increase in GA loading as fibers were increasingly covered by the polymeric additives, GA–chitosan complexes were less likely to adsorb to fibers, hence the diminishing return. Figure 5(c) exhibits the saturated water absorption for various cellulose fiber networks. It can be seen that the saturated water uptake was 69% for control and it decreased with increasing GA dosage. This was likely due to the coverage of fiber surface with the cross-linked GA–chitosan products that governed the swelling of cellulose fibers and consequently the water uptake. Accordingly, the wet-strength retention, defined as the ratio of the wet-strength of treated paper after saturation with water to the dry strength of the control, increased with increasing GA dosage. The wet-strength retention was 32% for the sample with a GA dosage of 0.04 g compared to about 7% for the control sample.

It is notable that the improvement in the wet-strength (1250% for GA dosage of 0.04 g) was much higher than that of wet-web strength (106% for GA dosage of 0.04 g). This is because during the drying process, fiber-fiber separation decreases and the GA–chitosan complexes are more likely to form bridges between adjacent fibers. Therefore, GA–chitosan had a larger impact in improving the wet-strength rather than the wet-web strength.

Effect of GA–Chitosan/Fiber Ratio

Figure 6 shows the effect of GA–chitosan/fiber ratio (by weight) on wet-web strength of cellulose fiber network at a constant GA/chitosan ratio of 0.2 g/1 g. As expected, wet-web tensile index increased with increasing GA–chitosan loading on the fiber and with increasing the solids content. The wet-web tensile index at solids content of 50% is plotted in Figure 6(b). This figure shows that the GA–chitosan loading had a diminishing return in terms of improving the wet-web tensile index of samples. The wet-web tensile index at 50% solids for GA–chitosan/fiber ratio of 0.2 g/1 g was 3.8 Nm g⁻¹, which showed an improvement of 192% comparison to the control sample (1.3 Nm g⁻¹). The effect of GA–chitosan/fiber ratio on dry tensile index was also studied as shown in Figure 7(a). The dry tensile index at 0.2 g/1 g GA–chitosan/fiber loading was 53.2 Nm g⁻¹ that was 117% larger than the control (24.5 Nm g⁻¹). By increasing the GA–chitosan loading, the dry tensile index increased and reached a plateau at ratios above 0.05 g/1 g. A similar trend was also found for wet-strength that exhibited an increase with increasing GA–chitosan loading [Figure 7(b,c)]. The wet tensile index at 50% solids for 0.2 g/1 g was 11.5 Nm g⁻¹ that was 1337% higher than that of the control sample (0.8 Nm g⁻¹). Once again, these findings may be explained based on the effect of polymer loading on fiber coverage. Similar to our earlier observation, the saturated water uptake decreased with increasing the amount of GA–chitosan [Figure 7(c)].

CONCLUSIONS

We developed a method to prepare cellulose fiber network with enhanced tensile strength properties using glutaraldehyde–chitosan complexes (GA–chitosan). GA–chitosan cross-linked polymers were prepared by reacting chitosan and glutaraldehyde. This material was applied on the surface of cellulose fibers in pulp suspension and was further cross-linked during the drying pro-

cess to form strong bridges between adjacent cellulose fibers, which significantly improved the strength properties of cellulose fiber network. In comparison with the control sample, wet-web tensile index at 50% solids, dry tensile index and wet tensile index at 50% solids were increased by as high as about 190, 115, and 1300%, respectively, after optimizing the formulation, thus demonstrating better reinforcement than using only chitosan as wet-strength additive. These enhancements in the strength properties indicate a significant increase in the fiber–fiber bonding that is expected to also improve other mechanical properties of paper such as out-of-plane tear resistance, bursting strength, and folding endurance. Compared with conventional strength additives such as PAE, the proposed GA–chitosan exhibits a sufficiently high cross-linking reaction rate at room temperatures and does not need high temperature curing that results in significant energy saving. The GA–chitosan additive developed in this study provides a useful approach to prepare high-performance value-added specialty wood-fiber based products.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support of this work by the NSERC Green Fibre Network.

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