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Original Article

Effects of shrimp chitosan on the physical properties of handsheets

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ABSTRACT

The effects of shrimp chitosan as an additive were determined on the physical properties of handsheets, especially: their brightness, opacity, surface roughness and surface water absorptiveness. Commercial, hardwood, bleached kraft pulp was beaten to attain 390 mL Canadian standard freeness and then made into four sets of handsheets by mixing each part of the beaten pulp slurry with shrimp-chitosan solution to obtain 0.00%, 0.25%, 0.50% and 0.75% (oven dry weight (o.d. wt.) of pulp), respectively, in accordance with standard test methods. All the sets of handsheets were conditioned for 1 wk and then tested for their mechanical and physical properties at $50 \pm 2\%$ relative humidity and 23 ± 1 °C. The results indicated that even though there were some substantial decreases in some physical properties of shrimp-chitosan-treated handsheets (brightness, surface roughness and surface water absorptiveness), their opacity was slightly increased. Most of the mechanical properties of shrimp-chitosan-treated handsheets such as the bursting index, folding endurance, tensile index, modulus of elasticity and tensile energy absorption were greatly increased with the addition of shrimp chitosan at 0.25% o.d. wt. of pulp to 0.50% o.d. wt. of pulp. However, there was no effect on the tearing strength by adding shrimp chitosan to the handsheets.

Introduction

Chitosan is a bio-material produced by the deacetylation of chitin, which is derived from shrimp or crab shell, with sodium hydroxide (Ifuku et al., 2013). Therefore, chitosan is widely used as an environmentally friendly product with antibacterial, biodegradable and non-toxic properties (Ashori et al., 2006; Sarwar et al., 2009; Nicu et al., 2011, 2013). As its chemical structure ($C_6H_{11}NO_4$) is very similar to cellulose, chitosan is easily absorbed onto the cellulosic surface of fibers due to chemical affinity and has been applied to improve some properties of cellulose-based material especially those of cellulose fibers and paper sheets (Lertsutthiwong et al., 2002, 2004; Nada et al., 2005; Ashori et al., 2006; Sarwar et al., 2009; Nicu et al., 2011, 2013). Even though chitosan has demonstrated its possible application in the paper-making process as a dry and wet strength additive (Lertsutthiwong et al., 2002; Nada et al., 2005; Ashori et al., 2006; Sarwar et al., 2009; Nicu et al., 2011, 2013), some properties of paper treated with chitosan as an additive have not yet been reported, such as brightness, opacity, surface roughness and surface water absorptiveness.

Therefore, the purpose of the current research was to clarify and demonstrate the effects of shrimp chitosan as an additive on the physical properties of handsheets, especially: their brightness, opacity, surface roughness and surface water absorptiveness.

Materials and methods

Preparation of chitosan solution

Dried shrimp chitosan (percentage > 90%; ash < 1%; moisture content < 10%) weighing 0.060 g was soaked with 600 mL of acetic acid (5% concentration) for about 40 min and then subjected to stirring for about 20 min, in accordance with the preparation procedure suggested by the shrimp-chitosan manufacturer (Marine Bio Resources Co., Ltd.; Samut Sakhon; Thailand). The objective was to produce a clear and colorless solution of shrimp chitosan. A pH level of 3.0 was maintained.

Handsheet production

In this study, the Technical Association of the Pulp and Paper Industry (TAPPI) test methods (Anonymous, 2002) were applied to the handsheet production and testing. A commercial, hardwood, bleached kraft pulp was beaten with a Valley beater (Laurentzen and Wettress; Stockholm; Sweden) to obtain 390 mL Canadian

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standard freeness according to the TAPPI T-200 standard. Four sets of handsheet production were conducted by mixing each part of the beaten pulp slurry containing 1.2 g of oven dry weight (o.d. wt.) of pulp with 0 mL, 30 mL, 60 mL and 90 mL of the chitosan solution to obtain 0.00% o.d. wt. of pulp, 0.25% o.d. wt. of pulp, 0.50% o.d. wt. of pulp and 0.75% o.d. wt. of pulp, respectively, in accordance with the TAPPI T-205 standard. Ten handsheets per set were produced. Deionized water was used during the production of the handsheets.

Handsheet testing

In accordance with the TAPPI T-205 standard, all the sets of handsheets were conditioned for 1 wk and then tested for their properties at 50 ± 2% relative humidity and 23 ± 1 °C. The mechanical properties of the handsheets—bursting strength (the TAPPI T-403 standard), folding endurance (the TAPPI T-511 standard), tearing resistance (the TAPPI T-414 standard), and tensile strength (the TAPPI T-494 standard)—were determined using a bursting strength tester (Laurentzen and Wettress; Stockholm; Sweden), a folding tester (Kumagai Riki Kogyo Co., Ltd.; Tokyo; Japan), an Elmendorf tearing tester (Laurentzen and Wettress; Stockholm; Sweden) and a tensile tester (EJA-series, Thwing-Albert Instrument Co.; West Berlin, NJ, USA), respectively. The physical properties of handsheets—brightness and opacity (to the TAPPI T-452 and T-425 standards), surface roughness (to the TAPPI UM 535 (Bendtsen) standard), and surface water absorptiveness (to the TAPPI T-835 (drop test) standard)—were also determined using an automatic reflectometer (Model-3, Kumagai Riki Kogyo Co. Ltd.; Tokyo; Japan), a roughness tester (Frank-PTI, Quality Testing Instruments; Vorchdorf; Austria) and a micropipette 100 μL (Eppendorf; Missisauga, ON, Canada), respectively. In this study, both sides of the handsheets (the top and the bottom sides) were tested for their surface roughness and surface water absorptiveness.

Results and discussion

Tables 1 and 2 show the changes in the physical and mechanical properties of the handsheets treated with shrimp chitosan. Some uncommon data were found concerning the effects of shrimp chitosan on the physical properties of the handsheets—brightness, opacity, surface roughness and surface water absorptiveness. As can be seen in Fig. 1, the brightness of shrimp-chitosan-treated handsheets significantly decreased. This was possibly because the handsheets treated with shrimp chitosan had a higher apparent density or fewer air voids in their structure, resulting in a decrease in the refraction and scattering of the light traveling in their structure as shown in Fig. 2. Casey (1981) theoretically stated that the brightness of handsheeets demonstrates the amount of diffusely reflected light caused by refraction and scattering. The difference between the refractive index of transparent cellulose fiber and that of air voids in the handsheet structure comprehensively affected the refraction and scattering of the light traveling throughout the structure. Khantayanuwong et al. (2006) also demonstrated that the brightness of recycled handsheets increased while their apparent density decreased. These phenomena were consistent with the effect of the changed apparent density of paper on its brightness due to beating and wet pressing (Casey, 1981). Furthermore, the decrease in brightness was possibly due to the increase in light absorption of the higher apparent density of handsheets (that is their opacity increased), even though Casey (1981) and Khantayanuwong et al. (2006) demonstrated that handsheets with a very low density or with a very high density could be transparent due to the transparency of air voids or due to lots of transparent material in the cellulose fibers in the handsheet structure, respectively.

Fig. 3 shows that both the top and bottom sides of shrimp-chitosan-treated handsheets demonstrated smoothness compared to the equivalent untreated ones, especially the handsheets treated with shrimp chitosan at 0.25% o.d. wt. of pulp. As can be seen, however, the smoothness of shrimp-chitosan-treated handsheets was not increased by increasing the amount of shrimp chitosan in the handsheets. This result possibly indicated that high amounts of shrimp chitosan applied to handsheet production might not be distributed uniformly throughout the surface of the handsheets even though a shrimp-chitosan film could form on the fiber surface (Lertsutthiwong et al., 2002).

Fig. 4 demonstrates the significant decrease in the water absorptiveness of the handsheets with an increase in the shrimp-chitosan content. Even though a significant decrease in the water absorptiveness of the handsheets occurred using a very small content of shrimp chitosan (0.25% o.d. wt. of pulp), the lower

Table 1
Physical properties of handsheets treated with various shrimp-chitosan contents.

Shrimp-chitosan content (% of o.d. wt. pulp)[a]	Apparent density (g/cm^3)	Brightness (%)	Opacity (%)	Bendtsen roughness (mL/min)		Water drop absorption (s)	
				Top side	Bottom side	Top side	Bottom side
0.00	0.60 ± 0.01[b]	81.8 ± 1.27	81.2 ± 0.78	680 ± 73	661 ± 71	12 ± 2	11 ± 1
0.25	0.62 ± 0.01	75.2 ± 0.48	82.1 ± 0.53	544 ± 114	551 ± 65	81 ± 5	78 ± 12
0.50	0.62 ± 0.01	75.6 ± 0.72	82.6 ± 0.88	575 ± 47	580 ± 87	187 ± 35	171 ± 21
0.75	0.61 ± 0.01	77.7 ± 0.27	82.8 ± 0.35	655 ± 77	583 ± 41	189 ± 14	170 ± 18

[a] % of oven dry weight pulp.
[b] Mean values are shown with the 95% confidence interval.

Table 2
Mechanical properties of handsheets treated with various shrimp-chitosan contents.

Shrimp chitosan content (% of o.d. wt. pulp)[a]	Burst index (kPa·m^2/g)	Folding endurance (double folds)	Tear index (mN·m^2/g)	Tensile index (Nm/g)	Modulus of elasticity (MPa)	Tensile energy absorption index (mJ/g)
0.00	2.39 ± 0.05[b]	23 ± 2	10.3 ± 0.32	42.9 ± 1.91	1594 ± 272	1193 ± 109
0.25	2.61 ± 0.24	31 ± 2	10.2 ± 0.15	46.9 ± 1.20	1943 ± 137	1493 ± 124
0.50	2.75 ± 0.30	34 ± 3	10.8 ± 0.20	48.6 ± 2.88	2037 ± 66	1522 ± 307
0.75	3.09 ± 0.16	35 ± 4	10.2 ± 0.09	49.3 ± 1.93	2060 ± 206	1582 ± 192

[a] % of oven dry weight pulp.
[b] Mean values are shown with the 95% confidence interval.

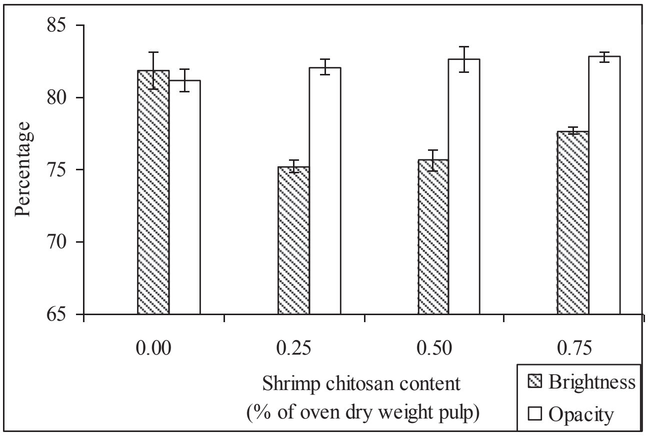

Fig. 1. Changes in brightness and opacity of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

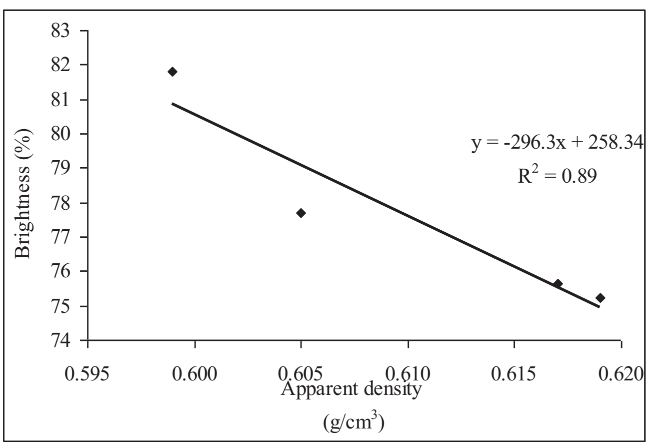

Fig. 2. Relationship between the changed apparent density and brightness of shrimp-chitosan-treated handsheets (R^2 is the coefficient of determination).

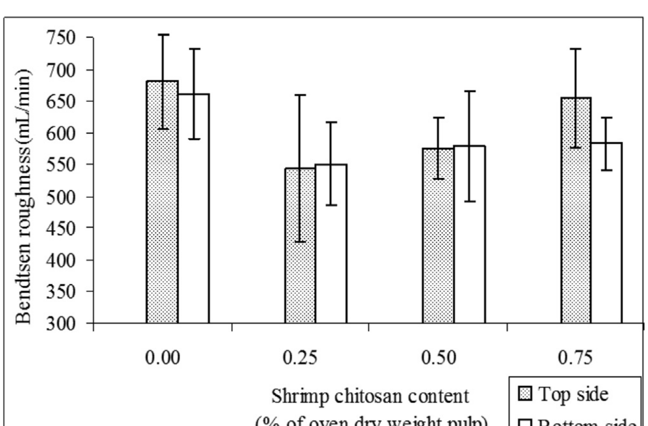

Fig. 3. Changes in surface roughness of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

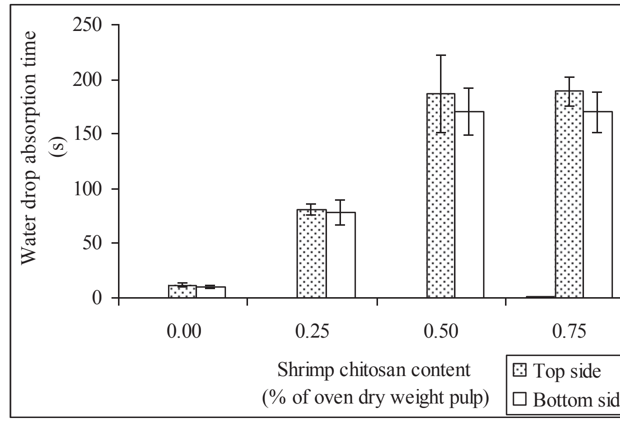

Fig. 4. Changes in water absorbability of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

capacity for water absorptiveness of the handsheets could be reached and leveled off if the handsheets were treated with shrimp chitosan at 0.50% o.d. wt. of pulp or 0.75% o.d. wt. of pulp. This result was not consistent with the hydrophilic property of shrimp chitosan due to its abundant hydroxyl groups. Therefore, the decrease in the water absorptiveness was possibly because the shrimp chitosan could form film-like structures on the fiber surface in the handsheets promoting a longer water-absorption time (Lertsutthiwong et al., 2002; Sarwar et al., 2009). As also can be seen in Fig. 4, there is slightly less capacity for water absorptiveness on the bottom side of the handsheets because the handsheets according to the TAPPI T-205 standard generally possess a slight luster on the bottom surface.

Figs. 5–7 demonstrate that most of the mechanical properties of handsheets (burst index, folding endurance, tensile index, modulus of elasticity and tensile energy absorption) were enhanced by the increased content of shrimp chitosan applied to the production of handsheets. Moreover, as can be seen, the level of most of these properties leveled off in the handsheets treated with shrimp chitosan at 0.50% o.d. wt. of pulp or 0.75% o.d. wt. of pulp while the bursting strength continued to increase with the addition of shrimp chitosan. This was consistent with the results reported by Lertsutthiwong et al. (2002) and Ashori et al. (2006), where paper sheets treated with chitosan at from 0.25% o.d. wt. of pulp to 0.5% o.d. wt. of pulp could increase their own strength to a greater degree than those treated with chitosan at from 0.5% o.d. wt. of pulp

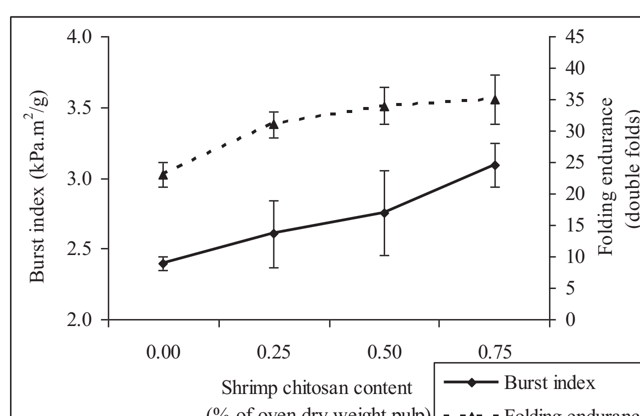

Fig. 5. Changes in bursting strength and folding endurance of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

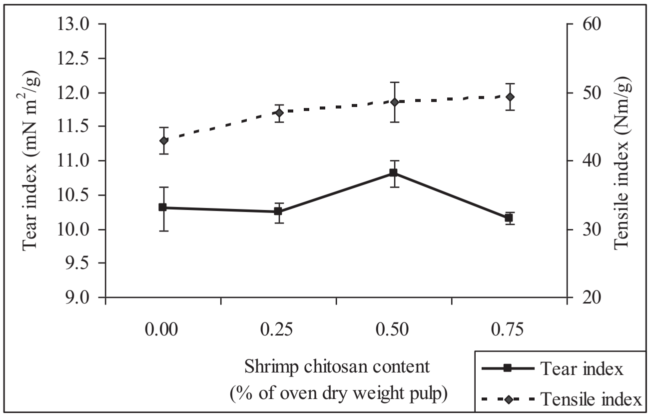

Fig. 6. Changes in tearing strength and tensile strength of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

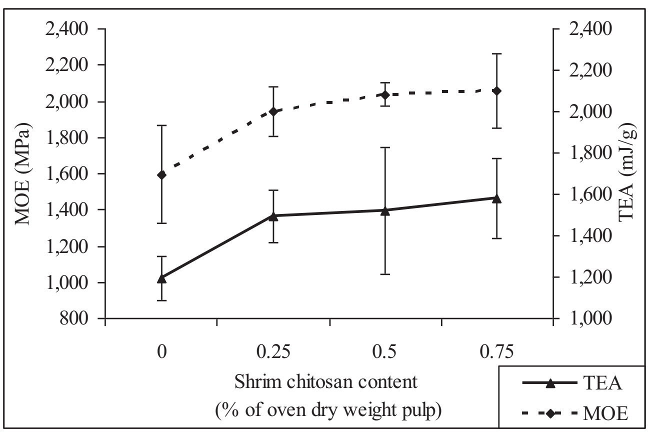

Fig. 7. Changes in modulus of elasticity (MOE) and tensile energy absorption (TEA) of shrimp-chitosan-treated handsheets with error bars showing the 95% confidence intervals.

to 1.0% o.d. wt. of pulp. However, it seems that the tearing strength was not affected by any level of shrimp chitosan in the handsheets, even though Lertsutthiwong et al. (2002) and Ashori et al. (2006) demonstrated that paper sheets treated with chitosan possessed higher tearing strength. Sarwar et al. (2009) also demonstrated that the tearing strength of handsheets could be increased primarily with the first 0.5% addition of chitosan. These results could emphasize that the tearing resistance of handsheets fundamentally relies only on fiber length in their structure, that is, all the handsheets were produced with the same fibrous raw material or pulp without any different treatment. Khantayanuwong et al. (2006) demonstrated that the portion of long fibers in recycled handsheets probably increased due to fines loss. Long fibers could produce a high level of tearing resistance in a handsheet due to the increase in the frictional drag work per fiber (Casey, 1981).

Thus, the opacity was slightly enhanced by the addition of shrimp chitosan while some other parameters tested (brightness, surface roughness and water absorptiveness) showed substantial decreases. Most of the mechanical properties of shrimp-chitosan-treated handsheets, such as the bursting index, folding endurance, tensile index, modulus of elasticity and tensile energy absorption, were substantially increased with the addition of shrimp chitosan at from 0.25% o.d. wt. of pulp to 0.50% o.d. wt. of pulp. However, there was no effect on the tearing strength from the addition of shrimp chitosan to the handsheets.

Conflict of interest

None.

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