The Effect of Chitosan into Mechanical and Optical Properties of Paper

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Abstract: Chitosan is one of a biomaterial non-toxic, biodegradable, and biocompatibility material. Chitosan has been studied as an additive in papermaking to enhance the properties of paper such as mechanical and optical properties. The aim of this research was to investigate the effect of chitosan on the properties of recycled paper. In process of papermaking, four different concentrations of chitosan (0.5%; 1%; 1.5%, and 2%) were added in 1% acetic acid. The efficiencies of chitosan in papermaking was examined by measuring and analyzing the properties of paper, in particular mechanical and optical properties. The results showed that with the increasing dosage of chitosan, the mechanical properties of paper, such as tensile strength increased while the water absorption of paper decreased. It also found that the brightness of paper was not affected by the addition of chitosan. The tensile index value of HVS paper was more significant than the newspaper. The optimum/peak concentration of chitosan in papermaking was obtained at concentration of 1.5%. Furthermore the water absorptiveness of HVS paper was lower than the newspaper. The application of chitosan concentrations from 0.5% to 2%, cannot trigger the increasing of brightness of paper, which remained constant with further increase of chitosan concentration. This research shows that chitosan is useful as an additive in the recycled papermaking to improve the mechanical properties of paper.

1 INTRODUCTION

Paper is one of the printed materials that is very needed in the printing and packaging industry. Paper is the printing component that will determine runnability and print quality. The properties of paper and papermaking will affect the print quality that will be produced. Paper is the required printing material. With the increasing world population and the higher consumption of paper usage, paper waste will also increase. Increased paper production will result in increasing raw materials for making wood paper from plants needed. Nowadays, with the increasing awareness of humans on the environment, recycled paper becomes essential in life, which has a positive impact on the environment, including saving natural resources. Recycling papermaking can be reduced excessive deforestation as raw material, reducing the level of pollution due to paper waste and paper processing and making processes are cheaper than making and processing paper from virgin pulp.

Paper is made from cellulose fibers that are added with additives such as fillers and sizing to improve the properties of paper it produces. The filler used to increase brightness, the opacity of paper, with fill the pores of the paper. Fillers consist of white pigment as inorganic compounds, such as calcium carbonate, china clay, titanium dioxide, and others. A number of these synthetic additives are non-biodegradable and and may cause negative effects to environment. Printing material should be non-toxic, eco-friendly, and biodegradable. The development and improvement of biodegradable materials has attracted increasing research interest.

Chitosan is increasingly used and applied in a wide variety of industries. Chitosan is a natural heteropolymer containing glucosamine and acetyl glucosamine. Chitosan has a unique characteristic that is cation, biodegradable, biocompatible, non-toxic, and has antimicrobial activity (Crini, 2008 and Patale, 2011). Chitosan has anti-termite activity, which can cause the paper to be stored for an extended period (Muryeti, 2018). Chitosan can absorb heavy metals such as Cu, Zn, Pb, Cd, and other heavy metals. Chitosan active sites either in the form of NH_2 or in the protonated state of NH_3^+ can adsorb heavy metals through the formation of chelates or ion exchangers (Mourya, 2010).

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Chitosan also has the ability as an adsorbent to dye such as mono azo dye, methyl orange, because chitosan a protonated state, the amine group in chitosan can bind to the sulfonate group of dyes (Chiou, 2006 and Zulkarnain, 2009).

The use of chitosan in various fields of modern industry is quite a lot including in the pharmaceutical, cosmetic, food, paper, textile, agriculture, membrane, and health industries (Shigemasa, 1995).

Chitosan is produced from the deacetylation of chitin and has the same chemical structure as chitin, consisting of long molecular chains and high molecular weight. The difference between chitin and chitosan is that each chitin ring is present in the acetyl group (-CH_3-CO) in the second carbon atom, whereas in chitosan there is an amine group (NH_2). Chitosan can be produced from chitin through a process of acetylation using reacting using high concentrations of alkali with a relatively long time and high temperatures.

Chitosan has relatively more amino groups compared to chitin, so it is more nucleophilic and basic. The crystallinity of chitosan caused by intermolecular and intramolecular hydrogen bonds. It is lower than that of chitin, making it easier to apply in several reagents. Chitosan is a biopolymer with abundance after cellulose. Chitosan is similar to cellulose in chemical structure but the C-2-hydroxyl group of cellulose is replaced by an amino group (Dutta, 2002). In previous studies, chitosan can be used as an additive to improve wet strength in papermaking and surface properties of paper for offset printing (Li Q, 1992). The biopolymers such as cellulose, chitosan, and chitosan-cellulose composite were either crosslinked or uncrosslinked, and they were added in a series of concentrations from 0.1% to 1.5% (Lertsutthiwong, 2002).

The study of the effect of chitosan additives on the properties of recycled paper such as news print has never been done. Based on this description, this research aimed to identify/investigate/assess the effect/impact of chitosan on the mechanical and optical properties of recycled paper.

2 MATERIAL AND METHOD

2.1 Materials

The materials used in this experiment were chitosan, acetic acid 1%, aquadest, and waste paper (newspaper and HVS). The instruments required and used for this research were laboratory glassware, analytical scale, blender, screen, Elrepho, tensile tester, Cobb tester, and oven.

2.2 Experimental Method

2.2.1 Preparation of Chitosan Solution

0.5 g, 1 g, 1.5 g, and 2.0 g of chitosan were weighed using an analytical balance. Then the chitosan is dissolved with 1% acetic acid. The mixture is stirred for 2 hours, so it is homogeneous.

2.2.2 Handsheet Production

Paper samples (HVS and newspaper) weighed as much as 50 g, then soaked in 10 L aquadest for 6 hours. After that, it is crushed using a blender. Pulp slurry by adding water with pulp and chitosan with various variations. Furthermore, a sheet of paper is made using screens, so that a wet sheet of paper is formed. Then the sheet of paper is dried in the oven. Moreover, prepared for further paper testing.

2.2.4 Characteristic of Paper

Properties of paper have been tested including the mechanical properties such as tensile strength and water absorption and the optical properties such as paper brightness. The capacity of water absorption of paper sheet was measured by using Cobb's test, according TAPPI T441 om-09 standard. The value of water absorption can be obtained from the equation below

$$\text{Water absorption (cobb)}x = 100\ (a-b) \qquad (1)$$

Where
a = weight of the sample paper after testing (gram)
b = weight of the sample paper before testing (gram)

Tensile strength was determined using tensile tester TAPPI T-494. The tensile strength test was conducted three times. Paper brightness was measured by using Elrepho test, according to TAPPI- 452 standard method. Brightness value shows the percentage reflectance of blue light at wavelength of 457 nm reflected from the surface of paper.

3 RESULT AND DISCUSSION

The Cobb test determines the amount of water that is taken up by a defined area of paper through one sided contact with water. Table 1 shows the test result of

water absorption of paper with various chitosan concentrations.

Table 1: Water absorption in various concentrations of chitosan

Concentration of Chitosan (%)	Water absorption (g/m^2)	
	HVS	Newspaper
0	69.78	98.52
0.5	72.69	92.35
1	63.61	85.78
1.5	52.97	72.54
2	47.36	70.92

HVS paper without chitosan had a Cobb value of 69.78 g/m^2. The addition of 0.5% chitosan concentration resulted in a Cobb value of 72.69 g/ m^2. At chitosan concentration of 1%, a Cobb value was 63.61 g/ m^2. While paper with the chitosan concentration of 1.5% had a Cobb value of 52.97 g/m^2. Furthermore, with the addition of chitosan concentration of 2%, Cobb value was 47.46 g/m^2.

The newspaper sample untreated with chitosan had a water absorption value of 98.52 g/m^2. The addition of chitosan at a concentration of 0.5% resulted in water absorption value of 92.35 g/m^2. Water absorption value were 85.78 g/m^2, 72.54 g/m^2 and 70.92 g/m^2 when treated with chitosan concentrations of 1%, 1.5% and 2% respectively. The data showed that the chitosan addition reduced the water absorption of paper made from HVS paper and waste newspaper, where the water absorption of waste newspaper is higher than HVS paper. Newspapers have more paper pores compared to HVS, and this causes the newspaper water absorption value is higher than the HVS. Both newspaper and HVS paper that does not contain chitosan have a higher absorption value than paper containing chitosan, and this is due to chitosan as an additive (sizing agent). This result was not consistent; chitosan has many hydroxyl groups so that it can bind to water, due to increasing the water absorption paper. In the previous research, water absorption decreased by increasing the concentration of chitosan. With the formation of the structure of the film layer on the surface of the fiber (Sarwar, 2009).

The tensile strength represents the maximum force needed to break a strip of paper. Tensile strength is one of the most important basic physical properties of paper. Therefore, it is necessary to increase paper quality by improving other factors, such as fiber length. Tensile strength is a measure of how resistant the paper is to a web break. The strength, length and bonding of fiber, degree of fiber refining, the direction of the fiber, and filler are the main sources of the tensile strength of paper (Khantayanuwong, 2017).

Table 2 shows the result of tensile strength measurement on paper.

Table 2: Tensile index of paper that contain of chitosan

Cencentration of chitosan (%)	Tensile index	
	HVS (Nm/g)	Newspaper (Nm/g)
0	23.67	17.25
0.5	35.26	20.71
1	41.79	32.58
1.5	45.32	35.74
2	40.85	35.90

HVS paper that did not contain chitosan had tensile index of 23.67 Nm/g, which exhibited lowest tensile strength. The addition of chitosan at a concentration of 0.5% resulted in a tensile index of 35.26 Nm/g. At chitosan concentration of 1%, a tensile index was 41.79 Nm/g. HVS paper with the chitosan concentration of 1.5% had tensile index of 45.32 Nm/g. Moreover, with the addition of chitosan concentration of 2 %, tensile index was 40.85 Nm/g and had no significant effect on tensile strength.

Furthermore this study showed that tensile index of newspaper was 20.71 Nm/g when treated with chitosan concentration of 0.5%. Tensile index were 32.58 Nm/g, 35.74 Nm/g, and 35.90 Nm/g when treated with chitosan concentration of 1%, 1.5% and 2% respectively. Tensile strength of HVS paper is higher than tensile strength of newsprint.

The tensile strength test showed that tensile index of HVS paper and newspaper increased with increasing of concentration of chitosan and this result is consistent with the previous research (Ashori, 2006). The results showed that chitosan at concentration of 1.5% can be identified as optimum concentration. However chitosan concentration addition of more than 0.5%, did not increase the tensile index. One factor that affects tensile strength is fiber length.

The chitosan's structure is resemble to cellulose. It should be compatible with the cellulose, thus making it possible to create strong bonding with fibers and giving the strength of paper (Nada, 2006).

Chitosan, which has hydroxyl and amine groups, can form hydrogen bonds with cellulose fibers, cellulose fibers to form strong bonds, this affects the tensile strength of the paper produced. Cellulose is held by hydrogen bonding, and these bonds influence the fiber cross-linking distance (Mucha, 2000)

Tensile strength is indicative of the strength derived from factors such as fiber strength, fiber length, and bonding. The tensile index of HVS paper is higher than the tensile index of newspaper, and this is because cellulose fibers from newspapers are secondary fibers from paper recycling. HVS paper made from primary fibers has more long fibers. Secondary fibers have fewer long fibers; this causes a higher tensile index for HVS compared to newspapers

Adding excessive chitosan will result in the strength of the paper being compliant. This is due to the paper pores filled by chitosan will reduce the braid between the fibers, resulting in reduced mechanical strength of the paper.

It also will cause the occurrence of dusting on the paper. Chitosan that is not attached to the surface of the paper will act on the image on the printing plate so that it will ultimately affect the course of print production and decrease the quality of printing.

When the surface-sized sheet is treated with chitosan solution, a portion of the additive solution penetrates with water into the fibrous structure. Interaction between chitosan and fiber would improve bonding strength and resistance of paper to water, due to the formation of amide bonds during the printing ink drying process. Interaction with amino groups of chitosan with fiber the presence of water, they can form ionic and amino bonds (Ashori, 2006).

The brightness of paper measures the amount of reflectance of blue light at wavelength of 456 nm reflected from the surface of paper. The results of the paper brightness test can be shown in Table 3.

Table 3: The brightness of paper in various concentration of chitosan

Concentration of Chitosan (%)	Brightness (%)	
	HVS	Newspaper
0	81.19	67.25
0.5	81.68	67.34
1	82.85	68.12
1.5	84.47	68.85
2	80.94	67.94

HVS paper that did not contain chitosan had paper brightness of 81.19%. The paper brightness were 81.68%, 82.85%, 84.47%, and 80.94% when treated with chitosan concentration of 0.5%, 1%, 1.5% and 2% respectively. The application of chitosan concentrations from 0.5% to 2%, cannot trigger the increasing of brightness of paper, which remained constant with further increase of chitosan concentration.

The paper brightness of waste newspaper without chitosan was 67.25%. The addition of 0.5% chitosan concentration resulted in paper brightness of 67.34%. The paper brightness were 68.12%, 68.85% and 67.94% when treated with chitosan concentration of 1%, 1.5% and 2% respectively.

The brightness value higher the number, the whiter the paper. The paper brightness was influenced by fillers, bleaching process, and OBA substances. HVS paper brightness value is higher than the brightness of the newspaper because the HVS paper raw material, which has a higher brightness value than the newspaper. The data obtained shows that there is no effect of chitosan on the value of paper brightness, both on HVS paper and newspaper. The brightness of HVS paper is greater than the brightness of the newspaper. Papers with large amounts of residual lignin will have lower brightness. The brightness of paper increased with an increasing of filler. The decrease brightness of paper both of HVS and newspaper was possibly due to the increase in light absorption of the higher apparent density of handsheet.

For further research, to increasing the mechanical properties of paper, chitosan should be combination with other such as carboxymethyl cellulose and starch to enhance the strength properties of paper.

4 CONCLUSION

Chitosan is a biomaterial that used as an additive in papermaking to improve paper properties. The application of chitosan into the paper will affect the properties of the paper produced, among others, the paper's tensile resistance and water absorption. The addition of chitosan does not affect the paper brightness. With the increasing of chitosan concentration, the tensile strength increased, but the water absorption of paper decreased. The application of chitosan concentrations from 0.5% to 2%, cannot trigger the increasing of brightness of paper, which remained constant with further increase of chitosan concentration. This study showed that chitosan at concentration of 1.5% can be identified as optimum concentration. The tensile index of HVS paper is greater than the tensile index of newspaper, whereas water absorptiveness of HVS paper is lower than water absorptiveness of newspaper. This research shows that chitosan is useful and effective as an additive in papermaking to improve the mechanical properties of paper.

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